

Characteristics and transport of atmospheric aerosols over the Namibian coast

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Abstract

It is well understood that on various scales in the atmosphere, the transport, dispersion, accumulation, transformation and deposition of aerosols is driven by atmospheric dynamics, meteorological conditions and topographical controls. This thesis presents the results of a series of inter-disciplinary research endeavours in environmental and atmospheric sciences to describe the spatial- and temporal variability in vertical atmospheric structures, transport pathways, and aerosol character over the Namibian coast. The unique topography, atmospheric conditions, variety of aerosol sources, and the presence of a semi-permanent stratocumulus cloud deck, make the Namibian coast of particular interest for this study and this region is a type of natural laboratory for studying the variability in these conditions. Recent international research efforts in the region include the *Observations of aerosol and cloud interactions* (Nasa-ORACLES: Zuidema et al., 2016) and the *Aerosols, Clouds and Radiation in southern Africa* (AEROCLO-SA: Formenti et al., 2019) campaigns. For the aforementioned reasons, the ground-based, Henties Bay Aerosol Observatory (HBAO; 22.090619°S, 14.272424°E), Namibia, makes *in situ* measurements of various physical and chemical properties of aerosols. These measurements within the Namibian boundary layer (BL) include black carbon (BC) intermittently from July 2012 to December 2015, and filter sampling of PM₁₀ aerosols from February 2016 to December 2017 (over 26 sampling weeks). These filters were analysed for element- and ion-concentrations. Additionally, publicly available datasets were used, such as the NOAA HYSPLIT kinematic back-trajectory model, radiosonde data, remote-sensed satellite data from MODIS, CALIPSO and COSMIC missions, synoptic charts, reanalysis meteorological datasets, and statistical- and mathematical models. Boundary layer height (BLH), characterised by the bulk Richardson number, at Walvis Bay, where radiosondes were released was linked to cloud- and surface cover, surface heating effects, and easterly wind components. The surface of MG across the region of interest was largely affected by changes in atmospheric moisture and cloud, and was not consistent with BLH as defined by the bulk Richardson number. Low-level inversions, identified by GPS-RO, were lowest, deepest and strongest in the spring. Their character was linked to surface-radiation interactions with cold sea surfaces, warm arid landscapes and low-level clouds in the region, and macroscale circulation, such as the southeast Atlantic and continental high-pressure systems. The effects of diurnal variability in surface temperatures extended deep into the atmosphere with stability peaking just before dawn. The character of low-level inversions along the coast also indicated the presence of the night-time Benguela jet stream. The geographical variability and springtime maximums coincided with maximum closed cloud cover over the SEA Ocean and biomass burning aerosol (BBA) plumes over the region. The character of elevated inversions was also linked to macroscale circulation, as well as the spatial and temporal distribution of radiation-absorbing aerosols emitted by biomass burning. The transport pathways to the site, conceptualised with the use of synoptic charts and trajectory analyses, helped to identify several major transport pathways to the

aerosol observatory, from marine and continental atmospheres or recirculated locally. An early peak in equivalent black carbon (eBC) in comparison to literature and satellite measurements were explained by the influence of localised low-pressure systems that either enhance (July) or inhibit transport (September) into the Namibian BL. In addition, lower eBC in the BL in September may be linked to increased stability when co-occurring inversions were at a maximum for the year. In addition to the *biomass burning* source, five major aerosol source types were identified from the apportionment by comparisons of mass ratios to known literature values and positive matrix factorisation (PMF). These sources are *sea salt* (component contributes $74.7 \pm 1.9\%$ of the total mass, characterised by Na^+ , Cl^- , Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-}), *mineral dust* ($15.7 \pm 1.4\%$, Si, Al, Fe, Ti, Ca^{2+} , Mn, P, F and V), *ammonium neutralised* ($6.1 \pm 0.7\%$, SO_4^{2-} , NH_4^+ , MSA, oxalate, and nitrate), *fugitive dust* ($2.6 \pm 0.2\%$, V, Cd, Pb, Nd and Sr) and *industry* ($0.9 \pm 0.7\%$, As, Zn, Cu, Ni and Sr). High fluoride concentrations ($25 \mu\text{g m}^{-3}$) could pose a serious health problem to the affected populations. Back-trajectory analyses showed how aerosols were circulated locally and transported over great distances from the ocean and subcontinent. Even though the HBAO is set in a remote environment, the transport and contribution of aerosols generated by both natural and anthropogenic processes mean that the site cannot be considered as pristine. The combined interdisciplinary methods used in this study, have proven useful in investigating the influence of vertical structures in the atmosphere, and the local- and long-range transport of air masses on the aerosol character and load at HBAO.

Keywords: aerosol character, atmospheric circulation, Namibian coast, source apportionment, transport pathways, vertical structure

Preface

Interactions between atmospheric dynamics and processes directly influence the transport of air masses, from the micro- and mesoscale processes near the surface where aerosols and their gaseous precursors are readily emitted, to the subsequent transport of these constituents over long distances. Atmospheric aerosols, or suspended particulate matter, have direct and indirect impacts on the physicochemical properties of the atmosphere through which they move. The result is complex feedbacks between aerosols, radiation, and clouds. Despite research into these interactions and their relevance to climate over southern Africa by remote sensing and intensive field campaigns (e.g. SAFARI-92, SAFARI-2000), our understanding is limited by uncertainties in the location, character and concentration of aerosols over climatically significant regions. More recently the AEROCLO-SA and NASA-ORACLES field campaigns focussed on aerosol interactions with the climatically-relevant stratocumulus cloud deck over the southeast Atlantic on the Namibian coast. This study aims to describe the transport of atmospheric constituents to a long-term observatory, namely the Henties Bay Aerosol Observatory (HBAO) on the Namibian coast. To address this aim, the thesis is composed of three separate articles, each presented in a separate chapter, and each addressing one of the objectives, which are to;

- (1.) analyse the vertical structure of the atmosphere over the west coast and evaluate the implications for air mass transport,
- (2.) evaluate the seasonality in black carbon at HBAO and create a conceptual model of predominant circulation patterns and atmospheric transport pathways over the Namibian coast, and
- (3.) characterise the chemical composition of the aerosols at HBAO and determine a transport climatology to HBAO to assist in understanding the aerosol composition.

Chapter 1 presents some background to the scientific problem, the motivation and intended contribution of this research to the meteorology and atmospheric science branches of geography. Next, the aims and objectives are presented. The final part of this chapter presents an in-depth literature review, which guides the reader through the relevant temporal and spatial scales of known atmospheric dynamics and processes over southern Africa and the Namibian coast, as well as the topic of atmospheric aerosols. The second chapter presents the research design and methodology, and describes the experimental methods and statistical models used to address each research objective. The third chapter presents the first article (not yet published) entitled, *Atmospheric stratification over the Namibian coast and surrounds*. The article makes use of three years of radiosonde data and eleven years of Global Positioning System Radio Occultation data to describe the characteristics in the spatial and temporal distribution of marine boundary layer heights and elevated inversion layers. Chapter four presents the second article entitled, *Three years of measurements of light-absorbing aerosols over coastal Namibia: seasonality, origin, and transport*, published in the

journal Atmospheric Chemistry and Physics. The article made use of measurements of equivalent black carbon to estimate black carbon concentrations arriving at the HBAO between July 2012 and December 2015. Synoptic maps from Era-interim reanalysis data and back-trajectories calculated using the NOAA HYbrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT) were used to study the links between the concentrations of black carbon particles and the meteorological conditions that give rise to different transport pathways over the region. Chapter five presents the third and final article entitled, *Chemical composition and source apportionment of the aerosol load at an observatory on the Namibian coast*, was published in the journal Atmospheric Chemistry and Physics. The article presents a study on the collection, analyses and chemical characterisation of elemental and ionic species of PM₁₀ aerosols arriving HBAO between February 2016 and December 2017. Source apportionment is done by comparison of mass ratios of elements to known literature values and PMF. Chapter six presents a summary of the results from the three articles and final concluding remarks. The appendices at the end of the document present other published work by the author; consent forms from co-authors for the published article, the supplementary data for each of the three articles and instrument calibration forms. Research funding and author contributions are presented with each respective article.

Opsomming

Dit word goed verstaan dat die vervoer, verspreiding, ophoping, transformasie en deponering van atmosferiese partikels op verskillende skale in die atmosfeer aangedryf word deur atmosferiese dinamika, meteorologiese toestande en topografiese kontroles. Hierdie tesis bied die resultate aan van 'n reeks interdisiplinêre navorsingspogings in omgewings- en atmosferiese wetenskappe om die ruimtelike en tydelike veranderlikes in vertikale atmosferiese strukture, vervoer patrone en chemiese karakter van atmosferiese partikels oor die Namibiese kus te beskryf. Die unieke topografie, atmosferiese toestande, verskeidenheid bronne van atmosferiese partikels en die teenwoordigheid van 'n semi-permanente stratocumulus wolkdek oor die Namibiese kus wat van besondere belang vir hierdie studie is, beteken dat hierdie streek 'n soort natuurlike laboratorium is om die wisselvalligheid in hierdie toestande te bestudeer. Onlangse internasionale navorsingspogings in die streek sluit die waarnemings van atmosferiese partikel- en wolkinteraksies in (Nasa-ORACLES: Zuidema et al., 2016) en die atmosferiese partikels, wolke en bestraling in suidelike Afrika (AEROCLO-SA: Formenti et al., 2019). Vir die bogenoemde redes, neem die *Hentiesbaai Aerosol Observatory* (HBAO; 22.090619 ° S, 14.272424 ° O), Namibië, *in situ* metings van verskillende fisiese en chemiese eienskappe van atmosferiese partikels. Hierdie metings binne die Namibiese grenslaag sluit in swart koolstof (BC), gemeet tussen Julie 2012 en Desember 2015, en PM₁₀ filtermonsterneming van vanaf Februarie 2016 tot Desember 2017 (meer as 26 monsternemingsweke). Hierdie filters is geanaliseer vir elementele- en ionkonsentrasies. Addisionele openbare datastelle word gebruik, soos die *NOAA HYSPLIT kinematic back-trajectory model*, radiosonde-data, afstandswaarnemende satellietdata van MODIS, CALIPSO en COSMIC-missies, sinoptiese weerkaarte, meteorologiese herontleding datastelle en statistiese en wiskundige modelle. Soos verwag, is atmosferiese grenslae en inversies beïnvloed deur die relatiewe posisies en intensiteit van makroskaalse sirkulasies, soos die hoëdrukstelsels oor die suidoostelike Atlantiese Oseaan en kontinent, oostelike golwe met gepaardgaande laedrukstelsels en troë. Die seisoenale wisselvalligheid in hierdie stelsels word verder beïnvloed deur mesoskaal en kleiner stelsels. Dit sluit in die interaksies tussen inkomende bestraling en koue see-oppervlaktes, warm droë landskappe en lae wolke in die streek, wat bydra tot die ingewikkelde karakter van die grenslaag. Die effekte van die daaglikse wisselvalligheid in oppervlaktemperatuur was tot diep in die atmosfeer teenwoordig, met stabiliteit wat net voor dagbreek 'n hoogtepunt bereik het. Die karakter van inversies het verband gehou met die ruimtelike en tydelike verspreiding van atmosferiese partikels wat vrygestel word tydens die verbranding van biomassa. Die vervoerpaaie na die terrein, gekonseptualiseer met die gebruik van sinoptiese kaarte en trajekontledings, het gehelp om verskeie belangrike vervoerweë na die HBAO te identifiseer, vanaf mariene en kontinentale bronne of plaaslik hersirkuleer. 'n Vroeë piek in ekwivalente swart koolstof (eBC) in vergelyking met literatuur en satellietmetings word verklaar deur die invloed van gelokaliseerde laedrukstelsels wat vervoer versterk (Julie) of verswak

(September) na die Namibiese grenslaag. Verder, kan laer eBC in die grenslaag in September gekoppel word aan verhoogde stabiliteit wanneer die inversies wat saam voorkom, 'n maksimum bereik vir die jaar. Bykomend tot die bron van biomassa verbranding, is vyf belangrike atmosferiese partikel brontipes geïdentifiseer vanaf die toedeling deur vergelykings tussen massaverhoudings en bekende literatuurwaardes en positiewe matriksfaktoriserings. Hierdie bronne is *seesout* (komponent dra by tot $74.7 \pm 1.9\%$ van die totale massa, gekenmerk deur Na^+ , Cl^- , Mg^{2+} , K^+ , Ca^{2+} en SO_4^{2-}), *minerale stof* ($15.7 \pm 1.4\%$, Si, Al, Fe, Ti, Ca^{2+} , Mn, P, F⁻ en V), *ammonia geneutraliseer* ($6.1 \pm 0.7\%$, SO_4^{2-} , NH_4^+ , MSA, oksalaat, en nitraat), *vlugtige minerale stof* ($2.6 \pm 0.2\%$, V, Cd, Pb, Nd en Sr) en *industrie* ($0.9 \pm 0.7\%$, As, Zn, Cu, Ni en Sr). Hoë fluoriedkonsentrasies ($25 \mu\text{g m}^{-3}$) kan 'n ernstige gesondheidsprobleem vir die aangetaste bevolking inhou. Terug-trajekontledings het getoon hoe atmosferiese partikels plaaslik versprei word en oor lang afstande vanaf die oseaan en subkontinent vervoer word. Ongeag die feit dat die HBAO in 'n afgeleë omgewing is, die vervoer en hidrae van atmosferiese partikels wat deur natuurlike en antropogene prosesse gegenereer word beteken dat die terrein nie as ongerep beskou kan word nie. Die gekombineerde interdisiplinêre metodes wat in hierdie studie gebruik is, is nuttig om die invloed van vertikale strukture in die atmosfeer en die plaaslike en langafstandvervoer van lugmassas op die partikelkarakter by HBAO te ondersoek.

Sleutelwoorde: atmosferiese partikel karakter, atmosferiese sirkulasie, Namibiese kus, bronverdeling, vervoerweë, vertikale struktuur

Dedication

Writing this thesis has been a sustained exercise in failing forward and ultimate growth. Thank-you's and I-couldn't-have-done-it-without-you's are owed to everyone who lent a critical ear, offered insights and encouraged me in this process. In general, thank you to all the individuals who strive to make this a better world for everyone who shares- and is yet to share this planet. May the next piece of writing from the book of Michael McCarthy, entitled *The Moth Snowstorm: Nature and Joy*, further inspire considerate and purpose-driven actions on our part.

"We can generalise or, indeed, monetise the value of nature's services in satisfying our corporeal needs, since we all have broadly the same continuous requirement for food and shelter; but we have infinitely different longings for solace and understanding and delight. Their value is modulated, not through economic assessment, but through the personal experiences of individuals. So we cannot say — alas that we cannot — that birdsong, like coral reefs, is worth 375 billion dollars a year in economic terms, but we can say, each of us, that at this moment and at this place it was worth everything to me. ...[B]ut we need to remake, remake, remake, not just rely on the poems of the past, we need to do it ourselves — proclaim these worths through our own experiences in the coming century of destruction, and proclaim them loudly, as the reason why nature must not go down."

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List of abbreviations

ABFZ	Angola Benguela Frontal Zone
AEROCLO-sA	Aerosols, Clouds and Radiation in southern Africa
AERONET	Aerosol Robotic Network
agl	above ground level
amsl	above mean sea level
AOD	aerosol optical depth
ARL	Air Resources Laboratory
ATN	attenuation of light
BC	black carbon
BL	boundary layer
BLH	boundary layer height
BUS	Benguela Upwelling System
CAB	Congo Air Boundary
CALIOP	Cloud-Aerosol Lidar with Orthogonal Polarization
CCN	cloud condensation nuclei
CDAAC	COSMIC Data Analysis and Archive Centre
CDO	Climate Data Operators
COSMIC	Constellation Observing System for Meteorology Ionosphere and Climate
DMS	dimethylsulphide
eBC	equivalent black carbon
ECMWF	European Centre for Medium-Range Weather Forecasts
GAW	Global Atmosphere Watch
GDAS	Global Data Assimilation System
GPS	Global Positioning System
HBAO	Henties Bay Aerosol Observatory
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory Model
IC	ion chromatography
ITCZ	Inter-Tropical Convergence Zone
LPDM	Lagrangian particle dispersion models
MBL	marine boundary layer
MERRA	Modern-Era Retrospective analysis for Research and Applications
MODIS	Moderate Resolution Imaging Spectroradiometer
MQL	minimum quantification limit

MSA	methanesulfonic acid
MSLP	mean sea level pressure
NCEP	National Centre for Environmental Prediction
NOAA	National Oceanic and Atmospheric Administration
NWP	Numerical Weather Prediction
ORACLES	Observations of Aerosol and Cloud Interactions Campaign
PM	particulate matter
PMF	positive matrix factorization
R^2	Pearson correlation coefficient
READY	Real-time Environmental Applications and Display System
RO	radio occultation
SAFARI	South African Fire Research Initiative
SANUMARC	Sam Nujoma Marine and Coastal Resources Research Centre
SAWS	South African Weather Service
Sc	stratocumulus cloud
SEA	southeast Atlantic
SST	sea surface temperature
TEOM	tapering element oscillating microbalance
TOA	top of atmosphere
UTC	Coordinated Universal Time
WD-XRF	wavelength-dispersive X-ray fluorescence
WMO	World Meteorological Organization
XRF	X-ray fluorescence

Chapter 1

Introduction & background

This chapter serves to introduce this study within the larger context of the research and provide essential background information from existing literature on the meteorological controls for aerosol transport, aerosol chemistry and trajectory modelling, specifically over Namibia and surrounds. The motivation for this study is presented by addressing the unique characteristics of the coastal desert environment in Namibia and gaps in the scientific body of knowledge that this study aims to address. An in-depth literature review of existing research allows for setting the broader context of the research and aids in the formulation of research questions, objectives, and a scope for the investigation, ultimately aimed at contributing to the existing science on aerosol character and transport over the Namibian coast.

1.1. Introduction to the scientific problem

Awareness of air pollution dates back to ancient Greece and the Middle Ages in London, and scientific investigation and regulation began in the United Kingdom in the 19th century, spurred by the hundred-fold increases in pollution with the onset of industrialisation (Jacobson, 2002, and references therein). Scientific discourse and research are ongoing due to uncertainties in the spatial and temporal distribution of pollutants, also the weather and climate impacts of these gases and aerosol in the non-linear and non-static earth-ocean-atmosphere system (Akimoto, 2003). To add to the uncertainty, socio-economic conditions, and human responses to changes in climate are also highly variable. Our ability to adapt to changing climate is closely linked with our understanding of the processes and dynamics in effect at different scales in the atmosphere. Feedback loops within the earth-ocean-atmosphere system demonstrate the known interactions between different components in the system (Andreae et al., 1995; Fan et al., 2016; Haywood et al., 2003a; Keil and Haywood, 2003). Increasing demands on natural, capital and energy resources in developed and developing populations influence both air quality and climate in different ways. Similarly, the state of the earth-ocean-atmosphere system directly influences our capacity for survival where, for example, planetary food security is subject to interannual climate variability. Scientific research allows us to contemplate and investigate these issues, thereby expanding our collective body of knowledge into the elusive nature of the atmosphere, describing the processes and interactions at play, and facilitating informed decision-making.

Both natural and anthropogenic processes are responsible for the production of atmospheric aerosols and their gaseous precursors. These include biomass burning, windblown mineral dust, mining activities (Annegarn et al., 1983; Dansie et al., 2017; Eltayeb et al., 1993; Heine and Völkel, 2010) and industrial activities (Freiman and Piketh, 2003) over continental southern Africa, and biogenic (Andreae et al., 1994) emissions from the continent and southeast Atlantic Ocean (Zhang et

al., 2010). Different emission sources are associated with different chemical profiles, also known as a source fingerprints, which can be identified by unique tracers or specific combinations of chemical species to determine the contribution of detected sources to the total aerosol load, known as receptor modelling (Hopke, 1991; Viana et al., 2008). A primary assumption of the use of tracers is that the elemental and ionic ratios remain constant over time in the atmosphere for each source being traced. The complexity and diversity of chemical profiles are related to the aerosol source, size, age and state, either primary species emitted from fresh emission sources or secondary species formed by photochemical reactions in gas-to-particle conversions (Fitzgerald, 1991; Viana et al., 2008). The effects of these processes on aerosols limit the detail of source profiling that can be done with the use of tracers alone.

Once formed, these aerosols are subject to various scales of motion and mixed into the ambient atmosphere (Buseck and Schwartz, 2014; Finlayson-Pitts and Pitts, 2000; Freiman and Tyson, 2000; Garstang et al., 1996; Piketh et al., 2002; Ramanathan et al., 2001). The residence time, and therefore transport, of aerosols depends on meteorological conditions and individual aerosol properties, such as size and hygroscopicity (Pöschl, 2005), and usually ranges from one to ten days for particulate matter (PM) smaller than or equal to 10 micrometres (PM₁₀) – a relatively short period as compared to greenhouse gases that may persist for years (Akimoto, 2003; Intergovernmental Panel on Climate Change: IPCC, 2013; Ramanathan et al., 2001). Despite the shorter residence time and transport distance as compared to greenhouse gases, aerosol impacts have been shown to extend to global scales and alter climate feedback loops (Bergstrom, et al., 2003; Eck et al., 2003; Haywood et al., 2003a, 2003b; IPCC, 2013; Jost et al., 2003; Keil and Haywood, 2003; Pöschl, 2005). Aerosols also modify the local and regional atmospheric composition. This impacts air quality and human health and has direct, indirect, and semi-direct interactions with solar and terrestrial radiation (Charlson et al., 1992; Hansen et al., 1997; Twomey, 1977).

The direct effect of aerosols describes particle interactions with incident radiation (Bergstrom et al., 2002; Chand et al., 2009). Black carbon is one of the most effective light-absorbing aerosols at all wavelengths of light from both incoming and outgoing radiation, and elevated smoke plumes have been studied in field campaigns and by satellite observations, reported in publications by Andreae et al. (1998), Bergstrom et al. (2003), Eck et al. (2003), Formenti et al. (2003a), Haywood et al. (2003a, 2003b), Sakaeda et al., (2011) and Painemal et al., (2014a). Absorbing aerosols, such as dust or black carbon, have implications for temperature distribution in the atmosphere and may induce an elevated heat pump effect as proposed by Lau et al. (2006). The indirect effect of absorbing aerosols is the ability of aerosols to act as cloud condensation nuclei, which indirectly modify the microphysical and optical properties, and alter the extent, reflectivity, and lifetime of clouds (Charlson et al., 1992; Johnson et al., 2004; Ramanathan et al., 2001; Twomey, 1977). The semi-direct effect is the capacity of aerosols to modify temperature and humidity profiles of the atmosphere (Hansen et al., 1997;

Johnson et al., 2004). The largest biases in climate models are due to erroneous sea surface temperature (SST) inputs (Grodsky et al., 2012; Li and Xie, 2012; Richter and Xie, 2008) and inaccurate parametrisations of aerosols and clouds, which result in under- or overestimations of the absorption of solar radiation, especially over the tropics and subtropics (IPCC, 2013; Randall, et al., 2007; Wang et al., 2014).

Remote sensing of clouds from space has made it possible to estimate the relative contribution of clouds to climate forcing and the earth's energy budget, the most important factor related to forcing in the atmosphere (Arakawa, 2004). This is significant to the southeast Atlantic and Namibian coast where a meridionally extended stratocumulus cloud (Sc) deck, one of three semi-permanent systems in the world, extends between 10–30°S, 10°W–10°E and tops the marine boundary layer (BL) at ~850 hPa (Muhlbauer et al., 2014; Wood, 2015). These Sc, which covers roughly 20% of the globe, have a high albedo and reflect more incoming short-wave radiation than both cirrus or cumulus clouds, and are therefore of global significance for the Earth's radiation balance (Johnson et al., 2004; Klein and Hartmann, 1993; Muhlbauer et al., 2014; Wood, 2015; Zuidema et al., 2009). Cloud fractions in the Namibian Sc deck range from >50% in the austral summer/autumn to <80% in winter/spring (Muhlbauer et al., 2014).

The ability of inorganic aerosols to act as cloud condensation nuclei (CCN) is well-understood and is determined by particle hygroscopicity (Martin et al., 2013), size and chemical composition (Fan et al., 2016). Particle size is of significance for CCN and the larger particles tend to form clouds at lower supersaturation levels (Hobbs et al., 2000). Soluble sea-spray aerosols are generally efficient CCN (Ayash et al., 2008; Pierce and Adams, 2006) as is coarse fraction dust when coated with a soluble material (Boucher, 2013). The variability in the physicochemical properties of aerosols and their relative locations to cloud height present large sources of uncertainties in regards to the aerosol-induced effects on various scales (Keil and Haywood, 2003; Koch and Del Genio, 2010; O'Dowd et al., 1999). As an example, in a coupled climate modelling study, Cabos et al. (2017), found biases in the incoming solar radiation and cloudiness over the South Atlantic Anticyclone, especially during the austral wintertime.

Ultimately, the atmospheric dynamics, which affect the thermodynamic structure and mass transport of atmospheric constituents, are themselves also impacted by the atmospheric constituents that are being transported. These simplified feedbacks are illustrated in Figure 1-1.

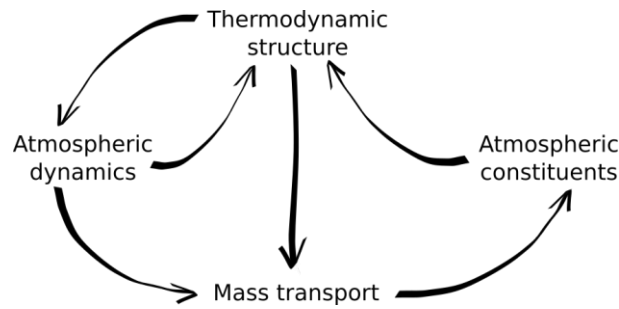


Figure 1-1. Simplified feedbacks between atmospheric processes and constituents.

The formation and dissipation of vertical structures, such as temperature inversions or steep isopycnal slopes in the atmosphere, depend largely on these interactions, in turn, affecting the advection and convection of air masses over both short and long ranges. The nature and extent of interactions in atmospheric processes and dynamics, the mechanisms influencing transport through the region, is especially important to understanding the impacts thereof on aerosol load and character parameterisations. The parameterisation of aerosols presents significant sources of uncertainties in regional and global models that estimate the impact on short-term climate forcing and long-term climate change (Carslaw et al., 2013; Charlson et al., 1992; Hansen et al., 1997; Keil and Haywood, 2003; Ramanathan et al., 2001).

1.2. Motivation for this research

Our understanding of population vulnerability to the variability of climate is limited by the data we collect. Although aerosols over southern Africa have been a subject of interest for some time now, uncertainties still exist regarding the physical and chemical properties and distribution thereof in the atmosphere (Di Biagio et al., 2017; Fan et al., 2016; Samset et al., 2018; Tsigaridis et al., 2013). Namibia and the southeast Atlantic are amongst the global areas of interest to study aerosols and their role on climate by interactions with clouds and radiation (De Graaf et al., 2014; Muhlbauer et al., 2014; Painemal et al., 2014a, 2014b; Wilcox, 2010; Zuidema et al., 2009).

Long-term studies to collect and chemically classify aerosols at a site on the coast offer a unique opportunity to study the variability in concentration, source and character of aerosols. *In situ* aerosol sampling is particularly useful in this region because the Sc deck limits the ability of satellites to identify the character of aerosols below them (Chand et al., 2009). The links in aerosol character and load to transport pathways at low-levels into the region can also be studied to determine the significance of these transport pathways. This would provide invaluable input for interactive aerosol parametrisations for this region and would allow for improved estimates of regional and global scale climate impacts of aerosols (Finlayson-Pitts and Pitts Jr, 2000; Kondratyev et al., 2006). This will also add to our understanding of how the variables in Figure 1-1 interact in the region and how the vertical structure and circulation patterns affect aerosol composition and load.

1.3. The study area

The Sam Nujoma Marine and Coastal Resources Research Centre (SANUMARC) of the University of Namibia, shown in Figure 1-2, was identified as a suitable site for an aerosol observatory. In 2012, the Henties Bay Aerosol Observatory (HBAO, www.hbao.cnrs.fr) was established with the aim of sampling aerosols on a long-term basis.

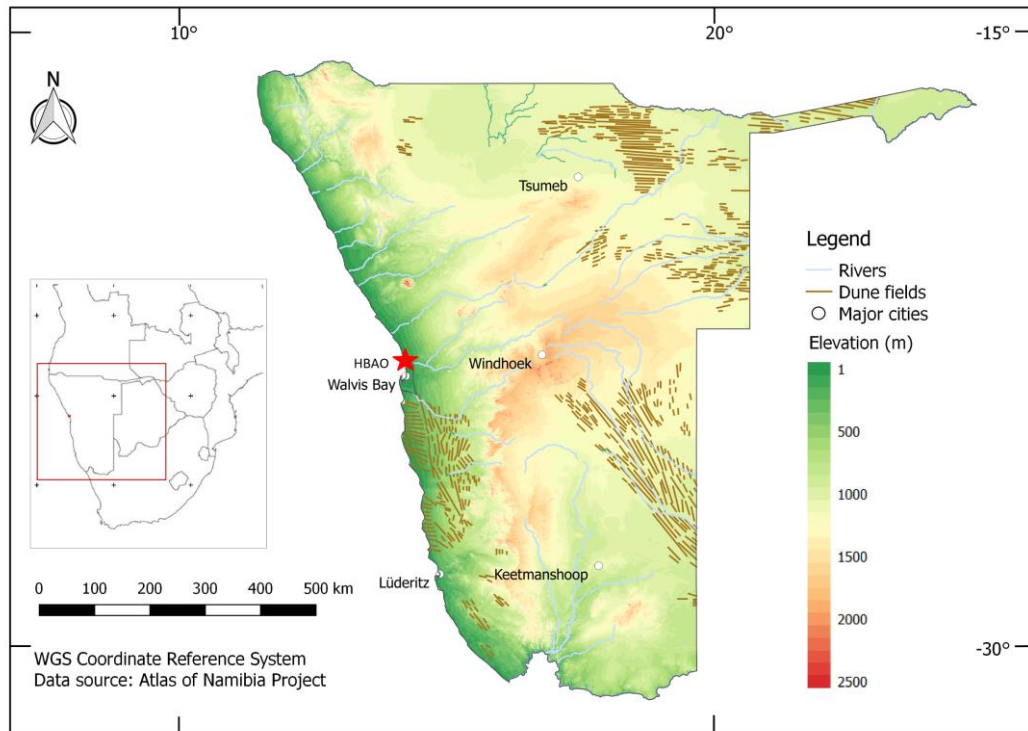


Figure 1-2. Elevation and locality map for Namibia. The HBAO at SANUMARC is indicated by the red star, just north of the major city, Walvis Bay.

HBAO is located at $22^{\circ}5'26.23''$ S, $14^{\circ}16'20.73''$ E, 100 m from the shoreline and 30 m above mean sea level (amsl) where the instruments operate from a roof terrace and adjoined laboratory below. Figure 1-3 shows photos taken three hours apart from the roof terrace where the sampling inlets are located, on 2 March 2017. The dry Omaruru river mouth exits into the sea 100 m north of the station and the Namibian Gravel Plains lie to the east.



Figure 1-3. View from the rooftop of the HBAO (30 m amsl) on 02/03/2017 at (top) 15:13 and (bottom) 18:16 where stratocumulus clouds are evident along the coast.

The coastal town of Henties Bay is just south of SANUMARC, and 100 km north of the second largest city in Namibia, Walvis Bay. The region is characterised by an arid environment with little to no vegetation covering the desert landscape along the coast. Henties Bay has a population of around 4 800 as reported by the most recent Namibia Population and Housing Census of 2011 (Namibia Statistics Agency, 2013), with very little traffic and no large-scale industrial activity in or around the town. Walvis Bay on the other hand, has a population of 62 100, with industrial areas, an airport and harbour, as well as surrounding mining activities.

1.4. Research aims and objectives

This study aims to describe the transport of atmospheric constituents to a site on the Namibian coast by studying the thermodynamic structure of the atmosphere, the transport pathways to the site and the chemical character of constituents in the atmosphere.

The specific objectives of the research are to:

- (1.) Analyse the vertical structure of the atmosphere over the Namibian coast and evaluate the implications for air mass transport.
 - (1.1) Identify stratified layers from radiosonde and GPS satellite radio occultation data.
 - (1.2) Describe the diurnal, seasonal and interannual variability in these structures over the Namibian coast.
 - (1.3) Evaluate the effects of these vertical structures on air mass transport through the region.
- (2.) Evaluate the seasonality in black carbon at Henties Bay Aerosol Observatory (HBAO) and create a conceptual model of predominant circulation patterns and atmospheric transport pathways over the Namibian coast.
 - (2.1) Measure and analyse the mass concentrations of equivalent black carbon (eBC) in the marine BL.
 - (2.2) Describe the importance and seasonality of eBC in the region.
 - (2.3) Identify the dominant transport patterns and quantify their contributions by coupling observations with calculations of air mass back-trajectories.
- (3.) Characterise the chemical composition of the aerosols at HBAO and determine a transport climatology to assist in understanding the aerosol composition.
 - (3.1) Measure and analyse the PM₁₀ elemental and water-soluble ionic aerosol composition in the marine BL.
 - (3.2) Analyse the temporal variability and apportion the measured chemical species to aerosol sources through receptor models.
 - (3.3) Investigate the geostatistical correlations in aerosol character and concentrations to local and long-range air mass transport.

1.5. Literature review

In alignment with the research objectives, this literature review will describe the macroscale circulation that sets the environment in which meso- to microscale circulation then develops. This section also describes the resulting vertical atmospheric structures, with a particular focus on what is known and what remains uncertain in how these conditions might affect air mass transport over the southern African subcontinent, and, specifically, the Namibian coast. Known perturbations to these circulation features are also described because these effects may describe anomalous features in air mass transport. Accordingly, major sources and known impacts of atmospheric PM₁₀ aerosols over the subcontinent and southeast Atlantic (SEA) Ocean are summarised. The existing uncertainties in aerosol character and concentrations, specifically within the BL of coastal Namibia, are also illustrated.

1.5.1. Scales of motion

Atmospheric processes and dynamics interact on different spatial and temporal scales in the atmosphere. These interactions are crucial to consider when inferring potential relationships in atmospheric mechanisms and controls for mass and momentum transport. The height, direction, and velocity of transport in the atmosphere is governed by these interactions; this includes the initial buoyancy of primary emissions (Burger, 2016), to transport enhanced or inhibited by atmospheric dynamics and circulation conditions (Cosijn and Tyson, 1996; Swap et al., 1996; Tyson et al., 1996) over varying landmasses and topographical features (Lengoasa et al., 1993). This manifests as variable concentrations and size distributions of constituents in the atmosphere, and also in varied local atmospheric impacts. The scales of motion in the atmosphere range from micro- to macroclimate as described by Orlanski (1975) and Oke (1988) presented in Figure 1-4. Figure 1-4 also gives the horizontal spatial and temporal scales of BL mixing processes, aerosol lifetime in the atmosphere, as well as the appropriate scales for interpreting trajectory models, each described in further detail in this literature review and the methods in Chapter 2.

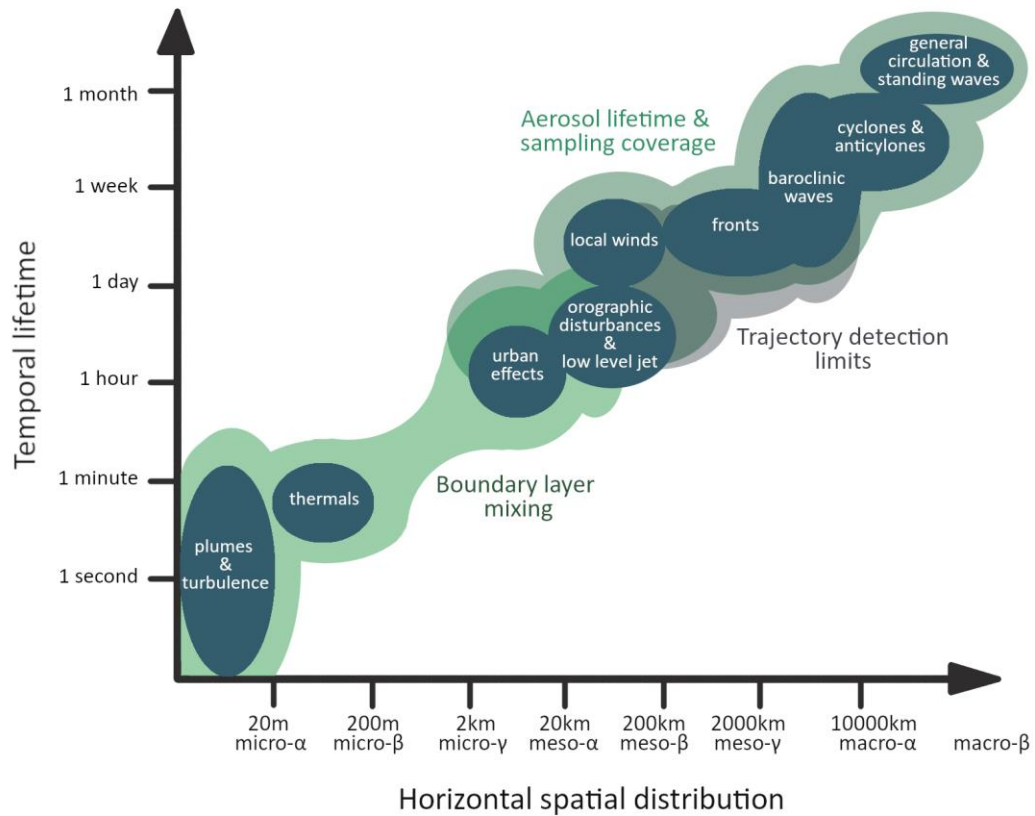


Figure 1-4. Temporal and horizontal spatial scales of motion in the atmosphere, adapted from Orlanski (1975) and Oke (1988), and the atmospheric processes at these different scales affecting the Namibian coast. The bubbles around these processes are informed by literature and indicate the scales relevant to boundary layer mixing, the detection limits for trajectories, typical aerosol lifetimes and aerosol sampling coverage at HBAO.

1.5.2. Macroscale circulation

The combined effects of Earth's rotation, as well as the spatial and temporal variability in incoming solar radiation across the globe, determine the relative location of macroscale convection and subsidence. This produces a globally distributed three-cell circulation system (Ahrens and Henson, 2014) as indicated in Figure 1-5. The seasonal intensification of pressure distribution and wind regimes are linked to the movement of the Inter-Tropical Convergence Zone (ITCZ: Waliser and Gautier, 1993), shown in Figure 1-5 and also in more detail in Figure 1-6.

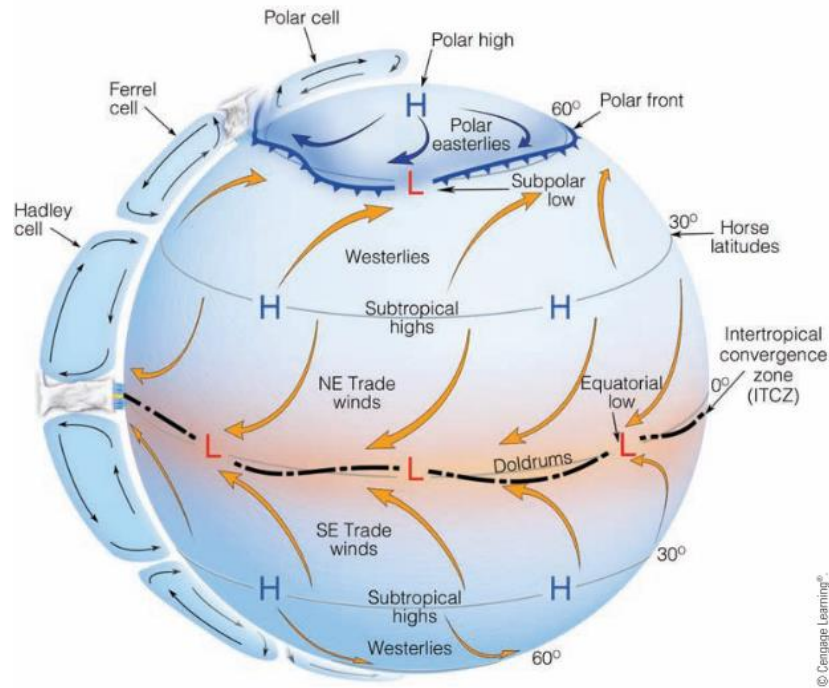


Figure 1-5. The idealised distribution of winds and surface pressure in the three-cell circulation system. Image courtesy of Ahrens and Henson (2014).

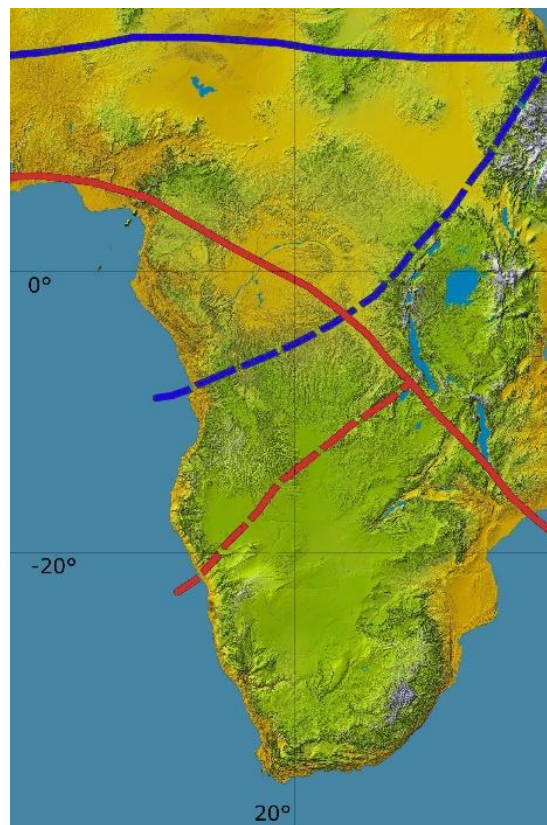


Figure 1-6. The relative positions of the Inter-Tropical Convergence Zone (solid line) and Congo Air Boundary (dashed line) in the austral summer (red) and austral winter (blue). The topographic heights are indicated by brown (lowest), to yellow, green and white (highest). The high-resolution image of topography over Africa was downloaded on 27 April 2020 from: <https://photojournal.jpl.nasa.gov/catalog/PIA04965>, courtesy of Nasa-JPL.

The ITCZ is a region where the northeast and southeast trade winds converge and are associated with enhanced convective activity. In the austral summer, the ITCZ moves south to around 17°S east of 30°E (Taljaard, 1994) and the associated barotropic easterly wave fluctuates between 15°S and 25°S (Tyson et al., 1996) between the surface and ~850 hPa. A secondary formation, the Congo Air Boundary (CAB), is also noteworthy for circulation over southern Africa, particularly in the austral summer when the CAB follows the migration of part of the ITCZ east of 30°E. The CAB may join a southward extending tropical temperate trough (TTT), marking an area of preferential low-pressure formation over the central subcontinent. A surface system, the west coast trough, forms along the west coast under conditions of active tropical convection and usually occurs in conjunction with a westerly wave to the south-west and divergence in the upper air (Tyson and Preston-Whyte, 2014). They are most frequently observed in the early summer and late autumn. Other isolated low-pressure systems near the coast, such as the Angolan low (Racz and Smith 1999), are associated with the inflow of moist, marine air masses.

These low-pressure systems are merely transient disturbances that perturb the mean circulatory fields over southern Africa, characterised by the descending subtropical limb of the Hadley cell. The macroscale subsidence and surface divergence fluctuate from south of 30°S in the austral summer to north of 30°S in the winter (Tyson and Preston-Whyte, 2014). Three distinctive subtropical high-pressure cells form under the subsidence and are labelled according to their relative positions, namely; the continental, southeast Atlantic and south Indian anticyclones (Swap et al., 1996; Tyson et al., 1996; Tyson and Preston-Whyte, 2014). The formation of these high-pressure cells up to 850 hPa can be seen in Figure 1-7, which gives the seasonally averaged (2009-2019) geopotential height of pressure levels at 1000 hPa, 850 hPa, 700 hPa, 500 hPa and 300 hPa, modelled by the modern-era retrospective analysis for research and applications version 2 (MERRA-2; GMAO, 2015a). High-pressure systems are seen year-round, but exert the greatest influence on circulation over southern Africa during the autumn and winter. The areas of preferential low-pressure formation can also be seen, particularly between 850 hPa and the surface.

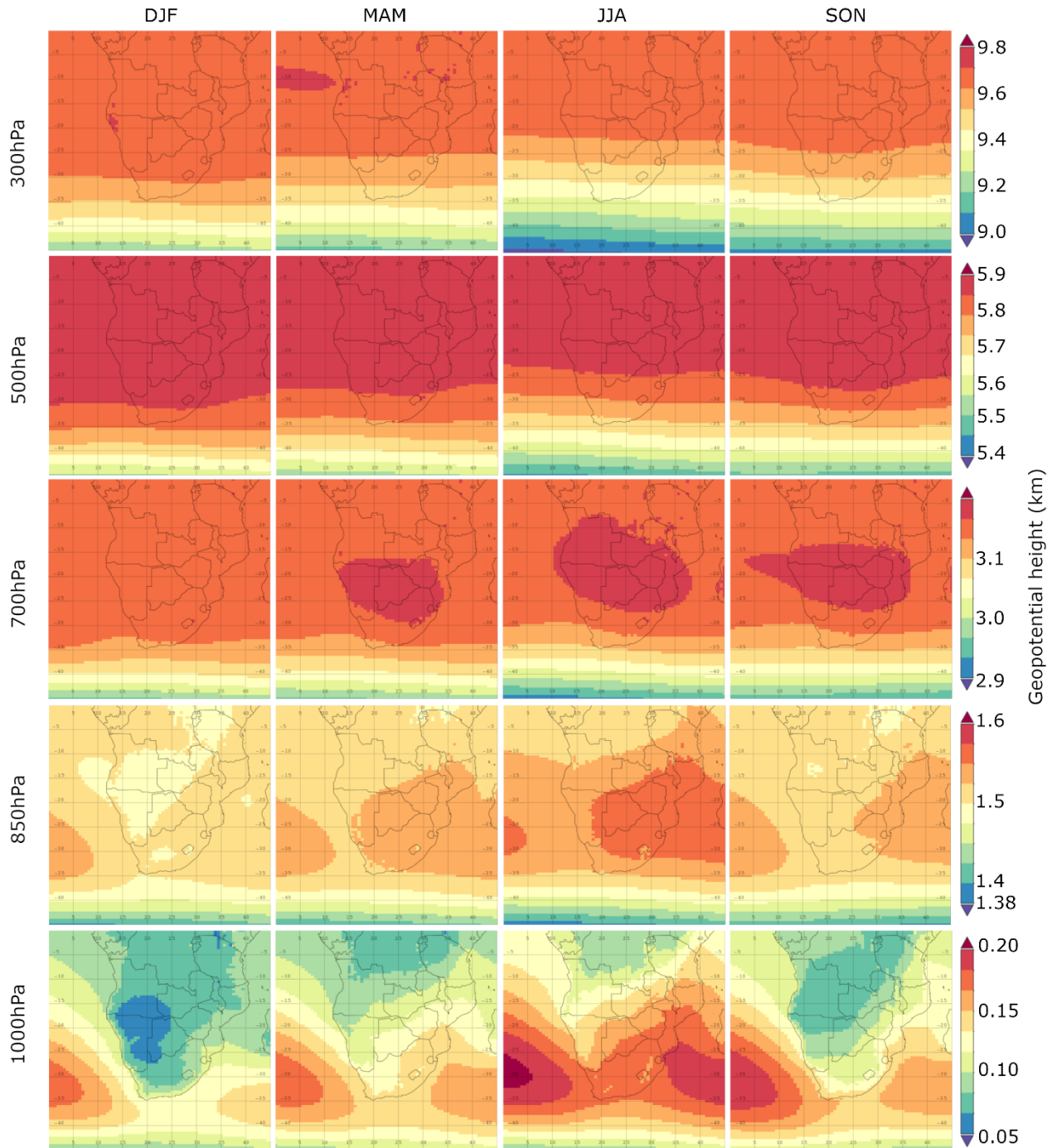


Figure 1-7. Seasonally averaged geopotential height for 2009 to 2019 from MERRA-2 data ($0.625^\circ \times 0.5^\circ$) (GMAO, 2015a) for pressure levels at 1000 hPa, 850 hPa, 700 hPa, 500 hPa and 300 hPa over southern Africa. Seasons are divided as follows: DJF (December, January and February), MAM (March, April and May), JJA (June, July and August) and SON (September, October and November).

To the east of the low-pressure trough, a warm ridge typically forms, producing cloud bands responsible for rainfall over central and eastern southern Africa (Cook et al., 2004; Preston-Whyte and Tyson, 1988). To the west, a cold and dry ridge typically forms (Preston-Whyte and Tyson, 1988; Taljaard, 1995a, 1995b) as surface divergence and anti-cyclonic circulation produces persistent stable atmospheric layers. In the transition from summer to winter, a band of suppressed convection

forms between the receding easterly lows and anticyclonic high-pressure (Cook et al., 2004), maintaining the dry and stable conditions on the subcontinental west coast year-round (Preston-Whyte and Tyson, 1988). The resulting climate on the Namibian coast is that of a typical coastal desert environment (Warner, 2004).

In winter the ITCZ retreats to approximately 10°N over Africa and the continental anticyclone centre undergoes a 5° to 6° northward shift joining a ridge across the subcontinent (Tyson and Preston-Whyte, 2014). The seasonal meridional shift of the subtropical Southeast anticyclone during the winter (7° to 13°) is far less pronounced than the zonal shift of the South Indian Anticyclone (24° to 30°), as can be seen in Figure 1-7. The displacement of these high-pressure cells influences the movement and amplitude of the westerly wave (winter peak) and ultimately the transport of air masses over the subcontinent.

The transient, baroclinic westerly wave disturbances occur with a periodicity of five to ten days across the mid-latitudes (Tyson et al., 1996) and rarely exceed a height of 1500 m (850 hPa) (Tyson and Preston-Whyte, 2014). These waves generally tilt to the west with height and account for up to 25% (35%) of the variance of the 500-hPa geopotential height in summer (winter) at 50°S (Tyson and Preston-Whyte, 2014). Tyson and Swap (1996) reported the greatest heights over South Africa during the spring and autumn months, and the more recent seasonal means for 2009 to 2019 from MERRA-2 reanalyses (Figure 1-7) showed slightly higher 500-hPa geopotential heights over South Africa during these seasons (5.89 km maximum) as compared to winter and summer (5.88 km maximum). The westerly wave is driven by the polar vortex where the year-round maximum wind speeds are found in the upper troposphere (Tyson and Preston-Whyte, 2014). Changes in conditions in the polar vortex would describe changes in the westerly wave's character, such as decreases in near-surface (10 m) wind speeds in what is known as the "global stilling phenomenon" that was observed between 1980 and 2010 by various studies across the globe (Nchaba et al., 2017; Young et al., 2011; Zheng et al., 2016) and the subsequent reversal thereof observed in more recent long-term observations (Zeng et al., 2019).

Westerly waves are associated with the formation of cold fronts that persist throughout the year and the zone of maximum occurrence of these fronts change little with season in the mid-latitudes (Preston-Whyte and Tyson, 1988; Taljaard, 1994; Tyson and Preston-Whyte, 2014). Cold fronts approaching the south-west coast of Southern Africa are the most common frontal feature and comprise 65% of cold fronts around southern Africa, although they very rarely move far up the west coast (Taljaard, 1994). Despite this, these fronts influence transport of marine air masses southerly along the west coast.

The macroscale subtropical jet stream, which forms part of the westerly disturbances in the austral winter, is associated with vertical wind shear at the upper troposphere around 200 hPa, of which the weaker counterpart is situated around 20°E and 30°S, 30 km above ground level (~10 hPa) blowing

at approximately 38 m s^{-1} (Taljaard, 1994). Although jet streams influence surface weather, airflow and the long-range transport of air masses, the limited spatial extent of this study does not include a detailed study of this macroscale subtropical jet stream. An additional, low-level nocturnal jet stream also forms along the west coast of southern Africa on meso- β scales, and is discussed in the next section.

Apart from affecting long-range transport, macroscale circulations and the resultant meridional wind stresses along the west coast also control the upwelling of ocean currents. Offshore of South Africa, over the southern part of the Benguela Upwelling System (BUS), high-speed southerly winds over the coastline are induced by the anticyclonic curvature offshore and subsequent deflection at the subcontinent and southerly flow along the coast, ultimately strengthening the upwelling of cold water in this region (Colberg and Reason, 2006; Jury and Courtney, 1995). The enhanced upwelling strengthens Eckman transport in the northward-flowing current and maintains this upwelling over the northern Benguela. The induced upwelling results in decreased sea surface temperatures (SST), which in turn impacts on mesoscale atmospheric processes. This is described in more detail in the next section.

1.5.3. Meso- to microscale circulation

Feedbacks in the earth-ocean-atmosphere system are interconnected. The large-scale oscillations in wind-energy impact on the dynamics in the ocean surface layers (Colberg and Reason, 2006). SST impacts on regional atmospheric dynamics (Chang and Philander, 1994; Desbiolles et al., 2018). Regional topography is also important for understanding smaller scale circulations and near-surface wind fields (Goldreich and Tyson, 1988; Lindesay and Tyson, 1990; Tyson and Seely, 1980). This is because turbulence and convection within and above the BL on mesoscales are dominated by eddies generated by forced convection (Desbiolles et al., 2018; Hermes and Reason, 2009; Lengoasa et al., 1993; Tyson and Preston-Whyte, 2014). Steep air temperature gradients over the semi-arid landscapes and the cold Atlantic Ocean can be seen in Figure 1-8.

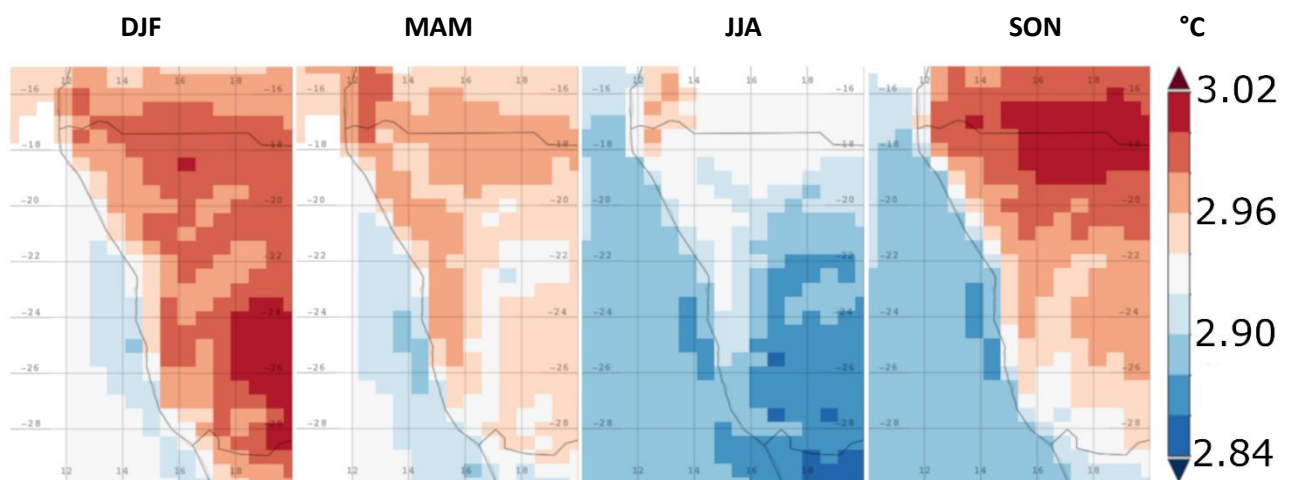


Figure 1-8. Seasonal means of air temperature at 10 m on $0.5^\circ \times 0.65^\circ$ grids, between 2009 and 2019, from MERRA-2 (GMAO, 2015b).

Offshore along the coast, the relatively warmer SST over the Angola basin (Monteiro et al. 2008; Shannon et al., 1987) are in contrast with the cold, upwelling waters in the Benguela current. These temperature gradients are responsible for the relative positions of coastal lows that track along the coast to the east (Lengoasa et al., 1993) and the Angolan low-pressure systems (Desbiolles et al., 2018). Colder SST also contributes to the stabilisation of the lower troposphere in this region (Cook et al., 2004; Nelson and Hutchings, 1983; Tyson and Preston-Whyte, 2014).

Atmospheric stability along the coast is enhanced by warm easterly to north-easterly moving, subcontinental air that heats adiabatically as it descends off the high escarpment. In the transitions between macroscale cyclonic and anti-cyclonic centres and ahead of cold fronts in the winter, infrequent steep pressure gradients form perpendicular to the coast, which results in the formation of mesoscale berg winds (Lengoasa et al., 1993; Tlhalerwa et al., 2005; Tyson and Preston-Whyte, 2014, and references therein). They often co-occur with shallow coastal low-pressure systems where the stable air above traps the cyclonic vorticity generated by the outflow of continental air (Tyson and Preston-Whyte, 2014). An example of such a coastal low is given in Figure 1-9. The combined effects of these systems are quick (hours) changes in temperature, wind speed and -direction, pressure, and vertical structures over short distances (20–50 km). These systems are characterised by cool air masses blowing onshore to the rear of the low-pressure system and warm air masses blowing offshore ahead of the system in the form of berg winds. Berg winds and coastal lows disrupt the diurnal rhythm in BL processes along the coast, which are largely determined by near-surface air flows. The transport of aerosols by these circulations are described in section 1.5.6.



28 November 2017

Figure 1-9. Corrected reflectance of true colour showing the formation of a localised coastal low-pressure formation (courtesy of MODIS (Platnick et al. 2015)).

The diurnal and seasonal variability in temperature gradients between land and ocean surfaces (Figure 1-8) often result in the formation of land and sea breezes (Markowski and Richardson, 2010;

Tyson and Preston-Whyte, 2014). The seasonal mean near-surface zonal wind components, at 2 m and 50 m and at a 50 km resolution, are given in Figure 1-10. Sea breezes and plain-mountain winds accompanied by anabatic airflow up the continental slope typically form near the surface and at the BL top during the day and in the summer. At night and in the winter, katabatic airflow by land breezes and mountain-plain winds typically dominate and are linked to shallower BL (Lindesay et al., 1990). The land breezes may be sustained into the summer at the top of the BL.

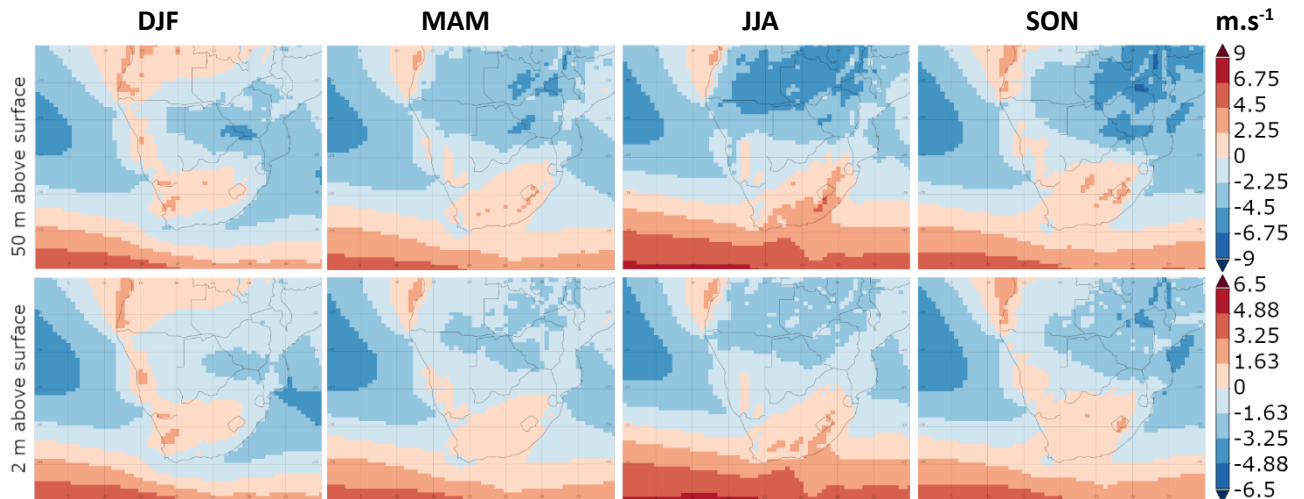


Figure 1-10. Seasonally averaged zonal mesoscale wind components with wind speeds averaged for 2009 to 2019 using MERRA-2 data (GMAO, 2008) at 2 m and 50 m above the surface over southern Africa and the southeast Atlantic. Positive (negative) values denote winds from the west (east). Seasons are divided as follows: DJF (December, January and February), MAM (March, April and May), JJA (June, July and August) and SON (September, October and November). Negative (positive) values indicate easterly (westerly) winds.

Differences in temperature near the surface and the overlying air often results in the decoupling of surface from upper air flows. Sufficient decoupling above the BL, results in the formation of the low-level, meso- β scale nocturnal Benguela jet stream along coastal Namibia (Nicholson, 2010). The core of maximum winds between 1000 hPa (~ 200 m amsl) and 925 hPa (~ 800 m amsl) was found to occur at around 450 km from the coast where mean winds were >10 m s^{-1} and moderate winds >6 m s^{-1} were present over the entire coastal upwelling region. These high wind speeds enhance turbulence and therefore mixing of air masses in the otherwise stable marine BL.

1.5.4. Perturbations to the general circulation

The mean temporal and spatial variability of circulations described in the previous sections are perturbed by two primary modes of climate variability over southern Africa linked to continental (Nicholson and Chervin, 1983; Gillett et al. 2006) and global-scale teleconnections (Marshall, 2003) in the ocean-atmosphere system. These perturbations are relevant for understanding the full range of known variability in circulation and the potential implications for air mass transport. The one interannual perturbation is the El Niño Southern Oscillation (ENSO: Harnack and Harnack, 1985) consisting of the El Niño and La Niña phases. These phases describe the meridional movement of

pressure cells in the Pacific Ocean (Monahan and Dai, 2004; Rasmusson and Carpenter, 1982), on average occurring once every two to seven years. The other perturbation is the standing Southern Annular Mode (SAM), which describes anomalies in zonal pressure between 40°S and 65°S on interannual time scales (Gong and Wang, 1999; Reason and Rouault, 2005).

Swart et al. (2015) illustrated the differences in the westerly wind jet position, width, and strength, which directly influence the SAM index (Monahan and Fyfe, 2008) from observations, models and reanalyses data. They found large discrepancies in the estimations from these different data due to lack of observations over the region. Although the magnitude of the forcing is highly variable, the consensus is that in the positive SAM phase (austral summer), the westerly jet moves south and increases in strength. The westerly wind belt widens with the high-wind speed sector, situated around 60°S (Swart and Fyfe 2012), while the lower wind speed sectors are just south of the subcontinent at 40°S (Thompson et al., 2011). The relationship in the movement of the westerly jet and pressure gradients related to the SAM index is not linear, however, as shown by Swart et al. (2015), changes in the SAM index depend on the latitudinal position of the westerly jet. Bigger changes in the SAM index were associated with changes in the position of a more northerly situated westerly wind (Swart et al., 2015).

Nchaba et al. (2017) studied surface and 850-hPa summer winds and found trends in the BUS linked to the SAM. The southward migration of the locus of westerly winds (i.e. the positive phase of SAM) results in the strengthening of the southeast Atlantic anticyclone and the weakening of low pressures over the subcontinent. Speeds of southerly winds along the coast also increase, which results in the improved ocean upwelling. Reason and Rouault (2005) found, by impacting the relative positions of circulation systems and the subtropical jet stream, that the wettest winters over the South African west coast were recorded during the positive SAM phase.

Similarly, ENSO affects SST in the south Atlantic and the subsequent change in pressure distribution, which affects circulation over the region (Howard et al., 2019; Jury, 1996; McHugh, 2006; Rouault et al., 2010). These authors found that during the El Niño phase, the mean latitude of tropical low-pressure systems shift northward, and during the La Niña phase they shift southward, increasing the occurrences of TTT (Pohl et al., 2009; Hart et al., 2010). Nchaba et al. (2017) reported a positive correlation in the ENSO phase and wind speeds at the surface and 850 hPa near the centre of the southeast Atlantic anticyclone, but little correlation with this macroscale oscillation near the coast. Colberg et al. (2004) studied the teleconnections with reanalyses data fed into a model of general circulation and reported a lag of one season from the shift of pressure cells in the Pacific that translate to the southeast Atlantic Ocean.

Another phenomenon observed over the Benguela region is the Benguela Niño (Shannon et al., 1987), not related to ENSO. During autumn and summer in some years, anomalous zonal and meridional circulation over the western tropical Atlantic Ocean affects the eastern Atlantic Ocean, with a lag time

of two (Florenchie et al., 2003) to three (Richter et al., 2010) months. This results in anomalous conditions in the Benguela current, a phenomenon characterised by weak southerly winds at the equator (Hardman-Mountford et al., 2003) and a change in wind fields over the cold Benguela ocean current. Although the region often experiences intrusions of warm, saline water from the equatorial Angolan current (Colberg and Reason, 2006; Shannon et al., 1987), during a Benguela Niño the change in wind fields results in a southward migration of the front between these currents. This leads to the subsequent depression of the thermocline and stabilisation of the water column; anomalous to the normal conditions.

1.5.5. Vertical structures in the troposphere

1.5.5.1. General features over southern Africa

A significant characteristic of the atmosphere is its thermodynamic vertical structure that describes atmospheric stability, and influences the transport and mixing of air masses away from the source (Burger, 2016; Cosijn and Tyson, 1996; Tyson and D'Abreton, 1998). As described in the previous sections, southern Africa is subject to circulation features across middle latitudes where the high-pressure systems produce subsidence below 500 hPa (Tyson and Preston-Whyte, 2014). The macroscale subsiding air heats adiabatically and may trap cool air below, often resulting in decoupling, stabilisation and stratification of the atmosphere (Painemal et al., 2014a; Wood and Bretherton, 2004). Atmospheric stability is described by temperature lapse rates and refers to the relative state of equilibrium of an air parcel and tendency thereof to move vertically. Stratified layers enhance (unstable) or inhibit (absolutely stable) air mass transport. Absolutely stable layers are those where the atmospheric lapse rate is smaller than the moist adiabatic lapse rate. These lapse rates are smaller than those of temperature inversion layers, which are also considered stable layers and therefore also inhibit the vertical movement and mixing in the atmosphere (Cosijn and Tyson, 1996; Tyson and Preston-Whyte, 2014).

Radiosonde climatologies by Cosijn and Tyson (1996), Garstang, et al. (1996) (for non-rain days), Tyson et al. (1996) and the Southern African Fire Atmosphere Research Initiative (SAFARI-92: Lindesay et al., 1996) field experiment identified four absolutely stable layers over the subcontinent at ~700 hPa (~3.5 km amsl), ~500 hPa (~4 to 6 km amsl), and ~300 hPa (~8 to 9 km amsl) with varying degrees of persistence and influence. The fourth layer is observed at ~850 hPa and associated with haze layers, such as the fog and Sc present along the coast (Muhlbauer et al., 2014; Preston-Whyte and Tyson, 1988; Wood, 2015). These four stable layers, along with the first elevated inversion over the subcontinental region, are given in Figure 1-11.

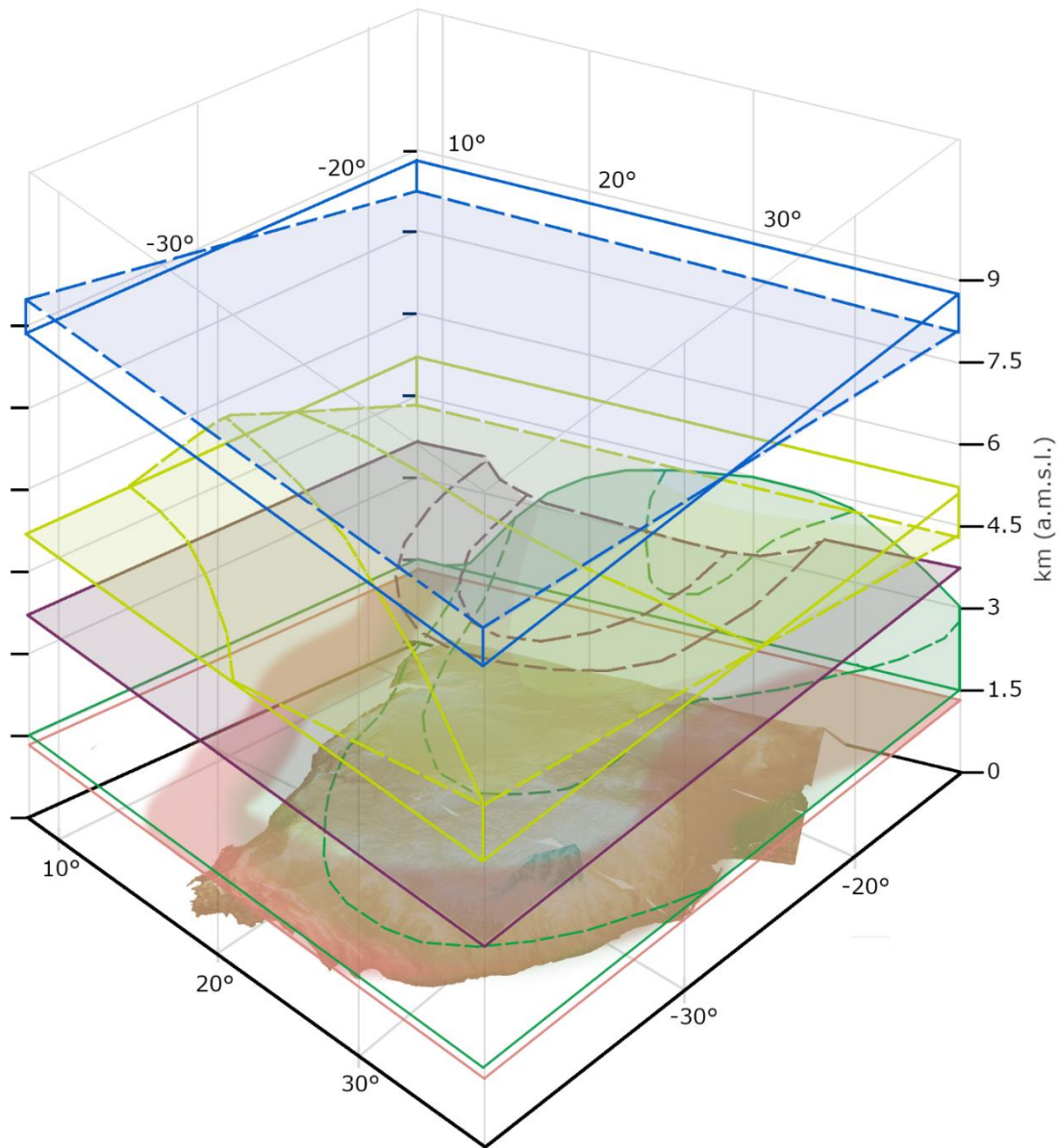


Figure 1-11. The average positions of the first elevated inversion over southern Africa (green, Preston-Whyte et al. 1977) and the four stable layers (Cosijn and Tyson, 1996) at 850 hPa (pink), 700 hPa (purple), 500 hPa (yellow) and 300 hPa (blue).

The effect of these stratified layers on the formation of clean air slots between highly polluted plumes over southern Africa was documented by Hobbs (2003). Clean air slots have also been recorded above (Costantino and Bréon, 2013) and below cloud (Wilcox, 2010), and above smoke layers (Haywood et al., 2004). The conditions and compositions of air trapped below these different stratified layers also differ (Costantino and Bréon, 2013; De Graaf et al., 2014; Hobbs, 2003; Tyson and D'Abreton, 1998) and therefore has significant potential to interact with moisture or incident radiation, and alter weather and climate feedbacks (Hansen et al., 1997; Haywood and Shine, 1995; Mishra et al., 2015). The long-range transport of continental air masses has been linked to the position of the 500 hPa stable layer (Cosijn and Tyson, 1996; Garstang et al., 1996; Tyson and D'Abreton, 1998). Additionally, transport of biomass burning (BB) aerosols over the Namibian coast has been reported in autumn

and winter (Das et al., 2017; Zuidema et al., 2018) coinciding with maximum subsidence under the influence of the continental high-pressure system. This is discussed in more detail in section 1.5.7.

The atmospheric BL is the lowest part of the troposphere near Earth's surface. Convection and turbulence in the BL are directly impacted by the surface temperature and roughness on meso- and smaller scales (Markowski and Richardson, 2010; Oke, 1988). The BL is also where most pollutants are emitted into the atmosphere (Pöschl, 2005). The BL has a pronounced diurnal cycle in contrast to the free atmosphere above. During the day, when surface heating generates convective currents and transfers moisture, heat and momentum, the layer is generally well-mixed (Markowski and Richardson, 2010). The height of the BL gives an indication of these processes and particularly the potential for dilution and transport of air masses within the BL. The in-depth study into the vertical structures over the region, undertaken in Chapter 3 of this thesis, investigates the seasonal variability of the boundary layer height (BLH) and the diurnal and seasonal variability of elevated inversions in more detail. The implications of these mesoscale circulations on air mass transport and the extent of mixing of these air masses into the marine BL at Namibia is also investigated in Chapters 4 and 5 of this thesis.

1.5.5.2. Measuring vertical atmospheric layers

Measurements of the height and character of BLs, stable layers and temperature inversions (absolutely stable) over Namibia and southern Africa are mainly made by ascents (descents) of traditional radiosondes (drop-sondes) (Jury, 2010; Tyson, 1997; Zunckel et al., 1996), satellite measurements such as GPS Radio Occultation (GPS-RO) (Ao et al., 2012; Chan and Wood, 2013; Ho et al., 2015), or reanalysis data that constitute a combination of observational and modelled data (Desbiolles et al., 2018; Ho et al., 2015; Von Engel and Teixeira, 2013). Previously, long-term radiosonde datasets for Windhoek have been used to characterise vertical structures and circulation features over central Namibia (Cosijn and Tyson, 1996; Jury, 2010) and jet-streams along the coast (Nicholson, 2010; Rife et al., 2010). Further studies were limited to short-term, intensive field campaigns focussed on BB plumes (Magi et al., 2003; Swap et al., 1996, 2003; Zunckel et al., 1996). More recently, studies utilising GPS-RO data have made use of this global coverage, twice daily data to describe diurnal and seasonal variability of structures such as BL (Ao et al., 2012; Chan and Wood, 2013; Guo et al., 2011) and cloud tops (Lin et al., 2010) on a global scale. These measurements are limited by the methods used to identify these structures, as well as various systematic and observational errors, described by Chen et al. (2011), Ho et al. (2015), Wang and Zhang (2008) and Wang et al. (2013), among others.

Generally, differences in reported BLH arise due to data coverage and the chosen definitions of what defines the BL top. This is based on assumptions about the conditions in a particular region and the limitations specific to the instruments used to make measurements in the vertical. In a global study, Von Engel and Teixeira (2013) estimated the BLH from European Centre for Medium-Range

Weather Forecasts (ECMWF) reanalysis data, using nine different definitions, and found a relationship of decreasing bias in different definitions toward higher latitudes. Von Engeln and Teixeira (2013) reported maximum BLHs of ~ 2.5 to 3 km over Namibia in austral spring, and the lowest mean BL of ~ 1.8 to 2.3 km over Namibia in the autumn. These BLHs decrease dramatically along the coast where the annual means were ~ 0.5 km – in good agreement with that reported by Preston-Whyte et al. (1977). They also reported little diurnal variability for the BLH along the coast, likely due to consistently stable conditions in this region whereas over the subcontinent, the radiative cooling results in a decrease in turbulence and decay of the well-mixed BL, strengthening the surface inversion and decreasing BLH. Chapter 3 of this thesis will investigate the vertical structures over Namibia and the southeast Atlantic in more depth and evaluate the implications thereof for air mass transport.

The two types of data used to describe these vertical structures in Chapter 3 are radiosonde and GPS-RO data. For both data types, observational errors in temperature and moisture measurements occur as the radiosonde sensor or GPS signal moves through cloud (Wang and Zhang, 2008; Wang et al., 2013). A comparison between these COSMIC GPS-RO data and nine radiosonde datasets by Wang et al. (2013) showed a relative error of the refractivity profile of $\pm 1.6\%$. The greatest observational errors were reported for the humid tropics (Kuo et al., 2004; Sokolovskiy, 2003), near the surface and in the summer ($\pm 2.5\%$) (Chen et al. 2011). These errors were ascribed to the sensitivity of GPS-RO signal refraction with horizontal and vertical changes in the partial pressure of water vapour (Hande et al., 2015; Seidel et al., 2010). Furthermore, in winter the errors are more latitude dependant than in the summer due to greater zonal moisture gradients. The biases between radiosonde and GPS measurements at Walvis Bay, Namibia are explored in Chapter 3.

1.5.5.3. Stable boundary layer

Along the Namibian coast, the year-round cold waters of the Benguela stabilise the lower atmosphere, which supports the use of the bulk Richardson number method (Hanna, 1969) that describes a BL topped by a statically stable layer. These conditions also justify the assumption that the BL is more moist than overlying air masses (Ao et al., 2012; Ho et al., 2015).

1.5.5.4. Cloud-topped and decoupled boundary layer

Considering the stable conditions over the west coast, another reasonable definition would be that of a cloud-topped BL (Von Engeln and Teixeira, 2013). The top of springtime Sc deck was quantified by model and satellite data by Painemal et al. (2014b), who found the biggest biases in the two measurements nearest the coast (± 0.4 km) corresponding to the region of the strongest winds and cold upwelling waters. The effects of subsidence over these cold surfaces results in the thinning of clouds in this region where mean depths along the length of the Namibian coast and to 10°E were < 0.2 km (Painemal et al. 2014b). Decoupling of the BL top from cloud bases presents a major limitation to this definition of the BL, and the extent of decoupling depends largely on latitudinal

position (Painemal et al., 2014b) and turbulence, which may lead to the breakup of clouds (Bretherton and Wyant, 1997) and increased decoupling. At latitudes below 20°S however, Painemal et al. (2014b) showed that low cloud fractions actually coincide with well-coupled conditions over the southeast Atlantic.

1.5.5.5. Inversion-topped boundary layer

Painemal et al. (2014b) showed how the core of the stratocumulus clouds are associated with the strongest temperature inversion, which would also inhibit vertical mixing. This ties in with the definition of a BL topped by a subsidence-induced temperature inversion (Seidel et al., 2010). Preston- Using radiosonde data, Whyte et al. (1977) estimated the height of the temperature inversion over the Benguela current to be between 400 m and 500 m. The surface inversion is strengthened at night, when radiative cooling sets in over the region as turbulence in the mixed layer decays, decoupling upper air from the surface (Lengoasa et al., 1993; Markowski and Richardson, 2010; Oke, 1988; Rife et al., 2010). The steepening temperature gradient results in the formation of low-level nocturnal jet streams associated with an area of maximum wind speeds near the top of an inversion layer (Lazaridis, 2011). Rife et al. (2010) studied the characteristics of low-level jets in different localities and identified a summertime nocturnal low-level jet core to be situated onshore around 300 m agl over 16.0°S and 15.6°E, reaching speeds of 14 m s⁻¹ and oriented parallel to the coast with mean south-south-westerly winds. The study by Rife et al. (2010) also found a significant contribution of topographic controls on the structure of these winds by variable temperature profiles over the ocean, coastal escarpment and continental plateau, inducing strong and abrupt wind formation, such as the low-level Benguela jet (Nicholson, 2010) discussed in section 1.5.3.

1.5.6. Air mass transport over southern Africa and the southeast Atlantic

The transport of air masses is either by advection, on horizontal scales, or convection, on vertical scales, which directly affects the concentrations and character of aerosols reaching the Namibian coast. The forcing mechanisms of this transport are macro- to micro-scale circulations. Several studies have investigated the mechanisms for transport over subtropical southern Africa (Tyson et al., 1996; Tyson, 1997; Piketh et al., 2002; Winkler et al., 2008) and from southern Africa into the tropical South Atlantic Ocean (Swap et al., 1996; Tlhalerwa et al., 2005; Das et al., 2017).

The variability in relative positions of diverging and converging pressure cells, as indicated by the seasonal variability in Figure 1-7, and the corresponding transitions between these circulations, result in different vertical structures and wind fields that influence the transport of atmospheric constituents over the region. Zonal winds, given in Figure 1-10, are particularly important for long-range transport of atmospheric constituents over southern Africa (Tlhalerwa, et al., 2012; Tyson et al., 1996). It is important to note that mean wind speeds between 1980 and 2010 showed continued decreases in a phenomenon known as the global stilling phenomenon, observed by various studies across the globe (Nchaba et al., 2017; Young et al., 2011; Zheng et al., 2016). More recently Zeng et al.

(2019) documented the reversal of this phenomenon, which would increase zonal transport of air masses and might alter the characteristics of air transport climatologies derived under conditions of lower wind speeds than we are experiencing today. This means that transport climatologies and estimations of aerosol mass transport pathways derived before the reported increase in zonal wind speeds from 2010, will be affected. Nonetheless, the transport mechanisms studied over the region are described below for reference.

Using trajectory and radiosonde climatology model analyses, Tyson et al. (1996) showed that total transport over the region occurred through discrete streams due to recirculation below the 500 hPa absolutely stable layer. Tyson et al. (1996) identified four characteristic circulation types associated with long-range transport over the subcontinent. These are the semi-permanent subtropical continental anticyclones, transient mid-latitude ridging anticyclones, quasi-stationary barotropic easterly disturbances, and transient baroclinic westerly disturbances. The mean percentage of transport and recirculation, as well as the frequency of occurrence for each of these circulation types over the subcontinent, is given in Figure 1-12, courtesy of Tyson et al. (1996).

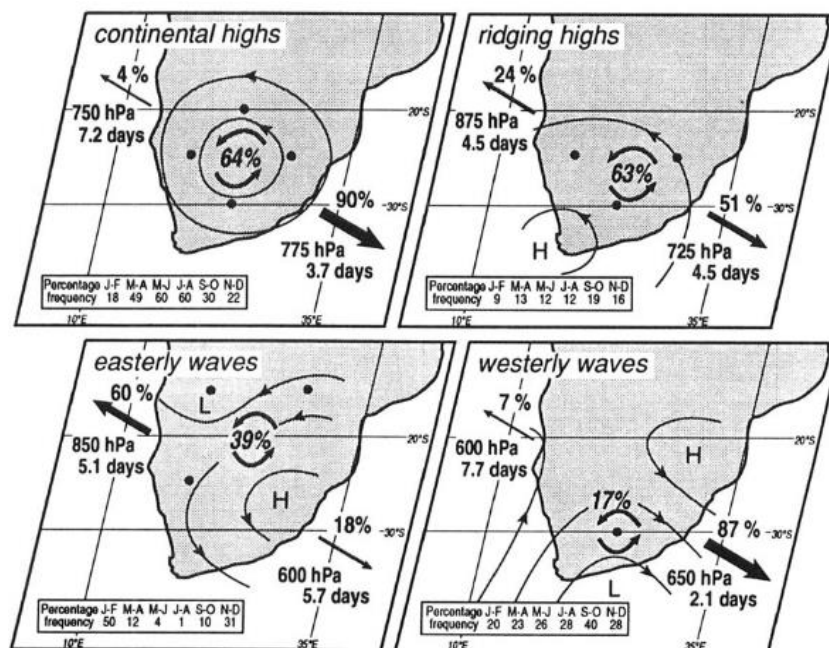


Figure 1-12. The mean percentage transport off and recirculation over the subcontinent, from the surface to 800 hPa, for each of the four major circulation patterns responsible for air mass transport over southern Africa, sourced from Tyson et al. (1996). Mean heights of the plume exiting the subcontinent off the west coast beyond 10°E and off the east coast at 35°E are also given along with the respective transit times.

In recirculating air streams, atmospheric pollutants may be held suspended for days under the combined effect of macroscale circulation in anticyclones over the subcontinent and offshore and mesoscale low pressures at the coast (Garstang et al., 1996; Tyson et al., 1996; Tyson and Swap, 1996). Tyson et al. (1996) found that under anticyclonic conditions, of the total aerosol loading emitted from the subcontinent south of 15°, approximately 4% exits the west coast at 750 hPa (after

seven days of recirculation over the subcontinent). Furthermore, they found that ridging highs resulted in 24% of the total aerosol load, emitted from the subcontinent south of 15°, exiting the west coast at 875 hPa (after four to five days) and westerly waves resulted in 7% exiting the west coast at 600hPa (after a week).

North of 15°S, the long-range easterly transport across the subcontinent is mainly influenced by planetary-scale southerly to easterly trade winds that blow at speeds of 5–10 m.s⁻¹ as compared to the north-easterly and north-westerly winds that blow at approximately half the speed (Preston-Whyte and Tyson, 1988; Taljaard, 1995a; Tyson and Preston-Whyte, 2014). Easterly disturbances are less frequent than the semi-permanent anticyclones and were only observed 4% of the time in Garstang et al.'s (1996) study; however, those disturbances were responsible for most of the advection off the west coast below 800 hPa and specifically between 10° and 20°S (Tyson et al., 1996). Observations between 1992 and 1998 by Tlhalerwa et al. (2012) also showed how the berg winds, associated with easterly transport, were the main agents of aerosol transport and deposition off the coast at Lüderitz and Keetmanshoop. A total of 72 752 tonnes of aeolian dust were transported offshore in the Keetmanshoop plume (in the south of Namibia), of which 982 tonnes were deposited within 100 km offshore in the nutrient-rich BUS. Further north, the Lüderitz dust plume transported 35 894 tonnes of dust in the south-easterly plume, of which 437 tonnes were deposited offshore. A further 36 537 tonnes were transported in the easterly plume, of which 3 018 tonnes were deposited offshore. Some 4 437 tonnes of the dust transported in the Lüderitz plume was transferred into the BUS (Tlhalerwa et al., 2005). The significance and further uncertainties regarding mineral dust transport into the South Atlantic are discussed in section 1.5.7. Although westerly disturbances are less effective at transporting subcontinental air masses off the west coast, approximately 7% of the transport is still off the west coast during westerly wave circulation (Tyson et al., 1996).

1.5.7. Atmospheric aerosols

The Namibian atmosphere is impacted by a combination of primary and secondary aerosols, either produced locally or transported over long distances (Andreae et al., 1998; Annegarn et al., 1983; Dansie et al., 2017; Das et al., 2017; Formenti et al., 1999; Freiman and Piketh, 2003). Aerosols are suspended particulate matter (PM) with sizes ranging from nano- to micrometres. Primary aerosols are directly emitted and usually constitute the large fraction PM greater than 1 µm. Secondary aerosols are formed by two processes in the atmosphere, i.e. by photochemical reactions and gas-to-particle conversions, or by the condensation or accumulation of material on existing particles (Buseck and Schwartz, 2014 and references therein). These secondary particulates are generally, but not exclusively, associated with anthropogenic emissions and are smaller than 1 micrometer (Buseck and Schwartz, 2014; Virkkula et al., 2006).

The concentrations and character of atmospheric aerosols transported through a region depend on the conditions at the source of the emission and the subsequent ageing (Kirkman et al. 2000;

Konovalov et al. 2017). It also depends on the spatial and temporal variability in circulation systems and vertical structures that enhance or inhibit transport on greater scales (Bretherton and Wyant, 1997; Das et al., 2017; Piketh et al., 2002; Swap et al., 1996). The accumulation, transport and dilution of aerosols directly affect local and regional air quality, human and ecosystem health, and climate.

Aerosols are known to modify the relative humidity profile, atmospheric stability and composition, as well as cloud microphysical processes (Sakaeda et al., 2011). Aerosols also interact with radiation both directly and indirectly, scattering incident solar radiation and absorbing terrestrial radiation (Ayash et al., 2008; Li et al., 2008). Tsigaridis et al. (2013) showed how the type and magnitude of this radiative forcing are largely dependent on the composition of these aerosols, and uncertainties in this regard are a direct result of the lack of knowledge on the aerosol composition. The magnitude and direction of forcing also depend on whether they are transported above, below or entrained into clouds (Carslaw et al., 2013; Costantino and Bréon, 2013). Furthermore, depending on their physical and chemical characteristics, aerosols can act as CCN, increasing the number concentration of cloud droplets and subsequently the cloud temperature and brightness which are significant determinants for the sign and magnitude of radiative forcing, and therefore, aerosols directly affect weather or climate (Formenti et al., 2019; Klein and Hartmann, 1993; Johnson et al., 2004; Muhlbauer et al., 2014; Wood, 2015; Zuidema et al., 2016).

The effects of aerosols described above are highly variable and the quantification thereof largely dependent on the aerosol concentration, character and relative location. Aerosols that might be expected over coastal Namibia, as identified by previous short-term studies, are discussed in more detail below, along with the potential significance for atmospheric processes or dynamics.

1.5.7.1. Marine aerosols

Oceans are a major source of atmospheric sea spray aerosols that comprise organic material from the ocean and inorganic coarse mode sea salts (Sciare et al., 2000), of which the spatial and temporal differences over the region can be seen in Figure 1-13. These aerosols are produced by mechanical processes such as bubble and wave breaking that increase proportionally to wind speeds (Colbeck, 2009). Similarly, the type and concentration of aerosols produced depend on the presence of these constituents in the so-called sea-surface micro-layer of the ocean (Hardy, 1982). Sea-spray aerosols, typically have radii in the order of 100 nm to >10µm (Boucher, 2013). Sea salt aerosols are effective CCN (Ayash et al., 2008; Pierce and Adams, 2006) and increased concentrations result in an increase in aerosol optical depth (AOD) over marine environments (Huang et al., 2010). The characterisation of sea-spray aerosols at the surface is therefore of great importance in this study, especially since satellite imagery is often obscured and unable to gather information down to the surface.

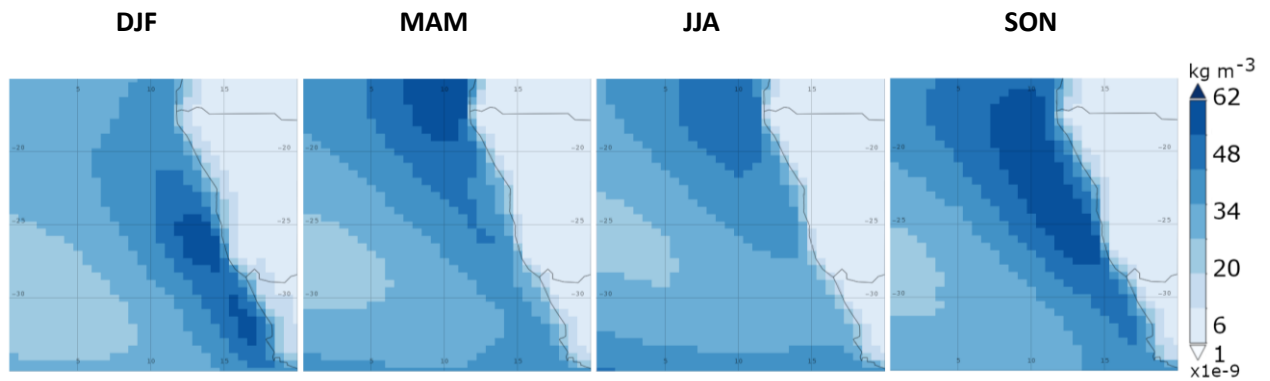


Figure 1-13. The seasonally averaged sea salt surface mass concentrations in kg m^{-3} on a $0.5^\circ \times 0.625^\circ$ resolution grid for 2015 to 2018 from MERRA-2 data (GMAO, 2015c).

Organic material contained in sea-spray aerosols measured off the west coast of southern Africa, such as *chlorophyll a* and biogenic sulphates, are generally emitted by the fertile BUS during the life and decomposition of marine algae (Andreae, et al., 1995; Formenti et al., 1999; Zorn, et al., 2008). An example of the high levels of *chlorophyll a* released by these colonies are indicated in the example of 11 June 2017, in Figure 1-14. The emissions from phytoplankton in the BUS peaks in April, August and December according to observations between 2000 and 2012 by Louw et al. (2016). The CLAW hypothesis, proposed by Charlson et al. (1987), suggests that primary dimethyl sulphide (DMS) emissions from phytoplankton are oxidised to form sulphates, which are good CCN, thereby

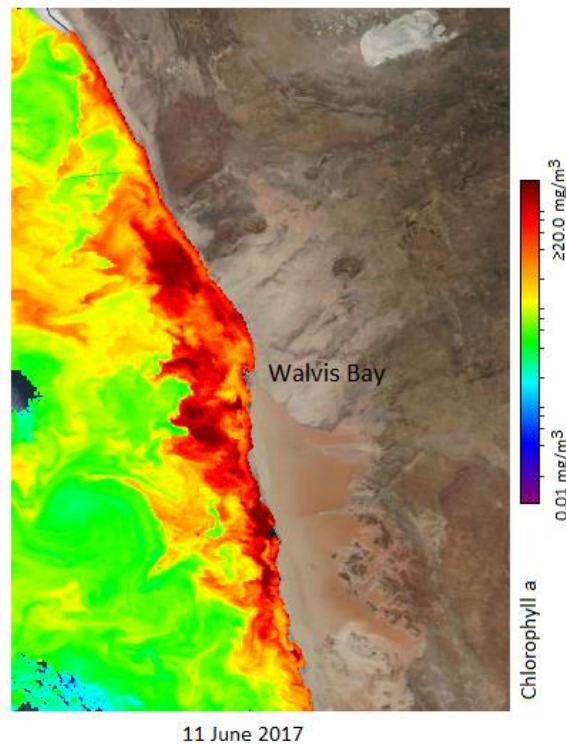


Figure 1-14. Corrected reflectance true colour image with chlorophyll a made by MODIS (Platnick et al., 2015) on 11 June 2017, showing increased chlorophyll a, indicating colonies of marine phytoplankton along the coast.

impacting cloud character and regional climate. Subsequent studies have supported this hypothesis (Andreae et al., 1995; Zorn et al., 2008).

Other biogenic emissions in the region are from ammonia emissions from fur seal colonies, of which there are 24 along the western coasts of South Africa and Namibia. Ammonia emissions from the Cape Cross Colony, approximately 150 km north of Walvis Bay, were measured by Theobald, et al. (2006) at a variety of ground-based stations around the site and showed mean concentrations between the site and 26 km from the site that ranged from 354 to $0.01 \mu\text{g m}^{-3}$. Unsurprisingly, the contribution of these natural sources is very hard to quantify due to the high variability and uncertainties in emissions, which extends into uncertainties in atmospheric composition and radiative forcing (Myhre et al., 2013).

1.5.7.2. Biomass burning aerosols

The southern African dry season, from mid-May to mid-October, is associated with extensive BB across the central subcontinent (Formenti et al., 2003a; Haywood et al., 2003b). The extent of the burnt areas, not limited to the biomass burning season, is given in Figure 1-15. Easterly transport results in the outflow of BB aerosols over the west coast (Piketh et al., 2002; Swap et al., 2003), as seen in Figure 1-16. Smoke from southern African BB consist of up to 10% minerals, such as, organic and black carbon, ammonium fine potassium-salts, such as potassium chloride and potassium and calcium-bearing sulphates and nitrates (Andreae et al., 1998; Andreae and Merlet, 2001; Feng et al., 2013; Formenti et al., 2003a, 2003b; Gordon et al., 2018; Li et al., 2003; Maenhaut et al., 1996). Biomass burning particulates range in diameter from 20 nm to 1.5 μm , are concentrated around 100

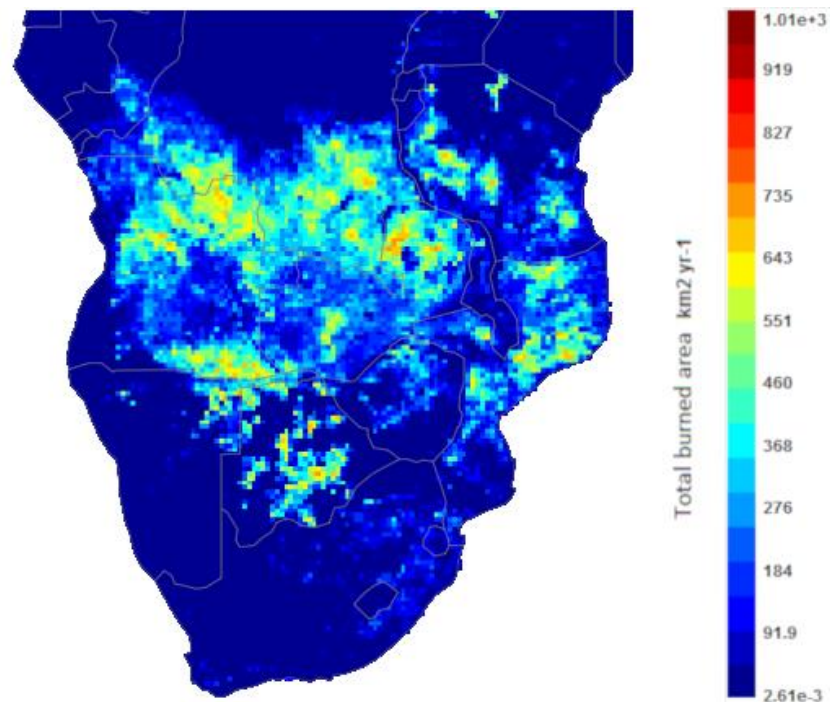


Figure 1-15. Total burned area between 2010 and 2015 over southern Africa, from publicly available Global Fire Emissions Database (GFEDv4) 0.25×0.25 data (Randerson et al., 2017).

to 600 nm and have a residence time of approximately 5 days (Ramanathan et al., 2001). Formenti et al. (2002) showed a bimodality in the volume size distribution of BB aerosols at different sites in southern Africa.

Black carbon is produced during combustion and is a relatively fast ageing species with a lifetime of several days to weeks (Li et al., 2003; Magi and Hobbs, 2003). BC is one of the most effective light-absorbing aerosols from both incoming and outgoing radiation, especially when released by flaming, as compared to smouldering, fires (Li et al., 2003). Elevated smoke plumes in southern Africa have been studied in field campaigns across southern Africa and by satellite observations as reported in publications by Lindesay et al. (1996, SAFARI-92), Andreae et al. (1998), Bergstrom et al. (2003), Eck et al. (2003), Formenti et al. (2003a), Haywood et al. (2003b), Swap et al. (2002, SAFARI-2000), Costantino and Bréon (2013), Zuidema et al. (2016, Nasa-ORACLES) and Formenti et al. (2019, AEROCLO-SA).

Absorbing aerosols above stratocumulus clouds, as can be seen in satellite imagery from MODIS in Figure 1-16, result in a thickening of- and increase in low-cloud cover (Wilcox, 2010). These aerosols may also impact cloud top height by resulting in a strong temperature inversion and a stable layer above the cloud, thus preventing convection and leading to a build-up of moisture within the BL (Adebiyi and Zuidema, 2016; Costantino and Bréon, 2013; Johnson et al., 2004; Muhlbauer et al., 2014). This constitutes a negative semi-direct forcing or surface cooling effect (Hansen et al., 1997; Johnson et al., 2004). Light-absorbing aerosols within the BL and below the clouds result in positive semi-direct forcing or a surface warming effect (Hansen et al., 1997; Johnson et al., 2004) and may lead to the evaporation of cloud droplets. The uncertainties arise in quantifying the magnitude of impacts on forcing. In a study using detailed global models, Myhre et al. (2013) found higher uncertainties particularly related to BC as compared to sulphates in smoke aerosols transported over the southeast Atlantic Ocean. This was explained by the variability in BC effects related to the relative location of these particles in the vertical.

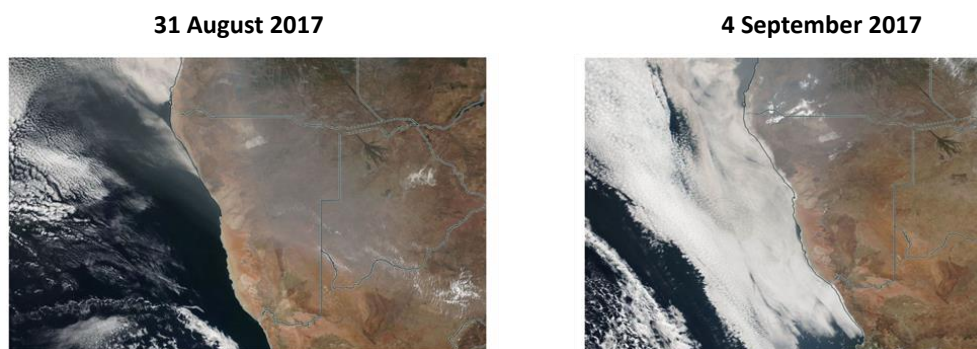


Figure 1-16. Corrected reflectance of true colour observed by MODIS (Platnick et al., 2015) instruments show the presence of smoke from southern Africa on 31 August 2017 and 4 September 2017.

1.5.7.3. Mineral dust

Rocky outcrops, dry river valleys and river mouths (fluvisol soil types), salt pans (solonchaks and solonetz soil types) such as Etosha and Makgadikgadi, Namib dunes, untarred roads and mining activities are some examples of the sources of regional windblown dust found in Namibia (e.g. Annegarn et al., 1983; Dansie et al., 2017; Eckardt and Kuring, 2005; Eltayeb et al., 1993; Prospero et al., 2002; Vickery et al., 2013; Washington et al., 2003). A map of the dominant soil types across Namibia is given in Figure 1-17. Under high wind speeds and favourable wind directions, geological parent materials undergo mechanical and chemical abrasion by loose sediment that is liberated from the surface as windblown or aeolian dust (Dansie et al., 2007; Vickery and Eckhardt, 2013). According to the theory of dust production described by Gillette and Goodwin (1974), particles with radii of 20 to 50 μm are liberated first, i.e. dune sand, regosols, arenosols and gypsisols. These large particles do not remain suspended for long and quickly settle back to the surface all the while colliding with other particles, resulting in size fractionation of liberated soils (Annegarn et al., 1983) to radii typically in the order of 100 nm to $>10\mu\text{m}$ for aeolian dust (Boucher, 2013). Formenti et al. (2014) refer to this as a “transfer function”. Ramanathan et al. (2001) suggested that crustal aerosols are generally inert and have a residence time of approximately 4 days, making them relatively simple to assign to a source due to limited chemical transformations.

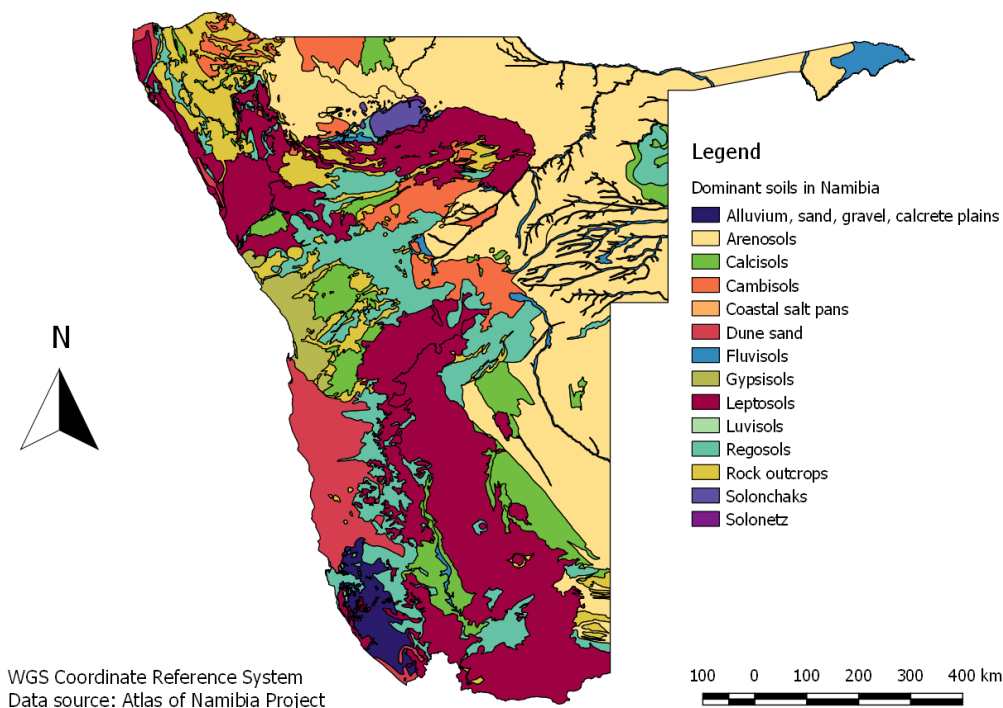


Figure 1-17. Dominant soil types in Namibia. Data source: Atlas of Namibia project (Mendelsohn et al., 2002).

MERRA-2 data of the seasonal average density of dust in the column of air, presented in Figure 1-18, confirms significant dust emissions from the Namibian coast (Prospero et al., 2002; Vickery et al., 2013; Washington et al., 2003). The significant transport of mineral dust into the coastal waters

offshore of Keetmanshoop and Lüderitz by berg winds (Tlhalerwa et al., 2005) was described in section 1.5.6. Dansie et al. (2017) also showed significant contributions to aeolian dust from ephemeral river valleys from the Namib desert to the north of HBAO. The load and character of mineral dusts arriving at the HBAO will contribute new data to the body of knowledge. This is important because coarse fraction dust can act as CCN when coated with a soluble material (Boucher, 2013) and the specific mineralogy and particle size of wind-blown dust impact the regional and global radiation budget (Di Biagio et al., 2017; Caponi et al., 2017), atmospheric chemistry and biological productivity in the oceans (Chester and Jickells, 2012).

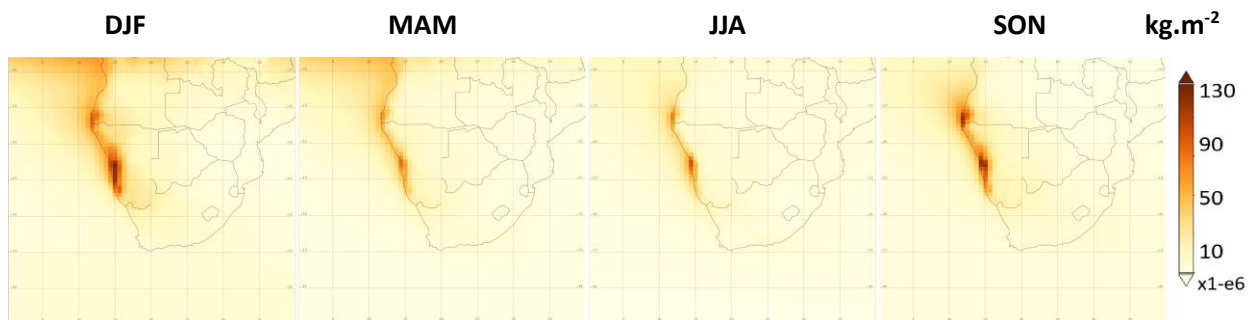


Figure 1-18. The seasonally averaged dust column mass density in kg m^{-2} on a $0.5 \times 0.625^\circ$ resolution grid for 2004 to 2015 from MERRA-2 data (GMAO, 2015d).

The input of minerals, such as iron, zinc and manganese, and nutrients, such as nitrogen and phosphorous, are essential for the growth and reproduction of phytoplankton (Chester and Jickells, 2012; Dansie et al., 2017; Jickells et al., 2005). Some trace metals contained in mineral dust (chromium, copper, nickel, manganese, or zinc) play a biological role in enzymes and as structural elements in proteins (Morel and Price, 2003). Excessive heavy metal concentrations are, however, detrimental and, as an example, the input of biologically available forms of copper into the ocean has been found to inhibit plankton growth in laboratory studies (Paytan et al., 2009) and over the western Mediterranean (Jordi et al., 2012). This study will provide invaluable data on the temporal variability in character and concentrations of mineral dust transported over the coastal site.

1.5.7.4. Anthropogenic aerosols

The aerosol emissions from commercial shipping along the Cape of Good Hope Sea Route have been investigated by several authors, including Hobbs et al. (2000), Zhang et al. (2010), Tournadre (2014) and Chance et al. (2015), for steam- and diesel-powered ships using low-grade diesel or navy distillate fuel. These emissions include sulphates and nitrates (Hobbs et al., 2000; Zhang et al., 2010) and heavy metals (Chance et al., 2015; Viana et al., 2009). Those aerosols emitted by steam-turbines had radii of $\sim 0.02 \mu\text{m}$ and those emitted by the diesel ships had larger radii of $\sim 0.03\text{--}0.05 \mu\text{m}$.

Namibia is not highly industrialised (Government of the Republic of Namibia, 2011), unlike the South African Highveld where anthropogenic fossil fuel combustion releases high concentrations of fine elemental sulphur and iron (Piketh et al., 2002) year-round. The subsequent formation and transport

of aerosols from industrial activities over the South African Highveld have been studied by Piketh et al. (1999a and 1999b) and Freiman and Piketh (2003). The seasonally averaged sulphate mass density over southern Africa is given in Figure 1-19, which clearly shows major contributions of sulphate over the subcontinent and Namibian coast.

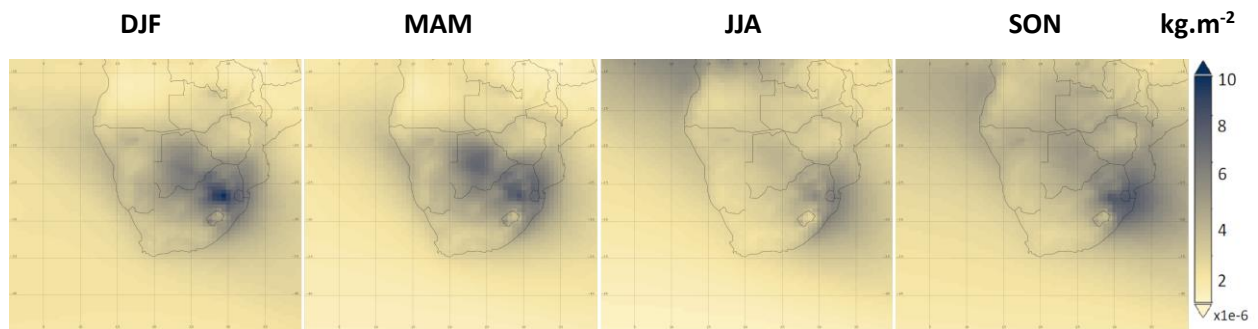


Figure 1-19. Seasonal averages of SO_4^{2-} column mass density in kg m^{-2} on a $0.5 \times 0.625^\circ$ resolution grid for 2004 to 2015 from MERRA-2 data (GMAO, 2015d).

This chapter presented an in-depth literature review on atmospheric aerosols and meteorology over the Namibian coast and southern Africa. This background context informed the motivation for the research, aims and objectives intended to fill the gap in scientific knowledge. This chapter showed that HBAO offers a unique opportunity for collecting and studying aerosol composition and interactions with meteorology over the Namibian coast. Furthermore, the characterisation of aerosols, identification of potential sources and their variability and links to transport pathways undertaken in this research will provide invaluable input for interactive aerosol parametrisations for this region.

Chapter 2

Research methodology

This chapter presents the research design and methodology of this study. The geographical setting in the coastal desert environment is presented along with the location of the aerosol observatory. The chapter then goes on to discuss the methods of collection, processing and analyses of radiosonde and Global Positioning System-Radio Occultation (GPS-RO) data of the vertical atmospheric structure. The vertical extent of interest is limited to conditions in the troposphere where aerosols are produced and transported. Synoptic charts and air mass back-trajectories are used to determine the dominant transport pathways and analyse links to aerosol character and load, and local wind speed and -direction. This is accompanied by a discussion of the availability, use and limitations of these data types. Then the methods for collecting, analysing and quantifying aerosols are presented along with a discussion on the instruments housed at the observatory, the measurements made and related uncertainties. Finally, the methods employed to ensure reproducible, robust statistical analyses and source apportionment are presented. The research design framework, outlining the strategies for collecting, processing and analysing the different data to address the three research objectives, is summarised in Figure 2-1.

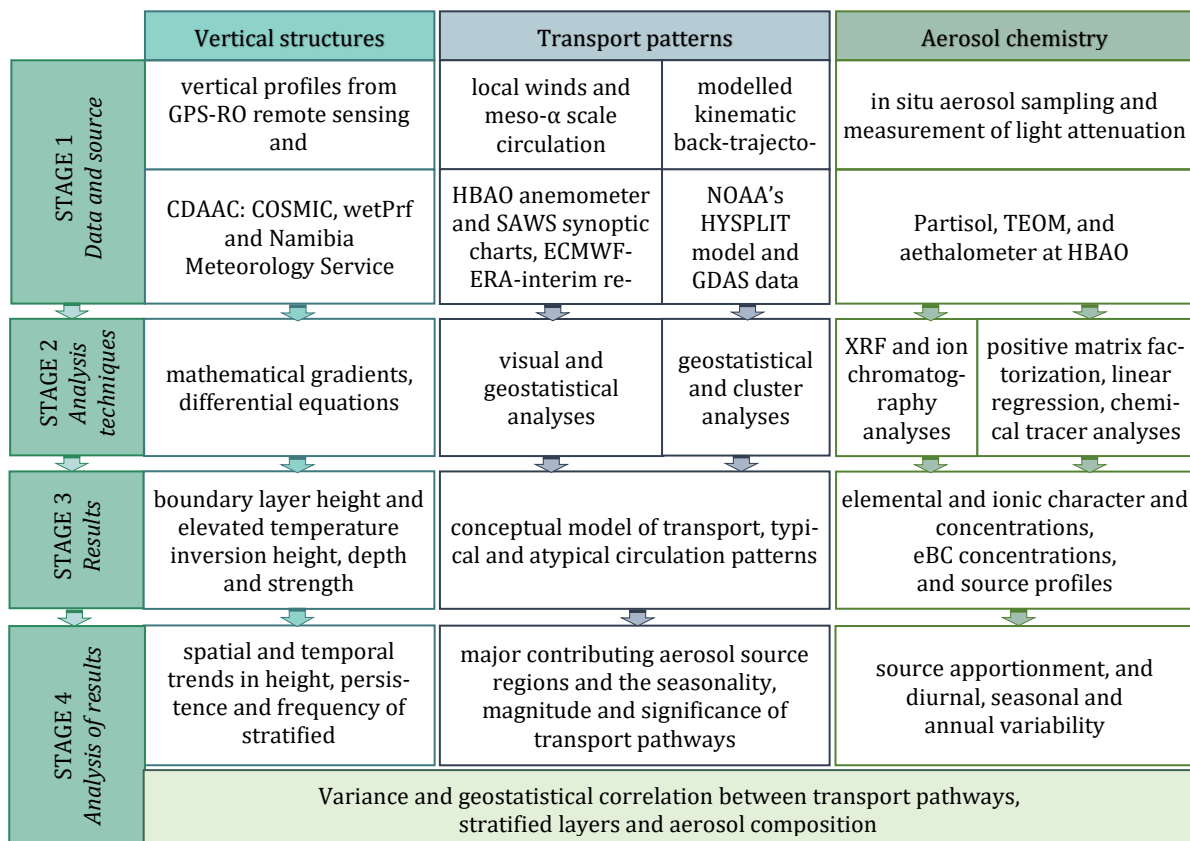


Figure 2-1. Flow diagram of the stages in this research design framework.

2.1. Analysis of atmospheric vertical structure

2.1.1. Radiosonde measurements

The radiosonde data used for this study were from an iMet-2-AA radiosonde instrument (<https://intermet.co/radiosondes/imet-2/>) released at Walvis Bay airport (22°58'43.5"S 14°38'28.4"E, 97m above mean sea level) by the Namibia Meteorology Service. A total of 335 soundings for 2015 were included in the analysis. These were launched almost daily at 10h00, with the exception of a few launched at 09h00 local time. Local Namibian time is UTC +1 in the winter between the first Sunday in April to the first Sunday in September. For the rest of the year, daylight savings time (UTC +2) is used. The instrument was operated according to the latest available World Meteorological Organization's (WMO) *Guide to Instruments and Methods of Observation* (2017). Standard variables measured by the radiosonde and used for this research were temperature, pressure, relative humidity, wind speed and - direction, and height above ground level (agl). Radiosonde measurements were all interactively quality controlled by the instrument to remove any erroneous values that may have resulted from automated statistical regression (WMO, 2017).

Temperature measurements were made by a bead thermistor. Humidity measurements were conducted with a thin film that has a Capacitor (E+ E) sensor, and calculated by the Bolton (Goff Gratch) formula (Nash et al., 2010). The design of the iMet radiosonde housing around the sensors has been optimised to minimise systematic errors, specifically radiation effects on temperature, above 15 km (dry bias), as well as sensor limitations to accurately measure temperature and humidity in a cloud (wet bias) (Wang and Zhang, 2008; Wang et al., 2013). Corrections were applied by the instrument software to account for the remaining solar radiation effects (Nash et al., 2010). A breakdown of the solar calibrations applied by the manufacturer is available upon request at <https://intermet.co/radiosondes/imet-2/>. As compared to 12 other radiosonde manufacturers, daytime temperature measurements made during the WMO Radiosonde Intercomparison in Yanjiang, China by the iMet was positively biased by a maximum of 0.3 K at 8 km (Nash et al., 2010). No corrections to the retrieved relative humidity were applied by the manufacturer. Random observational errors, which cannot be corrected for, include radiosonde drift of up to 200 km due to vertical winds during the instrument's ascent (McGrath et al., 2006; Seidel et al., 2011). Standard radiosonde datasets do not include uncertainty estimates. The inherent bias and limitations of the instruments were taken into account when analysing the stability indices from radiosonde data.

Preston-Whyte et al. (1977) found the lowest subsidence inversion, which indicated boundary layer height (BLH) in the absence of a surface inversion over the Benguela current, exceeding a height of 500 m. Considering this and to exclude surface inversions from the analyses, the profiles were analysed for BLH between 400 m and 2500 m. Refer to section 3.3.2. for the specific indices used to identify BLH.

2.1.2. Satellite measurements

Limb soundings of the atmosphere by radio occultation (RO) of signals from low earth orbiting GPS satellites are used to calculate the bending angle of the signal as it changes phase and amplitude with its passage through the atmosphere. GPS data provide stable, long-term measurements for weather and climate analyses (Ao et al., 2012; Ho et al., 2009; Lin et al., 2010; Von Engel and Teixeira, 2013) and have been used extensively in astronomical applications with other GPS satellites to retrieve self-calibrating, near-global coverage of high spatial resolution observations of vertical atmospheric profiles (Karayel and Hinson, 1997; Kursinski et al., 1997, 2001; Rocken et al., 2000).

In this study, GPS-RO observations over Namibia and offshore in the southeast Atlantic Ocean between 2007 and 2017 were used to analyse the long-term variability of temperature inversions and stable layers, particularly above the low-level stratocumulus clouds in the region. The sampling frequency over the area of interest is given in section 3.2.1. These observations were made by the Constellation Observing System for Meteorology, Ionosphere, and Climate (COSMIC) mission, which has been in operation since 2006 (Anthes et al., 2008). Quality checks are made at retrieval so that observations of systematic negative refractivity biases and multipath propagation of the signal can be corrected by retrieving bending angle profiles by wave optics (Ao et al., 2003; Xie et al., 2010). Data are further post-processed (*cosmic*, May 2014 - 2017) and re-processed (*cosmic2013*, 2007 - April 2014) (Sokolovskiy et al., 2006) and made publicly available at the Data Analysis and Archive Centre (CDAAC: <http://cosmic-io.cosmic.ucar.edu/cdaac/index.html>, <https://cdaac-www.cosmic.ucar.edu/cdaac/status.html>).

Observations of the refractivity of the COSMIC GPS-RO signal were processed by dry and wet retrieval algorithms. The wet retrievals were used in this thesis. Wet retrieval algorithms (O'Sullivan et al., 2000) assume that temperature is quadratically related to the natural logarithm of pressure documented in O'Sullivan et al. (2000). This was tested and validated by Shyam (2019). Processing by CDAAC also involved applying 1-D var moisture corrections from the European Centre for Medium-Range Weather Forecasts (ECMWF) to the signal's bending angle, which compensates for the high sensitivity of the signal to moisture (Hande et al., 2015; Ho et al., 2015; Kuo et al., 2004; Seidel, 2010). Finally, the Able inversion (Sokolovskiy, 2001) was applied to the bending angle, which produced the refractivity profile. From here, following Bean and Dutton (1968) and assuming a neutral atmosphere, the temperature, pressure, and moisture of the atmosphere were estimated as follows:

$$N = 77.6 \frac{P}{T} + 3.73 * 10^5 \frac{P_w}{T^2}, \quad (\text{Equation 2-1})$$

where T is temperature, P is pressure and P_w is vapour pressure. In the tropical, lower-troposphere, these observations have a vertical resolution of approximately 100 m (Guo et al., 2011; Hande, 2015). Due to the occultation angle, the horizontal resolution in the troposphere is approximately 160 km (Sun et al., 2013).

Uncertainties are mostly due to the sensitivity of the GPS signal to atmospheric moisture resulting in increased refractivity. Ao et al. (2003) reported refractivity biases of -10% below 2 km, and Alexander et al. (2014) reported approximately -0.2% below 8 km. The passage of a signal through cloud may cause super-refraction, and even with the applied corrections, once the signal has been super-refracted, no reliable information about the atmospheric structure can be collected beyond this point (Sokolovskiy, 2003). The result is that often GPS signals are unable to penetrate to the surface. Additionally, uncertainties in variables, such as temperature, which were derived from the refractivity profiles, are a direct result from moisture content (Alexander et al. 2014; Kursinski et al., 1997; Sokolovskiy, 2003). Despite post- and re-processing procedures, very high-temperature gradients over 30°C/100 m were found in only four observations of all retrieved observations over the region between 2007 and 2017 and were excluded from further analyses.

Other observational errors, tested by Chen et al. (2011), are the seasonal, vertical and latitudinal dependence of observational errors of the COSMIC GPS-RO profiles. Chen et al. (2011) showed that observational errors in refractivity across latitudes are greatest in the winter due to greater zonal variability in specific humidity. Within the troposphere, Chen et al. (2011) showed an almost linear decrease in observational errors with height.

With the limitations and uncertainties in mind, GPS-RO data were used to identify the diurnal and seasonal variability in temperature inversions and stable layers between 2007 and 2017 over Namibia and the southeast Atlantic Ocean. Refer to section 3.4.1. for the comparison and validation of GPS and radiosonde data.

2.1.3. Stability indices

The specific stability indices used in these analyses were selected because they were deemed most useful to describe the state of equilibrium in the Namibian atmosphere, based on previous literature findings and described in section 1.5.5.1. Stability is best described by the rate of change of the measured air temperature with height as compared to the standard dry and moist adiabatic lapse rates. Statically stable layers, as seen in Figure 2-2, are not limited to inversions, and include any layer of air where the measured lapse rate is smaller than the dry adiabatic lapse rate (DALR) of 0.98°C / 100 m (Bohren and Albrecht, 1998; Tyson and Preston-Whyte, 2014).

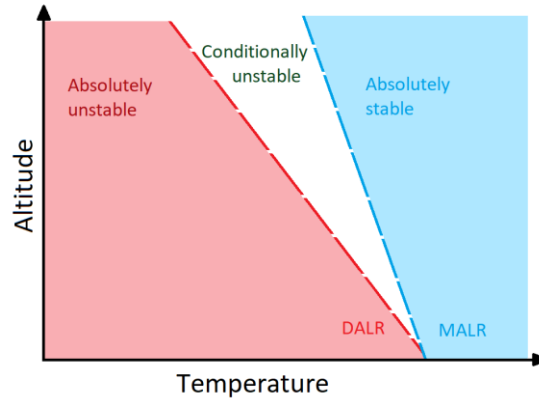


Figure 2-2. Static stability of the atmosphere indicated by the relation of the environmental lapse rate to the dry (DALR) and the moist adiabatic lapse rates (MALR). Adapted from Tyson and Preston-Whyte (2014).

Temperature is an important indicator of stability, and across southern Africa, anticyclonic circulations tend to form subsidence-induced temperature inversions. For both radiosonde and GPS data, the environmental lapse rate was calculated by

$$\text{Environmental lapse rate (}^{\circ}\text{C/100 m)} = \frac{T_{p2} - T_{p1}}{Z_{p2} - Z_{p1}} * 1000, \quad (\text{Equation 2-2})$$

where Z is height above ground level (agl). Temperature inversions were identified by a negative lapse rate between 2 and 10km. Inversion depth was calculated by subtracting the height at the top of the inversion from the height at its base. Inversion strength was calculated as the total change in temperature through the depth of the inversion.

As described in section 1.5.5., different definitions of BL top may be assumed, based on the regional conditions. The first definition of BLH considered for Walvis Bay was that of a statically stable BL (discussed in section 1.5.5.3.), which was approximated by using the bulk Richardson number (R_N) method given by Hanna (1969) and following the example of Korhonen et al. (2014).

$$BLH_{R_N} = R_N \frac{(u_h^2 + v_h^2)}{(g/\theta_{v_0}) * (\theta_{v_h} - \theta_{v_0})} \quad (\text{Equation 2-3})$$

In Equation 2-3, BLH is the point where the critical number is greater than zero (Korhonen et al., 2014; Sørensen et al., 1996). $u(v)$ denotes the change in horizontal (vertical) wind components across the same layer at altitude (h), and the surrounding air (o) and g is gravitational acceleration. Potential temperature (θ) was calculated according to Poisson's equation (Bohren and Albrecht, 1998) for each radiosonde as

$$\theta = T \left(\frac{P_o}{P} \right)^{\frac{DALR}{c_p}}, \quad (\text{Equation 2-4})$$

where T is temperature (K), P is pressure (hPa), P_o is pressure at 1 000 hPa standard pressure level, and c_p is the heat capacity of dry air, which together come to an exponent of $2/7$.

A second useful indicator of stability is the point where virtual potential temperature (VPT) at a point in the profile is the same as at the surface (Seidel et al., 2010), approximated with

$$VPT = \theta \times (1 + 0.61 \cdot w). \quad (\text{Equation 2-5})$$

The mixing ratio (w) was approximated with

$$w = \left(0.62197 \times \frac{e_s}{P - e_s}\right) * \frac{RH}{100}, \quad (\text{Equation 2-6})$$

where RH is relative humidity and saturation vapour pressure (e_s) was approximated by using reference values for the enthalpy of vapourisation (sublimation) at 0°C for each measurement over water (ice) when the temperature was over (under) 273.15 K and at a reference at 0°C saturation vapour pressure (e_{so}) of 6.11 hPa, as follows:

$$\ln e_{so}^{e_s} = 19.83 - \frac{5417}{T}, \text{ or} \quad (\text{Equation 2-7})$$

$$\ln e_{so}^{e_s} = 22.49 - \frac{6142}{T}. \quad (\text{Equation 2-8})$$

The third definition was that of a BL topped by a surface-based inversion (discussed in section 1.5.5.5.) (Tyson et al., 1977). The first two definitions provide for more turbulent BLs, whereas temperature inversions result in the most stable BL conditions. These BLHs were identified as the lowest point in the profile where the temperature gradient changed from negative to positive.

A fourth definition was specific to a cloud-topped or decoupled BL (discussed in section 1.5.5.4.), calculated as the point of the minimum gradient of refractivity, as in Equation 2-1. This is generally used for GPS data (Ao et al., 2012) but has also been used on radiosonde data for comparative studies (Ho et al., 2015). Vapour pressure (Pw , hPa) was calculated as follows:

$$Pw = e_s(Td). \quad (\text{Equation 2-9})$$

Dew point temperature (Td) was approximated using T and relative humidity (r) from the August-Roche-Magnus formula and the recommended coefficients detailed in Alduchov and Eskridge (1996), as follows:

$$Td = 243.04 \times \frac{\ln\left(\frac{r}{100}\right) + \left(\frac{17.625 \cdot T}{243.04 + T}\right)}{17.625 - \ln\left(\frac{r}{100}\right) - \left(\frac{17.625 \cdot T}{243.04 + T}\right)}. \quad (\text{Equation 2-10})$$

2.2. Analysis of air mass transport

The section that follows presents the methods for data collection and processing, applicability and limitations to weather maps and kinematic trajectory calculations for analysing the transport of air masses.

2.2.1. Wind speed and -direction

Measurements of local wind speed and -direction were made with two anemometers located on the rooftop: First, a Campbell Scientific 05103 (Figure 2-3), which was then replaced with a Vaisala WXT530

from September 2017 onwards. Measurements were stored as five-minute averages. These averages were plotted on wind roses to describe the variability of winds that corresponded to each nine-hour filter sampling period, which is described in section 2.3.2.



Figure 2-3. Campbell Scientific 05103 anemometer on the rooftop of HBAO.

2.2.2. Synoptic weather maps

Atmospheric circulation over the area of interest is characterised by its location in the low latitudes (0° - 30° S), tropics (0° - 23.5° S) and sub-tropics (23.5° - 40° S). Hand-drawn synoptic maps covering the region of interest were obtained from the website archives of the South African Weather Service (SAWS, 2017). These synoptic maps capture meso- α pressure at the surface and show locations of high- and low-pressure systems and also frontal zones. The limitations of synoptic charts lie in the fact that they are drawn by meteorologists and have low spatial resolution, both horizontally and vertically. These maps were only used for describing the position and subsequent airflow in these macroscale circulation patterns during sampling periods.

2.2.3. Kinematic back-trajectory modelling

To analyse the long-range transport patterns and links to aerosol composition, three-dimensional kinematic back-trajectories were calculated using the National Oceanic and Atmospheric Administration's (NOAA) HYbrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT; Stein et al., 2015), run through the Air Resources Laboratory (ARL) (Stein et al., 2015) Real-time Environmental Applications and Display sYstem (READY) software (Rolph et al., 2017). This model uses a hybrid calculation method between the Lagrangian and Eulerian approaches to model atmospheric transport (Stein et al., 2015) through the depth of the atmosphere and on a latitude-longitude grid. The Lagrangian approach to trajectory modelling uses a moving frame of reference to calculate the advection of an air mass and allows for the realistic representation of turbulence in the planetary BL. This approach also satisfies the well-mixed criterion, which assumes that air masses that have undergone uniform initial mixing within the BL will remain well-mixed when transported. The Eulerian approach uses a fixed frame of reference to calculate the changing concentrations as the air mass moves over the grid (Stein et al., 2015).

Trajectories cannot reproduce the exact movement of air masses through the atmosphere; however, continued improvements in modelling capabilities, data resolution and reanalysis methods mean that trajectories effectively model transport pathways on meso- α scales (Chance et al., 2015; Cheng et al., 2013; Nyanganyura et al., 2008; Stohl et al., 2002; Tshehla and Djolov, 2018). Trajectories are unable to model smaller scale parameters such as jet streams, rainout and low inversion layers or micro-scale electrostatic forces generated between individual particulates (heightened effects in conditions of higher relative humidity; He et al., 2019), and these interactions are therefore approximated in the model and by the meteorological data (Stohl, 1998; Tshehla and Djolov, 2018). Trajectories have proven useful in classifying source-receptor relationships so long as the limitations and uncertainties are properly considered (Beaver et al., 2008; Borge et al., 2007; Brankov et al., 1998; Dorling and Davies, 1995; Piketh et al., 1999a; Rozwadowska et al., 2010; Sciare et al. 2000).

Three-dimensional wind fields and meteorological conditions from numerical weather prediction models (NWP, Kimura, 2002) are incorporated into the hybrid trajectory calculations. Naturally, the accuracy of these calculations is greatly dependant on the quality and resolution of these data. The National Centre for Environmental Prediction's (NCEP) Global Data Assimilation System (GDAS) (Saha et al., 2006) model produces six-hourly wind field reanalysis data on mandatory pressure levels in a gridded 3D model by combining surface, hybrid sigma-pressure level data from airborne and spaceborne measurements. Two resolutions are available; $1^\circ \times 1^\circ$ horizontal resolution with 23 pressure surfaces (20-1000 hPa) and $0.5^\circ \times 0.5^\circ$ horizontal resolution with 55 pressure levels. The GDAS0.5° has the advantage of higher vertical and horizontal resolution as compared to GDAS1° (Su et al., 2015) but the disadvantage is that it is in hybrid-sigma coordinates and does not include vertical velocity in the dataset. The vertical velocity for GDAS0.5° is mathematically resolved through the divergence method and is therefore solely based on modelled data (Draxler et al., 2016).

The use of modelled turbulence and vertical velocity data as the driving meteorology for trajectory models presents a major source of uncertainties (Su et al., 2015). Processes such as turbulent mixing, convection, advection and precipitation influence the vertical and horizontal movement of air on scales smaller than what trajectory models can resolve (Stohl, 1998). This is an inherent source of uncertainty in trajectory calculations (Su et al., 2015). These uncertainties increase when strong convection is not reflected in data for horizontal wind speeds, but in the absence of deep convection, such as over the Namibian coast and western southern Africa, the modelled vertical velocity was deemed suitable for the region of interest based on previous studies (Crawford et al., 2017; Fuelberg et al., 1996; Nyanganyura et al., 2008; Stohl, 1998).

2.3. Aerosol chemical composition

2.3.1. Aerosol black carbon measurements

Measurements of equivalent black carbon (eBC) concentration were performed at HBAO to evaluate the level of background pollution at the site. Measurements were performed by a single-wavelength

aethalometer (model AE-14U, Magee Sci., Berkeley, CA, USA), shown in Figure 2-4, operating at 880 nm at five-minute time resolution and stored on a data logger (model CR-1000, Campbell Sci. Ltd.).

Air was sampled from a PM₁ inlet (BGI Inc., Waltham, MA) at a flow rate of 3.5 (± 0.1) L min⁻¹. The inlet was located on the rooftop of the sampling station and connected to the instrument by a straight stainless-steel pipe of approximately 4 m in length. The exact sampling dates are given in section 4.2.1.

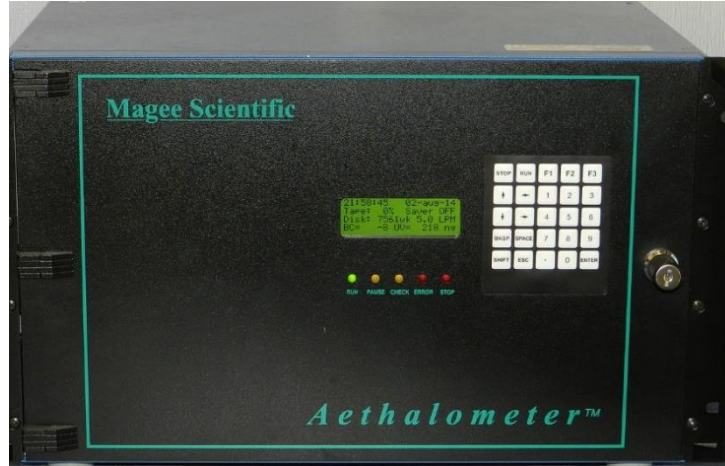


Figure 2-4. The single-wavelength aethalometer (model AE-14U, Magee Sci., Berkeley, CA, USA) operating at HBAO.

The operating principle of the aethalometer consists of measuring optical attenuation of light (ATN) through a pure quartz fibre tape. Black carbon is effective at absorbing all wavelengths of light, although it is most efficient in the near-infrared portion of the spectrum, justifying the measurement of ATN at this wavelength (Kirchstetter et al., 2004; Caponi et al., 2017). The relationship between the ATN by equivalent eBC particles deposited on a filter and their mass concentration (expressed in µg m⁻³) is based on the Lambert–Beer law describing light extinction through a medium, and requires various empirical correction terms. The equation is

$$eBC = \frac{1}{MAC_{BC}} \left(\frac{1}{C \cdot R(ATN)} \right) \left(\frac{A}{V} \frac{\Delta ATN}{\Delta t} \right), \quad (\text{Equation 2-11})$$

where **MAC_{BC}** is the mass absorption efficiency of eBC (units of m² g⁻¹). The **C** parameter considers the multiple scattering effects of aerosols embedded in the filter and the filter fibres. The **R(ATN)** term accounts for the shadowing effect when aerosols accumulate on the filter. The specific units of the chosen values for the **C** and **R(ATN)** are detailed in Collaud Coen et al. (2010), Saturno et al. (2017) and Weingartner et al. (2003) and described in section 4.2.1. **A** denotes the area of the filter covered by aerosols and **V** the volumetric flow rate (1 m³/hour for 9 hours). The $\frac{\Delta ATN}{\Delta t}$ term describes the change of attenuation with time.

Uncertainties in the conversion of eBC to mass concentrations are related to the chosen input parameters and correction factors. These parameters and assumptions made are described in detail in section 4.2.1. The original dataset was screened to eliminate spikes and peaks lasting less than 2 hours, generally associated with open fires for barbecuing meat.

2.3.2. Aerosol sample collection

Samples of PM₁₀ aerosols were collected in 2016 and 2017 to characterise chemical composition, quantify mass concentrations and apportion the main local and distant sources and associated transport pathways. A certified PM₁₀ inlet (Rupprecht and Patashnick, Albany, New York, USA) is connected by straight stainless-steel pipes (to avoid particle losses) to an automated sequential air sampler (model Partisol Plus 2025i, Thermo Fisher) operated at a flow rate of 16.67 L min⁻¹. The inlet and Partisol sampler are shown in Figure 2-5.



Figure 2-5. The PM₁₀ inlet on the rooftop of the HBAO connected by a straight stainless steel pipe to the Partisol in the room below.

The Partisol collected aerosol samples on nucleopore polycarbonate filters (47-mm) (in Figure 2-8) with 1- μ m diameter straight, cylindrical pores. Polycarbonate nucleopore filters are not prone to water absorption, but to prevent clogging of pores in the humid coastal boundary layer (BL), the Partisol cabin is warmed and filters are kept dry. Furthermore, after sampling and during transport, filters are stored in a cool, dark place to minimise losses by volatile species such as ammonium, nitrate or other organics (International Atomic Energy Agency, 1997).



Figure 2-6. Sampled nucleopore filters ready for analysis.

To evaluate potential contamination on the filters, a blank filter was also collected during sampling by the Partisol, which passed through the Partisol directly into the sampling magazine. These were then used to determine the detection limits for different species on the filters, described below.

2.3.3. Aerosol sample analysis

All the filter samples collected at HBAO were analysed at the Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) in France. The polycarbonate filters were first analysed with Wavelength-dispersive X-ray fluorescence (WD-XRF) to yield the mass concentrations for 24 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Pb, Nd, Cd and Ba). The concentrations of 15 water-soluble ions (propionate, formate, acetate, methanesulfonic acid (MSA), Cl⁻, Br⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, oxalate, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) were obtained by Ion Chromatography.

The polycarbonate membranes are well suited to these analyses because they collect aerosols on the upper surface, scatter very little of the X-ray radiation due to their very low trace metal content, and have minimal interference with the characteristic radiation absorbed or generated by the particulates (International Atomic Energy Agency, 1997).

The working principle of WD-XRF is described in Arai (2006) and Watson et al., (1999). The process involves bombarding a sample with X-rays, which excite electrons from the inner orbital that emit characteristic secondary X-rays. The wavelengths (λ) of X-ray photons emitted from different elements are associated with characteristic gaps in the atomic absorption spectrum. The emitted X-rays are counted by a photon counter (Watson et al., 1999). The WDXRF technique uses individual crystals, whose structures are composed by regularly repeating lattice planes in an isometric system, to select the energy of the fluorescent X-ray characteristics of each element based on the relationship with the Bragg diffraction angle (Kawahara and Shoji, 2006), written as follows:

$$2d_{hkl} \sin(\theta_{hkl}) = \lambda, \quad (\text{Equation 2-12})$$

where d^{hkl} is the distance between lattice planes, denoted by the Miller indices (hkl) and a is the lattice parameter.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \quad (\text{Equation 2-13})$$

The WD-XRF apparatus at LISA is a PW-2404 spectrometer (Panalytical), shown in Figure 2-7.



Figure 2-7. Wavelength X-ray dispersive instrument at LISA.

The calibration of the XRF apparatus was conducted with certified mono- and bi-elemental standard samples by Micromatter Inc. (attached in Appendix D-1). To account for relative analytical uncertainty, the net peak intensity for different elements is multiplied by the sensitivity factors (approximately 5%) determined during calibration to give the raw masses in $\mu\text{g}/\text{filter}$ (Watson, 1999).

Each chemical species was analysed three times by this non-destructive procedure, and variable components in the XRF analyser, such as the collimator, voltage, crystal and detector, were changed according to the group of species being measured (Kawahara and Shoji, 2006; Watson, 1999).

The measured concentrations were blank-corrected to account for the contribution of the filter composition to the XRF measurements and any contamination. The blank filters were analysed and any raw masses below the quantification limit (QL) were excluded from the dataset. QL was calculated as

$$QL = 10 \times \sqrt{sd} . \quad (\text{Equation 2-14})$$

The minimum detection limit (MDL) for each of the detected chemical species was calculated as follows:

$$MDL = 3 \times \sqrt{sd} , \quad (\text{Equation 2-15})$$

where **sd** is the standard deviation of the raw masses measured for each element on the blank filters. The MDLs were subtracted from the raw masses measured for each respective chemical species on the sampled filters. These blank-corrected masses were then divided by the surface area of the deposit on the filter (12.557 cm^2) to calculate the mass per unit area ($\mu\text{g m}^{-2}$).

The mass per unit area was corrected for small levels of self-attenuation, which describes the auto-absorption of X-rays within large particles, by applying a correction factor, as in Table 2-1 such as that suggested by Formenti et al. (2010), for dust samples.

Table 2-1. Size-resolved correction factors applied to surface densities from XRF measurements.

Species	Cl	S	Na	Mg	Al	Si	P	K
Correction factor	0.9	0.9	0.53	0.67	0.77	0.76	0.88	0.91

Finally, the concentration of aerosols in a volume of air ($\mu\text{g m}^{-3}$) was calculated using the fixed sampling flow rate of $1 \text{ m}^3 \text{ hr}^{-1}$ for a total of nine hours over the entire surface area deposited on the filter.

Ion chromatography (IC) analysis was performed with a Metrohm Professional IC 850 device (Figure 2-8). Firstly, a solution of the aerosols was made by soaking the polycarbonate filters in ultra-pure water and according to protocols detailed in Metrohm (2009). The solution passes into a separator column that is coated in a conductive resin, which can accommodate a limited number of either cations or anions in ion-exchange sites. Any additional ions leave the tube and the quantity is measured by a conductivity detector.



Figure 2-8. The Metrohm IC 850 device (injection loop of 100 μl) used for ion chromatography analyses at LISA. Photo by: Fadi Lahmidi.

This detector produces a plot (chromatograph), which was compared to those of known reference materials to identify the ionic species (ISO Guide 34:2009, ISO Guide 35:2017). The species was quantified by comparing the peaks on the chromatograph to standard curves of the ion concentrations (Metrohm, 2009). The quantifications are therefore directly affected by and relative to the calibration by standard solutions of the ions. The uncertainty of water-soluble ionic concentrations (also expressed in ng m^{-3}) was within 5%, the maximum uncertainty obtained during calibration by standard certified mono- and multi-ionic solutions (attached Appendix D-2). Specific operational procedures and sampling dates are detailed in Chapter 5, section 5.2.1.

2.4. Statistical analysis

All statistical methods employed were guided by the work of Wilks (2011) on statistical methods in the atmospheric sciences. This aided in ensuring that the data were appropriately processed, analysed and interpreted, that robust and applicable statistical procedures were used, uncertainties were sufficiently considered and described, and predictors to describe data were based on well-researched methods to best describe the progression of atmospheric circulation and variability in chemical profiles. Statistical analysis of the chemical datasets obtained by the Partisol sampling was done to characterise the types of sources contributing to the measured aerosol load.

2.4.1. Linear regression

The linear regression technique of comparing inter-elemental ratios (Bowen, 1979) was applied to the data to test the variance and correlations between locally detected chemical species and known ratios in regional sources of aerosols (Pöschl, 2005). The limitations of using linear regression models for this type of data are in the variability of exact chemical profiles derived for similar sources. Industrial and commercial shipping emissions, for example, can differ by trace impurities and grade of the fuel used (Mazzei et al., 2008; Piketh et al., 2002; Viana et al., 2009) and biomass burning emissions differ by the type of vegetation burnt (Andreae and Merlet, 2001; Formenti, et al., 2003). These inherent

uncertainties were compensated for by using a range of potential mass ratios as reported in the literature and also using various measures of statistical correlation between species known to originate from the same type of source, described in more detail in the respective articles. Additionally, the background concentrations were accounted for by identifying stationarity in the data and peak episodes identified as those that varied greatly from this slowly-moving background (De Gouw and Jimenez, 2009).

2.4.2. Positive matrix factorisation

Multivariate factor analysis in the form of positive matrix factorization (PMF) was used to determine the aerosol source profiles and source contributions from the measured concentrations. The principle of PMF analysis are described in Lee et al. (1999) and Paatero and Tapper (1994). The PMF was run on the EPA (Environmental Protection Agency) PMF version 5.0 software, available from <https://www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses>. The model uses a least-squares matrix factorisation algorithm:

$$X_{ij} \approx \sum_{k=1}^p g_{ik} f_{kj} + \varepsilon, \quad (\text{Equation 2-16})$$

where input data X is a non-negative matrix of i sample numbers and j chemical species with measurement uncertainties in matrix ε . Variable g is the basis matrix ($i \cdot k$) and f is the coefficient matrix ($k \cdot j$) for the number of factors p , or unique sources, contributing to the dataset. Matrix X is approximated by multiplying columns of the basis matrix g with each entry in the coefficient matrix f . The columns of matrix g hold the contribution of the chemical species to the observation and matrix f contains the source profile. The uncertainties related to aerosol filter sampling and analyses are contained in matrix ε .

Uncertainties in PMF solutions relate to the subjective selection of the number of sources to be considered in the model solution and differing initial positions for the model iterations. To overcome these uncertainties, multiple runs with randomised starting positions were used to determine the optimal solution in the multidimensional PMF space. The optimal number of solutions was selected based on the lowest Q(robust) goodness-of-fit parameter. The Q(robust) parameter for each of these runs was compared to determine the variability between the initial base run and subsequent runs, thereby indicating the stability of the solutions. Solutions were only considered stable when the same number of sources were resolved for multiple runs from various initial positions.

After selecting the optimal solution, the error estimation was done by displacing chemical species in the model and testing the rotational ambiguity of the solutions (Norris et al., 2014; Paatero et al., 2014). ‘Fpeak’ rotations with strengths between -0.5 and 1.5 were tested to further optimise the source solutions. From these analyses, the solution with the smallest uncertainties and greatest stability was selected as the most physically meaningful and representative solution.

This chapter presented the research design and methodology used to address the objectives of this research. Uncertainties remain unavoidable and are inherent in weather and climate studies due to our limited understanding and the complexity of interactions. The limitations and inherent bias in the methods and data were discussed and are accounted for in the research where possible. Robust lines of inquiry were sought by combining different data types and using various analyses techniques to handle these data.

Chapter 3

Vertical atmospheric structures

This chapter presents the results of an investigation into the vertical structure of the atmosphere over Namibia and part of the southeast Atlantic. An eleven-year, long-term study of the vertical structure over Namibia and the southeast Atlantic was conducted, which entailed the collection, processing, and analyses of high-resolution vertical profile data from radiosonde and GPS-radio occultation measurements. The horizontal distribution, as well as diurnal, monthly and seasonal trends of these structures were studied. The article is titled, *Atmospheric stratification over the Namibian coast and surrounds*, and the author of this thesis contributed the full data analysis of the vertical profiles, as well as the final compilation and writing of the document with inputs from co-authors. This work is intended for submission to the International Journal of Climatology or Journal of Atmospheric Research. No co-author consent is included since the paper is not in its final published format with author and co-author contributions still subject to change.

Author contributions

- Danitza Klopper performed the analysis of radiosonde and COSMIC data with inputs from Roelof Burger.
- Danitza Klopper wrote the paper with contributions from Stuart J. Piketh, Roelof Burger and Paola Formenti.
- Simon Dirkse (and co.) collected the radiosonde data at Walvis Bay.

ARTICLE 1: Atmospheric stratification over the Namibian coast and surrounds**Danitza Klopper¹, Stuart Piketh¹, Roelof Burger¹, Paola Formenti², Simon Dirkse³**¹ School of Geo- and Spatial Science, Unit for Environmental Sciences and Management, North-West University, Potchefstroom, South Africa² Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris-Est-Créteil, Université de Paris, Institut Pierre Simon Laplace, Créteil, France³ Namibia Meteorology Service, Windhoek, Namibia**Corresponding author:** Danitza Klopper (danitzaklopper@gmail.com)

Abstract. We currently have a limited understanding of the spatial and temporal variability in vertically stratified atmospheric layers over Namibia and the southeast Atlantic (SEA) Ocean. Stratified layers directly influence the transport and dilution of local and long-range transported atmospheric constituents. These constituents have a variety of direct and indirect interactions with solar radiation. To address this, our study uses one year of radiosonde data from Walvis Bay, Namibia, and eleven years of global positioning system radio occultation (GPS-RO) signal refractivity data over the greater area of interest. The seasonal variability in boundary layer height (BLH) along the coast, characterised from radiosonde data by the bulk Richardson number, was shown to be linked to cloud- and surface cover, surface heating effects, and easterly wind components. Radiation interactions with earth's surfaces were also evident in the year-round stability of the surface-based inversion over the cold sea surfaces. The minimum gradient (MG) of refractivity, calculated from these two datasets were in good agreement in cloud-free conditions. The surface of MG across the region of interest was largely affected by changes in atmospheric moisture and cloud, and was not consistent with BLH as defined by the bulk Richardson number. The GPS-RO data was used to characterise the diurnal, seasonal and interannual variability in temperature inversion height, depth and strength. In a comparison between co-located GPS-RO to radiosonde temperature profiles, we find good agreement in cloud-free conditions with an absolute temperature difference of $-0.15 \pm 0.70^\circ\text{C}$ between 0.5 and 7 km amsl and 0.60 ± 0.40 between 7 and 10 km. The low-level inversions, identified by GPS-RO, were lowest, deepest and strongest in the spring. The character of these inversions was linked to the interaction of radiation with surfaces and macroscale circulation. The character of low-level inversions along the coast also indicated the presence of the night-time Benguela jet stream. The geographical variability and springtime maximums coincided with maximum closed cloud cover over the SEA Ocean and biomass burning aerosol (BBA) plumes over the region. The formation of elevated inversions was also linked to diurnal variability in solar inputs (to a lesser extent than low-level inversions), macroscale circulation systems and more notably the presence of BBA plumes.

Keywords. inversions, boundary layer, Namibia, southeast Atlantic, stable layers, vertical structure

3.1. Introduction and background

Southern Africa is positioned in the tropics and middle latitudes and primarily affected by the high-pressure belt under the descending limb of the Hadley circulation cell (Tyson and Preston-Whyte, 2014). Large-scale subsidence of air masses below 500 hPa along this high-pressure belt results in the adiabatic heating of layers aloft, which traps, stabilises, and often decouples the lower troposphere, resulting in the formation of stratified atmospheric layers (Wood and Bretherton, 2004; Painemal et al., 2014; Tyson and Preston-Whyte, 2014). Mean vertical motions within the boundary layer (BL), the lowest stratified layer, controls the depth- and dilution of atmospheric constituents and their potential to be transported into the overlying air. Circulation in the southeast Atlantic (SEA) anticyclone and low sea-surface temperatures induced by upwelling in the Benguela Current contribute to the stabilisation of the lower troposphere over the Namibian coast with the effect peaking in the austral summer (Taljaard, 1995; Cook et al., 2004; Tyson and Preston-Whyte, 2014; Gordon et al., 2018). This results in a decrease in temperature with altitude that is smaller than the adiabatic lapse rate (Warner, 2004). These climatic conditions are conducive to frequent fog formation near the surface in the Namibian coastal desert environment. Temperature is an important indicator of stability. With sufficient stabilisation, vertical mixing is suppressed and the surface flows become decoupled from the upper air. In these conditions, fast-moving, diurnally-varying jet streams (Rife et al., 2010) such as the low-level Benguela jet, form (Nicholson, 2010).

The greater area of interest, given in Figure 3-1, extends between 15°–30°S and 0°–20°E. This area was divided into three regions, namely, *coastal margin* (outlined in blue in Figure 3-1), *ocean* to the west, and the *subcontinent* to the east. These regions were selected based on a priori information on where conditions in the vertical would differ most from one region to the next, such as the boundary layer height (BLH) and the height, depth, and strength of stratified layers. Additionally, Walvis Bay (22°58'43.5"S 14°38'28.4"E, 97 m above mean sea level) as indicated in Figure 3-1, represents a coastal site within this region. Winds generated by steep thermal gradients that form between the marine and continental atmospheres are a significant modulator of the BLH in Namibia. The BLH varies on both diurnal and seasonal scales (Lengoasa et al., 1993; Cook et al., 2004; Markowski and Richardson, 2010). Near the surface and at the BL top, cool-marine air masses are transported in sea breezes and plain-mountain winds. These form most commonly in the daytime and summer (Lindesay et al., 1990). The great escarpment (elevation higher than 1000 m above sea level, as seen in Figure 3-1) acts as a physical topographical barrier to atmospheric transport from the west below this elevation (Gille et al., 2005; Tyson and Preston-Whyte, 2014). Easterly, mountain-plain winds and offshore warm continental air as land breezes and berg winds typically form at night in the winter (Tlhalerwa et al., 2005). These breezes are sometimes sustained into the summer at the top of the BL (Lindesay et al., 1990). Berg winds often co-occur with coastal lows that recirculate local air and may cause higher variability in BLH (Lengoasa et al., 1993; Tyson and Preston-Whyte, 2014).

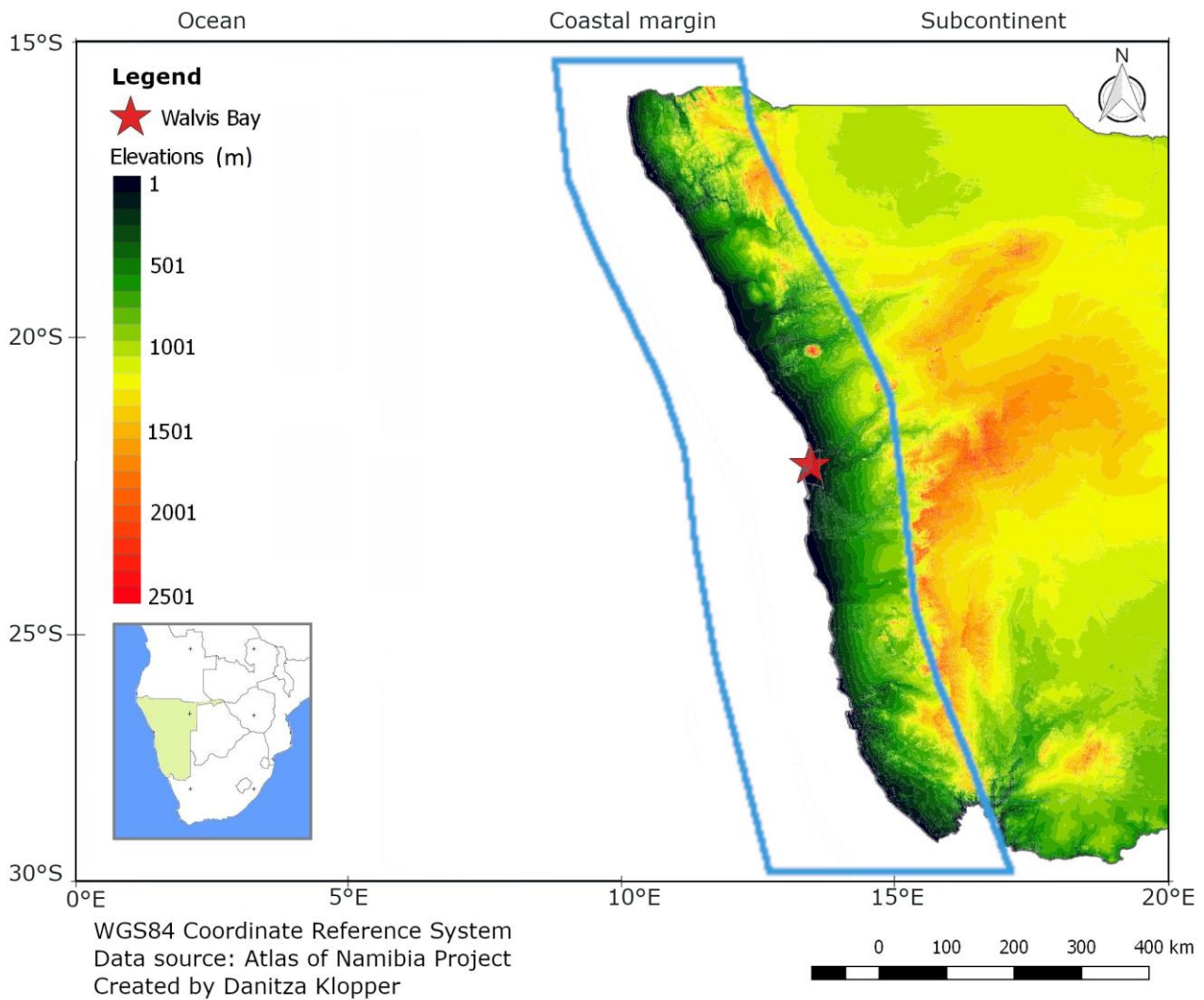


Figure 3-1. Relief map of Namibia over the area of interest. Walvis Bay is indicated by the red star.

Another important modulator of BLH, is the lifetime and fraction of low-cloud cover (Davis et al., 2020). Under clear sky conditions, incident surfaces are subject to the maximum incoming solar flux at noon. Convective atmospheric heating over the semi-arid desert landscapes is greater than that over cool, upwelling coastal waters. High humidity and suppressed vertical cloud growth at the top of the BL often results in the formation of a semi-permanent stratocumulus cloud (Sc) deck along the Namibian coast (Wood, 2015). This deck extends to geographical boundaries between 10°–30°S and 10°W–10°E (Klein and Hartmann, 1993; Muhlbauer et al., 2014), where cloud fractions range from approximately 50 to 75% in the summer/autumn and winter/spring (Muhlbauer et al., 2014). In the presence of clouds, incoming solar radiation is intercepted at cloud top, limiting the convective heating at the surface and resulting in an overall lower BLH as compared to clear sky conditions (Davis et al., 2020). The 850 hPa stability structure only formed below the elevation of the continental plateau.

Above the BL, once released, the subsequent vertical mixing and dilution of atmospheric constituents in the troposphere is largely dependent on the location and conditions in the stratified layers aloft, and is greatest under unstable conditions (Cosijn and Tyson, 1996; Tyson and D'Abreton, 1998; Burger, 2016). Previous studies by Cosijn and Tyson (1996), Garstang, et al. (1996) (for non-rain days), Tyson et al.

(1996), Freiman and Piketh (2003) and the Southern African Fire Atmosphere Research Initiative (SAFARI 2000, Swap et al., 2003) field campaign, have shown that the large-scale transport and recirculation of aerosols from industrial pollution in the south African Highveld and biomass burning fires over the southern African subcontinent occurs in stable layers. In the free troposphere, these studies identified four stable layers with varying degrees of persistence, at 850hPa (approximately 1.5 km), 700 hPa (approximately 3.5 km), 500 hPa (approximately 4-6 km) and 300 hPa (approximately 8-9 km).

Over the Namibian coastal troposphere, the atmospheric composition is shaped by the short- and long-range transport of air masses from southern Africa and the SEA Ocean (e.g. Swap et al., 1996; Zunckel et al., 1996; Tlhalerwa et al., 2005; Das et al., 2017; Chazette et al., 2019; Mallet et al., 2019; Klopper et al., 2020; Pennypacker et al., 2020). The characteristics of the aerosols contained within those air masses, and how they are distributed vertically, determine their ability to modify temperature and moisture conditions (Costantino and Bréon, 2013; Dagan et al., 2016) and interact with incident radiation (Johnson et al., 2004; Mishra et al., 2015), ultimately modifying weather and climate on local to global scales (Hansen et al., 1997; Myhre et al., 2013). Their vertical distribution also affects satellite retrievals of both cloud and aerosol properties (e.g., Haywood et al., 2004; Li et al., 2020).

The study of the stratification of air over southern Africa has garnered much interest over the years and to date, studies have made use of traditional radiosondes released daily or more frequently during short-term intensive field campaigns. A lack of spatial and temporal data coverage, however, has resulted in descriptions that are often coarse on spatial scales and overly generalised (e.g., Preston-Whyte et al., 1977; Cosijn and Tyson, 1996; Swap et al., 1996). The high specific heat capacity of moist, marine air flowing onshore would generally result in smaller variability in BLH at a coastal site, as compared to the outflow of warm, dry continental air masses (Davis et al., 2020). Cool sea-breezes have also been found to inhibit the noontime convective development of the BLH (Davis et al., 2020). The modulating effects on the height and variability of the forenoon and noontime BLH, under the influence of on- or offshore flow, as well as under the effects of clear or cloudy skies, are summarised in Figure 3-2.

In this paper, we present the first long-term study of the variability in the atmospheric discontinuities over the Namibian region. This was done using two datasets, namely radiosonde data (2015) from Walvis Bay airport (collected by the Namibia Meteorology Service), and global positioning system radio occultation (GPS-RO) data from the Constellation Observing System for Meteorology, Ionosphere, and Climate (COSMIC) spaceborne mission. The radiosonde data were collected at Walvis Bay in 2015 and the GPS-RO data were collected between 2007 and 2017 over the region of interest as given in Figure 3-1. These high spatial and temporal resolution data are analysed to provide a statistical view of the variability of temperature inversions over the greater Namibia and SEA. Additionally, the day-to-day and seasonal variability of the BLH is investigated at Walvis Bay, which represents a site within the coastal margin.

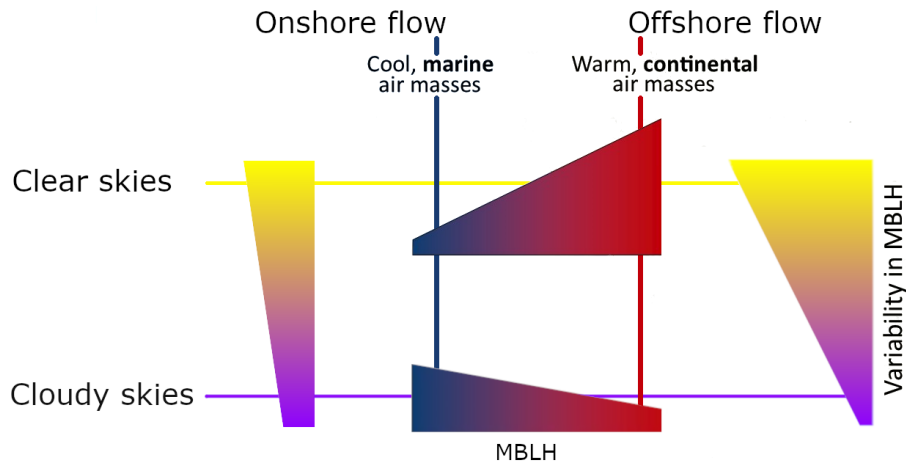


Figure 3-2. Conceptual model of how the convective MBLH along the coast would theoretically vary in the forenoon and at noontime depending on the source of the air mass, either marine or continental, and relative to cloudy or clear sky conditions (Davis et al., 2020).

3.2. Dataset

3.2.1. COSMIC GPS-RO data

Limb-soundings of the atmosphere are made by the low earth-orbiting Global Positioning System (GPS) of the COSMIC satellite mission that has been operational since 2006 (Anthes et al., 2008; Rocken et al., 2000). The raw data are processed by the COSMIC Data Analysis and Archive Centre (CDAAC) inversion software, utilising a Radio Occultation (RO) technique. This data is contained in the “dry atmospheric retrieval profiles”, or “atmPrf” dataset, with a vertical resolution of approximately 50–100 m in the troposphere (Guo et al., 2011; Hande, 2015). The horizontal resolution in the troposphere is approximately 160 km, due to the occultation angle (Sun et al., 2013). These data cover the globe and make measurements over the region of interest several times a day (Guo et al., 2011; Hande, 2015) which reduces any potential bias in diurnal sampling.

The Abel inversion algorithm is applied to retrieve refractivity (**N**) from bending angle profiles by wave optics, perform quality control, as well as correct the observations for systematic negative refractivity biases and multipath propagation of the signal (Ao et al., 2003; Sokolovskiy, 2003; Xie et al., 2006). The optimised refractivity profile is related to temperature (**T**, K), pressure (**P**, hPa) and vapour pressure (**P_w**) of the layer according to Equation 3-1 (Bean and Dutton, 1968; Guo et al., 2011).

$$N = 77.6 \frac{P}{T} + 3.77 * 10^5 \frac{P_w}{T^2} \quad (\text{Equation 3-1})$$

To correct the sensitivity of the signal to moisture (Kuo et al., 2004; Seidel, 2010; Hande et al., 2015; Ho et al., 2015), a “1-D var” moisture correction from the European Centre for Medium-Range Weather Forecasts (ECMWF) is applied to the “atmPrf” dataset to produce the “wetPrf” dataset used in this study (O’Sullivan et al., 2000; Shyam, 2019). In the tropical, lower troposphere, the “wetPrf” dataset has a vertical resolution of approximately 100 m (Guo et al., 2011; Hande, 2015). It is important to note that even with the applied corrections, no reliable information about the atmospheric structure can be

collected below the point where the refractivity signal is super-refracted (Sokolovskiy, 2003). The uncertainties in these measurements due to high humidity, are related to the sensitivity of GPS-RO signal refraction, with vertical changes in the partial pressure of water vapour (Seidel et al., 2010; Hande et al., 2015). Chen et al. (2011) tested observational errors and measured the seasonal, vertical and latitudinal dependence of observational errors of the COSMIC GPS-RO profiles. They found that errors decreased with height in the troposphere and reported greater errors in summer due to added moisture in the lower troposphere. Consequently, in winter the errors are more latitude dependant than in the summer due to greater zonal moisture gradients.

Vertical refractivity profiles for 2007 to 2017 extending between 15°–30°S and 0° to 20°E were used to analyse the long-term variability in stable discontinuities near the surface and up to 10 km. The frequency of measurements is summarised in Figure 3-3, showing the uneven spatial and temporal distribution across the three regions identified in Figure 3-1. Months with less than 10 measurements per region were excluded from the analyses and are indicated by the blank spaces in Figure 3-3. The number of valid profiles available for each region was 18475 (ocean), 4007 (coast) and 4369 (subcontinent).

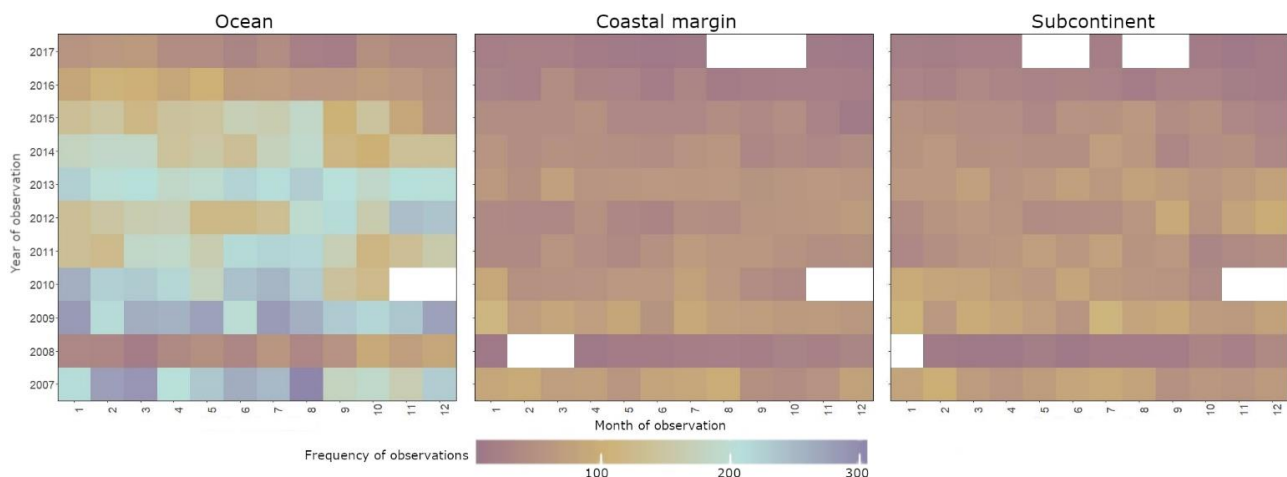


Figure 3-3. Frequency of COSMIC GPS-RO measurements by month and year made over the ocean, coast and subcontinent. Note the different colour scales.

3.2.2. Radiosonde data

Radiosonde data used in this study were measured at Walvis Bay airport by the Namibian Meteorology Service using an iMet-2-AA radiosonde instrument, which was operated according to the latest available World Meteorological Organization's (WMO) *Guide to Instruments and Methods of Observation* (2017). Standard variables contained in the dataset are temperature, pressure, wind speed and -direction, relative humidity, and height on a 50 m vertical resolution. These measurements were all interactively quality controlled to remove any erroneous values by automated statistical regression (WMO, 2017). A total of 335 soundings for 2015 were included in the analyses. Radiosondes were launched almost daily at 10h00, except for several launched at 09h00 local time. In 2015, local Namibian time was UTC +1 in

the winter between the first Sunday in April to the first Sunday in September. For the rest of the year, daylight savings time (UTC +2) was used.

3.3. Data analysis

3.3.1. Point of minimum gradient in refractivity

The refractivity of the bending angle of GPS-RO profiles correspond best to atmospheric moisture, and therefore, assuming that the top of the BL marks a sharp transition from the free troposphere to a more dense, moist, and refractive layer, the height of the BL was estimated by the height of the point of the relative minimum gradient (MG) in the refractivity profile (Xie et al., 2006; Sokolovskiy et al., 2007; Guo et al., 2011; Ao et al., 2012; Ho et al., 2015). The definition assumes a neutral atmosphere, following the equation of Bean and Dutton (1968) as given in Equation 3-1. Ho et al. (2015) used the MG method to calculate BLH from GPS-RO and showed that this method is especially useful in conditions where the layer is defined by a large change in moisture, such as at the top of the BL. Compared to observations by Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) space-borne sensors, the GPS-RO BLH defined by the point of MG, had good correlation to cloud top height (0.85) with a standard deviation of 150 m (Korhonen et al., 2014). Use of the MG method to determine BLH proved to be reliable in the southeast Pacific off South America (Ho et al., 2015), which shares similar climatic conditions in the coastal desert environments, including the semi-permanent Sc formations (Warner, 2004). Considering that the Sc tops the marine boundary layer at ~850 hPa (Muhlbauer et al., 2014; Wood, 2015). Ao et al. (2012) found that the GPS-RO compared well with Era-interim reanalyses meteorological data for climatological studies but overestimated the BLH by up to 500 m. GPS-RO also showed greater variability than the era interim data, especially in the tropics.

3.3.2. BLH from radiosonde data

Different definitions for BLH are considered in an attempt to derive a robust estimation following the examples of Seidel et al. (2010) and references therein. Three of the definitions are considered to be more traditional approaches to quantification from radiosondes, while a fourth definition is assumed for direct comparisons with COSMIC GPS-RO refractivity profiles.

1/ Assuming the stabilisation of the lower atmosphere by the year-round cold waters of the Benguela, the BL top is defined as the top of this statically stable layer, calculated using the bulk Richardson number (R_N) method as in Korhonen et al. (2014) and references therein. The general equation is given by Hanna (1969) and adapted by Korhonen et al. (2014) as follows:

$$R_N(h) = \frac{g(h-h_0)}{\theta(h)} \frac{[\theta(h)-\theta(h_0)]}{u(h)^2 + v(h)^2}, \quad (\text{Equation 3-2})$$

where θ is potential temperature, g is gravitational acceleration, u (zonal) and v (meridional) denote wind components at the surface (h_0) and at given altitude (h). A critical bulk Richardson number

($R_N(h)$) greater than zero identifies the height above the statically stable flow in the BL (Sørensen et al., 1996; Korhonen et al., 2014).

2/ The BLH may also be defined as the top of a surface-based inversion, which would stabilise surface layers and inhibit vertical mixing.

3/ The parcel method (Seibert et al., 2000) identified BLH as the point where the virtual potential temperature (VPT) aloft is the same as at the surface and defined as the height at which a parcel would be in equilibrium with its surroundings (Seidel et al., 2010).

4/ BLH is defined as the point of MG in the refractivity profile, also used to determine BLH from GPS-RO profiles. As described in section 3.3.1. This is done to make a comparison of measurements made by radiosonde and those made by COSMIC GPS-RO following the example of Xie et al. (2012) and Hande et al. (2015) Radiosonde profiles of pressure, temperature, and moisture were converted into a refractivity profile according to Equation 3-1.

Preston-Whyte et al. (1977) reported a minimum height of 500 m for the subsidence inversion over the Benguela Current. Considering this, and to exclude surface inversions from the analyses, a range of 400–2500 m height above ground level (agl) is set in which to find the BLH.

3.3.3. Subsidence inversions

Both GPS-RO and radiosonde measurements are made in height above mean sea level (amsl). To exclude surface inversions, heights amsl were converted to height agl by extracting the elevation for each coordinate point from a Shuttle Radar Topography Missions, 30 m raster data elevation model (SRTM, 2013). The profiles were then limited to 0.5 and 10 km agl, and the height amsl were retained for the final analyses. Temperature profiles were derived from the refractivity using Equation 3-1. It is important to note that these temperatures are derived from the refractivity and not measured directly, therefore introduce uncertainties which are largely dependent on the moisture content of the atmosphere and the algorithm applied or retrieval method used (Wang et al., 2013). The saturation mixing ratio, mixing ratio, and dew point temperatures were then calculated from these variables according to Bohren and Albrecht (1998).

The valid radiosonde temperature profiles were also limited to between 0.5 and 10 km agl, to exclude surface inversions. The measurements are then converted into height amsl, considering the 91 m surface altitude at Walvis Bay airport. These temperature profiles were analysed for inversions, defined by an increase in temperature with height. The strength of these inversions, describing the stability in the atmosphere, were calculated as the change in temperature per 100 m interval. Inversion depth was calculated as the distance through which the inversion persists. Shallow isothermal layers directly above or below the inversion were not included in the calculation of the inversion depth.

3.4. Results and discussion

3.4.1. Comparisons between radiosonde and COSMIC GPS-RO data

3.4.1.1. Temperature profiles

The inability of all GPS-RO observations to extend down to the surface means that some information may be lost that is otherwise captured by the radiosonde measurements. To investigate this issue, temperature profiles were compared for five case studies, when the GPS-RO profiles were within one cardinal degree of the Walvis Bay position and two-hours from the radiosonde release (Figure 3-4). The comparison for GPS-RO to radiosonde profiles, excluding those taken on 2015/07/04, had an absolute (and standard deviation) temperature difference of $-0.15 \pm 0.70^{\circ}\text{C}$ between 0.5 and 7 km amsl. Between 7 and 10 km, an absolute difference of $0.60 \pm 0.40^{\circ}\text{C}$ was found. The mean temperature difference measured by the two methods compared well with $-0.20 \pm 1.50^{\circ}\text{C}$ reported by Wang et al. (2013) for global comparisons made of temperature profiles up to 10 km. The profiles measured on 4 July 2015 (measurements were taken one hour apart) show an extreme temperature lapse rate in the GPS-RO

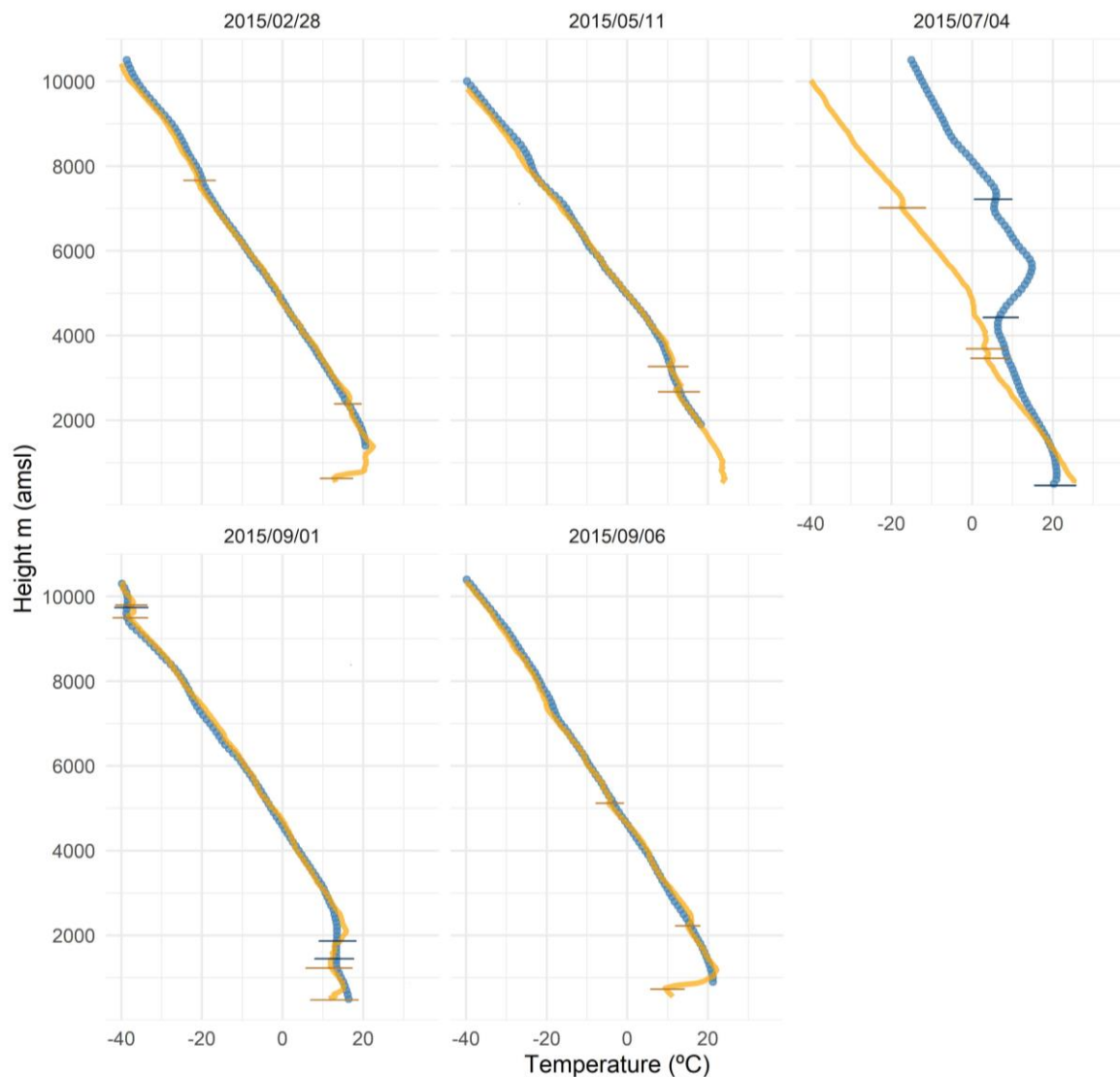


Figure 3-4. Five instances of nearly co-located temperature profiles from GPS-RO (blue) and radiosonde (orange) data. Base heights of temperature inversions identified in each of these profiles are marked accordingly in these colours.

measurement when compared to the lapse rates found in the other profiles in Figure 3-4. To determine the source of the error, additional GPS-RO profiles taken within three cardinal degrees and three hours of the radiosondes released from Walvis Bay (to account for large differences in humidity by location and time of day) were compared. This confirmed the large discrepancies between the lapse rates in these profiles and that of 4 July. This suggests that the GPS-RO measurement was the source of the error. Variability in atmospheric moisture is a major source of errors, as discussed in section 3.2.1.. Considering that the other profiles in the vicinity did not show this extreme lapse rate, despite also being taken through an overcast atmosphere as seen in daily MODIS Cloud Fraction data (Platnick et al., 2017), meant that there was another, unknown reason for this extreme derived temperature profile

Inversion base heights identified in each profile are also indicated in Figure 3-4. Despite the good general agreement in temperature profiles, base heights of temperature inversions differ as a result of the higher vertical spatial resolution of radiosondes as compared to GPS-RO. Furthermore, radiosonde measurements were not taken at regular height intervals, which may also contribute to this variability.

3.4.1.2. Boundary layer height

An additional comparison is done on thirteen co-located GPS-RO measurements, taken within three hours and two cardinal degrees of the radiosonde release. The comparison is between the BLH estimated by the MG method from GPS-RO data to those estimated by the MG and bulk R_N methods from radiosonde data (Figure 3-5). When using the MG method on both datasets, the comparison shows good agreement for most of the points.

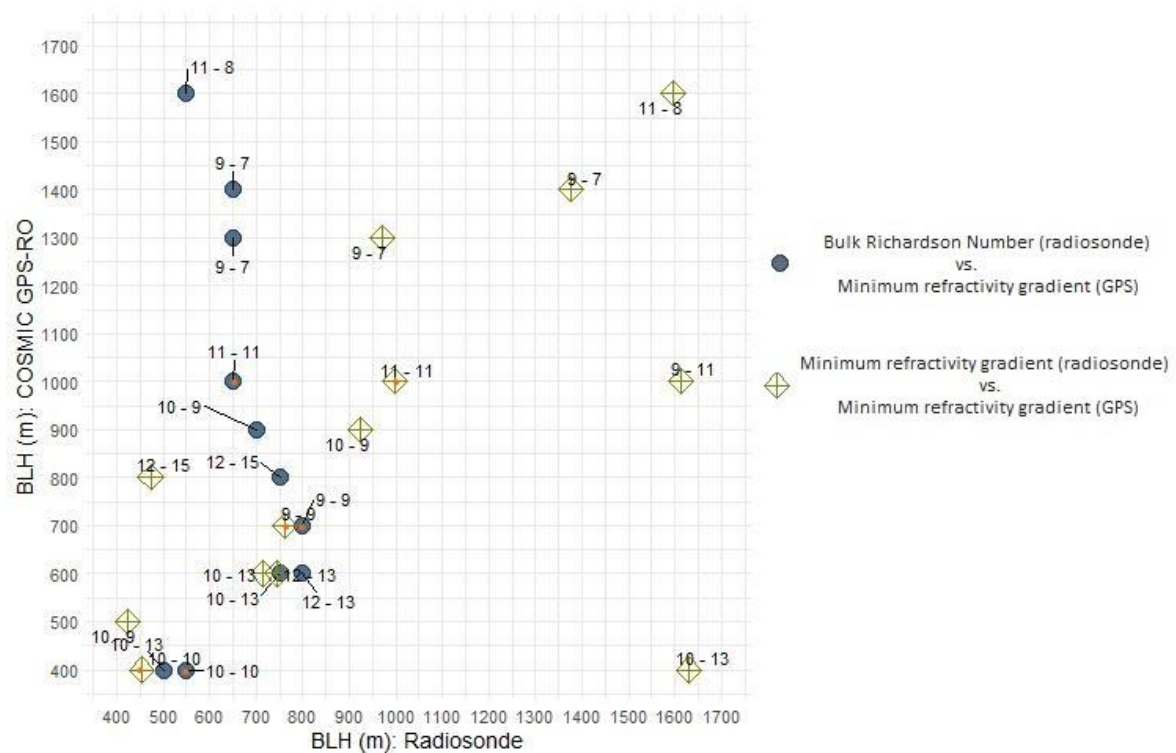


Figure 3-5. Scatterplots of BLH identified in radiosonde and COSMIC GPS-RO profiles. The points are labelled by the hour of radiosonde – GPS measurement. Points with an orange centre indicate measurements made within the same hour.

Three of these co-located measurements were made within an hour of one another in March, April and May. The BLH estimated by MG from the two datasets for these three points showed that GPS-RO was negatively biased and the standard deviation between measurements was 30 m. This is in good agreement with that reported by Ao et al. (2003). These three co-located profiles were taken in clear skies, as observed in daily MODIS Cloud Fraction data (Platnick et al., 2017). Considering that our differences are smaller than the vertical resolution of GPS profiles, our comparison reveals very good agreement between the two datasets for the region in cloud-free conditions.

The biggest differences were coincident with measurements taken two to three hours apart and may therefore be a function of humidity which changes by location and time of day. As mentioned before, atmospheric moisture poses the greatest challenge for both GPS-RO and radiosonde sensors, to measure temperature and humidity, with the effect peaking in the presence of clouds (Wang and Zhang, 2008; Wang et al., 2013). Furthermore, GPS-RO signals are unable to penetrate to the surface beyond a point of superrefraction, which may contribute to the overestimation of BLH with the MG method in the presence of Sc's (Ao et al., 2012). The errors related to COSMIC GPS-RO data in comparison with different radiosonde data were described in detail by Wang et al. (2013), who reported a relative error in the refractivity profile of $\pm 1.6\%$ (3% at 1000 hPa and 0.5% at 300h Pa), with the greatest biases reported in the tropics under high humidity conditions (Sokolovskiy, 2003; Kuo et al., 2004). As a result of higher humidity near the surface, Ao et al. (2003) reported refractivity biases of -10% below 2 km, and Alexander et al. (2014) reported approximately -0.2% below 8 km. Ho et al. (2015) also reported a negative bias (with a standard deviation of 140 m) over the south-eastern Pacific.

These biases and observational errors in radiosondes (Wang and Zhang, 2008; Wang et al., 2013) and GPS-RO profiles (Chen et al., 2011), as well as spatial and temporal mismatches in measurements and measurement resolution, have been the main reasons for a statistical difference in the retrieval of vertical atmospheric structures. Other causes of discrepancies between the two methods are the chosen definitions for structures, such as BL top. This is evident in Figure 3-5 where the BLHs estimated by MG method from GPS-RO underestimated radiosonde BLH defined by R_N by an average of 220 ± 530 m. The spatial and temporal variability in the BLH is described in section 3.4.2.1. Overestimations by the MG method increased above 800 m amsl at higher wind speeds. This also corresponds to the height where the probability of open and disorganised mesoscale cellular convection (MCC) cloud morphologies starts to decrease and the probability of closed MCC increased (more solid Sc layers) (Muhlbauer et al., 2014). Ho et al. (2015) have shown how BLH over the southeast Pacific corresponds well to the location of the cloud top, identified from satellite observations, with mean differences of 90 m. This is lower than the differences in BLH defined by the MG and R_N methods (Figure 3-5). Several key differences in conditions between the SEA and southeast Pacific include a smaller diurnal variability in the Sc deck and an overall lower BLH in the Atlantic due to strong inversion conditions (Painemal et al., 2014, and references therein). This indicates that the BLH identified by the MG and R_N methods do not identify the same structure in the atmosphere. and the biggest difference is assumed to be due to cloud morphologies and

location, and wind components included in the R_N definition. Although the two datasets show good agreement in pressure, temperature, and moisture conditions, the bulk R_N was more reliable at identifying physical processes associated with a BL than the MG method which is linked to cloud top. The layer in the atmosphere identified by the MG method is real and still relevant to air mass transport and vertical distribution of atmospheric constituents. Radiosondes prove useful in identifying smaller scale vertical structures whereas GPS-RO data are useful for long-term studies over larger geographical areas.

3.4.2. Spatial and temporal variability in low-level discontinuities

3.4.2.1. Boundary layer height and point of minimum gradient of refractivity

Monthly mean BLH for 2015 (the only complete year of measurements), estimated by the different methods described in section 3.3.2., is given in Table C-1.1. The BLH, defined as the point where VPT is equivalent to that at the surface, remained stable around 430 ± 20 m, as did the top of the surface-based inversion (500 ± 140 m) (Table C-1.1.). Stability in the lower troposphere is influenced by micro- to mesoscale interactions with radiation. This includes interactions with clouds, and the varying surface cover and atmospheric conditions over the ocean, coastal desert environment and subcontinental escarpment (Lengoasa et al., 1993; Cook et al., 2004; Tlhalerwa et al., 2005; Tyson and Preston-Whyte, 2014). The year-round cold upwelling currents offshore of Walvis Bay, which decrease in intensity slightly in the summer (Nelson and Hutchings, 1983; Boyd and Agenbag, 1985; Cole and Villacastin, 2000), and the resulting lack of convective activity near the surface, may explain the stable BLHs estimated by these definitions. The year-round cold air temperatures near the surface are evident in the temperature profiles taken over Walvis Bay (Figure 3-6).

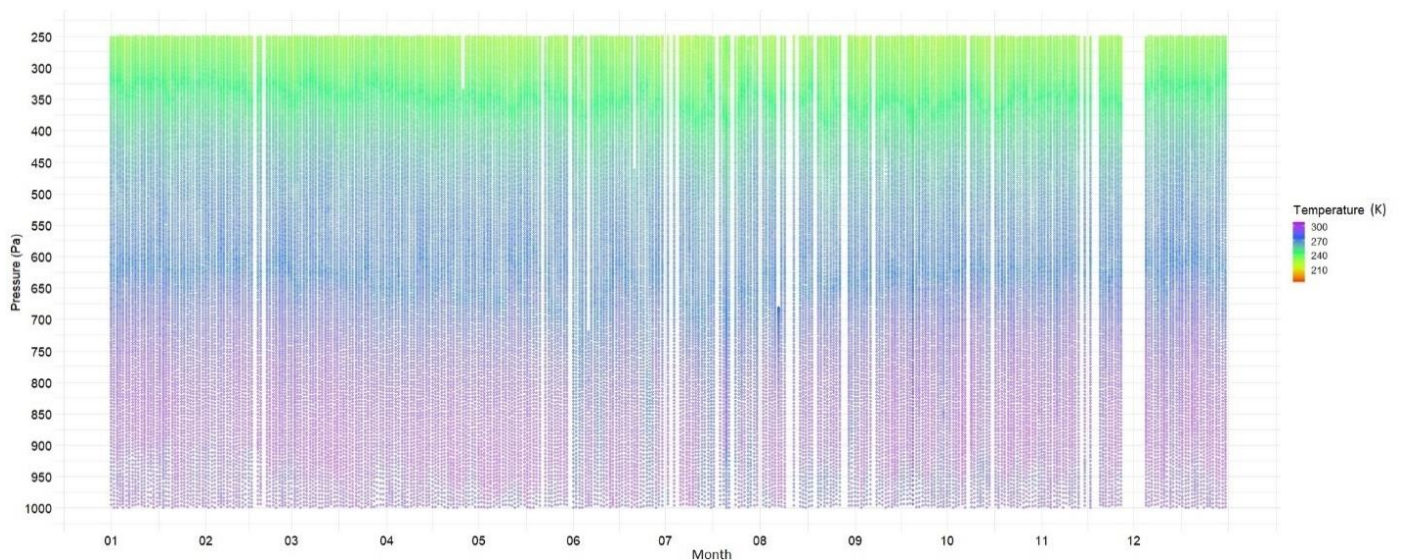


Figure 3-6. Temperature profiles taken by radiosondes released from Walvis Bay in 2015.

The bulk R_N definition found the monthly mean minimums in the austral autumn (730 ± 190 m) and maximums in the summer (1000 ± 230 m) of 2015 (Figure 3-7). BLH were similar to values derived by Von Engel and Teixeira (2013) offshore along the Namibian coastal margin, although the seasonal trend in 2015 differed. Our seasonal minimum was in the autumn whereas Von Engel and Teixeira (2013)

found a wintertime minimum, particularly over land. The variability in the R_N BLH over Walvis Bay could be linked to the frequency of occurrence and monthly variability in cloud fractions, as given in Figure 3-7, and are interpreted accordingly. Muhlbauer et al., (2014) reported increasing frequencies of both closed and open cloud MCC formation towards the open ocean in all seasons whereas the opposite trend was observed for disorganised MCC which decreased in frequency of formation towards the open ocean. Higher frequencies of closed MCC, which prevent surface heating, were associated with less monthly variability and higher base heights for the BL in the second half of the year. The increased frequency of open MCC during winter, when surface heating over the region is at a seasonal maximum, corresponds to the high BLH as seen in Figure 3-7. Gupta et al., (2020) showed how cloud-top entrainment of biomass burning aerosols during September also increased BLH.

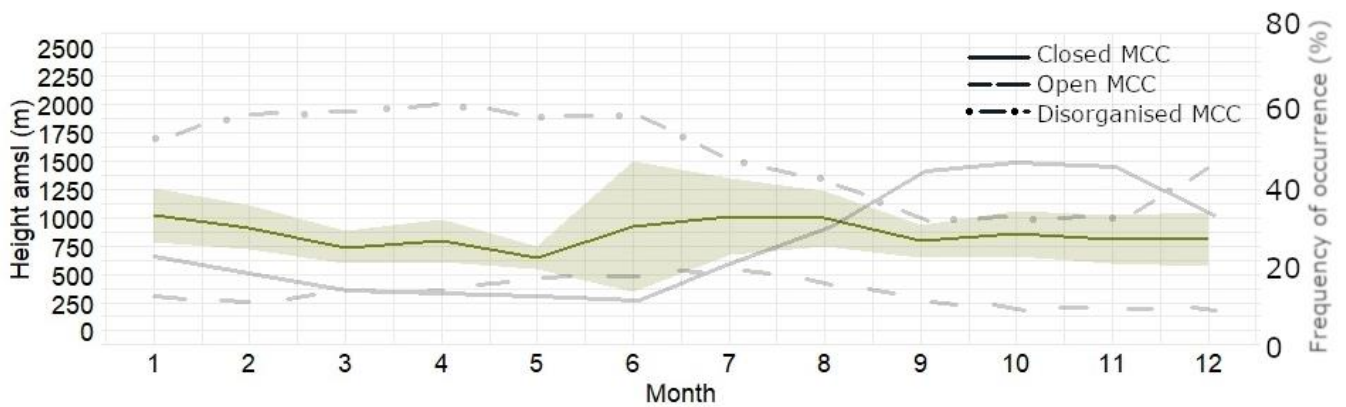


Figure 3-7. Time series for 2015 of the monthly mean mid-morning MBLH calculated for Walvis Bay from radiosonde data calculated by the Bulk Richardson number. On the secondary axis, the frequency of closed, open and disorganise mesoscale cellular convection (MCC) over the southeast Atlantic is given (Muhlbauer et al., 2014).

In addition, the high BLH in the second half of the year may be attributed to the inflow of warm, continental air masses (Davis et al., 2020) which is supported by the distinct decrease in the height of easterly wind components measured by radiosondes released from Walvis Bay (Figure 3-8). This supports the findings of Davis et al. (2020) as was illustrated in Figure 3-2.

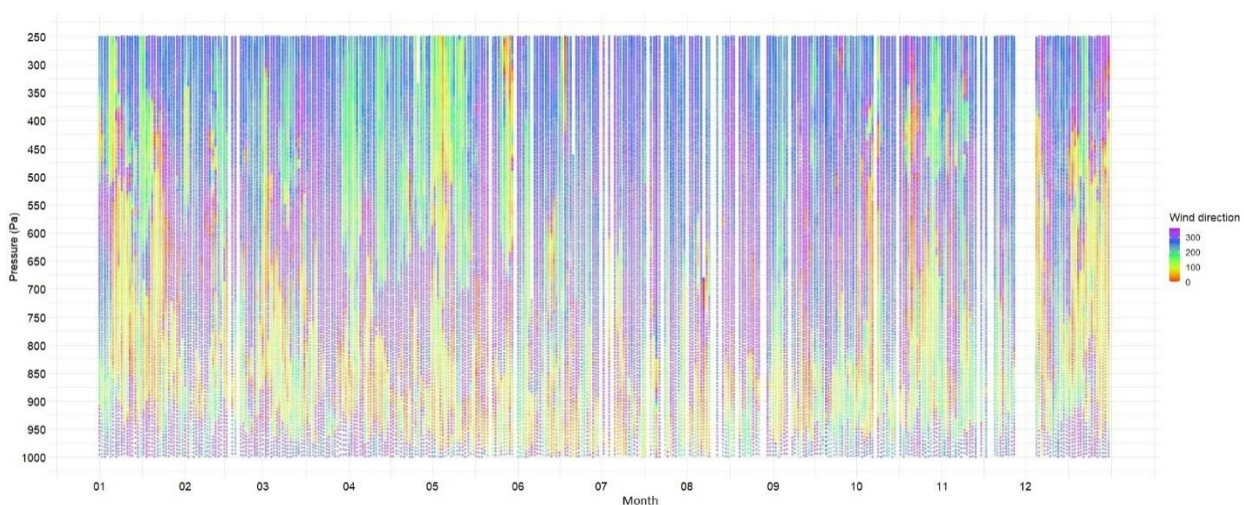


Figure 3-8. Wind direction profiles measured by radiosondes released from Walvis Bay in 2015.

The point of MG of refractivity identified from the GPS-RO profiles was assumed to be consistent with an isopycnal surface and is consistent with cloud top in supersaturated conditions. Over the ocean, zonally averaged base heights for MG of refractivity in Figure 3-9, show a slight increase with distance from the coast. A similar westward increase in stratocumulus inversion base heights (200 m to 700 m) over the ocean was simulated in a global model run for a 10-day case study in August 2016 (Gordon et al., 2018). Along the coastal margin, these base heights were highest between 20° and 25°S in all seasons. Over the ocean, this surface varied least across latitudes. The small variability over the ocean is in good agreement with the effect that clouds have on preventing convection below, reported by Davis et al. (2020). The latitudinal variability over the ocean in base heights for MG of refractivity was most

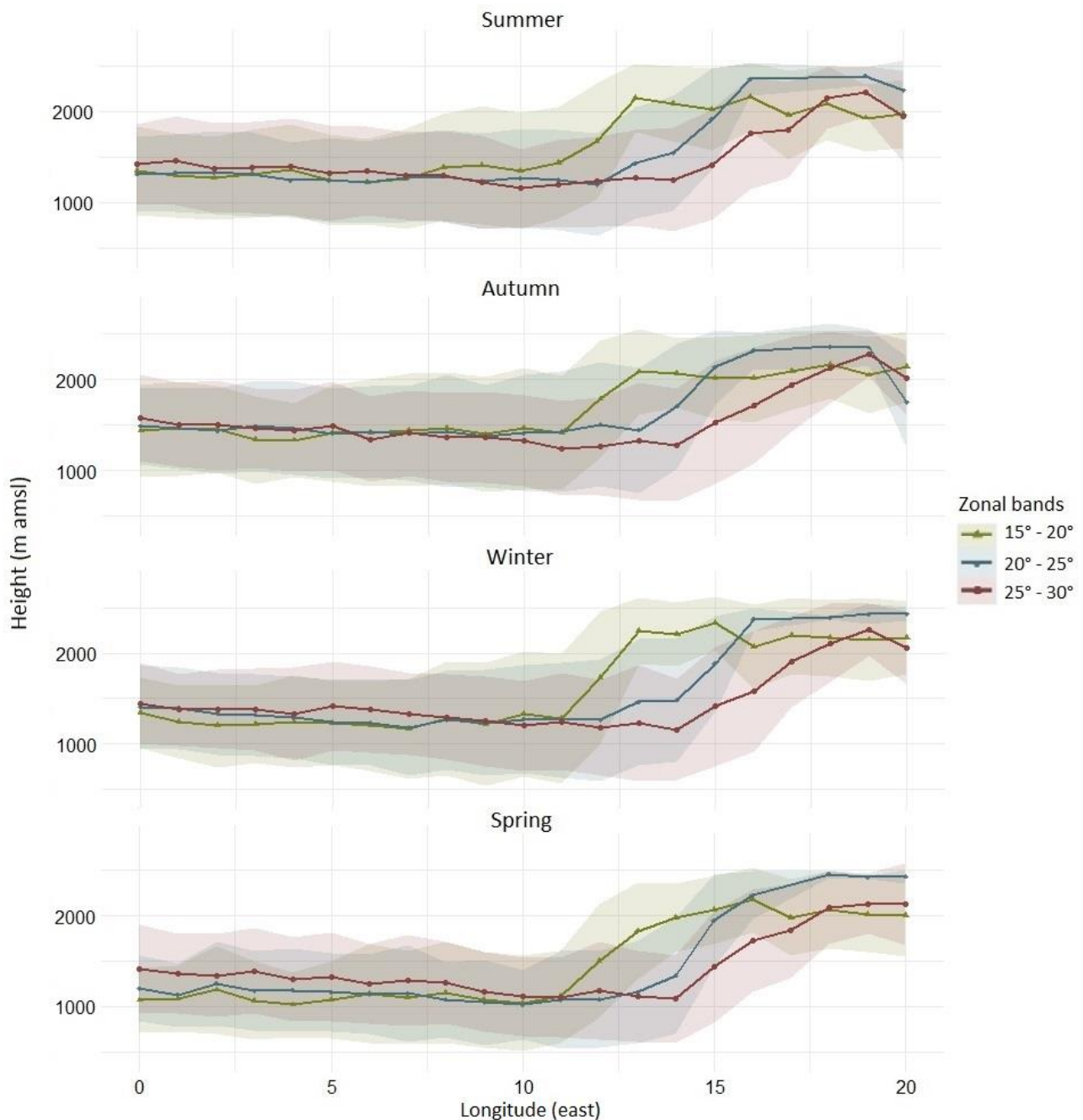


Figure 3-9. Five-degree zonally averaged seasonal means and standard deviations of the points of MG of refractivity from GPS data. The coastline position varies from 12°-13°E in the 15°-20°S band, from 13°-15°E in the 20°-25°S band, and from 15°-17°E in the 25°-30°S band.

exaggerated in the spring (Figure 3-9) when the occurrence of closed MCC peaks over the region (Figure 3-7). In the transition from marine to subcontinental atmospheres the base height increases by 400-800 m. The exact position of the dramatic increase in height from marine to continental atmospheres over the coast shows small seasonal differences. Generally, this surface was highest in autumn and lowest in spring. No clear connection to the strength of the anticyclonic circulation could be determined.

3.4.2.2. Temperature inversions

There was no correlation (0.34) between the height of MG and temperature inversion layers (not shown). Unlike the MG surface, mean base heights of low-level temperature inversions over the open ocean decreased towards higher latitudes, by 300 m in the winter/spring and 200 m in the summer/autumn. Low-level inversions formed most frequently over the ocean, and especially between 20° and 25°S. Stability over the ocean and along the coastal margin is enhanced to the east and south of the SEA anticyclone (Cosijn and Tyson, 1996). The latitudinal variability may be linked to the strength of the anticyclonic circulation that undergoes seasonal changes in latitudinal position. The system exerts a year-round influence on circulation over the region and subsidence peaks in the winter (Tyson and Preston-Whyte, 2014). In the winter, macroscale stability may also be induced in the low to mid-troposphere over temperate regions ahead of cold fronts (Preston-Whyte et al., 1977; Tyson and Preston-Whyte, 2014). Despite these macroscale stability-inducing systems, wintertime inversions were not necessarily stronger, deeper, nor more frequently observed in the GPS-RO data, as presented in Tables 3-1 to 3-3. These tables give a seasonal summary of the low-level (0.5 and 2.5 km) and elevated inversion (2.5 to 10 km) characteristics across latitudinal bands over the region. The generally stable conditions in the region are disturbed by the highly transient westerly waves (autumn and winter), and less transient easterly waves (spring and summer). Over the region, quasi-stationary barotropic easterly low-pressures, which move in direct response to surface heating over the semi-desert landscapes of southern Africa (Tyson and Preston-Whyte, 2014), fluctuate between 15° and 25°S (Tyson et al., 1996). Towards the locus of these transient low-pressures, enhanced convective activity and the resultant instability disturb the mean circulatory field between the surface and approximately 850 hPa, over central and northern Namibia (Garstang et al., 1996; Tyson and Preston-Whyte, 2014). This is the main driver of the decreasing frequency of surface inversions measured towards lower latitudes and low frequency of inversion formation over the subcontinent (Tables 3-1 to 3-3). In the spring, and to a lesser degree, summer, inversions over the subcontinent may still form under the influence of a band of suppressed convection found between the approaching easterly lows and weakening influence of anticyclones (Cook et al., 2004; Preston-Whyte et al., 1977). North of 20°S, springtime inversions were lowest, strongest and deepest as compared to other seasons. The latitudinal variability in inversion strengths was also most exaggerated in the spring, where over the ocean, inversion strengths increased towards lower latitudes (Tables 3-1 to 3-3). Besides the effects of macroscale circulation, this variability also coincides with the geographical extent of closed MCC formation over the SEA (Muhlbauer et al.,

2014) and potentially overlying radiation-absorbing biomass burning aerosol plumes in spring, discussed in regards to elevated discontinuities in the next section.

Table 3-1. Seasonal mean and standard deviation of the base heights (m amsl), depths (m), strengths ($^{\circ}\text{C}/100\text{ m}$) and strength throughout the depth ($^{\circ}\text{C}/\text{depth}$) of low-level (0.5 – 2.5 km agl) and elevated inversions (2.5 – 10 km agl) identified in COSMIC GPS-RO data. These data are summarised by season (Su.=DJF, A.=MAM, W.=JJA and Sp.=SON) for the 15° to 20°S zonal band over the region of interest that is divided into ocean, coast and subcontinent. The table also shows the number of inversions measured.

		0.5 – 2.5 km			2.5 – 10 km		
		Ocean	Coast	Subcontinent	Ocean	Coast	Subcontinent
Height (m)	Su.	950 $\pm$ 390	740 $\pm$ 260	1730 $\pm$ 350	5590 $\pm$ 1980	5070 $\pm$ 1500	4230 $\pm$ 1260
	A.	1020 $\pm$ 330	870 $\pm$ 300	1480 $\pm$ 270	5960 $\pm$ 1150	6370 $\pm$ 1240	6540 $\pm$ 1160
	W.	1000 $\pm$ 350	700 $\pm$ 190	2430 $\pm$ 60	5920 $\pm$ 1540	5940 $\pm$ 1360	5710 $\pm$ 1610
	Sp.	830 $\pm$ 240	820 $\pm$ 280	1530 $\pm$ 110	6160 $\pm$ 1060	6320 $\pm$ 990	6500 $\pm$ 1060
Depth (m)	Su.	400 $\pm$ 200	400 $\pm$ 200	200 $\pm$ 100	200 $\pm$ 300	200 $\pm$ 300	300 $\pm$ 200
	A.	400 $\pm$ 200	300 $\pm$ 200	200 $\pm$ 100	200 $\pm$ 100	200 $\pm$ 200	200 $\pm$ 200
	W.	300 $\pm$ 200	300 $\pm$ 200	400 $\pm$ 100	200 $\pm$ 300	200 $\pm$ 200	200 $\pm$ 200
	Sp.	400 $\pm$ 200	500 $\pm$ 300	200 $\pm$ 100	200 $\pm$ 200	200 $\pm$ 200	200 $\pm$ 200
Strength ($^{\circ}\text{C}/100\text{ m}$)	Su.	0.57 $\pm$ 0.36	0.46 $\pm$ 0.27	0.35 $\pm$ 0.19	0.34 $\pm$ 0.3	0.35 $\pm$ 0.23	0.33 $\pm$ 0.23
	A.	0.55 $\pm$ 0.33	0.41 $\pm$ 0.25	0.31 $\pm$ 0.21	0.32 $\pm$ 0.19	0.34 $\pm$ 0.25	0.35 $\pm$ 0.25
	W.	0.49 $\pm$ 0.35	0.43 $\pm$ 0.3	0.28 $\pm$ 0.14	0.34 $\pm$ 0.23	0.36 $\pm$ 0.28	0.33 $\pm$ 0.22
	Sp.	0.78 $\pm$ 0.43	0.51 $\pm$ 0.32	0.42 $\pm$ 0.34	0.43 $\pm$ 0.25	0.44 $\pm$ 0.41	0.44 $\pm$ 0.3
Strength ($^{\circ}\text{C}/\text{depth}$)	Su.	2.32 $\pm$ 2.49	1.69 $\pm$ 1.63	0.52 $\pm$ 0.67	0.95 $\pm$ 3.02	0.86 $\pm$ 2.6	0.9 $\pm$ 1.84
	A.	2.08 $\pm$ 1.9	1.19 $\pm$ 1.17	0.4 $\pm$ 0.27	0.49 $\pm$ 0.62	0.91 $\pm$ 3.37	0.74 $\pm$ 2.49
	W.	1.48 $\pm$ 1.77	1.03 $\pm$ 1.04	1.27 $\pm$ 0.96	0.99 $\pm$ 4.06	0.86 $\pm$ 2.65	0.57 $\pm$ 0.95
	Sp.	2.98 $\pm$ 2.31	2.28 $\pm$ 1.88	0.54 $\pm$ 0.66	0.82 $\pm$ 1.99	0.97 $\pm$ 3.68	0.82 $\pm$ 1.37
Number of inversions	Su.	1115	190	47	138	82	244
	A.	831	123	12	231	124	192
	W.	753	84	3	203	111	217
	Sp.	912	164	35	315	155	277

Table 3-2. Same as for Table 3-1, but for inversions in the 20° to 25°S zonal band.

		0.5 – 2.5 km agl			2.5 – 10 km agl		
		Ocean	Coast	Subcontinent	Ocean	Coast	Subcontinent
Height (m)	Su.	1080 $\pm$ 450	900 $\pm$ 410	1950 $\pm$ 380	6200 $\pm$ 2240	5370 $\pm$ 1810	4860 $\pm$ 1510
	A.	1040 $\pm$ 350	880 $\pm$ 300	1660 $\pm$ 180	6010 $\pm$ 1400	6290 $\pm$ 1070	6420 $\pm$ 1160
	W.	1090 $\pm$ 410	790 $\pm$ 270	1640 $\pm$ 280	6240 $\pm$ 1750	6130 $\pm$ 1430	6010 $\pm$ 1330
	Sp.	930 $\pm$ 350	820 $\pm$ 330	1650 $\pm$ 160	6310 $\pm$ 1390	6550 $\pm$ 1120	6570 $\pm$ 990
Depth (m)	Su.	400 $\pm$ 200	400 $\pm$ 200	300 $\pm$ 200	200 $\pm$ 200	200 $\pm$ 300	300 $\pm$ 300
	A.	400 $\pm$ 200	400 $\pm$ 200	200 $\pm$ 200	200 $\pm$ 200	200 $\pm$ 200	200 $\pm$ 200
	W.	300 $\pm$ 200	300 $\pm$ 200	200 $\pm$ 200	200 $\pm$ 300	200 $\pm$ 100	200 $\pm$ 200
	Sp.	400 $\pm$ 200	500 $\pm$ 300	200 $\pm$ 100	200 $\pm$ 200	200 $\pm$ 200	200 $\pm$ 100
Strength ($^{\circ}\text{C}/100\text{ m}$)	Su.	0.44 $\pm$ 0.31	0.32 $\pm$ 0.19	0.32 $\pm$ 0.19	0.32 $\pm$ 0.24	0.37 $\pm$ 0.32	0.43 $\pm$ 0.32
	A.	0.49 $\pm$ 0.32	0.37 $\pm$ 0.23	0.21 $\pm$ 0.08	0.32 $\pm$ 0.19	0.41 $\pm$ 0.29	0.38 $\pm$ 0.29
	W.	0.45 $\pm$ 0.33	0.3 $\pm$ 0.2	0.62 $\pm$ 1.25	0.34 $\pm$ 0.29	0.37 $\pm$ 0.21	0.39 $\pm$ 0.26
	Sp.	0.58 $\pm$ 0.37	0.4 $\pm$ 0.24	0.32 $\pm$ 0.18	0.44 $\pm$ 0.28	0.46 $\pm$ 0.31	0.47 $\pm$ 0.31
Strength ($^{\circ}\text{C}/\text{depth}$)	Su.	1.98 $\pm$ 2.46	1.14 $\pm$ 1.27	0.96 $\pm$ 1.24	0.61 $\pm$ 1.06	1.08 $\pm$ 3.66	1.26 $\pm$ 2.89
	A.	1.95 $\pm$ 2.17	1.46 $\pm$ 1.37	0.44 $\pm$ 0.48	0.52 $\pm$ 0.86	0.85 $\pm$ 2.09	0.95 $\pm$ 2.94
	W.	1.61 $\pm$ 2.12	0.8 $\pm$ 0.89	0.48 $\pm$ 0.50	0.87 $\pm$ 5.48	0.52 $\pm$ 0.77	0.67 $\pm$ 1.47
	Sp.	2.24 $\pm$ 1.99	1.77 $\pm$ 1.54	0.49 $\pm$ 0.49	0.95 $\pm$ 2.56	1.04 $\pm$ 2.91	0.79 $\pm$ 0.98
Number of inversions	Su.	1590	166	62	253	108	186
	A.	1327	208	7	259	195	179
	W.	1155	104	17	279	135	197
	Sp.	1268	236	32	306	160	216

Table 3-3. Same as for Table 3-1, but for inversions in the 25° to 30°S zonal band.

		0.5 – 2.5 km agl			2.5 – 10 km agl		
		Ocean	Coast	Subcontinent	Ocean	Coast	Subcontinent
Height (m)	Su.	1240 ± 520	1310 ± 590	1730 ± 410	6320 ± 2250	6010 ± 2240	5440 ± 1790
	A.	1110 ± 400	960 ± 370	1420 ± 190	5880 ± 1410	6390 ± 1290	6570 ± 1140
	W.	1180 ± 460	980 ± 490	1720 ± 450	6180 ± 1720	6040 ± 1730	5720 ± 1280
	Sp.	1110 ± 470	1080 ± 470	1720 ± 390	5830 ± 1890	6590 ± 1620	6430 ± 1280
Depth (m)	Su.	400 ± 200	400 ± 200	300 ± 200	200 ± 200	300 ± 300	200 ± 100
	A.	300 ± 200	300 ± 200	200 ± 200	200 ± 200	200 ± 100	200 ± 200
	W.	300 ± 200	300 ± 200	400 ± 800	200 ± 200	200 ± 300	200 ± 100
	Sp.	400 ± 200	300 ± 200	300 ± 200	200 ± 200	200 ± 200	200 ± 200
Strength (°C/100m)	Su.	0.47 ± 0.37	0.26 ± 0.15	0.32 ± 0.19	0.36 ± 0.26	0.34 ± 0.27	0.44 ± 0.26
	A.	0.43 ± 0.31	0.34 ± 0.25	0.26 ± 0.12	0.38 ± 0.28	0.43 ± 0.26	0.45 ± 0.32
	W.	0.42 ± 0.32	0.27 ± 0.17	0.26 ± 0.22	0.4 ± 0.34	0.43 ± 0.29	0.41 ± 0.25
	Sp.	0.46 ± 0.32	0.31 ± 0.21	0.24 ± 0.17	0.4 ± 0.39	0.49 ± 0.31	0.5 ± 0.38
Number of inversions	Su.	2.20 ± 3.13	0.92 ± 0.93	0.83 ± 0.90	0.76 ± 1.36	0.9 ± 1.94	0.67 ± 0.71
	A.	1.68 ± 2.14	1.09 ± 1.00	0.54 ± 0.54	0.93 ± 2.52	0.7 ± 0.88	0.94 ± 1.53
	W.	1.76 ± 2.78	0.72 ± 0.81	0.54 ± 0.51	0.69 ± 1.87	1.11 ± 3.58	0.63 ± 0.92
	Sp.	1.79 ± 2.23	0.99 ± 0.99	0.86 ± 1.28	0.78 ± 1.42	0.98 ± 1.65	1.34 ± 5.57
	Su.	1221	157	56	348	115	61
	A.	1085	162	16	169	113	77
	W.	994	128	20	258	104	83
	Sp.	1065	158	31	288	101	91

Our seasonal mean inversion strengths per 100 m for low-level temperature inversions (Table 3-4) measured by radiosonde data at Walvis Bay were in the order of the 2–5°C for summer and 3–4.5°C for winter over the Benguela reported by Preston-Whyte et al., (1977). Over the ocean and coastal margin, and towards lower latitudes, mean depths estimated from GPS data (Tables 1 to 3) were in agreement with 400 – 500 m reported by Preston-Whyte et al. (1977) and 500 m reported by Cosijn and Tyson (1996) for the west coast and Namibia. The low-level inversions identified in the GPS data, situated around 1.5 km amsl over the ocean and coast and around 2.2 km over the subcontinent, corresponds to the height of the 850 hPa stable layer described by Cosijn and Tyson (1996).

Diurnal variability was compared between measurements made in the morning (03h00 to 09h00 UTC), noon (09h00 to 13h00 UTC), afternoon (13h00 to 17h00), and night (17h00 to 03h00). On diurnal scales, this inversion layer formed more frequently at night and in the early morning, as seen in Tables C-1.2 to C-1.4., when atmospheric stability was greatest. Diurnal variability in inversion strengths and base heights was smallest along the coastal margin, likely as a result of the stabilising effect of the cold upwelling waters along the coast. The influence of diurnally varying land- and sea-breezes could not be identified in the data, despite them being known to form under steep pressure gradients between land and sea during the coldest or warmest times of the day (Markowski and Richardson, 2010; Tyson and Preston-Whyte, 2014). Along the coast, the frequently occurring, morning and night-time inversions at low-levels (Tables C-1.2. to C-1.4.) may indicate the presence of the weak counterpart of the low-level Benguela jet stream, for which Nicholson (2010) reported a temperature lapse of 2°C between 850 and 700 hPa (approximately 1 450–3 000 m, ie. inversion strength of 0.13°C/100m). For the stronger counterpart, Nicholson (2010) reported a temperature lapse of 7°C between 850 and 925 hPa

(approximately 750–1 450 m, i.e. inversion strength of 1°C/100 m). Of all those night-time inversions measured along the coastal margin, only 2.2% had strengths of at least 1°C/100 m and may be indicative of this stronger jet stream.

Table 3-4. Same as for Table 3-1, but for inversions identified in data from radiosondes released at Walvis Bay airport.

		0.5 – 2.5 km agl	2.5 – 10 km agl
Height (m)	Su.	980 ± 350	5990 ± 1420
	A.	910 ± 330	5260 ± 1370
	W.	1160 ± 570	5020 ± 2070
	Sp.	1020 ± 430	5940 ± 1850
Depth (m)	Su.	150 ± 120	60 ± 40
	A.	160 ± 120	70 ± 40
	W.	140 ± 110	90 ± 50
	Sp.	170 ± 120	70 ± 40
Strength (°C/100m)	Su.	0.01 ± 0.01	0.01 ± 0
	A.	0.01 ± 0.01	0.01 ± 0.01
	W.	0.01 ± 0.01	0.01 ± 0
	Sp.	0.01 ± 0.01	0.01 ± 0.01
Strength (°C/depth)	Su.	2.72 ± 2.59	0.55 ± 0.56
	A.	2.16 ± 2.09	0.44 ± 0.45
	W.	1.91 ± 2.23	0.73 ± 0.78
	Sp.	3.27 ± 3.43	0.52 ± 0.42
Number of inversions	Su.	183	44
	A.	144	65
	W.	73	82
	Sp.	177	52

3.4.3. Spatial and temporal variability in elevated discontinuities

3.4.3.1. Temperature inversions

The monthly and seasonal means (and standard deviations) of inversions identified between 2.5 and 10 km were only calculated for those periods that had vertical profiles for at least 80% of the days in the time of interest. Tables 3-1 to 3-3 also give the seasonal summaries of the elevated inversion character. As with the low-level inversions, the highest frequency of elevated inversions was measured over the open ocean between 20° and 25°S. The lowest frequency of formation was along the coastal margin north of 25°S and over the subcontinent between 25° and 30°S (Tables 3-1 to 3-3). Seasonal mean base heights for temperature inversions above 2.5 km agl, given in Figure 3-10, decreased slightly towards the open ocean across all latitudes in the summer with only a slight decrease in the spring. The most notable latitudinal variability was seen in the winter where base heights decrease drastically over the subcontinent. Low base heights over the subcontinent during the winter and autumn suggests a link to the migration of the high-pressure belt, which was theorised by Cosijn and Tyson (1996). This includes the SEA anticyclone and continental anticyclones which adiabatically heat subsiding air and have been linked to the formation of inversions as high as 500 hPa (Preston-Whyte et al., 1977; Cosijn and Tyson, 1996). Despite the increased subsidence under these high-pressure conditions, wintertime inversions

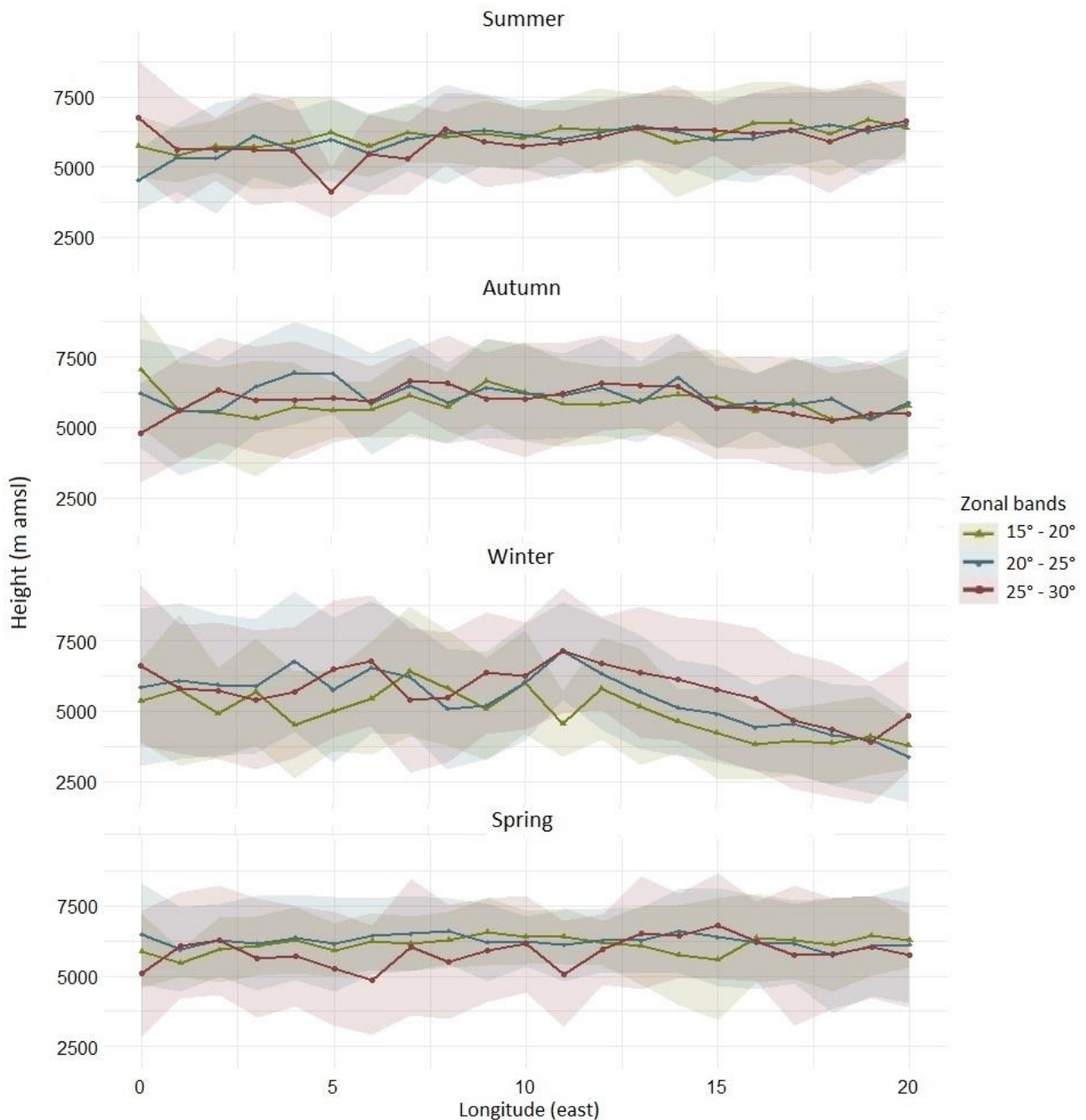


Figure 3-10. Five degree zonally averaged seasonal means and standard deviations of inversion base heights for elevated inversions between 2.5-10 km.

over the subcontinent were among the weakest throughout the year, whereas springtime inversions were strongest. The resultant variability in atmospheric stratification has tremendous implications for emitted pollutant concentrations in the atmosphere. Radiation interactions with atmospheric pollutants may also contribute to the strengthening of existing inversions. The transport of biomass burning smoke over southern Africa has been a topic of interest due to the implications of the constituents contained in these plumes for weather and climate (Haywood and Shine, 1995; Hansen et al., 1997; Shinozuka et al., 2020). Radiation-absorbing aerosols, such as black- (Formenti et al., 2018; Gordon et al., 2018) and brown carbon (Feng et al., 2013), and greenhouse gases such as ozone, interact directly with radiation, which alter the temperature and moisture profiles of the atmosphere (De Graaf et al., 2014). A seasonal

maximum in radiation-absorbing black carbon concentrations released in BB over southern Africa occurs in June to October (Chiloane et al., 2017; Swap et al., 2003). These plumes are transported off the west coast by the easterly wave from autumn to the end of winter when subsidence under the influence of the continental high-pressure system is at a maximum. Formenti et al. (2018) reported increased black carbon concentrations within the BL between April and September with a maximum in June. These plumes are transported over the south Atlantic as far Ascension Island between June and October (Wu et al., 2020) and were specifically observed above clouds in September and October (Zuidema et al., 2018).

No clear diurnal trend could be identified for elevated discontinuities. Diurnal variability in base heights was smallest along the coast over the cold, upwelling waters and greatest over the subcontinent where atmospheric temperature changes more rapidly. This is indicative of the impacts of solar inputs over the varying land surfaces. Across all three regions, the number of inversions was lowest at noon and in the afternoon when the input of solar radiation is at a maximum. There was also a slightly higher incidence of deeper inversions during this time, although depths generally remained around 0.2 ± 0.3 km. Over the subcontinent, the influence of diurnally varying solar inputs was also evident in the higher morning and night-time inversion strengths per 100 m. Variability in inversion strength throughout the depth was greatest along the coast and smallest over the ocean (Tables C-1.2. to C-1.4.). This high variability along the coast may be as a result of the variability in the inflow of warm, dry continental air masses and cool, moist marine air masses. The diurnal variability in the character of elevated inversions at high latitudes may be dampened by the increased influence of the high-pressure belt towards higher latitudes.

3.4.4. Co-occurring inversions

Multiple layers of inversions measured at different altitudes in the same profile are frequently detected in the atmosphere over the study region. Instances of these co-occurring elevated inversions between 0.5–10 km, indicated as a percentage of the total number of inversions measured, are given for diurnal (Table 3-5) and monthly variability (Table 3-6). Over the subcontinent and along the coast, the instances of co-occurring inversions were at a minimum around noon and the afternoon, whereas the maximum instances were measured in the morning and at night. The higher frequency of night and morning measurements are largely due to enhanced stability without the input of solar radiation. Over the ocean, diurnal variability was smallest. Over the ocean, the maximum number of co-occurring inversions was measured between 0.6 and 1.5 km. The small diurnal variability in the heights and number of co-occurring inversions over the ocean were likely a result of the high specific heat capacity of the atmosphere, where temperature changes are smaller than over the subcontinent. Along the coast, the maximum number of co-occurring inversions was measured between 0.6 and 1 km and then between 5.6 and 6.6 km. Over the subcontinent, the greatest number of co-occurring layers were present between 1.4 and 1.7 km, 5.4 to 5.7 km, 6 to 6.5 km and 7.7 to 7.9 km.

Table 3-5. The percent of inversions co-occurring with each other in the same profile as a function of the total, summarised by time of day and over the ocean, coast and subcontinent.

	Morning	Noon	Afternoon	Night
Ocean	14.6	14.9	13.6	13.8
Coast	18.0	14.8	14.8	17.4
Subcontinent	9.9	7.1	9.7	10.9

On monthly scales, the frequency of co-occurring inversions was between one in five and one in ten for GPS profiles over the ocean (14.2%), along the coast (16.8%) and over the subcontinent (9.9%), and for inversions measured by radiosonde at Walvis Bay (16.0%). This was about half of that (one in five) reported by Cosijn and Tyson (1996) for the subcontinent. The additional stratification, stabilisation and decoupling induced by multiple elevated inversions inhibit vertical motions and result in the formation of both heavily polluted plumes and clean air slots, an observed but not yet fully understood phenomena over southern Africa (Hobbs, 2003). These clean air slots have been observed adjacent to plumes of pollution (Hobbs, 2003) or cloud (Costantino and Bréon, 2010), and also above (Haywood et al., 2004) and below smoke layers (Wilcox, 2010) with varying differences in the thickness and location of those gaps (LeBlanc et al., 2020). No causal relationship between pollution plumes and number of co-occurring inversions is being suggested, but some interesting correlations were found.

Table 3-6. The percent of inversions co-occurring with another in the same profile as a function of the total, summarised for each month and over the ocean, coast and subcontinent.

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Ocean	14.8	11.7	13.4	10.2	12.5	11.1	13.1	14.1	18.8	21.1	14.7	12.9
Coast	19.9	15.0	15.5	12.3	12.6	9.6	13.5	15.0	21.9	22.9	16.8	17.8
Walvis Bay	13.6	14.8	4.8	10.3	16.7	25.0	16.7	20.1	20.1	9.5	8.3	18.5
Subcont.	9.4	7.5	8.2	7.9	10.1	6.6	7.9	9.6	15.7	14.5	9.6	7.7

Across all three regions, the maximum instances of co-occurring inversions measured by GPS-RO were recorded in September and October (Table 3-6). The instances of co-occurring inversions had the greatest seasonal variability along the coastal margin, with a maximum of 22.9% in October and a minimum of 9.6% in June. The inversions measured by radiosonde data at Walvis Bay also saw an increase in the frequency of co-occurring inversions between May and September. This coincides with the most intense anticyclonic circulation over the subcontinent. The general trend of the monthly variability across all four regions was a sharp decline after the October maximum, except for high incidences of multiple inversions in the coastal margin in January. Monthly variability was smallest over the ocean where the SEA anticyclone exerts a year-round influence over the region. Instances of co-occurring inversions also decreased towards lower latitudes over the region. This may be explained by the smaller influence of high-pressure cells at lower latitudes and is also in good agreement with the decreasing gradient of absorbing aerosol concentrations (De Graaf et al., 2014; Zuidema et al., 2018). The mechanism for the formation of these inversions is, therefore, subsidence and adiabatic heating.

3.5. Conclusions

This study of 11 years of GPS refractivity and temperature profiles and one year of radiosonde data at Walvis Bay provides a novel, in-depth look at the spatial and temporal variability of stable layers in the atmosphere over Namibia and the SEA Ocean adjacent to the coast. This paper drew from previous work in the region to understand how the meso- and macro scale circulation features affect the thermodynamic structure of the atmosphere.

A direct comparison of temperature profiles from GPS to radiosonde profiles found differences consistent with previous findings over the region by Wang et al. (2013). Furthermore, the identification of the point of minimum gradient in the refractivity profiles was also in good agreement. GPS-RO temperature measurements were negatively biased to radiosondes between 0.5 and 7 km and positively biased between 7 and 10 km. The study of an exceptional case found extreme temperatures measured by GPS-RO possibly linked to the high moisture content. The vertical resolution of the two datasets was noted as the reason for different inversion base heights identified in the profiles. Future studies would benefit from identifying profiles with excessive temperature lapse rates to investigate the causes of this.

The comparison also revealed that the MG was more consistent with cloud top than BLH. This reaffirms the importance of identifying real structures consistent with BLH and not other structures that may share similar characteristics to the BL, such as sharp moisture and temperature gradients. Furthermore, the variability in topographic features on the surface and radiative interactions over different landscapes and low-level clouds in the region contribute to the complex character of the BL and low-level inversions.

The BLH was best defined by the bulk R_N definition. The variability in BLH calculated by this method was linked to macroscale circulation and surface heating effects. High wintertime BLHs coincide with low cloud cover and the inflow of warm, dry continental air masses. The sensitivity of GPS signal propagation to atmospheric moisture means that despite identifying the large-scale variability, it would be useful for future investigations to separate measurements for cloudy and cloud-free conditions. The MG surface over the ocean shows a slight westward increase, similar to the simulated westward increase in the inversion at the base of the stratocumulus cloud. The transitional zone across the coastline, where the height of this surface increases by 400-800 m over the subcontinent, varies by latitude. No seasonal link to the strength of anticyclonic circulation could be determined.

The low-level inversion was present year-round over the ocean and coast. North of 20°S, the lowest, strongest and deepest inversions were measured in the springtime. Small variability (on diurnal and seasonal scales) in low-level inversions and the surface of MG of refractivity may be the result of the stabilising effect of the cold waters and cloud cover along the coastal margin. Latitudinal variability may be explained by the seasonal changes in the location and strength of anticyclonic circulation. The low-level inversion was deepest and strongest along the coastal margin at night and in the early morning, coinciding with the presence of the Benguela jet stream. Unlike previous studies, this inversion was observed over the subcontinent although very rarely. The character of these inversions was linked to

macroscale circulation systems. The elevated inversions were influenced by the same surface radiative effects and macroscale circulation systems as the low-level inversions; however, at these levels, no link to cloud character was established, but rather to the seasonality and distribution of radiation-absorbing biomass burning plumes. Accordingly, greater stability over the region was observed in spring when these plumes were present over the ocean.

Cases of multiple co-occurring elevated inversions were observed 10 to 20% of the time. Across all three regions, these inversions formed preferentially below 1.7 km. Over the subcontinent and coast, another preferential height for inversions was between 5.5 and 6.5 km and over the subcontinent around 7.7 to 7.9 km. Maximums in co-occurring inversions were measured in September and October across all three regions, coinciding with the maximum in radiation-absorbing aerosols over Namibia (Eck et al., 2003). Considering that springtime inversions were stronger than inversions measured during the winter when the high-pressure belt exerts the greatest influence on circulation over the region (evident in the significant decrease in base heights), it might be reasonable to suggest that the radiative properties of aerosols transported in burning plumes significantly affect regional atmospheric stability.

Data availability. COSMIC GPS-RO data and ECMWF data were obtained from the COSMIC Data Analysis and Archive Center (CDAAC), available at <http://cosmic-io.cosmic.ucar.edu/cdaac/index.html>. The openair package for R is found in Carslaw and Ropkins (2017). Radiosondes were collected and provided by the Namibia Meteorology Service.

Author contributions. DK analysed the data with contributions by RB and SJP. DK wrote the paper with contributions from SJP, RB and PF. SD made the measurements and compiled the radiosonde data.

Competing interests. PF is guest editor for the ACP Special Issue “New observations and related modelling studies of the aerosol–cloud–climate system in the Southeast Atlantic and southern Africa regions”. The remaining authors declare that they have no conflicts of interests.

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The article presented in this chapter gave in-depth analysis of the temporal and spatial variability in atmospheric vertical structures over Namibia and the southeast Atlantic. This included the study of marine boundary layer height and the height of elevated inversions.

Chapter 4

Seasonality, origin and transport of light-absorbing aerosols

This chapter fulfils the objective of creating a conceptual model of atmospheric transport pathways over the Namibian coast, specifically with regard to black carbon (BC) measured at Henties Bay Aerosol Observatory (HBAO). This was done by, first, investigating the topographic and meteorological controls on air mass transport and identifying ‘typical’ and ‘atypical’ conditions. Trajectories were classified into different envelopes to identify typical transport pathways towards HBAO. The variability in measurements of BC, made by an aethalometer at HBAO between 2013 and 2015, are divided according to the associated transport pathway. This allowed for a discussion on the seasonality and atmospheric relevance of these transport pathways to BC mass concentrations. The article is titled, *Three years of measurements of light-absorbing aerosols over coastal Namibia: seasonality, origin, and transport*. The author of this thesis contributed the full data analysis regarding transport patterns and the final compilation and writing of the document with inputs from co-authors. This paper has been accepted for publication in the journal *Atmospheric Chemistry and Physics*, issue 18, pp. 17003–17016, 2018, doi: 10.5194/acp-18-17003-2018. Consent from co-authors is attached under appendix B-1.

Author contributions

- Paola Formenti, Stuart John Piketh, Andreas Namwoonde, Samuel Mafwila, Edosa Omoregie, Wolfgang Junkermann and Willy Maenhaut designed the experiments and the sampling site.
- Paola Formenti, Stuart John Piketh, Andreas Namwoonde, Mathieu Cazaunau, Anaïs Feron, Cécile Gaimoz, Stephen Broccardo, Nicola Walton, Karine Desboeufs and Mattheus Hanghome performed the experiments.
- Paola Formenti and Stuart John Piketh performed the full data analysis with contributions by Danitza Klopper, Guillaume Siour and Roelof Burger.
- Paola Formenti and Stuart John Piketh, Danitza Klopper and Roelof Burger wrote the paper with comments from all co-authors.

ARTICLE 2: Three years of measurements of light-absorbing aerosols over coastal Namibia: seasonality, origin, and transport

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Abstract. Continuous measurements between July 2012 and December 2015 at the Henties Bay Aerosol Observatory (HBAO; 22°S, 14°05'E), Namibia, show that, during the austral wintertime, transport of light-absorbing black carbon aerosols occurs at low level into the marine boundary layer. The average and standard deviation of daily concentrations of equivalent black carbon (eBC) over the whole sampling period is 53 ($\pm$ 55) ng m⁻³. Peak values above 200 ng m⁻³ and up to 800 ng m⁻³ occur seasonally from May to August, ahead of the dry season peak of biomass burning in southern Africa (August to October). Analysis of 3-day air mass back-trajectories shows that air masses from the South Atlantic Ocean south of Henties Bay are generally cleaner than air having originated over the ocean north of Henties Bay, influenced by the outflow of the major biomass burning plume, and from the continent, where wildfires occur. Additional episodic peak concentrations, even for oceanic transport, indicate that pollution from distant sources in South Africa and maritime traffic along the Atlantic ship tracks could be important. While we expect the direct radiative effect to be negligible, the indirect effect on the microphysical properties of the stratocumulus clouds and the deposition to the ocean could be significant and deserve further investigation, specifically ahead of the dry season.

4.1. Introduction

Aerosol particles of natural and anthropogenic origin affect the Earth's climate and modulate the greenhouse effect of long-lived gases (Boucher et al., 2013). The extent of this modulation depends on their nature, in particular on their chemical composition and size distribution determining their interactions with radiation and clouds. Current understanding suggests that atmospheric aerosols increase the global outgoing shortwave radiation, enhancing the atmospheric albedo, thereby counteracting the warming effect of greenhouse gases (Boucher et al., 2013). However, light-absorbing aerosols, such as black carbon (BC) from fossil fuel combustion and biomass burning, can reduce the amount of outgoing radiation at the top of atmosphere (TOA), finally adding to the greenhouse effect (Haywood and Shine, 1995; Jacobson, 2001; Chung and Seinfeld, 2002; Bond and Bergstrom, 2006; Koch and Del Genio, 2010; Bond et al., 2013). The heating radiative effect of BC aerosols is either enhanced or suppressed if they are above or below clouds, respectively (Keil and Haywood, 2003; Koch and Del Genio, 2010). The local heating induced by light absorption below clouds could modify the cloud properties by enhancing the vertical motion and increasing the cloud cover and liquid water content (Koch and Del Genio, 2010). Finally, by entrainment into clouds, BC-containing aerosols could cause the cloud to evaporate and rise (Hansen et al., 1997) and reduce the cloud mean drop size diameters, increase droplet concentrations and henceforth reflectivity (Seinfeld and Pandis, 1997). These processes are relevant to the western coast of southern Africa, pointed out by the latest Intergovernmental Panel for Climate Change (IPCC) report as a region where future warming and reductions in precipitation should be severe (Maúre et al., 2018).

The west coast of southern Africa is characterised by a persistent and extended stratocumulus cloud deck topping a shallow, stable marine boundary layer (MBL) maintained by the cold sea-surface temperatures of the Benguela Current (Cook et al., 2004; Tyson and Preston-Whyte, 2002), and by high loading of light-absorbing aerosols, mostly from seasonal biomass burning in the austral dry season (Swap et al., 2003), but possibly from various local and distant anthropogenic activities including ship traffic and energy production (Piketh et al., 1999a; Formenti et al., 1999; Tournadre, 2014). Stratocumulus clouds are highly reflective and efficient in modifying the net radiative balance at TOA (Boucher et al., 2013). However, the mechanisms by which they could interact with light-absorbing aerosols, and the direct and indirect effects of those interactions on the regional radiative budget, are largely unknown (Keil and Haywood, 2003; Flato et al., 2013; Myhre et al., 2013).

To address these questions, a large observational effort was initiated in the last few years by a number of coordinated intensive airborne and ground-based field campaigns, analysis of space-borne observations, and climate modelling (Zuidema et al., 2016). These experiments focused on the dry season period between July and October when biomass burning aerosols contribute by optically dense plumes with instantaneous aerosol optical depth (AOD) systematically larger than 0.5 at mid-visible wavelengths (Swap et al., 2003). The emission, transport and direct radiative effect of light-absorbing carbonaceous

aerosols by biomass burning aerosols also motivated previous experiments, such as the Southern African Regional Science Initiative (SAFARI 2000; Swap et al., 2003).

However, little is known about the aerosol concentrations and properties outside this season. To fill this gap, this paper presents the first results of the mass concentrations of light-absorbing carbonaceous aerosols on the Atlantic coast of Namibia from 3 years of observations at the Henties Bay Aerosol Observatory (HBAO; 22°S, 14°05' E) long-term ground-based surface station.

Measurements of the mass concentrations of equivalent black carbon (eBC) recorded between July 2012 and December 2015 in the marine boundary layer below the stratocumulus deck are analysed to gather new knowledge on importance and seasonality. Observations are coupled with calculations of air mass back-trajectories to identify the dominant transport patterns and quantify their contributions. A comparison to the MERRA-2 model reanalysis is performed.

4.2. Methods

Surface observations of aerosol particles are conducted at the Henties Bay Aerosol Observatory (HBAO; <http://www.hbao.cnrs.fr/>, last access: 12 November 2018), a recent regional station in the Global Atmosphere Watch (GAW) programme of the World Meteorological Organization (WMO). The research centre is located on the Sam Nujoma Marine and Coastal Resources Research Centre (SANUMARC) of the University of Namibia in Henties Bay (22°S, 14°05'E), Namibia (Figure 4-1).

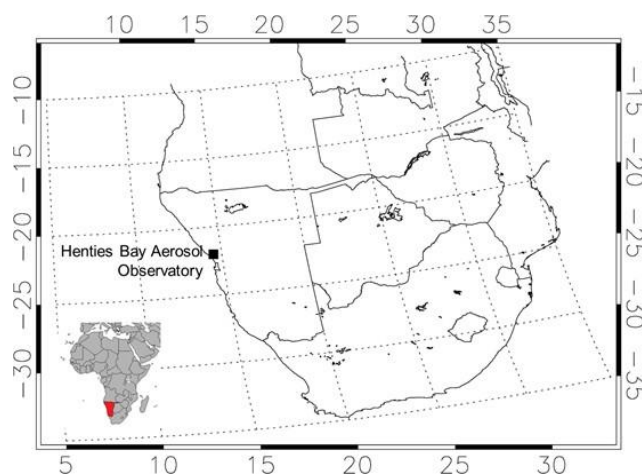


Figure 4-1. The geographic location of Henties Bay Aerosol Observatory (HBAO).

Henties Bay is a small town in an arid environment with no vegetation, no industrial activity and very little traffic. Energy usage is predominantly a mix of electricity and gas, with some solid fuel combustion (wood) due to low availability (Andreas Namwoonde, *personal communication*, 2017). The monitoring site, situated on the university campus, is located on the coast approximately 100 m from the shoreline. To the east are the Namibian gravel plains, 3 km to the south of the campus is the town of Henties Bay and to the north is the Omaruru riverbed (river mouth approximately 100 m from SANUMARC). The population of Henties Bay ranges between 4600 and 6000 inhabitants, according to the Namibia 2011

Population and Housing Census Main Report (available at <http://cms.my.na/assets/documents/p19dmn58guram30ttun89rdrp1.pdf>, last access: 12 November 2018).

4.2.1. Measurements of light-optical attenuation

Instruments at HBAO operate from a roof terrace at approximately 30m above mean sea level. The terrace hosts the sampling inlets, from which air is drawn into a laboratory room located underneath by straight stainless-steel pipes to avoid particle losses. The optical attenuation of light (ATN) by aerosol particles smaller than 1 μm in aerodynamic diameter was measured by a single-wavelength aethalometer (model AE-14U, Magee Sci., Berkeley, CA, USA) operating at 880 nm and sampling at 3.5 (± 0.1) L min^{-1} from a certified PM_{10} inlet (BGI Inc., Waltham, MA). The physical principle of operation of the aethalometer is detailed in Hansen et al. (1984). Measurements were performed at a 5 minute time resolution and stored on a data logger (model CR-1000, Campbell Sci. Ltd.). The original dataset was screened to eliminate spikes and peaks lasting less than 2 h, generally associated with open fires for barbecuing meat. The data record extended from July 2012 to December 2015, with an extended data gap between January and July 2014 due to instrument maintenance.

The Lambert-Beer law relates the temporal variation in the measured light attenuation (ATN) due to aerosol particles collected on a quartz fibre tape to the mass concentration of eBC (in $\mu\text{g m}^{-3}$). This is based on the fact that BC is the strongest light absorber in the near-infrared (Kirchstetter et al., 2004; Caponi et al., 2017). The operational equation linking eBC to the attenuation (ATN) measured by the aethalometer is

$$\text{eBC} = \frac{1}{\text{MAC}_{\text{BC}}} \left(\frac{1}{C \cdot R(\text{ATN})} \right) \left(\frac{A}{V} \frac{\Delta \text{ATN}}{\Delta t} \right) \quad (\text{Equation 4-1})$$

where A represents the area of the aerosol deposited on the filter, V the volumetric flow rate and $\Delta \text{ATN} / \Delta t$ is the variation rate of attenuation with time. The terms C and $R(\text{ATN})$ account for measurement artefacts that artificially increase absorption estimated from attenuation measurements. The term C takes into account the multiple scattering effects on the filter due to both the filter fibres and the aerosol particles embedded in it. The factor $R(\text{ATN})$ accounts for the shadowing effect occurring with time as high concentrations of absorbing particles are collected on the filter. Published values of the C parameter at 660 and 880 nm range between 1.75 and 6.3 depending on the nature of the light-absorbing aerosols, the measurement environment and finally on the parameterisation of the corrections (Weingartner et al., 2003; Arnott et al., 2005; Schmid et al., 2006; Collaud-Coen et al., 2010; Segura et al., 2014; Saturno et al., 2017; Di Biagio et al., 2017). These authors show that, regardless of location, values below 3.5 are appropriate for moderately absorbing aerosols whose single scattering albedo (ω_0) is above 0.8 at 660 nm. For Mace Head, a coastal site with prevailing marine North Atlantic air masses, Collaud-Coen et al. (2010) reported a mean C value of 3.44 (0.21), which we used for HBAO, neglecting any possible wavelength dependence. The parameterisation of the shadowing effect $R(\text{ATN})$ depends on ω_0 ; henceforth, on the availability of concurrent measurements of the scattering coefficient. This is the

case at HBAO, where scattering is measured on the PM_{10} and not on the PM_1 fraction as attenuation is preventing a meaningful estimate of ω_0 . In this case, Collaud Coen et al. (2010) recommended the Weingartner et al. (2003) correction, leading to a mean value of the R parameter of 0.93, which we assumed for the further analysis. The other crucial parameter in Eq. (4-1) is the mass absorption efficiency of eBC (MAC_{BC} , units of $m^2 g^{-1}$). Many authors have reported values in the range $5-20 m^2 g^{-1}$ at wavelengths between 550 and 870 nm and related this variability to the chemical state and age of BC aerosols (Liousse et al., 1993; Petzold et al., 1997; Martins et al., 1998; Kirchstetter et al., 2003; Hansen, 2005; Bond and Bergstrom, 2006; Knox et al., 2009; Subramanian et al., 2010; Bond et al., 2013; Zanatta et al., 2016). More recently, Zuidema et al. (2018) reported that the MAC_{BC} at 648 nm at Ascension Island, farther west than HBAO, and at times in its outflow, varied between $14.1 m^2 g^{-1}$ in June and $10.7 m^2 g^{-1}$ in July to October. When extrapolated, these values result in a MAC_{BC} at 870 nm between 7.9 and $10 m^2 g^{-1}$. Their average and standard deviation ($9.0 \pm 1.5 m^2 g^{-1}$) were retained in our analysis.

4.2.2. Supporting data

In 2013, the mass concentration of particles of diameters smaller than $2.5 \mu m$ in equivalent aerodynamic diameter ($PM_{2.5}$) was sampled by a tapering element oscillating microbalance (TEOM, model 1400a, Rupprecht and Patashnick, Albany, NY, USA) operating from a certified $PM_{2.5}$ inlet (also from Rupprecht and Patashnick). The total flow rate at the inlet was $16.7 L min^{-1}$ to ensure the correct functioning of the inlet, and the sampling flow rate driving the aerosol-laden air to the microbalance was $3 L min^{-1}$. The temperature of the sample stream was kept constant at $50^\circ C$. Three-dimensional air mass back-trajectories are calculated using the NOAA HYbrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT; Stein et al., 2015). The model uses the $1^\circ \times 1^\circ$ latitude-longitude grid reanalysis meteorological database. The 6 h reanalysis archive data are generated by the NCEP's GDAS (NCEP: National Centres for Environmental Prediction; GDAS: Global Data Assimilation System) wind field reanalysis. Further information can be found at <https://rda.ucar.edu/datasets/ds083.2/> (last access: 12 November 2018).

ERA-Interim reanalysis data (Dee et al., 2011) from the European Centre for Medium Range Weather Forecasts (ECMWF) are used in the analysis of synoptic-scale circulation patterns associated with the identified dominant air mass transport to Henties Bay. The 6-hourly (00:00, 06:00, 12:00, 18:00 UTC) analysis data ($0.75^\circ \times 0.75^\circ$) at mean sea level pressure (MSLP – variable 151.128) and the 500 hPa geopotential height (ZG500 – variable 129.128) are used for this study. Datasets were normalised (MSLP/100 and ZG500/100) using Climate Data Operators (CDO) (Schulzweida et al., 2006) and plotted with 2 and 10 hPa isobaric intervals for MSLP and the 500 hPa level, respectively. Surface BC concentrations predicted by the Modern-Era Retrospective analysis for Research and Applications, Version 2 (MERRA-2; Gelaro et al., 2017) sampled at HBAO and a number of other sites (Zuidema et al., 2016) are used for comparison.

The HTAP_V2 dataset is used for gridded emission of anthropogenic BC for the year 2010 (Janssens-Maenhout et al., 2015). It consists of $0.1^\circ \times 0.1^\circ$ grid maps. HTAP_V2 uses nationally reported emissions combined with regional scientific inventories in the format of sector-specific grid maps.

The grid maps are complemented with EDGARv4.3 data for those regions where data are absent. Anthropogenic activities producing BC aerosols comprise aviation, transportation, energy production, industries, ship traffic, residential and agricultural burning.

4.3. Results

4.3.1. Temporal variability in eBC concentrations

Figure 4-2 shows daily and monthly averages of the eBC concentrations measured at HBAO between July 2012 and December 2015. Daily averages excluded spikes and peak values occurring on short timescales, less than 1–2 h, resulting from contamination of local activities (episodic traffic and occasional open fires for barbecuing meat). The daily mean average of $53 (\pm 55) \text{ ng m}^{-3}$ is in accordance with previous observations in remote locations of the world shown in Table 4-1 (Bodhaine, 1995; Andreae et al., 1995; Derwent et al., 2001; von Schneidmesser et al., 2009; Marinoni et al., 2010; Sheridan et al., 2016). Andreae et al. (1995) found eBC mass concentrations lower than 50 ng m^{-3} along a cruise transect at 19°S over the south-east Atlantic between Brazil and Angola, except when approaching the African continent, when concentrations increased in the range $50\text{--}150 \text{ ng m}^{-3}$, indicating a strong continental influence in this otherwise pristine environment. Additional published research, also in Table 4-1, reports absorption coefficients that would lead to comparable eBC concentrations (Bodhaine, 1995; Clarke, 1989; Quinn et al., 1998). For contrast, eBC mass concentrations in lofted layers above the marine boundary layer in the range $0.1\text{--}6 \mu\text{g m}^{-3}$ were reported for aged biomass burning haze (Kirchstetter et al., 2003; Formenti et al., 2003; Eatough et al., 2003), and up to $5\text{--}40 \mu\text{g m}^{-3}$ for fresh biomass smoke plumes (Kirchstetter et al., 2003).

Table 4-1. Values of mass concentrations of equivalent black carbon (eBC) from measurements published in the literature for remote regions worldwide. When available, the specific attenuation σ_{BC} used to convert the measured attenuation to eBC is also reported.

Location	eBC (ng m^{-3})	$\sigma_{\text{BC}, 880 \text{ nm}}$ (m^2g^{-1})	Reference
Tropical South Atlantic off southern Africa, 19°S	50–150	10	Andreae et al. (1995)
Nepal Climate Observatory – Pyramid, Himalaya	160 ± 296	6.5*	Marinoni et al. (2010)
Summit, Greenland	< 340	-	von Schneidmesser et al. (2009)
Mace Head, Ireland	47–74	11 ± 3	Derwent et al. (2001)
South Pole, Antarctica	0.01–50	19	Bodhaine (1995)

*At 635 nm – measurements were conducted with a Multi-Angle Absorption Photometer (MAAP 5012, Thermo Electron Corporation).

Figure 4-2 also shows an apparent seasonal variability in eBC, further highlighted by the monthly means and by the comparison with $\text{PM}_{2.5}$ mass concentration measurements performed at the site during 2013, which, conversely, did not display any particular seasonal cycle (Fig. C-2.1 in the appendices), likely

because they were dominated by sea salt. Concentrations increase in the austral winter from May to July, and decrease from August to April. The increase from May to July is well captured by the MERRA-2 reanalysis (also shown in Fig. 4-2), according to which, however, concentrations only start decreasing after September.

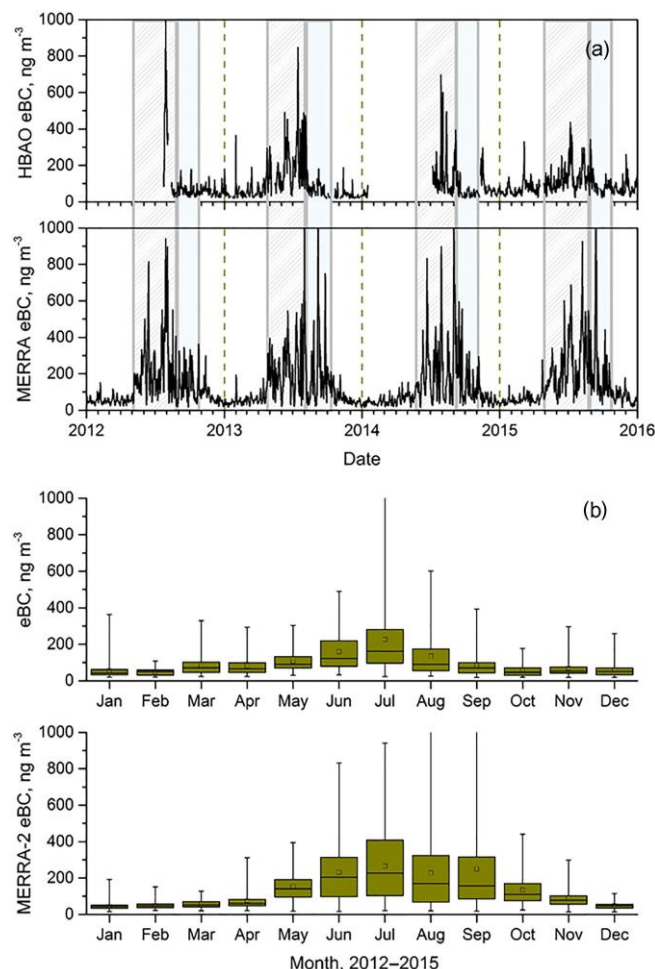


Figure 4-2. (a) comparisons of the time series of daily eBC mass concentrations (ng m^{-3}) measured at HBAO and predicted by the MERRA-2 reanalysis. The light grey boxes indicate periods of increasing concentrations. The light blue boxes indicate periods of decreasing concentrations; (b) box and whisker plot representation of the respective monthly variability.

The observed seasonality is somewhat surprising in that it precedes the seasonal maximum of the biomass burning fire season in southern Africa, peaking in the austral dry season from August to October (Swap et al., 2003). As previously stated in this paragraph, data constituting the time series have been screened to exclude short-term variability (less than 1–2 h time intervals) to exclude isolated and episodic sources. Peaks of eBC driving the seasonal increase in the May-to-August period are long-lasting, extending between 6 and 11 h, and occurring during both daytime and night-time. This suggests that transport is the cause of the seasonal peaks. The following section explores this hypothesis and attempts the quantification of attribution of eBC peaks to specific transport patterns.

4.3.2. General atmospheric circulation driving air mass transport

Transport to the west coast of Namibia is influenced by four general circulation patterns: baroclinic westerly waves, barotropic easterly waves, the semi-permanent south Atlantic high-pressure and a continental high-pressure circulation. The relative influence of each circulation pattern is highly seasonal and influenced by the meridional migration towards the north in austral winter and to the south in summer. The origin of the air parcel over the Southern Ocean is linked to the passage of a westerly wave and front that propagates towards the subcontinent from the south-west. These are Rossby waves that form as a result of the extratropical temperature gradient with a maximum impact on the weather over southern Africa in winter. The easterly waves are trade winds that are associated with the position of the Inter-Tropical Convergence Zone (ITCZ) that reaches a maximum over the subcontinent during summer (Tyson and Preston-Whyte, 2014; Taljaard, 1994). The semi-permanent high-pressure system (anticyclone) results from the descending limb of the Hadley circulation that interacts with the aforementioned waves. The south Atlantic high-pressure system will ridge behind a passing westerly wave in the direction of maximum cold air advection. Conversely, a strengthening anticyclone will block propagations of these waves and induce a strong persistent continental high-pressure. Air masses reaching the sampling station have been found to originate from the adjacent Atlantic Ocean and various locations over the continental subcontinent. Coastal lows are induced along the west coast of Namibia and result in the offshore flow ahead of westerly waves. This low-pressure system forms localised cyclonic circulation that includes onshore flow in the north and offshore flow in the south of the low-pressure cell (Tlhalerwa et al., 2005; Tyson and Preston-Whyte, 2014).

4.3.3. Identification of air mass transport pathways impacting HBAO

Three-day back-trajectories calculated daily between July 2012 and December 2015 are grouped according to the progression of the general synoptic circulation patterns and assigned to eight geographical sectors according to the position of their end point (shown in Fig. 4-3). Four sectors (G1 to G4) correspond to oceanic air masses and sectors G5 to G7 to transport from the continent. The last sector (G8) describes air masses recirculating around the sampling site for most of the 3-day period. Figure 4-3 also shows the 2010 BC aerosol regional emission HTAP_V2 inventory grid map from anthropogenic activities. Emissions are low in Namibia and neighbouring regions such as Botswana and west-central South Africa. Areas of higher emissions are Angola (with a hotspot in correspondence with the capital city Luanda); coastal South Africa, particularly to the east; but also to the south in the Cape Town greater area, but mostly in the South African Highveld (27°S, 28°W) where energy production is concentrated. The open-ocean and coastal ship tracks are also evident.

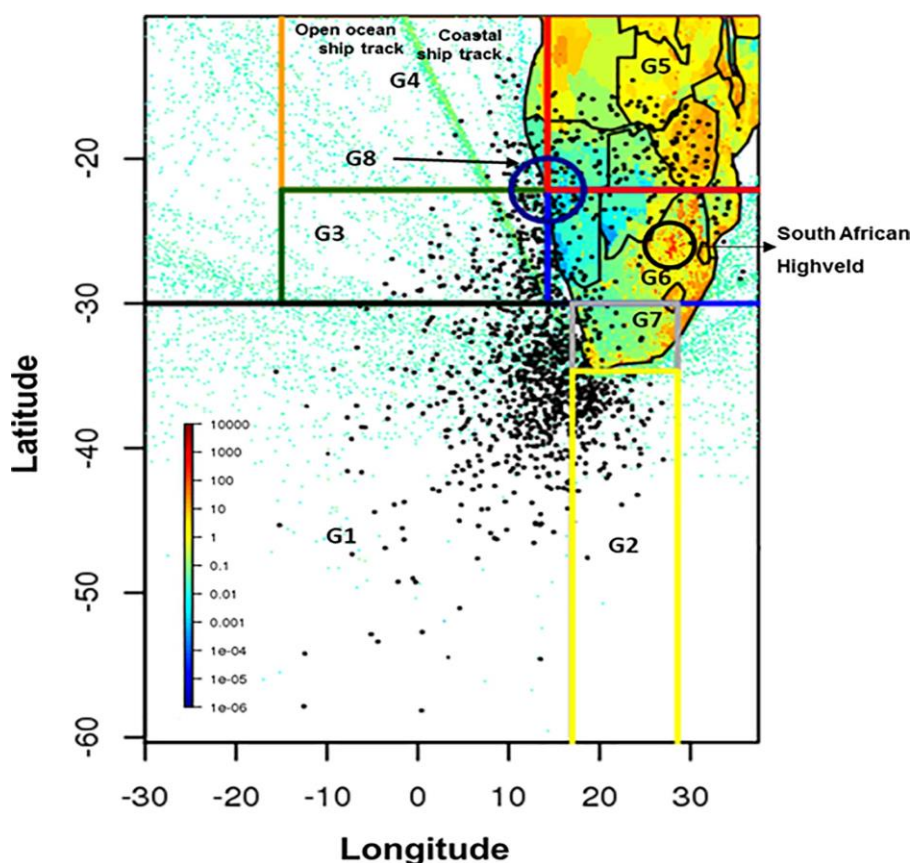


Figure 4-3. Geographical boundaries of the sectors used to classify the air mass back-trajectories superimposed to the emission grid maps at $0.1^\circ \times 0.1^\circ$ of BC aerosols from anthropogenic activities for the year 2010 provided by the HTAP_V2 inventory. Emissions are expressed in tonnes.

The monthly distribution of fire counts from 2012 to 2015 provided by MODIS/Aqua is shown in Fig. 4-4. Although some interannual variability exists, the image record is consistent in showing that the fire season in southern African starts towards April and extends until October. The major source areas are north of Namibia (Angola, Zambia), in South Africa (to the east and along the south coast) and in Mozambique. In Namibia, fire counts are seen towards the north, around the Etosha pan desert.

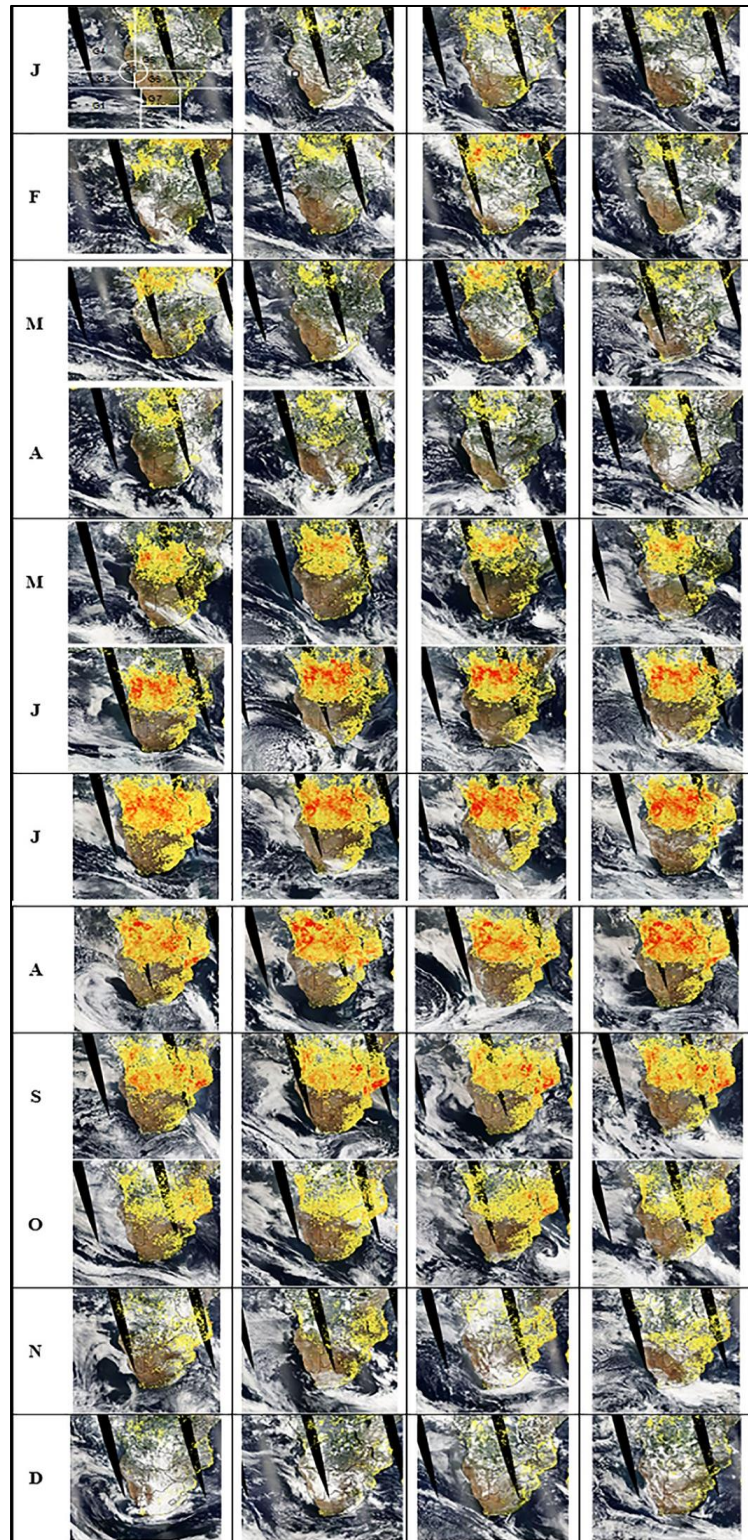


Figure 4-4. Fire counts per pixel from MODIS/Aqua provided by the NASA Fire Information for Resources Management System (FIRMS). Colours range from yellow (1 fire count per pixel) to red (> 100 fire counts per pixel). The underlying image is the corrected reflectance (true colour) measured by MODIS/Aqua on the first day of each month.

The seasonal contribution of these air mass transport pathways is shown in Fig. 4-5. Sectors G1 to G4 represent the most common air flow pathway (73 % out of 1279 calculated back-trajectories). The southern Atlantic Ocean transport (G1 and G2) is the dominant surface circulation along the west coast, resulting from the northward-moving limb of the surface south Atlantic high-pressure. Air masses originate over the southern Atlantic Ocean, as far south as 55°S (sector G2, representing approximately 66 % of the air mass occurrences). During summer this is predominantly a function of the most southerly location of the centre of the South Atlantic High (Fig. 4-6).

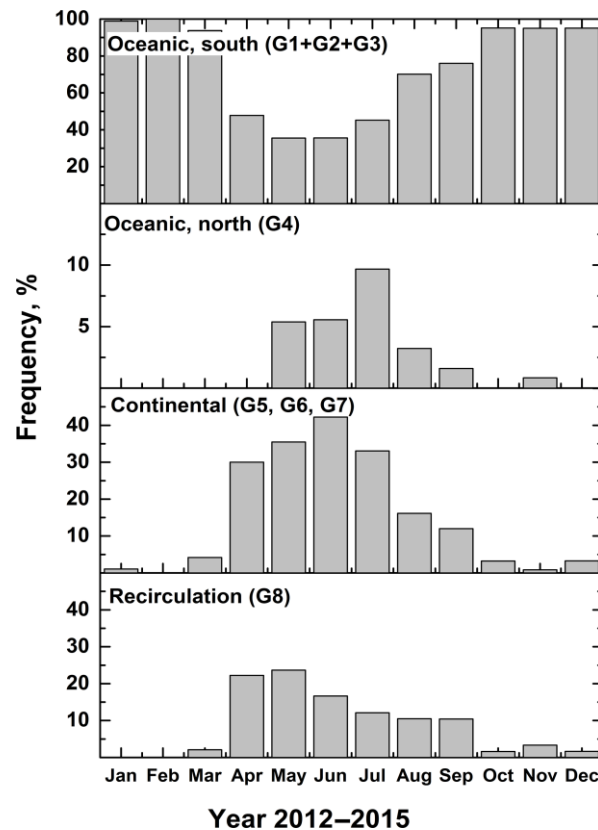


Figure 4-5. Seasonal variation in the transport pathways of air masses reaching HBAO between 2012 and 2015.

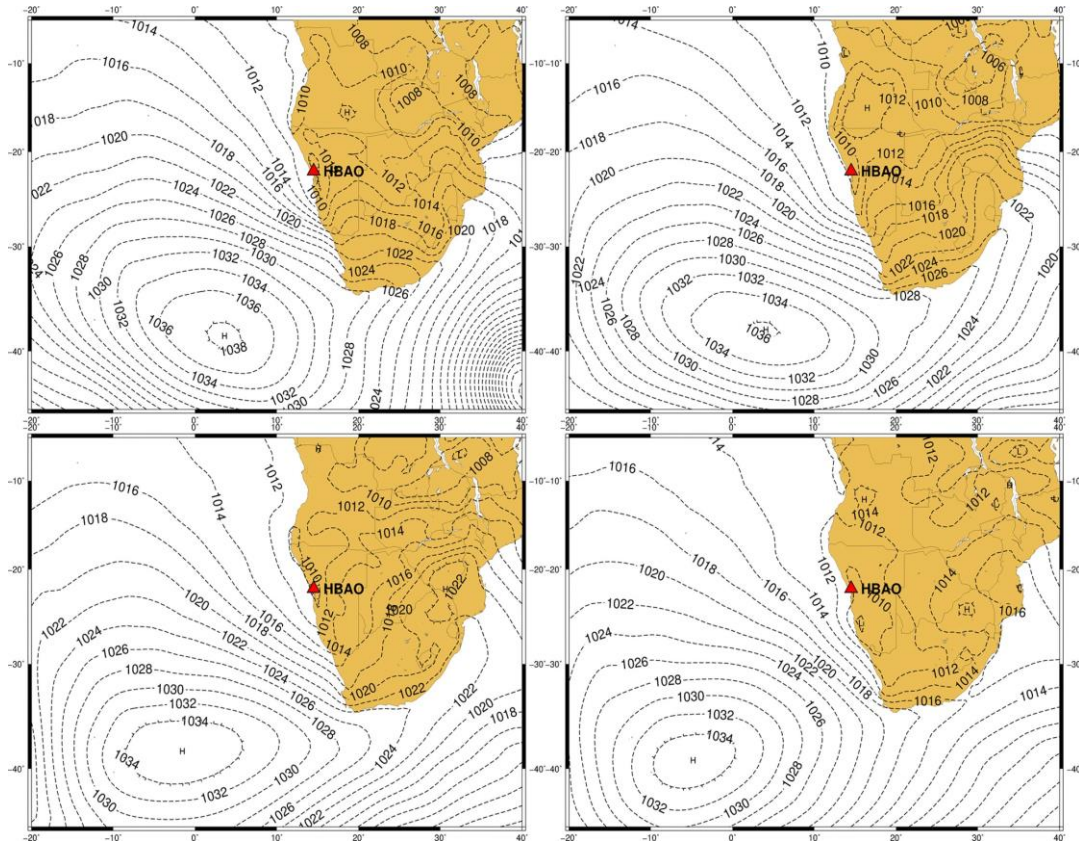


Figure 4-6. Case study of mean sea level pressure over the subcontinent and adjacent South Atlantic Ocean for 16–19 November 2014 illustrating the synoptic circulation that results in the transport of air masses from sector G1.

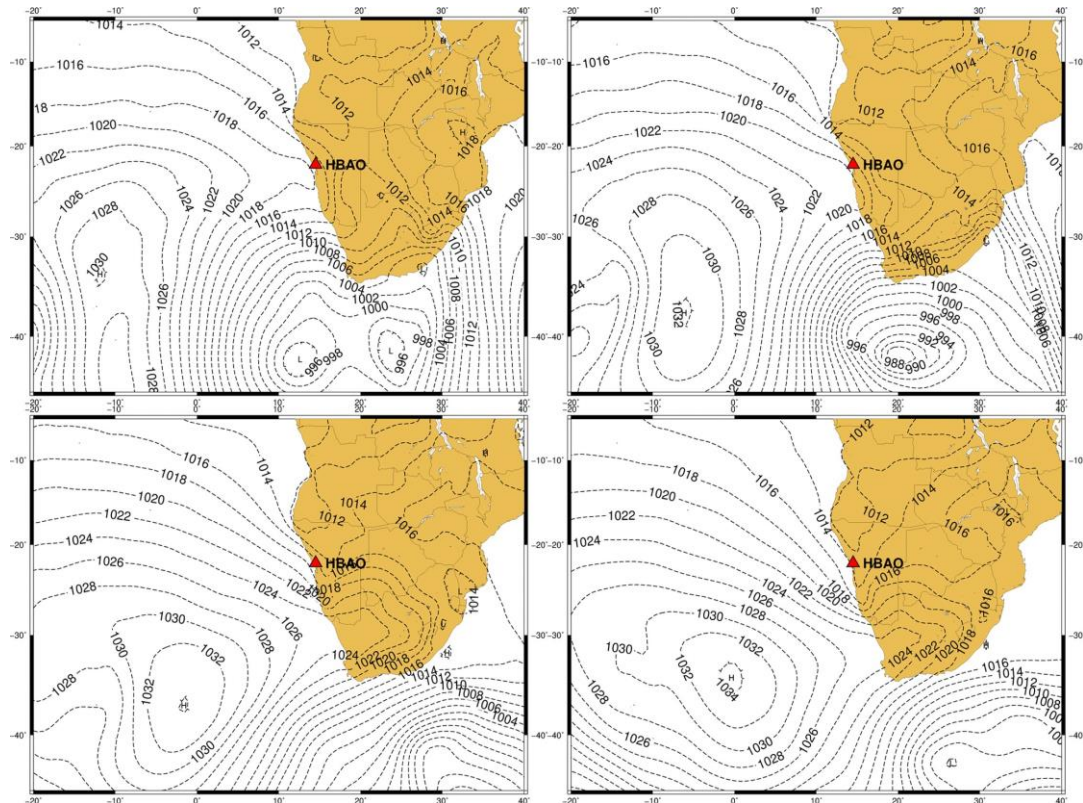


Figure 4-7. Case study of mean sea level pressure over the subcontinent and adjacent South Atlantic Ocean for 1–4 June 2013 illustrating the synoptic circulation that results in the transport of air masses from sector G2.

In winter transport results from a complex interaction between the westerly waves propagating from the south-west over the subcontinent and the re-establishment of the South Atlantic High in the westerly waves' wake. Initially, air transport is towards the east and is then directed northwards along the west coast to Namibia (Fig. 4-7). The distance covered by these air masses is several thousand kilometres due to the high wind speeds associated with the initial transport in the cyclonic circulation. Sectors G3 and G4 describe transport from the tropical regions of the Atlantic Ocean. The onshore flow towards the sampling site forms as a westerly wave advances. A shallow, localised cell of low-pressure (cyclonic circulation) is induced along the west coast with a diameter of approximately 200 km. Towards the north of the cell onshore flow occurs, while in the southern portion of the cell the flow is offshore. This circulation has also been shown to induce the dust plumes that blow off the Namibian coast over the Atlantic Ocean from ephemeral river beds along the west coast of Namibia (Dansie et al., 2017). The low-pressure, referred to as a coastal low, then propagates southwards behind the surface front. It is possible for air that is moved offshore in the easterly wave over Angola to be caught up in this more near-shore circulation.

Transport to HBAO from the continent (sectors G5–G7) occurred on 19% of the total days. These transport pathways are directly linked to the position of the easterly wave over the subcontinent as well as the position of the trough line associated with the wave. As pointed out earlier, the position of the easterly wave is highly seasonal. In general, air is transported across the subcontinent and exits to the Atlantic Ocean in the easterly transport. The low-pressure trough moves across the subcontinent. The position of the trough also determines the exact pathway of transport as well as the sector in which air masses originate. If the trough is situated along the west coast it forms a west coast trough that facilitates flow along and close to the west coast. During summer the easterly wave reaches to the southern tip of southern Africa. This leads to transport of air from areas of South Africa, including the highly industrialised South African Highveld region (Fig. 4-8a). In winter the easterly wave seldom reaches south of 25°S. Air masses during this season are more likely to originate over the central portion of southern Africa (Fig. 4-8b).

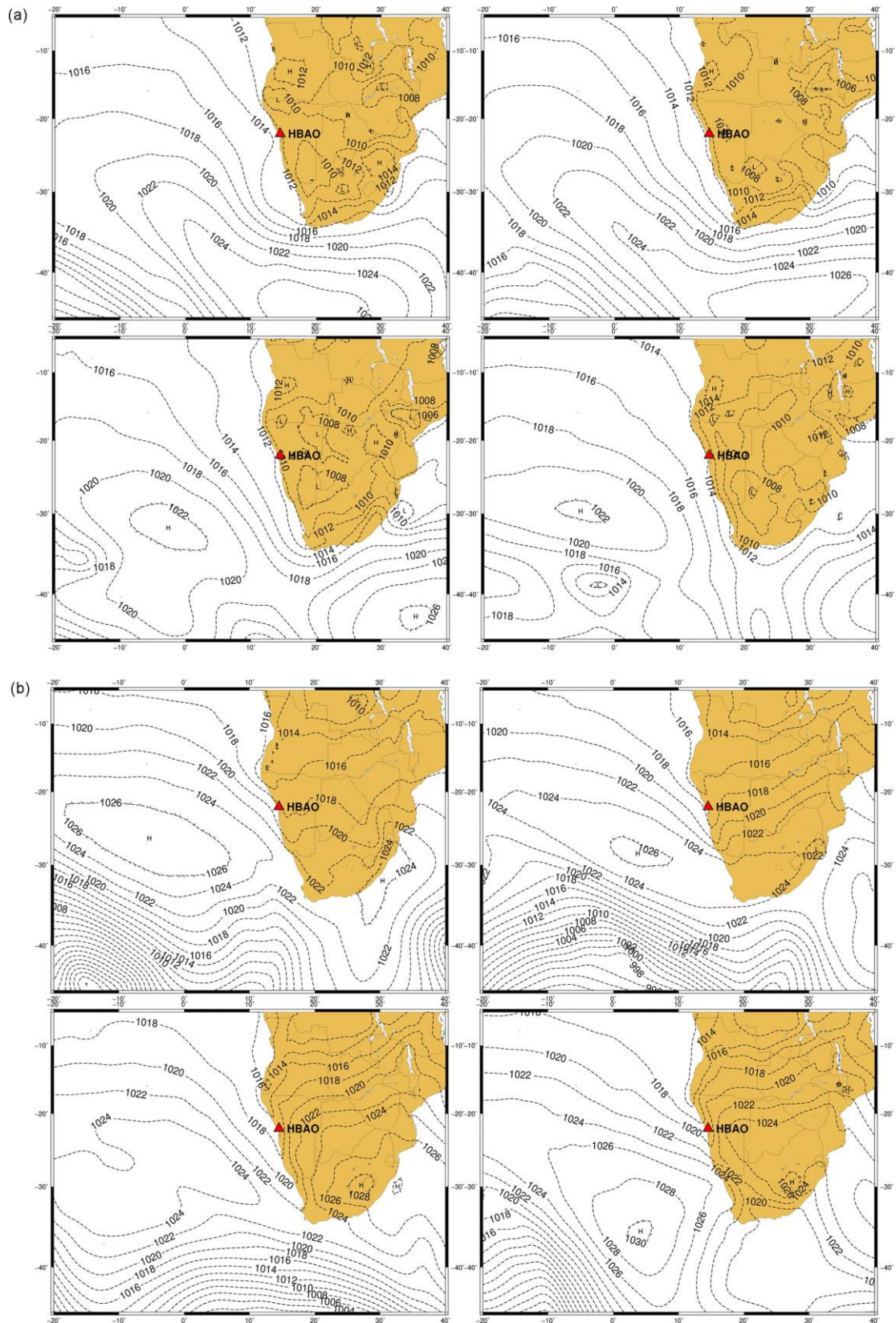


Figure 4-8. Case study of mean sea level pressure over the subcontinent and adjacent south Atlantic Ocean for (a) summer (10–13 December 2013) and (b) winter (6–10 July 2013) illustrating the synoptic circulation that results in the transport of air masses from sectors G5 to G7.

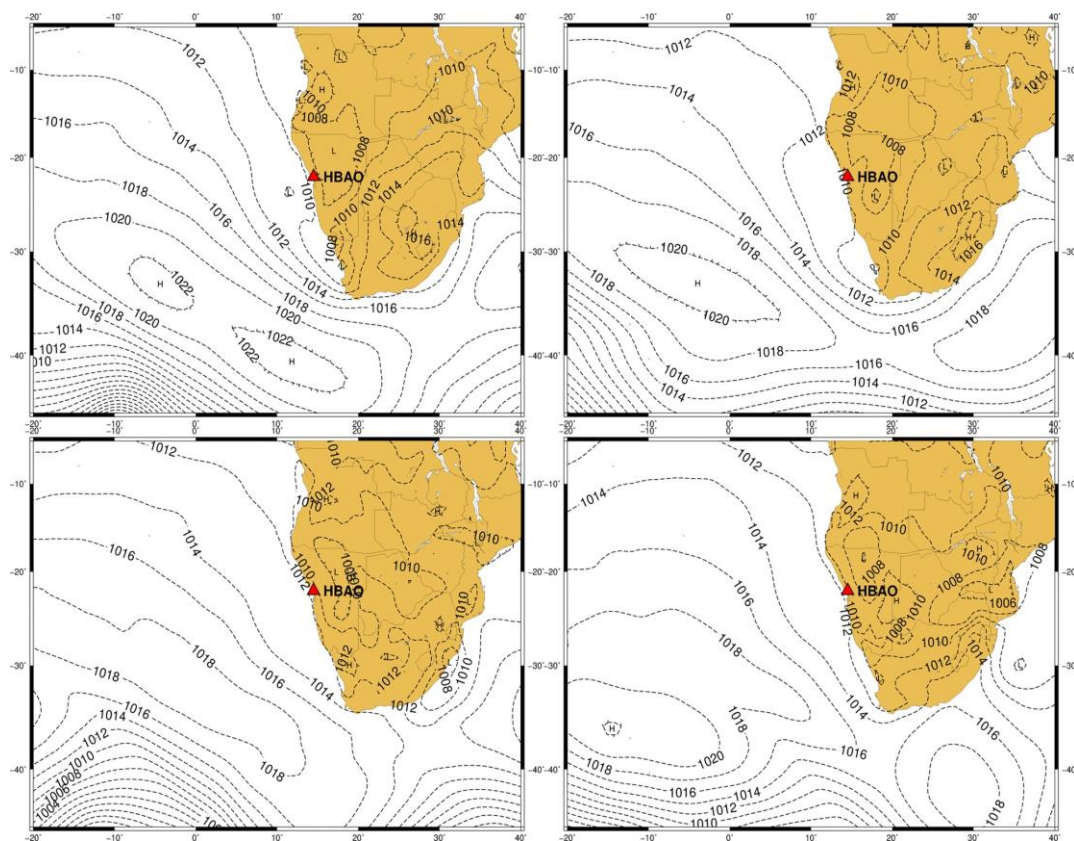


Figure 4-9. Case study of mean sea level pressure over the subcontinent and adjacent south Atlantic Ocean for 13–16 December 2012 illustrating the synoptic circulation that results in the transport of air masses from sector G8.

Finally, sector G8 is associated with air masses originating within 100 km of HBAO (Fig. 4-9), either from land or from the ocean, and representing about 8% of the air mass occurrences (Fig. 4-5). This circulation, only occurring in the second half of each year (Fig. 4-5), is linked to the formation of a low-pressure heat cell close to the west coast of Namibia centred at about the latitude of Henties Bay. Despite this being cyclonic-flow the circulation is closed (Fig. 4-9) and therefore represents transport from close to the sampling site. The heat low is always embedded in an easterly wave or west coast trough. Centres of low-pressure form along the west coast producing local and mesoscale circulation from the interior of Namibia to the coast. This flow pattern is distinguishable from a coastal low as it is centred on the subcontinent, whereas the coastal low is always centred on the coast just offshore.

4.3.4. Contribution of air transport patterns to the measured eBC

Figure 4-10 illustrates the contribution of the air mass sectors G1–G8 to the eBC mass concentrations measured at HBAO and those estimated by the MERRA-2 reanalysis. This has been done by calculating the distribution of eBC values per group.

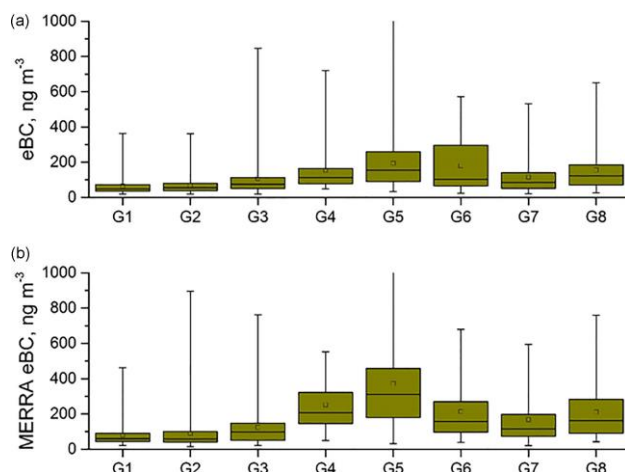


Figure 4-10. Contribution of air mass sectors to the eBC concentrations at HBAO from (a) our measurements and (b) MERRA-2 re- analysis.

Although the absolute values differ by a factor of 2–3, measurements and reanalysis show some consistent temporal features. Episodic high values of eBC concentrations occur independently of the origin of the air mass. The southern Atlantic oceanic air masses (sectors G1, G2 and G3) and the continental G7 sector, corresponding to the low population density semi-arid region of the Karoo, in South Africa, display the lowest concentrations. In particular, the oceanic sectors are characterised by a south-to-north gradient, the highest mean concentrations being from sectors G4, offshore northern Namibia and Angola, comparable to those from the continental sectors G5 and G6, as well as G8, representing recirculating air masses. Measurements at HBAO indicate that the contributions of sectors G5 and G6 are equivalent, while sector G5 is the largest contributor according to the MERRA-2 reanalysis.

4.4. Discussion and conclusions

This paper presents the first long-term time series of equivalent black carbon (eBC) concentrations in the marine boundary layer on the south-east Atlantic coast offshore southern Africa. Observations were conducted at the Henties Bay Aerosol Observatory (HBAO), in Namibia, between July 2012 and December 2015.

Higher concentrations of eBC on the western coast of southern Africa are observed from April to July within continental and marine air masses north of 30°S (sectors G4, G5 and G6). Daily eBC peak concentrations at HBAO do not exceed 800 ng m⁻³, and are seldom larger than 200 ng m⁻³, lower than measured at Ascension Island, approximately 1500 km downwind of coastal Namibia and located along the main outflow pathway from southern Africa to the Atlantic Ocean (Swap et al., 1996, 2002; Adebiyi and Zuidema, 2016; Zuidema et al., 2018). The seasonality of the eBC concentrations observed at HBAO corresponds to the seasonal shift from southern to northern circulation at the surface and is in phase with the April onset of the fire season in southern Africa (Fig. 4-4). The seasonal increase at HBAO is also well captured by the MERRA-2 reanalysis model, but it occurs earlier than reported by Zuidema et al. (2018) at Ascension Island (June to August). This seems to indicate that HBAO is on a minor branch of the transport pathway of the continental biomass burning smoke plume from continental southern

Africa compared with the biomass burning plumes that reach Ascension Island. The MERRA-2 reanalysis shows higher concentrations than measured at HBAO and suggests that the period of high concentrations should persist until September rather than August as in the HBAO measurements. This points to the inherent degree of uncertainty in our estimates. The correction factors (filter loading and multiple scattering corrections) needed to convert the measured attenuation into eBC concentration values are assumed and not evaluated from concurrent measurements, and set to fixed values as the aerosol at HBAO would derive from a single source type. We do not deal with potential changes in the aerosol properties due to ageing. Differences could also be due to the representation of the timing and extent of a southward shift of the easterly wind during summer. Although these issues cannot be resolved with the present dataset, they question the representation of the transport of smoke plumes at the subcontinental scale of southern Africa.

There is no doubt that the transport of wildfire smoke is the major regional source of the eBC aerosols for the western coast of Namibia. However, the presence of episodic outliers and the relatively elevated concentrations observed for oceanic air masses originating south of HBAO (sectors G1 to G3 in Fig. 4-5) suggests that additional sources could contribute to the load of light-absorbing aerosols in the marine boundary layer. In particular, the contribution of the coastal and open-ocean maritime shipping routes in the South Atlantic Ocean (Tournadre, 2014; Fraser et al., 2016; Johannson et al., 2017) and that of long-range continental anti-cyclonic transport from the industrial areas of the South African Highveld, shown in Fig. 4-3 (Piketh et al., 2002), should be further explored.

By the very rough assumption of the mass fraction of black carbon (BC) to the total fine aerosol (10 %; Bond et al., 2013), we estimate that the mean fine mass of aerosols containing eBC would be $0.5 (\pm 0.5) \mu\text{g m}^{-3}$. For comparison, the mean $\text{PM}_{2.5}$ mass concentration at HBAO was $14 (\pm 11) \mu\text{g m}^{-3}$ in 2013 (Fig. C-2.2, appendices).

These aerosols below clouds would have a negligible direct radiative effect. There are almost no AERONET measurements of the aerosol optical depth (AOD) at HBAO concurrent to the eBC data series. However, Fig. C-2.2 (appendices) shows the time series of the AERONET level 2.0 AOD of the fine and coarse mode aerosols (AOD_F and AOD_C) evaluated by the O'Neill et al. (2003) algorithm between December 2011 and May 2012, and then from May to December 2015. Figure C-2.2 (appendices) shows that the AOD_F varies significantly from background values in the December 2011–May 2012 period (average 0.05 ± 0.03) to peak values of 0.4 and higher during August, September and October 2015, when the transport of biomass burning occurs in the free troposphere (Swap et al., 2003). The AOD_C , essentially contributed by sea salt, is relatively invariant with time. There is no process other than biomass burning that would inject aerosols above the marine boundary layer, henceforth we can consider the mean value for December 2011–May 2012 as a reasonable evaluation of the optical depth of the fine mode of aerosols below clouds, including eBC.

The eBC aerosols might act on the microphysical properties of the local stratocumulus clouds. At Ascension Island, Zuidema et al. (2018) demonstrated the good correlation between the concentrations of refractory BC and cloud condensation nuclei (CCN) at supersaturations exceeding 0.2%. A similar effect should be expected at HBAO and could be important, outside but also during the biomass burning season as the entrainment of biomass burning aerosols from the free troposphere may be inhibited by the thermal inversions clear air slots separating the elevated plumes and the marine boundary layer (Keil and Haywood, 2003; Haywood et al., 2003; Hobbs et al., 2003). Finally, by deposition, these low-level aerosols could act on the biological activity for the oligotrophic South Atlantic Gyre in summer, providing soluble nutrient species, such as dissolved nitrogen, phosphorous and iron (Guieu et al., 2005; Luo et al., 2008; Paris et al., 2010).

In conclusion, the chemical apportionment of the AOD_F below cloud and the hygroscopic properties of the eBC aerosols at HBAO deserves exploration by future refined experiments.

Data availability. Original data for measured light-attenuation at HBAO are distributed by the French national AERIS data centre (<https://www.aeris-data.fr/direct-access-icare-2/>, last access: 12 November 2018). Treated data can be obtained by email request to the first author of this paper.

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/acp-18-17003-2018-supplement>, attached in the Appendix of this thesis.

Competing interests. The authors declare that they have no conflict of interest.

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(<http://www.geiacenter.org/>, last access: 12 November 2018) and is part of AERIS, the French data service for Atmosphere (<http://www.aeris-data.fr/>, last access: 12 November 2018). MERRA-2 data are available at MDISC, managed by the NASA Goddard Earth Sciences (GES) Data and Information Services Centre (DISC). Thanks are due to A. Da Silva (NASA/Goddard Space Flight Centre, Global Modelling and Assimilation Office, Greenbelt, MD, USA) for making the extractions at HBAO available.

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The article presented in this chapter evaluated the seasonality in eBC measured in the marine boundary layer, identified the dominant transport patterns and quantified the contributions of eBC from different air mass transport pathways.

Chapter 5

Chemical composition and source apportionment

This chapter introduces the second article that addresses the objective of chemical characterisation of aerosols and also transport pathways over the Namibian coast. Filter samples of PM₁₀ aerosols were collected at HBAO and analysed by ion chromatography and X-ray fluorescence. The resultant chemical dataset was evaluated by mathematical models (e.g. PMF, linear regression) to determine the sources of aerosols and also to analyse the diurnal, seasonal and annual variability in aerosol sources contributing to the overall mass load. These chemical profiles were geo-statistically compared with modelled transport pathways. The article is titled, *Chemical composition and source apportionment of atmospheric aerosols on the Namibian coast*, and the author of this thesis contributed the full data analysis of the chemical dataset and the final compilation and writing of the document with inputs from co-authors. This article was submitted for the special issue of the journal Atmospheric Chemistry and Physics, volume 20, issue 24, pp. 15811–15833, 2020, doi:10.5194/acp-20-15811-2020. Consent from co-authors is attached under appendix B-1.

Author contributions

- Danitza Klopper, Paola Formenti, Stuart J. Piketh, Andreas Namwoonde, Mathieu Cazaunau and Anaïs Feron performed the filter sampling and operated the wind sensor.
- Patrick Hease, Servanne Chevaillier, Fadi Lahmidi, Cécile Mirande-Bret, Sylvain Triquet and Zirui Zeng performed the XRF and IC analysis of the collected samples.
- Danitza Klopper performed the back-trajectory calculations, analysis of wind data and PMF.
- Danitza Klopper and Paola Formenti performed the analysis of the chemical analysis and integration of the dataset.
- Danitza Klopper and Paola Formenti wrote the paper with contributions from Stuart J. Piketh.

ARTICLE 3: Chemical composition and source apportionment of atmospheric aerosols on the Namibian coast

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Abstract. The chemical composition of aerosols is of particular importance to assess their interactions with radiation, clouds and trace gases in the atmosphere, and consequently their effects on air quality and the regional climate. In this study, we present the results of the first long-term dataset of the aerosol chemical composition at an observatory on the coast of Namibia, facing the southeast Atlantic Ocean. Aerosol samples in the mass fraction of particles equal to or smaller than 10 μm in aerodynamic diameter (PM_{10}) were collected during 26 weeks between 2016 and 2017 at the ground-based Henties Bay Aerosol Observatory (HBAO; 22°6'S, 14°30'E, 30 m above mean sea level). The resulting 385 filter samples were analysed by X-ray fluorescence and ion-chromatography for 24 inorganic elements and 15 water-soluble ions. Statistical analysis by Positive Matrix Factorisation (PMF) identified five major components, *sea salt* (mass concentration mean and standard deviation: $74.7 \pm 1.9\%$), *mineral dust* ($15.7 \pm 1.4\%$), *ammonium neutralised* ($6.1 \pm 0.7\%$), *fugitive dust* ($2.6 \pm 0.2\%$) and *industry* ($0.9 \pm 0.7\%$). While the contribution of sea salt aerosol was persistent, as the dominant wind direction was south-westerly and westerly from the open ocean, the occurrence of mineral dust was episodic and coincided with high wind speeds from the south-southeast and the north-northwest, along the coastline. Concentrations of heavy metals measured at HBAO were higher than reported in the literature from measurements over the open ocean. V, Cd, Pb and Nd were attributed to fugitive dust emitted from bare surfaces or mining activities. As, Zn, Cu, Ni and Sr were attributed to the combustion of heavy-oils in commercial ship traffic across the Cape of Good Hope sea route, power generation, smelting and other industrial activities in the greater region. Fluoride concentrations up to $25 \mu\text{g m}^{-3}$ were measured, as in heavily polluted areas in China. This is surprising and a worrisome result that has profound health implications and deserves further investigation. Although no clear signature for biomass burning could be determined, the PMF *ammonium neutralised* component was described by a mixture of aerosols typically emitted by biomass burning, but also by other biogenic activities. Episodic contributions with moderate correlations between NO_3^- , nss-SO_4^{2-} (higher than $2 \mu\text{g m}^{-3}$) and nss-K^+ , were observed, further indicative of the potential for an episodic

source of biomass burning. Sea salt accounted for up to 57% of the measured mass concentrations of SO_4^{2-} and the non-sea salt fraction was contributed mainly by the *ammonium neutralised* component, and small contributions from the *mineral dust* component. The marine biogenic contribution to the *ammonium neutralised* component is attributed to efficient oxidation in the moist marine atmosphere of sulphur-containing gas-phase emitted by marine phytoplankton in the fertile waters offshore in the Benguela Upwelling System. The data presented in this paper provide first-ever information on the temporal variability of aerosol concentrations in the Namibian marine boundary layer. This data also provide context for intensive observations in the area.

Keywords: aerosols, chemical composition, transport, Namibia, positive matrix factorisation

5.1. Introduction

Atmospheric aerosol particles are emitted from both natural and anthropogenic sources. Depending on their chemical and physical characteristics, airborne aerosol particles modify the Earth's radiative budget by scattering and absorbing solar and terrestrial radiation and by altering cloud lifetime and microphysical- and optical properties (Seinfeld and Pandis, 2006). The variability in their source distribution and short lifetime in the atmosphere (typically less than 10 days for particles below 1 μm in diameter, and shorter for larger particles) results in an uneven horizontal and vertical spatial distribution of concentrations and physicochemical properties (Seinfeld and Pandis, 2006). As a consequence, their effects on regional atmospheric dynamics and processes are unevenly spread and constantly changing, in stark contrast to the long-lived greenhouse gases, which are well-distributed around the globe (Boucher, 2013).

The Namibian coast, and more generally the southeast Atlantic region of southern Africa, is amongst the global areas of interest to study aerosols and their role on Earth's climate (De Graaf et al., 2014; Muhlbauer et al., 2014; Painemal et al., 2014a, b; Wilcox, 2010; Zuidema et al., 2009). Local meteorological conditions in this arid environment are sustained by the effect of cold ocean currents in the Benguela Upwelling System (BUS), one of the strongest oceanic upwelling systems in the world, with very low sea surface temperatures all year round, reaching a minimum in the austral winter (Cole and Villacastin, 2000; Nelson and Hutchings, 1983). This has a stabilising effect on the lower troposphere, resulting in the formation of a semi-permanent stratocumulus (Sc) cloud deck extending between 10–30°S, 10°W–10°E, that tops the marine boundary layer at ~850 hPa (Muhlbauer et al., 2014; Wood, 2015) and is of global significance for Earth's radiation budget (Klein and Hartmann, 1993; Johnson et al., 2004; Muhlbauer et al., 2014; Wood, 2015).

The region is also known for its high marine phyto- and zoo-plankton specifically in the northern BUS (Louw et al., 2016). The marine biogenic activity results in the release of gaseous compounds containing sulphur (dimethylsulphide (DMS), SO_2 , H_2S ...) to the atmosphere (Andreae et al., 1994), whose oxidation, particularly in this marine environment, could produce new aerosol particles contributing to the cloud

droplet number concentration of the Sc clouds (Charlson et al., 1987; Andreae et al., 1995). The region is also known for the seasonal transport above the Sc of optically-thick and wide-spread smoke layers of biomass burning aerosols emitted from forest fires in southern Africa in the austral dry season (August to October; Lindesay et al., 1996; Swap et al., 2003).

Despite their relevance, very limited research has been conducted to assess the seasonal cycle and long-term variability of the aerosol mass concentration and chemical composition in the region (Andreae et al., 1995; Annegarn et al., 1983; Dansie et al., 2017; Eltayeb et al., 1993; Formenti et al., 1999, 2003b; 2018; Zorn et al., 2008). To fill this gap, the long-term surface monitoring Henties Bay Aerosol Observatory (HBAO) was established in 2012 on the campus of the University of Namibia's Sam Nujoma Marine and Coastal Resources Research Centre (SANUMARC), along the Namibian coast (22°S; 14°E). HBAO faces the open ocean in an arid environment, far from major point sources of pollution. Episodically through the year, and seasonally between April to end of July, the station is affected by polluted air masses containing light-absorbing aerosols, mostly from vegetation burning (Formenti et al., 2018).

In this paper, we present the results of the very first long-term measurements of aerosol elemental and water-soluble ionic composition from the analysis of filter samples in the mass fraction of particles equal to or smaller than 10 μm in aerodynamic diameter (PM_{10} fraction) that were collected during 26 non-consecutive sampling weeks in 2016 and 2017. The paper looks into the temporal variability of measured elemental and water-soluble ionic concentrations and yields the first source apportionment to the PM_{10} loading. The research presented in this study is also relevant to the recent intensive observational efforts that took place in Namibia in 2016 and 2017 (Zuidema et al., 2016). Specifically, it provides the long-term context to the intensive filter sampling that was conducted in Henties Bay as part of the Aerosols, RadiatiOn and CLouds in southern Africa (AEROCLO-SA) project (Formenti et al., 2019).

5.2. Experimental methods

The HBAO station of Henties Bay, Namibia (22.09°S, 14.26°E; 30 m above mean sea level (amsl) <http://www.hbao.cnrs.fr/>, last access: 22 September 2020) is situated 100 m from the shoreline and is surrounded by an arid environment with little to no vegetation, as shown in Figure 5-1. Henties Bay is located approximately 100 km north of Walvis Bay, the largest commercial harbour of Namibia (Namport, 2018). Formenti et al. (2018) showed that the location can be considered as baseline for a large part of the year (August to late April), but May to end of July it is impacted by the synoptic transport of light-absorbing aerosols, most likely from vegetation burning in southern Africa and possibly but episodically by anthropogenic sources, such as heavy-fuel combustion by commercial ships travelling

along the coast, especially along the Cape of Good Hope sea route (eg. Chance et al., 2015; Tournadre, 2014; Zhang et al., 2010).

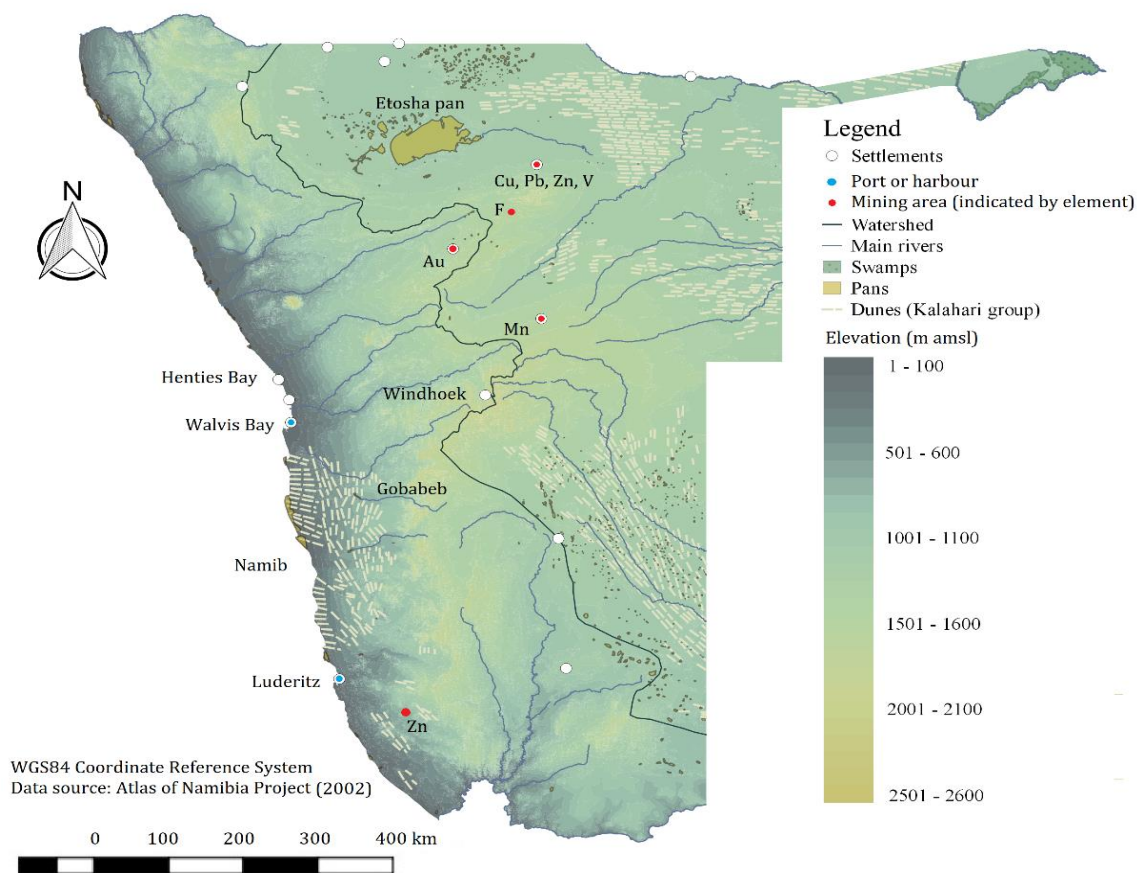


Figure 5-1. Geographical map of Namibia with elevation as a shaded gradient and some of the known emission sources in the region, such as major urban settlements and airports, harbours, pans and swamps, mineral-rich mining operations, labelled by the major element begin mined, and dune fields of the Kalahari stratigraphic group (Atlas of Namibia project, 2002).

5.2.1. Aerosol filter sampling and analysis

An automated sequential air sampler (model Partisol Plus 2025i, Thermo Fisher Scientific, Waltham, MA USA) was used to collect aerosol particles on 47-mm Whatman Nucleopore polycarbonate filters (1- μm pore size). Air was sampled at a flow rate of $1 \text{ m}^3 \text{ h}^{-1}$ through a certified inlet (Rupprecht and Patashnick, Albany, New York, USA) located on the rooftop terrace above the instrument, and collecting aerosols particles of aerodynamic diameter lower than $10 \mu\text{m}$ (PM_{10} fraction).

Individual filter samples were collected for 9 hours during the day (from 9 h to 18 h UTC) and during the night (from 21 h to 6 h UTC) on an intermittent week on/week off schedule. One blank sample per week was collected. The whole dataset consisted of 385 samples during 2016 and 2017.

Elemental concentrations of 24 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Pb, Nd, Cd, Ba) were obtained at LISA by wavelength-dispersive X-ray fluorescence (WD-XRF) using a PW-2404 spectrometer (Panalytical, Almelo, Netherlands), according to the protocol previously described by Denjean et al. (2016). The relative analytical uncertainty on the measured atmospheric

concentrations (expressed in ng m^{-3}) is evaluated as 10%. This represents the upper limit uncertainty, taking into account:

- The uncertainty related to the uniformity of the aerosol deposit on the filters, and the scaling error that can occur due to the fact that the area of the deposit, which is analysed is smaller than the area of the aerosol deposit;
- The statistical error on the photon counts, in particular for trace elements whose concentrations are close to their detection limits;
- The percent error on the certified mono- and bi-elemental standard concentrations (Micromatter Inc., Surrey, Canada) used for calibration of the XRF apparatus;
- For the lightest elements ($Z < 20$, Na to Ca), the choice of the correction factor to account for the self-attenuation of the X-ray signal, in particular for particles larger than $1 \mu\text{m}$ in diameter (Formenti et al., 2010). Constant correction factors (Table C-3.1.) were estimated through the sampling period assuming a mean diameter of $4.5 \mu\text{m}$ to represent the average coarse particle size.

The concentrations of 16 water-soluble ions (F^- , propionate, formate, acetate, methanesulfonic acid (MSA), Cl^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , oxalate, Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) were obtained at LISA by ion chromatography (IC) with a Metrohm IC 850 device (injection loop of $100 \mu\text{l}$). For anionic species, the IC was equipped with MetrosepA supp 7 (250/4.0mm) column associated with a MetrosepA supp 7 guard pre-column heated at 45°C . For simultaneous separation of inorganic and short-chain organic anions, elution has been realised with the following elution gradient (eluent weak: $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ (0.28/0.1mM) and eluent strong: $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ (28/10mM): 100% eluent weak from 0 to 23.5 minutes; then 15% eluant strong from 23.5 to 52 minutes and 100% eluent weak to finish. The elution flow rate was 0.8 ml min^{-1} . For cationic species, IC has been equipped with a Metrosep C4 (250/4.0mm) column associated to a Metrosep C4 guard column heated at 30°C . Elution has been realised with an eluant composed with 0.7 mM of dipicolinic acid and 1.7mM of nitric acid. The elution flow rate was 0.9 ml min^{-1} . The uncertainty of water-soluble ionic concentrations (also expressed in ng m^{-3}) is within 5%, the maximum uncertainty obtained during calibration by standard certified mono- and multi-ionic solutions. For each chemical species, the minimum quantification limit (MQL) was calculated as 10 times the square root of the standard deviation of the concentration of laboratory blank samples, corresponding to filter membranes prepared as actual samples but stored and analysed without exposure to external air. Only values above MQL are included in further analyses.

A quality-check assessment of the analysis was performed by comparing the concentrations of Cl, Mg, K, Ca, Na and $\text{MSA}+\text{SO}_4^{2-}/\text{S}$ measured by IC and XRF (Figure C-3.1.). The comparison revealed a good linear correlation between the two datasets, with the coefficient of determination (R^2) exceeding 0.85 for all the elements. However, some differences in the slopes of the linear correlations are observed when comparing the 2016 and 2017 datasets for Cl^-/Cl , Na^+/Na , and Mg^{2+}/Mg . Mass ratios were 1.3 ± 0.1 (2016) and 1.0 ± 0.1 (2017), 1.3 ± 0.1 (2016) and 0.9 ± 0.1 (2017), and 2.0 ± 0.1 (2016) and 1.7 ± 0.2

(2017) for Cl^-/Cl , Na^+/Na , and Mg^{2+}/Mg , respectively. Conversely, no annual dependence was observed in the slopes of the linear correlations for the mass ratios of Ca^{2+}/Ca (0.8 ± 0.1), K^+/K (0.6 ± 0.1) and $\text{MSA}+\text{SO}_4^{2-}/\text{S}$ (2.7 ± 0.4). The molar ratio of $\text{MSA}+\text{SO}_4^{2-}/\text{S}$ was 8.0 ± 1.2 for 2016 and 7.8 ± 0.9 for 2017. These values are in general terms consistent with expectations that these elements, mostly but not exclusively composing sea salt, should be predominantly soluble in water. However, ratios higher than unity are obtained for Cl^-/Cl in 2016 and Na^+/Na in 2017, and Mg^{2+}/Mg for both years. No specific sampling nor analytical problems were found. However, the further comparison of their proportions to those expected for seawater (Seinfeld and Pandis, 2006) as well as the possibility that the choice of a mean, time-independent self-attenuation correction factor for Na and Mg would be erroneous, suggested to discard the XRF results and only use the values obtained by IC for those three elements. For Ca^{2+}/Ca , K^+/K and $\text{SO}_4^{2-}/\text{S}$, ratios are consistent with previous observations in marine environments impacted by mineral dust (Formenti et al., 2003a).

5.2.2. Local winds, air mass trajectories and synoptic meteorology

Local wind speed and -direction were measured with two anemometers also located on the rooftop of HBAO, first, a Campbell Scientific 05103, replaced with a Vaisala WXT530 from September 2017 onwards. Measurements were stored as 5-minute averages. Wind data was available for all of 2016 and 55% of the aerosol sampling periods in 2017 (no wind data were available during 19 – 26 May and 7 – 14 July 2017).

The NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2015) was used to evaluate the origin and transport pathway of air masses to HBAO. Seventy-two-hour back-trajectories were run every hour for each 9-hour long filter sampling period starting at a height of 250 m above ground level (agl), which effectively models transport into the marine boundary layer (MBL, with a minimum height of ~500 m over the BUS; Preston-Whyte et al., 1977). This choice also considered the model vertical resolution (23 levels throughout the atmospheric column). The first model vertical level is at 1000 hPa (approximately 110 m amsl) and the next is at 975 hPa (approximately 300 m amsl). The Global Data Assimilation System (GDAS) reanalysis dataset with a $1^\circ \times 1^\circ$ resolution, provided by the National Centre for Environmental Prediction (NCEP), was used. This was preferred to the $0.5^\circ \times 0.5^\circ$ resolution dataset where the vertical velocity is absent and has to be calculated from the divergence, introducing uncertainties into the model. Trajectories were run through the Rstudio interface using the `rich_iannone/splitR` (available from <https://github.com/rich-iannone/splitr>, last access: 10 December 2020) and `Openair` (Carslaw and Ropkins, 2017) packages from the open-source libraries.

As a complement, publicly available daily synoptic charts provided by the South African Weather Service (SAWS, www.weathersa.co.za/home/historicalsynoptic; last accessed 20/02/2020) were analysed for the synoptic-scale induced flow.

5.3. Source identification and apportionment

The identification of the origin of the aerosols, complementary to the analysis of the air mass back trajectories and local wind speed and -direction, was undertaken by examining the temporal correlations of the elemental and ionic concentrations to known tracers, and additionally by positive matrix factorisation (PMF).

5.3.1. Ratios to unique tracers

The identification and quantification of the aerosol types contributing to the total particle load at HBAO were done by investigating the linear correlation of measured elemental and ionic concentrations and their mass ratios to unique tracers of the atmospheric particulate matter source types expected in the region. These are:

- Sea salt aerosols, traced by Na^+ constituting 30.6% of the aerosol mass in seawater (Seinfeld and Pandis, 2006);
- Marine biogenic emissions during the life cycle of marine phytoplankton in the BUS (Nelson and Hutchings, 1983) and traced by the concentrations of particulate MSA, a unique product of the oxidation of gaseous DMS (Seinfeld and Pandis, 2006);
- Wind-blown mineral dust liberated from the surface of pans and ephemeral river valleys (Annegarn et al., 1983; Eltayeb et al., 1993; Heine and Völkel, 2010; Dansie et al., 2017), but also during /road construction and mining activities (KPMG, 2014). Mineral dust is traced by elemental aluminium, representing aluminosilicate minerals and contributing on average 8.13% of the global crustal rock composition by mass (Seinfeld and Pandis, 2006), and by the non-sea salt (nss) fraction of Ca^{2+} to represent calcium carbonate. This is justified by the specific mineralogy of Namibian soils, which are enriched in gypsum (CaSO_4OH) and calcite (CaCO_3), and presenting calcium content higher than the world average (Annegarn et al., 1983; Eltayeb et al., 1993). The apportionment of the sea-salt (ss) and non-sea salt (nss) Ca^{2+} fractions was done using the nominal mass ratio of $\text{Ca}^{2+}/\text{Na}^+$ in seawater (0.021; Seinfeld and Pandis, 2006). The evaluation of the mass concentration of calcium carbonate was done by multiplying the measured nss- Ca^{2+} mass concentration by the CaCO_3/Ca mass ratio of 2.5;
- Heavy-oil combustion from industry and commercial shipping as well as mining activities traced by elements such as Ni, V, Pb, Cu, Zn (Ettler et al., 2011; Becagli et al., 2017; Johansson et al., 2017; Křibek et al., 2018; Sinha et al., 2003; Soto-Viruet, 2015; Vouk and Piver, 1983), and;
- Seasonal transport of biomass burning aerosols traced by nss- K^+ (Andreae et al., 1998; Andreae and Merlet, 2001). Nss- K^+ was calculated from measured K^+ assuming the mass ratio K^+/Na^+ of 0.036 as in seawater (Seinfeld and Pandis, 2006).

5.3.2. Positive matrix factorisation

Multivariate statistical methods such as positive matrix factorisation (PMF) are widely used to identify components or 'source' profiles and explore source–receptor relationships using the trace element

compositions of atmospheric aerosols (e.g., Schembari et al., 2014; Hopke and Jaffe, 2020). The PMF uses weighted least-squares component analysis to deconvolute the matrix of observed values ($\mathbf{X}$) as $\mathbf{X} = \mathbf{GF} + \mathbf{E}$, where $\mathbf{G}$ and $\mathbf{F}$ are the matrices representing the component scores and component loadings, respectively, and $\mathbf{E}$ is the matrix of residuals equal to the difference between observed and predicted values (Paatero and Tapper, 1994; Paatero et al., 2014).

In this paper, the multivariate PMF statistical analysis was conducted with the EPA (Environmental Protection Agency) PMF version 5.0 (Norris et al., 2014). The XRF and IC datasets were combined by retaining only elements/ions measured above the MQL in more than 70 samples (that is, at least in 20% of the collected values). This criterion excluded Ba, Br⁻, PO₄⁻ and Mn²⁺. Occasional missing values in the retained elements/ions were replaced by the species median value, as recommended by Norris et al. (2014). Uncertainties for missing values were replaced by a dummy value (99999) to ensure that these samples do not skew the model fit (Norris et al., 2014). In order to weight the concentrations according to their amount, a relative uncertainty of 10%, 20% and 60% was attributed to each value of concentration in the input matrix based on their ratio to their respective MQL (larger than 3.3, comprised between 1.25 and 3.3, and comprised between 1 and 1.25, respectively). The final input matrix comprised 385 observations of 33 chemical species. The water-soluble ionic form instead of the elemental form was retained for Mg, Na, Cl, K, Ca and S.

Based on the temporal correlation, the PMF analysis resolves the chemical dataset into a user-specified number of components ('sources'). No completely objective criterion exists for selecting the number of components and so the model was run considering potential solutions of three to seven sources. Each of these models were run 100 times using randomised seeds. For each of these runs, the robustness-of-fit was compared and the estimation of the error range of each solution was done by running a classical bootstrap analysis, displacing chemical species in each modelled component and testing the rotational ambiguity of the solutions, and finally also by running a supplementary bootstrap analysis enhanced by displacement of component elements (Norris et al., 2014; Paatero et al., 2014). *Fpeak* rotations with strengths between -0.5 and 1.5 were tested to further optimise the component solutions.

5.4. Results and discussion

5.4.1. Meteorological conditions during sampling

The characteristic synoptic circulation patterns identified over the west coast of southern Africa that are significant for this study include continental-anticyclonic circulation, the southeast Atlantic anticyclone, west coast troughs and barotropic easterly waves, transient baroclinic westerly waves and coastal low-pressure systems (Tyson and Preston-Whyte, 2014). Formenti et al. (2018) found that anticyclonic circulation, both in the form of the South Atlantic anticyclone and the continental anticyclone, is the most persistent circulation patterns over the west coast of Namibia.

Figure 5-2 shows weekly composite maps of calculated air mass back trajectories (their gridded frequency plot is shown in Figure C-3.2.). Southerly and south-westerly transport occurred year-round and easterly transport mainly occurred during late autumn (May), winter (June, July and August) and early spring (September, October and November). Large scale north-easterly air mass transport towards HBAO was restricted to the austral autumn and winter when continental anticyclonic flow dominated the circulation patterns in the lower and mid-troposphere. The majority of air masses arriving in the MBL are of marine origin from the southern and south-eastern Atlantic and show the transport of marine air masses toward the subcontinent, divergence at the escarpment and southerly flow, induced along the coast. Most of the air masses were transported over coastal waters offshore and along the west coast of South Africa and Namibia and just inland to the north-northeast of HBAO from the sub-continent. Continental plumes arriving at HBAO are transported easterly between 15° and 22°S and from as far as 36°E.

Emissions along these preferred pathways may be of great significance in shaping the regional aerosol background. Some of the known transport regimes are associated with mid-tropospheric easterly winds, responsible for transport off the subcontinent (Swap et al., 1996; Tyson et al., 1996). To the north of HBAO, Adebisi and Zuidema (2016) observed continental plumes transported off the coast, especially under anticyclonic circulation over the subcontinent and the southeast Atlantic Ocean. Tlhalerwa et al. (2012) found berg winds, an easterly perturbation, to be the main agents of aerosol transport and deposition off the coast at Luderitz, around 500 km south of HBAO, and easterly winds in the boundary layer may transport dust from the subcontinent into the ocean.

The weekly and hourly variability of local surface winds is illustrated in Figures 5-3 and 5-4, respectively. On average the wind is characterised by low speeds during the daytime ($4.7 \pm 2.2 \text{ m s}^{-1}$ with only 0.3% calm) and at night ($3.3 \pm 2.1 \text{ m s}^{-1}$ with 0.6% calm conditions). The low wind speeds are typical for regions frequently experience anticyclonic circulation. The highest wind speeds were recorded for southerly winds, which were persistent throughout the sampling period, except during January 2017 (Figure 5-3). The highest wind speed was recorded in the austral spring in both years and reached a maximum of 18.9 m s^{-1} in the week of 13–20 November 2017.

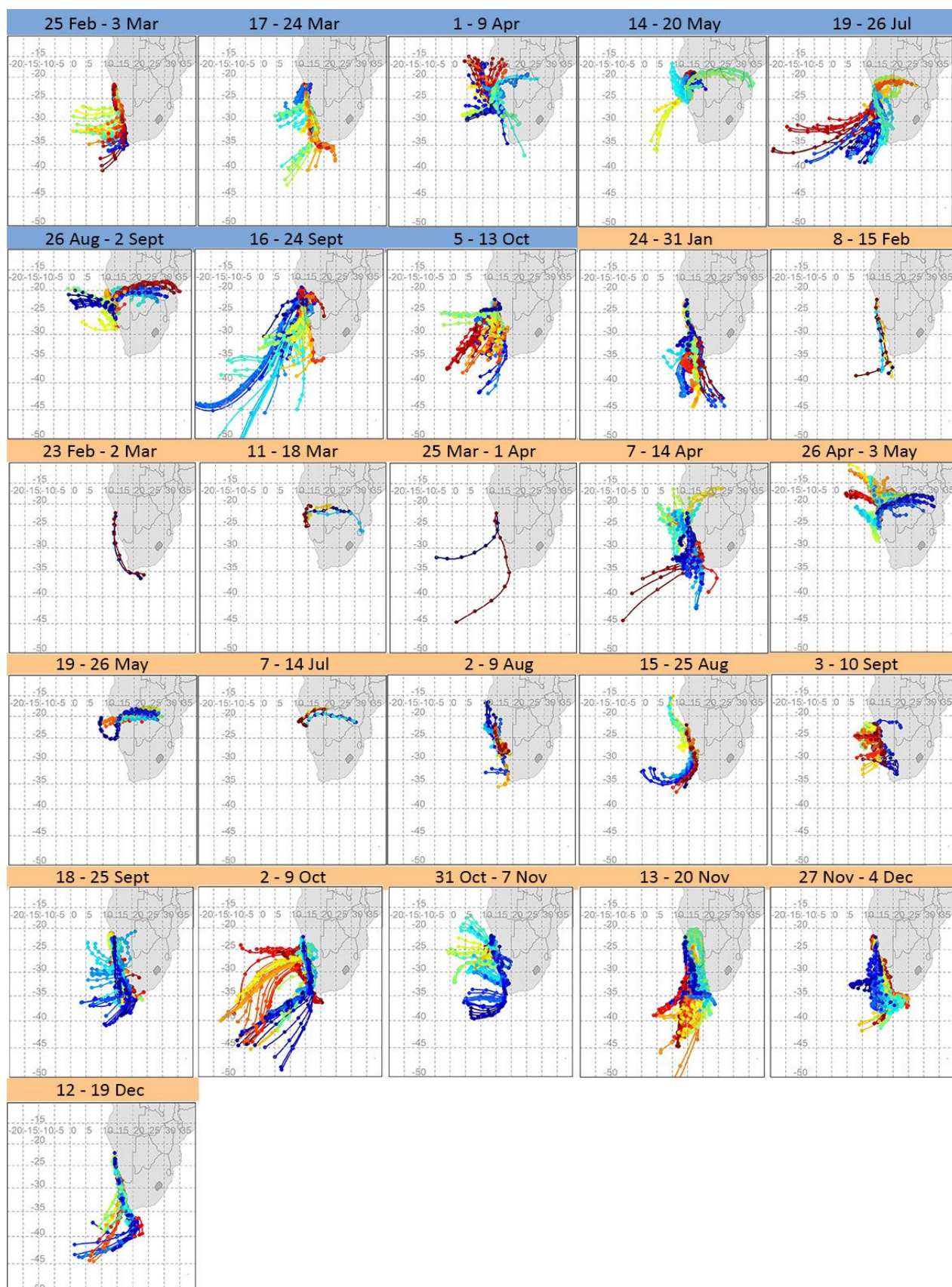


Figure 5-2. Composite maps of 72-hour back-trajectories for every filter sampling period in 2016 (dates in blue) and 2017 (dates in orange). From these composite maps, a clear distinction can be made between marine air masses and those of continental origin and the potential for variability from these regions in terms of distance travelled and trajectory pathway. The colours are only used to differentiate one set of trajectories from another.

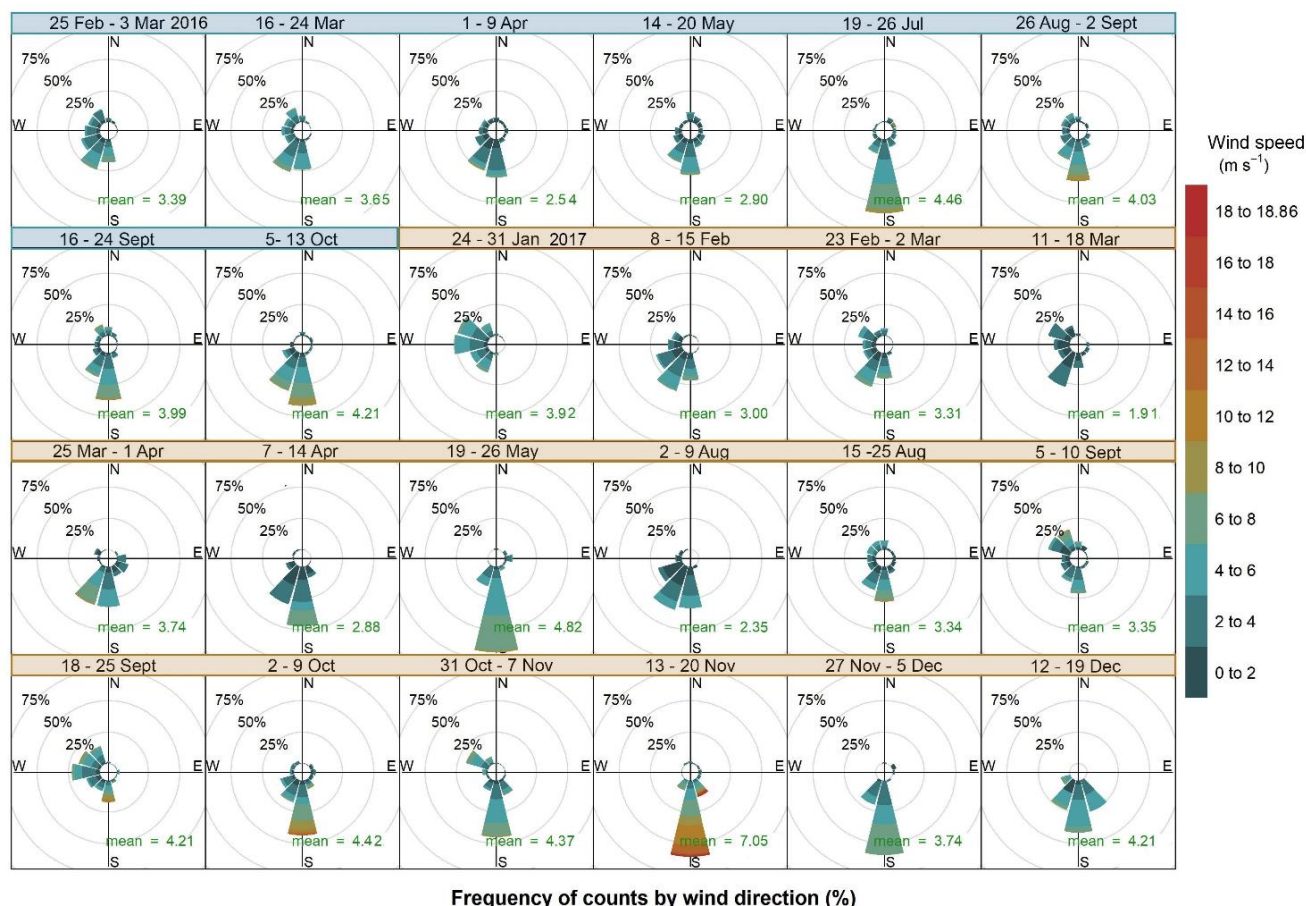


Figure 5-3. Wind roses showing the wind speed, direction and frequency of occurrence corresponding to each aerosol sampling week in 2016 (dates in blue), and 2017 (dates in orange). The arithmetic mean wind speed for each week is reported in green. For 7–14 July 2017 no surface wind data is available.

Another feature that is promoted by anticyclonic flow is thermally-induced land and sea breezes. Sea breezes were a common daytime occurrence at HBAO. The sea breeze is typically characterised by southerly and south-westerly winds. The wind direction is partly a function of the shape of the coastline at Henties Bay and the overlying gradient flow. The daytime land breeze was not observed as frequently as the onshore sea breeze flows. This supports the conclusion that the mechanisms for onshore flow are a combination of local and large-scale circulation. ENE and northerly winds were seen in July 2016 reaching a maximum speed of 13 m s⁻¹ (mean wind speed of 4.5 ± 2.2 m s⁻¹ for the week of 19-26 July 2016). These are the land breezes that are also most likely to develop on clear stable nights. The northerly flow, in particular, occurred in the early evening and mid-morning (Figure 5-4), with no seasonal dependence. Overall, it is important to note that the sea-breeze winds during the day are well defined in the data. At night the land breeze is much less important at Henties Bay than one might expect at a coastal site. This is almost certainly driven by the small thermal gradient that exists between the ocean and land temperatures at night. In the absence of a well-defined gradient, the land breeze does not develop on most nights.

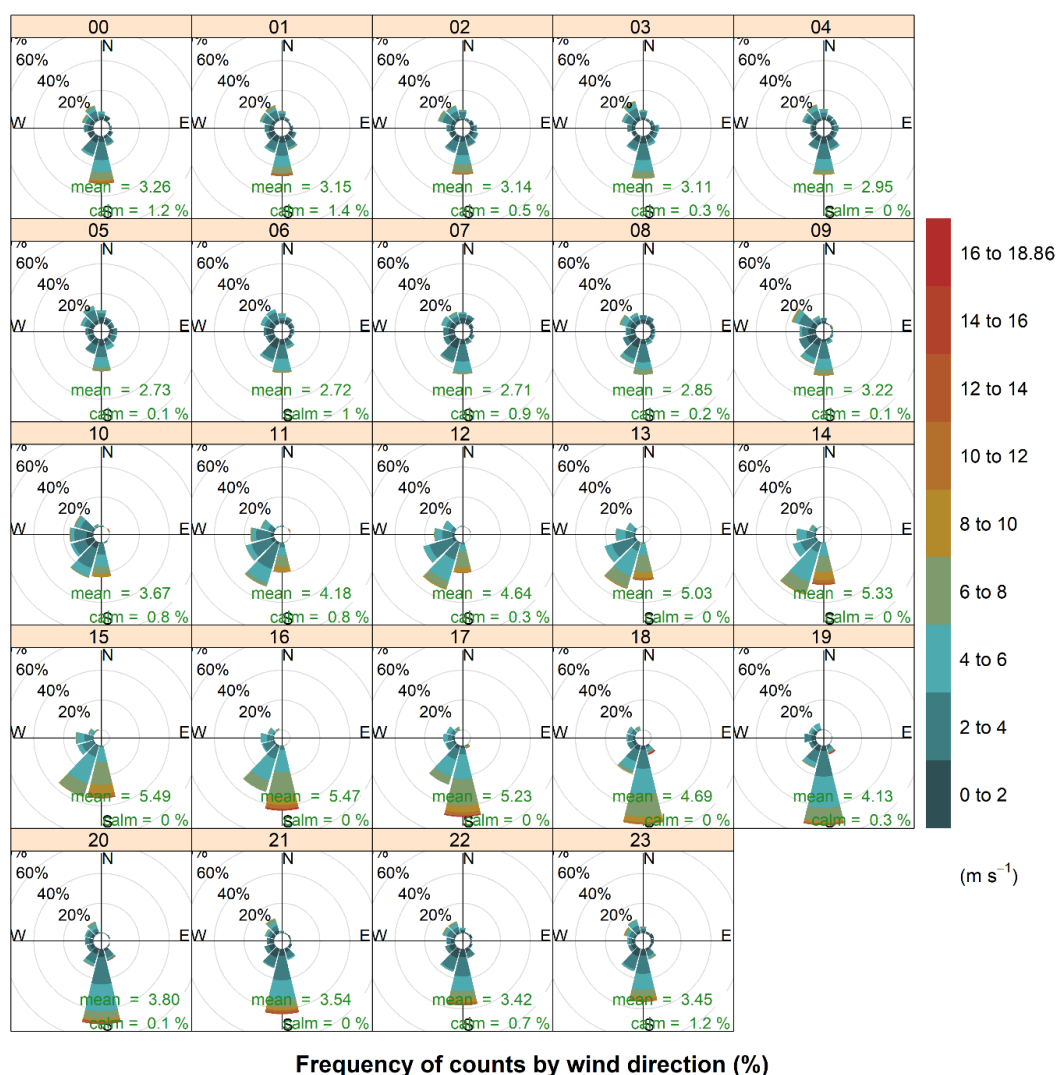


Figure 5-4. Hourly wind roses during the aerosol sampling at HBAO. The arithmetic means and percentage of calm conditions, when wind speeds are below detection, is reported in green. Time is in UTC. For 7–14 July 2017 no surface wind data is available.

Direct westerly winds occur less frequently at the site. The winds could be observed during the day and the night indicating that they are not exclusively established as sea breeze cells. The wind speeds for westerly flow conditions never exceeded 6 m s^{-1} . Easterly winds were only observed during the warmer months (January to March and September to December, Figure 5-3), and during the night-time sampling periods (21 to 9 UTC), when their speeds remained below 4 m s^{-1} (Figure 5-4). This local circulation is driven by easterly wave or tropical easterly circulation that moves southward during the summer months.

5.4.2. Variability and apportionment of measured concentrations

A summary of the measured elemental and water-soluble mass concentrations (arithmetic mean, standard deviation and range of variability) at HBAO during 2016 and 2017 is provided in Table 5-1. The time series of the mass concentrations of the source tracers discussed in section 5.3.1 are shown in Figure 5-5.

Table 5-1. Summary statistics of elemental and water-soluble ionic concentrations measured at HBAO. The second column indicates the number of samples for which values were above the minimum quantification limit (MQL). The arithmetic means with standard deviations (SD) and range of mass concentrations (minimum and maximum) are given in ng m⁻³.

Chemical species	Number of samples	Mean $\pm$ SD	Range
Cl	385	13216 $\pm$ 7987	17 - 50041
S	383	1346 $\pm$ 645	1 - 4386
Ca	366	885 $\pm$ 768	75 - 6862
Fe	383	367 $\pm$ 458	3 - 3687
Na	380	8435 $\pm$ 5752	18 - 42688
Mg	380	1178 $\pm$ 792	1 - 6416
Al	379	478 $\pm$ 581	2 - 4739
Si	374	1687 $\pm$ 2102	5 - 17016
P	352	10 $\pm$ 8	1 - 72
K	379	511 $\pm$ 359	8 - 3076
Ti	367	39 $\pm$ 47	1 - 363
Mn	295	13 $\pm$ 11	1 - 86
Zn	182	12 $\pm$ 7	1 - 42
Cr	228	8 $\pm$ 6	1 - 31
V	334	8 $\pm$ 5	1 - 38
Ba	100	9 $\pm$ 7	1 - 34
Co	261	8 $\pm$ 5	1 - 32
Cu	228	13 $\pm$ 9	1 - 48
Nd	296	15 $\pm$ 11	1 - 61
Ni	278	8 $\pm$ 6	1 - 33
Sr	251	77 $\pm$ 63	2 - 346
Cd	214	735 $\pm$ 1124	1 - 6776
As	221	191 $\pm$ 317	1 - 1092
Pb	193	75 $\pm$ 89	1 - 509
F ⁻	375	3356 $\pm$ 3201	110 - 25240
Acetate	90	27 $\pm$ 36	11 - 235
Propionate	79	46 $\pm$ 21	12 - 162
Formate	322	23 $\pm$ 12	5 - 73
MSA	330	63 $\pm$ 38	11 - 232
Cl ⁻	376	13980 $\pm$ 9834	117 - 76008
Br ⁻	17	44 $\pm$ 15	27 - 77
NO ₃ ⁻	364	232 $\pm$ 432	26 - 8167
PO ₄ ⁻	41	60 $\pm$ 62	27 - 397
SO ₄ ²⁻	376	3602 $\pm$ 1853	81 - 14331
Oxalate	379	121 $\pm$ 53	13 - 474
Na ⁺	376	10199 $\pm$ 6853	32 - 52987
NH ₄ ⁺	376	205 $\pm$ 126	25 - 1747
K ⁺	373	413 $\pm$ 265	23 - 1976
Mn ²⁺	7	41 $\pm$ 35	22 - 117
Ca ²⁺	371	727 $\pm$ 618	35 - 5232
Mg ²⁺	370	1168 $\pm$ 768	29 - 5585

An *Fpeak* strength of 0.5 was used to retain the best PMF solution whose five components (*sea salt*, *mineral dust*, *ammonium neutralised*, *fugitive dust* and *industry*) are shown in Figure 5-6. The relative contribution of those components to the total estimated mass is shown in Figure C-3.3. *Sea salt* accounted for the largest fraction of the mass concentration (74.7 $\pm$ 1.9%). Mineral dust accounted for 15.7 ($\pm$ 1.4%) of the evaluated total mass concentration. The remaining fraction was accounted by three components characterised by secondary species and heavy metals, *ammonium neutralised* (6.1 $\pm$ 0.7%), *fugitive dust* (2.6 $\pm$ 0.2%) and *industry* (0.9 $\pm$ 0.7%). However, the major tracers of the *sea salt*

component, Na^+ and Cl^- , were ubiquitous in all components, not surprising considering the continuous inflow of marine air to HBAO. As it can be seen in Figure 5-6, Na^+ and Cl^- contributed to $35.2 \pm 5.8\%$ of their mass to the mineral dust component, to $47.4 (\pm 1.9\%)$ of the mass of the *fugitive dust* component, and to $1.3 (\pm 17.8\%)$ of the mass of the *industry* component).

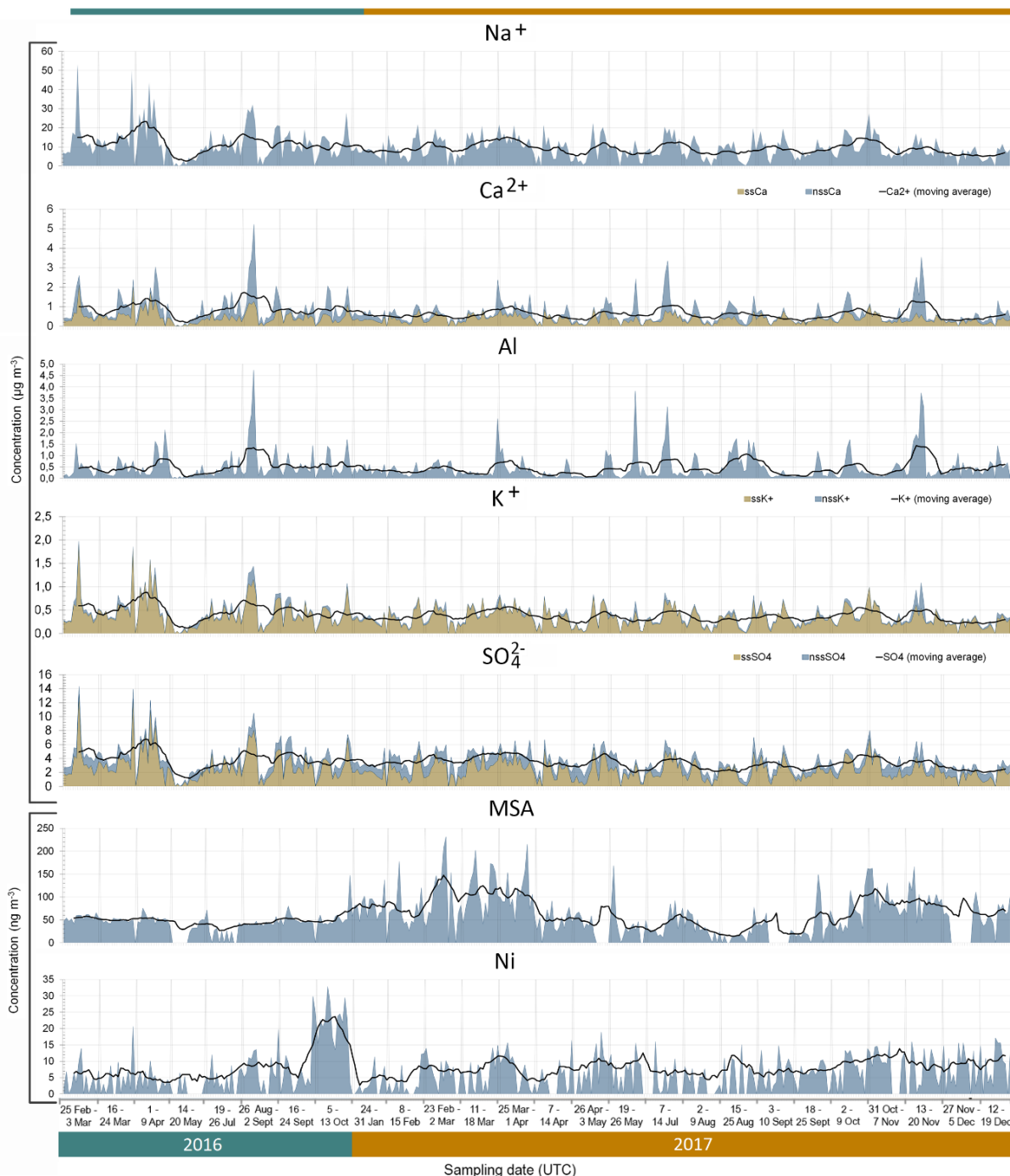


Figure 5-5. Time series (datetime in UTC) of measured concentrations for Na^+ , Ca^{2+} , Al, K^+ , SO_4^{2-} , MSA and Ni (shaded area). The solid black line indicates the calculated 10-point moving average. The sea salt (ss) components for Ca^{2+} , K^+ and SO_4^{2-} is indicated by the orange shaded areas, the non-sea salt (nss) fraction is represented by the blue shaded areas. The time series is non-consecutive and is divided into the 26 sampling weeks by the light grey vertical lines.

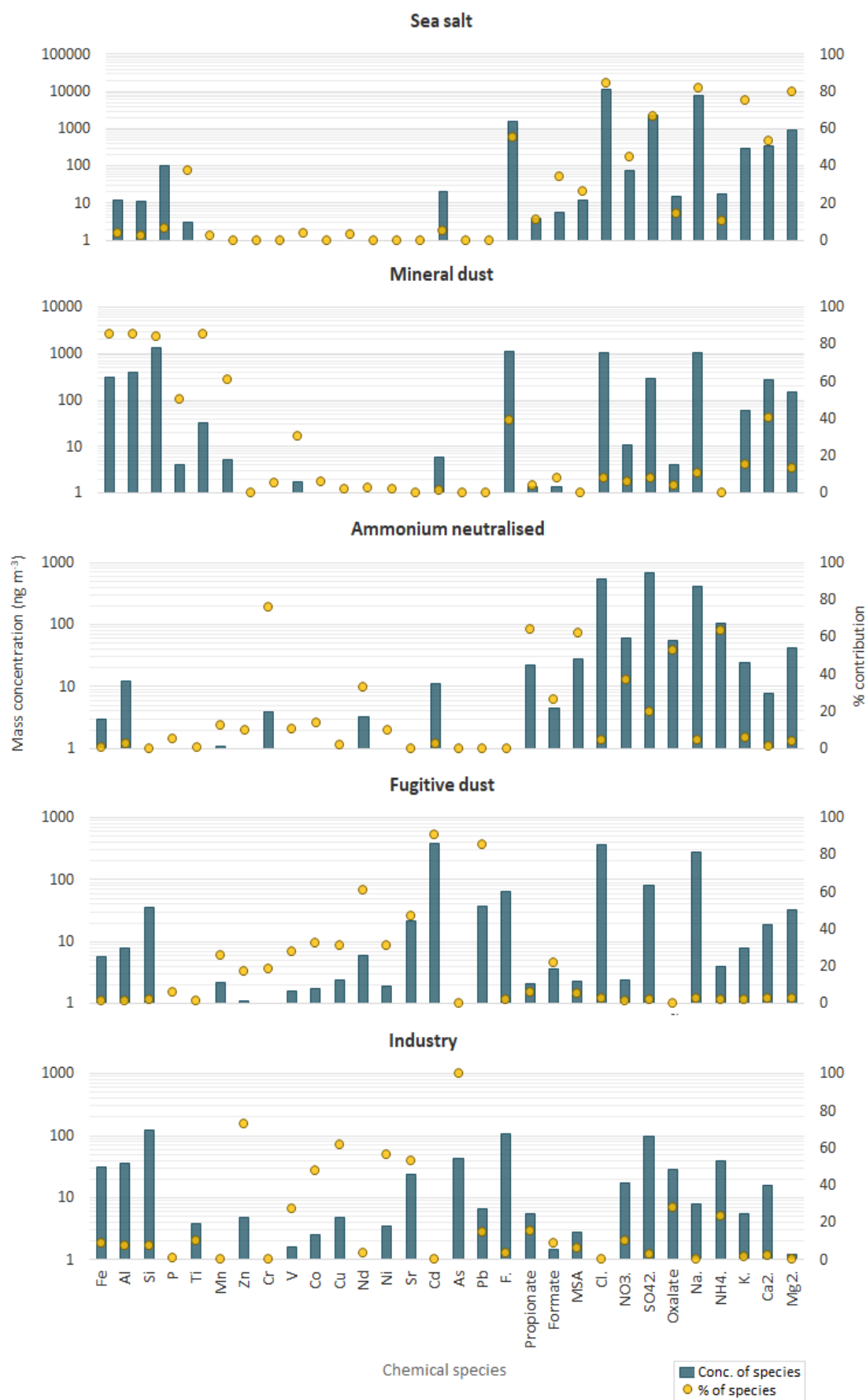


Figure 5-6. Profiles of the five components identified by the PMF analysis. Blue bars denote the mass concentrations of individual elements/ionic species (left logarithmic axis, ng m^{-3}) while the yellow points indicate the percent of species attributed to the source (right axis).

5.4.2.1. Sea salt

As expected, the major tracers of sea salt aerosols (Cl^- , Na^+ , Mg^{2+} and K^+) were sampled in high concentrations (up to 76, 53, 5.6 and $2.0 \mu\text{g m}^{-3}$, respectively) throughout the sampling periods. Their time variability, illustrated in Figure 5-5 by the example of Na^+ , was very similar and characterised by a significant continuous background that could be represented by a 10-point moving average (that is, 90 hours). The calculated mean background concentration was $10.1 \pm 3.6 \mu\text{g m}^{-3}$. No seasonal cycle was evident due to the dominance of southerly and south-westerly winds transporting marine air masses onshore (Figure 5-3).

The PMF *sea salt* component was represented by Na^+ , Cl^- , Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-} (Figure 5-6), and accounted for $74.7 \pm 1.9\%$ of the total aerosol mass (Figure C-3.3.). Table 5-2 shows the mass ratios of Cl^- , Mg^{2+} , K^+ , Ca^{2+} , F^- and SO_4^{2-} to Na^+ for 2016 and 2017, calculated as the slopes of their linear regression lines, and evaluated by the coefficient of determination (R^2). This table also gives the slope of the linear regression lines for the PMF *mineral dust* component. The experimental values were compared with average ratios in seawater (Seinfeld and Pandis, 2006). The average Cl^-/Na^+ mass ratio was 1.4 ± 0.1 in 2016 and 1.3 ± 0.1 in 2017 (also consistent for the PMF *sea salt* component), lower by 25% than the value expected in seawater of 1.8. This difference has previously been reported in fresh sea salt in acidic marine environments (e.g., Zhang et al., 2010), and is attributed to Cl^- depletion via reactions between NaCl and sulfuric- and nitric acids. A very good correlation was observed between the ratios of Mg^{2+} (0.12 ± 0.01) and K^+ (0.04 ± 0.01) to Na^+ in this data set and the value reported for sea water (Table 5-2) (Seinfeld and Pandis, 2006). Conversely, the linear correlation between Ca^{2+} and Na^+ (not shown) was less pronounced ($R^2 = 0.61$ and 0.42 in 2016 and 2017, respectively). The $\text{Ca}^{2+}/\text{Na}^+$ mass ratio was systematically higher than in seawater (0.04), indicating the contribution of crustal calcium typical of the Namibian soils (see section 5.4.2.2).

Table 5-2. Annual arithmetic mean mass ratios of Cl^- , Mg^{2+} , K^+ , Ca^{2+} , F^- and SO_4^{2-} with respect to Na^+ for 2016 and 2017. The Pearson coefficient of the linear regression (R^2) is reported. Mass ratios for average seawater from Seinfeld and Pandis (2006) are shown for comparison. Standard deviations are indicated as SD.

	2016		2017		PMF <i>sea salt</i> component	Average seawater
	Mean $\pm$ SD	R^2	Mean $\pm$ SD	R^2	Mean $\pm$ SD	Mass ratio
Cl^-/Na^+	1.35 ± 0.11	0.99	1.34 ± 0.11	0.99	1.38 ± 0.06	1.80
$\text{Mg}^{2+}/\text{Na}^+$	0.12 ± 0.01	0.99	0.11 ± 0.01	0.99	0.11 ± 0.01	0.12
K^+/Na^+	0.04 ± 0.01	0.98	0.04 ± 0.01	0.93	0.04 ± 0.01	0.04
$\text{Ca}^{2+}/\text{Na}^+$	0.07 ± 0.04	0.61	0.07 ± 0.05	0.42	0.04 ± 0.01	0.04
$\text{SO}_4^{2-}/\text{Na}^+$	0.36 ± 0.14	0.95	0.42 ± 0.23	0.85	0.28 ± 0.01	0.25
F^-/Na^+	0.38 ± 0.24	0.53	0.32 ± 0.35	0.33	0.19 ± 0.01	0.000122

Using the average seawater ratio, the mean sea-salt (ss) Ca^{2+} concentration was estimated as $470 \pm 360 \text{ ng m}^{-3}$ and $360 \pm 210 \text{ ng m}^{-3}$ for 2016 and 2017, respectively. The mean non-sea-salt (nss) Ca^{2+} concentration was 420 ± 520 and $270 \pm 400 \text{ ng m}^{-3}$, respectively for the two years, representing 47% and 42% of the mean measured Ca^{2+} concentrations. Similarly, for both 2016 and 2017, the ss and nss

components of K^+ were estimated as $367 \pm 246 \text{ ng m}^{-3}$ and $44 \pm 54 \text{ ng m}^{-3}$ respectively, accounting for 89% and 11% of the K^+ mass. The PMF estimated that *sea salt* contributed to $53.0 \pm 1.6\%$ of the calcium and $75.1 \pm 2.4\%$ of the K^+ mass.

The mean F^-/Na^+ mass ratio measured at HBAO was 0.39 ± 0.29 in 2016 and 0.32 ± 0.29 in 2017 and was 0.19 ± 0.01 for the PMF *sea salt* component, enriched by two to four orders of magnitude to the average seawater composition (mass ratio 1.2×10^{-4} ; Table 5-2).

5.4.2.2. Mineral dust

The PMF *mineral dust* component, composed by Si, Al, Fe, Ti, Ca^{2+} , Mn, P, F^- and V (Figure 5-6), accounted for $15.7 \pm 1.4\%$ of the total estimated mass. The time series of Al and $nss\text{-}Ca^{2+}$ (Figure 5-5) were analysed to investigate the temporal variability of airborne mineral dust at Henties Bay. The mean concentrations of mineral dust elements Al, Fe, Ti and Si were higher for night-time sampling between 21 and 06 UTC, and lower in the day (9 to 18 UTC), in correspondence of easterly winds, which were only observed at night and in the early morning (Figure 5-4).

Differently from sea salt, the occurrence of mineral dust was not continuous but episodic. Episodes of mineral dust corresponded to times when the concentrations of Al and $nss\text{-}Ca^{2+}$ exceeded background values (modelled as the 10-point moving average) for a minimum of 3 consecutively sampled filters. Similar time variability was observed for elemental Fe, Si, Ti and P (not shown). Overall, 19 episodes of mineral dust were identified during the two years of sampling (Table C-3.2.).

The mean mass concentration of elemental Al was $556 \pm 643 \text{ ng m}^{-3}$ in 2016 and $446 \pm 551 \text{ ng m}^{-3}$ in 2017, while values peak as high as $4.7 \text{ } \mu\text{g m}^{-3}$ (Table 5-1). To the best of our knowledge, no other measurements of Al are available in Namibia for comparison. Our arid sampling site is surrounded by loose sand, gravel plains (Matengu et al., 2019) and the deep Omaruru river valley directly north of the sampling site which is also a recognised source of mineral dust to the offshore waters (Tlhalerwa et al. 2012). While mostly characterised by gravels, some clay-rich deposits are found around the river valley approximately 17 km northeast of HBAO (Matengu et al., 2019). The relatively low aluminium concentrations measured at HBAO suggest that these are not a major local source for the site. The $nss\text{-}Ca^{2+}$ annual mean at HBAO ($703 \pm 644 \text{ ng m}^{-3}$ in 2016 and $428 \pm 437 \text{ ng m}^{-3}$ in 2017) is similar to the concentrations (mean 425 ng m^{-3} and maximum of 800 ng m^{-3}) measured in central Namibia at Gobabeb, in the Namib Desert ($23^{\circ}45'S$, $15^{\circ}03'E$; Annegarn et al., 1983). This is also the case for Fe, whose annual mean concentrations at HBAO ($372 \pm 480 \text{ ng m}^{-3}$ in 2016 and $338 \pm 433 \text{ ng m}^{-3}$ in 2017) compare well with the average of 246 ng m^{-3} (Annegarn et al., 1983).

Table 5-3 shows the mass ratios for major components of mineral dust as well as some heavy metals (V and Ni). Overall, Si, Fe, and Ti showed very good correlations to Al as expected for mineral dust ($R^2 > 0.9$). The average mass ratio of Si/Al was 3.7 ± 1.0 in 2016 and 3.4 ± 0.8 in 2017, lower than the average values of 4 to 4.6 expected in global soils and crustal rock (Seinfeld and Pandis, 2006). This is attributed

to the size-fractionation during aeolian erosion of soils producing airborne dust. As a matter of fact, our average values are consistent with those obtained for particles less than 10 μm in diameter by Eltayeb et al. (1993) at Gobabeb. Our averages, generally higher than in mineral dust from north Africa (Formenti et al., 2014), compare well with the value (3.4) reported by Caponi et al. (2017) for mineral dust aerosols generated in a laboratory experiment from a soil collected to the northeast of HBAO. The average Fe/Al ratio was 0.74 ± 0.19 in 2016 and 0.76 ± 0.18 in 2017 (0.8 ± 0.3 for the PMF solution), lower than the ratio of 1 reported by Eltayeb et al. (1993). The same is observed for the Ti/Al ratio, which was 0.07 ± 0.22 in 2016 and 0.06 ± 0.03 in 2017 (0.08 ± 0.01 in the PMF solution), while approximately 0.15 in Eltayeb et al. (1993).

Table 5-3. Annual arithmetic mean mass ratios of mineral dust tracers with respect to Al for 2016 and 2017. The Pearson coefficient of the linear regression (R^2) is reported. Mass ratios for previous publications are shown for comparison. Standard deviations are indicated as SD.

	2016		2017		Dust episodes		PMF <i>mineral dust</i> component	Literature values
	Mean $\pm$ SD	R^2	Mean $\pm$ SD	R^2	Mean $\pm$ SD	R^2	Mean $\pm$ SD	
Si/Al	3.7 ± 1.0	0.96	3.4 ± 0.8	0.96	3.5 ± 0.4	0.94	3.50 ± 0.13	$2.87 - 6.13^a$, 3.41^b , 4.63^c
nss-Ca ²⁺ /Al	1.3 ± 0.7	0.89	1.4 ± 0.7	0.83	1.4 ± 0.9	0.60	0.70 ± 0.02^s	$0.35 - 6.06^a$, 0.19^c
Fe/Al	0.74 ± 0.19	0.96	0.76 ± 0.18	0.97	0.76 ± 0.41	0.97	0.80 ± 0.03	$0.65 - 1.06^b$, 0.53^c
V/Al	0.03 ± 0.03	0.37	0.02 ± 0.02	0.26	0.02 ± 0.03	0.31	0.01 ± 0.01	0.0014^c
Ti/Al	0.07 ± 0.02	0.96	0.06 ± 0.03	0.97	0.08 ± 0.02	0.97	0.08 ± 0.01	$0.09 - 0.15^a$, 0.07^c
P/Al	0.03 ± 0.02	0.81	0.05 ± 0.02	0.59	0.02 ± 0.01	0.72	0.01 ± 0.01	0.007^d
Fe/nss-Ca ²⁺	0.54 ± 0.23	0.94	0.65 ± 0.23	0.83	0.76 ± 0.41	0.60	1.14 ± 0.03^{ss}	$0.18 - 1.86^a$, 0.58^b , 2.77^c
nss-K ⁺ /Al	0.13 ± 0.11	0.81	0.11 ± 0.10	0.59	0.08 ± 0.06	0.61	0.16 ± 0.01^{sss}	$0.251 - 0.452^a$
V/Si	0.01 ± 0.01	0.39	0.01 ± 0.01	0.26	0.01 ± 0.01	0.33	0.010 ± 0.001	0.0003^c
F ⁻ /Al	11.6 ± 8.4	0.73	9.7 ± 8.4	0.64	6.2 ± 2.9	0.57	2.8 ± 0.1	–
nss-SO ₄ ²⁻ /nss-Ca ²⁺	3.8 ± 2.4	0.42	6.1 ± 4.0	0.03	2.6 ± 5.7	0.11	1.1 ± 0.2	2.4^e

^a Eltayeb et al., (1993) from various sites around the Central Namib

^b Annegarn et al. (1983): Gobabeb, Namibia

^c Seinfeld and Pandis (2006): average chemical composition for soils globally

^d Formenti et al., (2003a): Cape Verde region

^e Mass ratio for gypsum

^s Ca²⁺/Al ratio

^{ss} Fe/Ca²⁺ ratio

^{sss} K⁺/Al ratio

The average nss-Ca²⁺/Al ratio was 1.3 ± 0.7 in 2016 and 1.4 ± 0.7 in 2017, however, for the strongest dust episodes (Al values higher than 1 $\mu\text{g m}^{-3}$) the ratio tended to 1 (Figure 5-7). This is in agreement with the specific mineralogy of Namibian soils that are rich in limestone and gypsum (Annegarn et al., 1983; Eltayeb et al., 1993). The PMF analysis attributed $40.5 \pm 0.6\%$ of the total Ca²⁺ mass to the *mineral dust* component, of the same order of magnitude than obtained from the chemical apportionment (nss fraction representing 47% of the total -Ca²⁺). The SO₄²⁻/Ca²⁺ mass ratio in the PMF *mineral dust* was 1.1 ± 0.2 , three to four times lower than that the nss-SO₄²⁻/nss-Ca²⁺ obtained from chemical apportionment and about half the mass ratio for gypsum, which, however, well coincided with the mass ratio obtained for when selecting the dust episodes only. The mean Fe/nss-Ca²⁺ ratio was 0.54 ± 0.23 in 2016 and 0.65

± 0.23 in 2017, higher than the value of 0.11 ± 0.10 reported by Caponi et al. (2017), pointing to the diversity in soil mineralogy, even at relatively small spatial scales.

As for nss-Ca^{2+} , values for $\text{nss-K}^+/\text{Al}$ ratios (Figure 5-7) were spread but ranged between 0.1 and 0.5 when Al concentrations exceeded $1 \mu\text{g m}^{-3}$. These values are in agreement with those for mineral dust sources in North Africa (Formenti et al., 2014). The PMF K^+/Al mass ratio was 0.16 ± 0.01 , in good agreement with the average $\text{nss-K}^+/\text{Al}$ (0.13 ± 0.12) by chemical apportionment and half of that reported in the literature (0.25 – 0.45, Eltayeb et al., 1993).

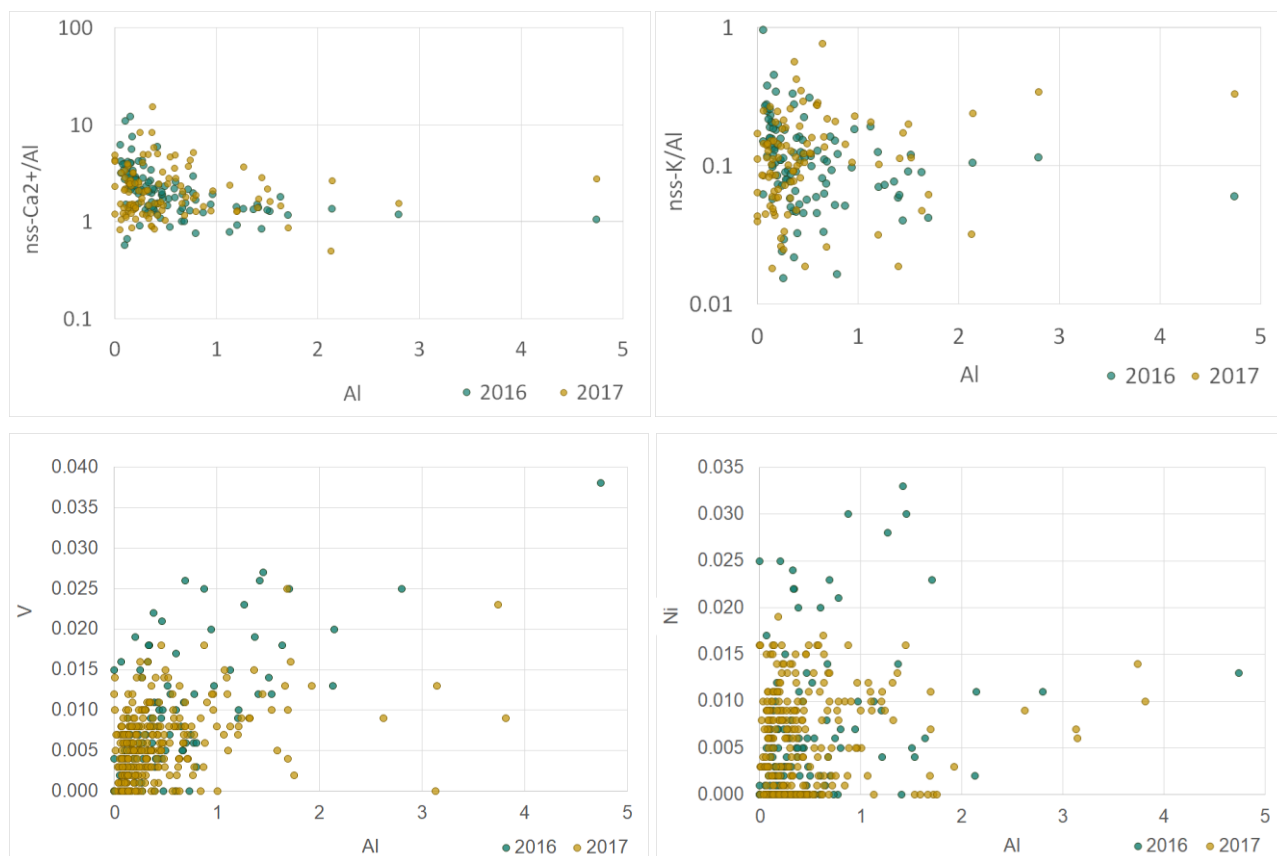


Figure 5-7. Scatterplots of $\text{nss-Ca}^{2+}/\text{Al}$ (top left), $\text{nss-K}^+/\text{Al}$ (top right), V (bottom left) and Ni (bottom right) ratios to Al for 2016 (blue) and 2017 (orange). Concentrations are expressed in $\mu\text{g m}^{-3}$. Note the logarithmic y-axes on the top plots.

The average phosphorus concentrations measured at HBAO were $11 \pm 9 \text{ ng m}^{-3}$ in 2016 and $14 \pm 4 \text{ ng m}^{-3}$ in 2017. Phosphorous was very well correlated with Al in 2016 ($R^2 = 0.92$) and only moderately correlated in 2017 ($R^2 = 0.66$). The P/Al mass ratio annual average was 0.03 ± 0.02 in 2016 and 0.05 ± 0.02 in 2017 (0.01 ± 0.01 in the PMF *mineral dust*). As was observed for the $\text{nss-Ca}^{2+}/\text{Al}$, the P/Al ratio tended to an asymptotic value of 0.02 when Al exceeded $1 \mu\text{g m}^{-3}$ (not shown). The PMF result is closer to that reported by Formenti et al. (2003a) for the outflow of Saharan dust to the North Atlantic Ocean (0.0070 ± 0.0004).

5.4.2.3. Heavy metals

The PMF identified two components characterised by heavy metals: a *fugitive dust* component (traced by V, Cd, Pb, Nd and Sr) and an *industry* component, characterised by As, Zn, Cu, Ni and Sr, representing 2.6 ($\pm 0.2\%$) and 0.9 ($\pm 0.7\%$) of the total estimated mass.

Vanadium and nickel are naturally occurring in mineral deposits in soils (Annegarn et al., 1983; Maier et al., 2013), but they are also known tracers of heavy-oil combustion, as reported in Becagli et al. (2017) and references therein. Their average concentrations at HBAO were $9 \pm 5 \text{ ng m}^{-3}$ (2016) and $7 \pm 6 \text{ ng m}^{-3}$ (2017) for V, and $8 \pm 7 \text{ ng m}^{-3}$ (2016) and $7 \pm 4 \text{ ng m}^{-3}$ (2017) for Ni. The highest V concentrations corresponded to south-south-easterly winds while high Ni concentrations were measured in the south-west wind sector (Figure C-3.4.). The annual mean values of V and Ni at HBAO are an order of magnitude larger than measured over the open ocean by Chance et al. (2015), higher than those reported by Hedberg et al. (2005) at towns affected by copper smelters and comparable to those measured by Isakson et al. (2001) at a Swedish harbour and by Becagli et al. (2017) in the central Mediterranean Sea downwind of a major shipping route.

Vanadium was well correlated with Al when Al exceeded $1 \mu\text{g m}^{-3}$ (R^2 around 0.4), whereas no correlation between Ni and Al were observed (Figure 5-7). Additionally, the correlation of V to Si, also used in the literature as a tracer of mineral dust, was evident while moderate (R^2 around 0.4), and no correlation was found for Ni. This differs from what was reported by Becagli et al. (2017), who found that neither V nor Ni were correlated to Si. In our dataset and the PMF *mineral dust* component (section 5.4.2.2), both V/Si and Ni/Si ratios were enriched by a factor of 10 or more to reference values for the upper continental crust (3.1×10^{-4} and 1.5×10^{-4} for V/Si and Ni/Si, respectively; Henderson and Henderson, 2009). The V/Ni mass ratio was 1.7 ± 1.1 for 2016 and 1.3 ± 1.3 in 2017, lower than reported by Lyyränen et al. (1999) and Corbin et al. (2018) for heavy fuel oil in diesel engines, and by Becagli et al. (2017) and Viana et al. (2009) in the Mediterranean basin ambient air (2.8–2.9 and 4–5, respectively).

All these elements, and furthermore their poor correlation (R^2 around 0.3), suggest that V and Ni do not necessarily have the same sources. Mining activities, likely in the Otavi mountain area (Boni et al., 2007), should account for the high concentrations of V, with additional contributions from heavy-oil combustion, where V is present as an impurity (Isakson et al., 2001, and references therein; Vouk and Piver, 1983). On the contrary, combustion of heavy-oils seems to be the primary source of Ni. This hypothesis is supported by the PMF analysis. The PMF apportionment of V and Ni concentrations (Figure C-3.5) clearly distinguishes the relative source contributions, and preferentially associates V with *mineral dust* and *fugitive dust* components, while Ni with the industry component.

Moderate to good correlations of V and Ni with Zn (R^2 of 0.42 and 0.55, respectively), Cu (0.55 and 0.73) and Pb (0.56 and 0.69) were observed in the dataset. Zn and Pb are found as impurities in bulk fuels for ships (Isakson et al., 2001) and also from copper smelting, as reported in central Chile (Hedberg et al. 2005) urban air in the United States of America (Ramadan et al., 2000). The mean concentration of Zn

at HBAO ($11 \pm 9 \text{ ng m}^{-3}$) was about two orders of magnitude higher than over the southeast Atlantic Ocean (Chance et al., 2015) and in air over the arid landscapes (Annegarn et al., 1983). Likewise, the mean Pb concentration ($75 \pm 89 \text{ ng m}^{-3}$) was three orders of magnitude higher than reported by Chance et al. (2015) for soluble Pb and comparable to values measured in the western Mediterranean by Denjean et al. (2016). The PMF separates the largest fractions of Zn and Pb into the *industry* and *fugitive dust* components, respectively. Although some of these heavy metals may be sourced from the commercial shipping route offshore, the mass ratios for tracer elements were not in agreement with our results and so we cannot conclusively state shipping heavy-oil combustion as the source of these heavy metals.

Average concentrations of Cu at HBAO were $8 \pm 6 \text{ ng m}^{-3}$, an order of magnitude higher than measured in windblown dust by Annegarn et al. (1983) in the central Namib but two orders of magnitude smaller than the average measured by Lee et al. (1999) in highly polluted Hong Kong (125.1 ng m^{-3}). Ettler et al. (2011) showed that copper ore mining and smelting operations in the Zambian Copperbelt are a significant source of potentially bioavailable copper, that, unlike phosphorus, has been found to inhibit plankton growth in laboratory studies (Paytan et al., 2009) and over the western Mediterranean (Jordi et al., 2012). Similar contamination of topsoil was found by Křibek et al. (2018) at operations in the Tsumeb mining district, Namibia ($19^{\circ}14'S$, $17^{\circ}43'E$). Average Cu concentrations were comparable to values $4.9 \pm 11.5 \text{ ng m}^{-3}$ reported for a town closer to smelters in Chile, and an order of magnitude smaller than in the urban environment of the capital city of Santiago ($77.5 \pm 78.2 \text{ ng m}^{-3}$; Hedberg et al., 2005). The Cu/Ni ratio (1.24 ± 0.20) in the PMF *fugitive dust* component was about half than reported for soil samples polluted by copper mine tailings from the Gruben River valley (2.03 ± 2.30 , Taylor and Kesterton, 2002).

The mean mass concentration of Cd was $1502 \pm 1458 \text{ ng m}^{-3}$ in 2016 and $219 \pm 163 \text{ ng m}^{-3}$ in 2017. The difference is mainly owing to high concentrations in October of 2016, which coincided with high concentrations in all other heavy metals, except for As. Cd concentrations in 2016 were less than that reported for airborne road dust ($7.4 \pm 7.8 \text{ } \mu\text{g m}^{-3}$) and our 2017 concentrations were in the order of that measured in ambient air ($0.14 \pm 0.04 \text{ } \mu\text{g m}^{-3}$) in the seaside city of Khobar, Saudi Arabia (El-Sergany and El-Sharkawy, 2011). The Cd/Pb ratio of 9.96 ± 0.21 for the PMF *fugitive dust* component was slightly higher than 7.14 ± 4.26 in the ambient air of the coastal desert environment in Khobar (El-Sergany and El-Sharkawy, 2011). The correlation of Pb, Nd and Sr the *fugitive dust* component may indicate contributions of non-micaceous kimberlites from a variety of source regions across southern Africa (Smith, 1983). The Sr/Nd ratio for the *fugitive dust* component (3.58) was close to 3.35 reported for Kimberlites at Uintjesberg in the Northern Cape of South Africa.

5.4.2.4. Fluoride

One of the striking features of Table 5-1 is the high mean concentration of F^- measured at HBAO ($4.3 \pm 4.0 \mu\text{g m}^{-3}$ in 2016 and $2.8 \pm 2.5 \mu\text{g m}^{-3}$ in 2017), with peak values as high as $25 \mu\text{g m}^{-3}$. Those annual mean concentrations were comparable to the mean 24-h fluoride concentrations measured between 1985 and 1990 over the South African Highveld by Scheifinger and Held (1997). The measured concentrations at HBAO were also comparable to those of heavily polluted areas in China (Feng et al., 2003), and significantly higher than reported for Europe, even in the polluted Venice lagoon (Prodi et al., 2009) or in areas nearby ceramic and glass factories (Calatrini et al., 1998). The peak values at HBAO were significantly higher than maxima reported by these authors and ranging between 1.4 and $2.9 \mu\text{g m}^{-3}$. The highest F^- concentrations were associated with south to easterly winds, that is, from the subcontinent (not shown). The very good correlation of F^- with nss-Ca^{2+} , shown in Figure C-3.6. (R^2 equal to 0.76 in 2016 and to 0.84 in 2017), yielded a mean mass ratio of 6.4 and 5.8, respectively, much higher than reported in groundwater, aerosols or precipitation in polluted environments (Feng et al., 2003; Prodi et al., 2009).

The strong relationship to nss-Ca^{2+} (and *a posteriori* to Ca^{2+}) drove the PMF apportionment (Figure C-3.7.), which attributed approximately the 94% of the F^- mass concentrations to the sea salt and mineral dust components ($55.1 \pm 1.9\%$ and $38.8 \pm 1.1\%$, respectively), and the remaining 6% to *fugitive dust* ($2.3 \pm 0.5\%$) and *industry* ($3.8 \pm 1.0\%$). Possible sources are the emission of fugitive dust during fluor spar mining of carbonatite related fluor spar deposits at the Okorusu Mine ($20^\circ 3'S$, $16^\circ 44'E$), but very likely also from the periodic surface mining occurring approximately 20 km south of HBAO to provide gravel for the construction of a major road between Swakopmund and Henties Bay, which started late in 2015 (Andreas Namwoonde, *pers. corr.*, 2017). The evaporation of fluoride rich water, leached into groundwater (Wanke et al., 2015, 2017) from fluoride-rich mineral deposits and soils, throughout the region and in the coastal waters (Compton and Bergh, 2016; Mänd et al., 2018), would also increase atmospheric F^- concentrations. In an analysis of borehole water in Namibia, roughly 80% of those sites surveyed were deemed unsafe to drink as a direct result of high fluoride concentrations (Christelis and Struckmeier, 2011).

5.4.2.5. Arsenic

The annual mean of the arsenic concentrations at HBAO was $22 \pm 16 \text{ ng m}^{-3}$ in 2016 and $239 \pm 344 \text{ ng m}^{-3}$ in 2017. The mean for 2017 is skewed due to two sampling weeks with very high concentrations in the order of those measured in rural and urban-industrial areas affected by mining and smelting emission sources (Hedberg et al., 2005; Šerbula et al., 2010).

The PMF analysis exclusively associated As the *industry* component along with large fractions of the Zn, Cu, Ni, Sr and Co. Known sources of atmospheric arsenic are biomass burning, heavy-oil combustion and non-ferrous metal smelting operations (Ahoulé et al., 2015; Gomez-Caminero et al., 2001). A possible local source could be the Tsumeb smelter in the northeast of HBAO (KPMG, 2014).

The PMF As/Zn, As/Pb and Zn/Pb ratios were 9.0 ± 0.3 , 6.4 ± 0.8 and 0.7 ± 0.1 , in good agreement with those reported by Hedberg et al. (2005) for a copper smelter plume in Chile (7.7, 4.5 and 0.6, respectively). This is in good agreement with the fact that no correlations between As to Al nor nss- Ca^{2+} were found, ruling out any major contribution of Inorganic arsenic in geologic formations released from mining operations or evaporated from soil and groundwater (Gomez-Caminero et al., 2001). Likewise, no discernible correlation between As and MSA was found, suggesting only a minor release of arsenic by marine algae and plankton (Sanders and Windom, 1980; Shibata et al., 1996).

5.4.2.6. Secondary aerosols and sulphates

The PMF *ammonium neutralised* (Figure 5-6) comprised secondary species such as SO_4^{2-} , NH_4^+ , MSA, oxalate, and nitrate, which accounted for $6.1 \pm 0.7\%$ of the estimated aerosol mass. The annual mean sulphate concentration measured at HBAO was $4.1 \pm 2.6 \mu\text{g m}^{-3}$ in 2016 and $3.4 \pm 1.4 \mu\text{g m}^{-3}$ in 2017 (Table 5-4), higher than previously measured over the southern Atlantic and Pacific oceans (Zhang et al., 2010) and comparable to springtime measurements in the Venice Lagoon (Prodi et al., 2009). As already discussed in Formenti et al. (2019), the highest concentrations were measured in spring and autumn, while minima occurred between May and August. SO_4^{2-} and Na^+ showed good correlation ($R^2 = 0.92$ in 2016 and 0.83 in 2017, Table 5-2). However, their annual mass ratios (0.36 ± 0.14 and 0.42 ± 0.23 in 2016 and 2017, respectively) were higher than the expected mass ratio in seawater (0.25; Seinfeld and Pandis, 2006), which was used as nominal reference to apportion SO_4^{2-} into its ss and nss fractions. As a result, up to 57% of the measured SO_4^{2-} mass concentration in the PM_{10} fraction was attributed to sea salt aerosols, while the nss-component was of the order of 43%. The PMF estimated that the *sea salt* component contributed to $66.6 \pm 0.4\%$ of the total sulphate mass. This is in agreement with previous observations in the south Atlantic Ocean (Andreae et al., 1995; Zhang et al., 2010; Zorn et al., 2008). On the contrary, at the remote Brand se Baai site along the Atlantic coast of South Africa (31.5°S, 18°E), Formenti et al. (1999) reported that sea salt accounted for about 92% of the total measured elemental sulphur concentrations.

The MSA concentrations measured at the site ranged between 10 and 230 ng m^{-3} (Table 5-1). The mean annual concentration was $63 \pm 39 \text{ ng m}^{-3}$, three times higher than the mean value of $20 \pm 20 \text{ ng m}^{-3}$ ($6.2 \pm 4.2 \text{ ppt}$) reported by Andreae et al. (1995) over the open ocean along 19°S, and lower than in the southeast Atlantic Ocean (Zhang et al., 2010; Table 5-4). As already described in Formenti et al. (2019), the MSA concentrations were higher in the austral summer and spring and lower in the austral winter. DMS is more efficiently oxidised in warmer conditions (Ayers et al., 1986; Huang et al., 2017), which explains the the higher daytime mean concentrations of marine biogenic products (MSA and nss- SO_4^{2-}) and lower means at night and in the winter. Springtime averages for MSA were in the range of that measured by Huang et al. (2017) during a springtime cruise over the South Atlantic and by Prodi et al. (2009) in the Venice Lagoon (Table 5-4). The mismatch of seasonality with respect to that of the

phytoplankton blooms (Louw et al., 2016) is already discussed by Formenti et al. (2019) and attributed to the spread of blooms in the BUS region depending on local conditions.

The MSA/nss-SO₄²⁻ ratio (Figure 5-8) displayed a large range of values (0.01 to 0.12), consistent with that reported in the literature at various geographical locations, especially in the southern Hemisphere (Table 5-4). The MSA/SO₄²⁻ mass ratio for the PMF component (0.04 ± 0.01) was in agreement with the MSA/nss-SO₄²⁻ from the chemical apportionment reported in Table 5-4. The strong seasonal dependence of MSA/nss-SO₄²⁻ is in agreement to that identified by Ayers et al. (1986) for marine biogenic sulphur in the Southern Hemisphere and suggests that the highest concentrations of nss-SO₄²⁻ in the PM₁₀ (nss-SO₄²⁻ larger than 2 µg m⁻³) are not necessarily associated to marine biogenic emissions. From measurements at the desert station of Gobabeb, in the Namib Desert, Annegarn et al. (1983) found that only the fine mode of the bimodal distribution of sulphur aerosols, that is, that bearing the lower mass concentrations, would be due to the oxidation of sulphur-containing gaseous emissions during the marine phytoplankton life cycle.

Table 5-4. Reported concentrations for marine biogenic and secondary aerosols for different locations, and especially in the southern hemisphere. Concentrations are in µg m⁻³ unless stated otherwise.

	SO ₄ ²⁻ (nss-SO ₄ ²⁻)	NH ₄ ⁺	NO ₃ ⁻	MSA	MSA/nss-SO ₄ ²⁻
Outflow Africa south of Cape Town, PM1^a	1.39	0.18	0.01	0.04	0.007 ^{aaa}
Southern Ocean south of Australia^b	-	-	-	0.02 - 0.2	0.24 ± 0.16
Cape Grim, Tasmania^c	11.9 ± 1.2 nmole/m ³	-	-	0.167 ± 0.027 nmole/m ³	0.063 ± 0.020
19°S offshore southern Africa^d	-	-	-	6.1 ± 4 ppt 6.3 ± 4.4 ppt	0.05 - 0.11
Southern Atlantic^e A = autumn, S = spring^f	1.95 ± 1.05 ^e	7.6 ± 13.9 ^e	1.05 ± 0.72 ^e	0.21 ± 0.30 ^e S: 0.05 ± 0.1 ^j A: 0.15 ± 0.1 ^j	0.11 ^e
Southern Pacific^e	2.10 ± 1.05	0 ± 0	0.12 ± 0.15	0.58 ± 0.60	0.27
Venice Lagoon^g W = winter, S = spring	W: 3.3 ± 1.0; S: 4.4 ± 1.2	W: 2.9 ± 0.6 S: 2.6 ± 1.0	W: 9.0 ± 2.4 S: 3.5 ± 2.9	W: 0.035 ± 0.017 S: 0.054 ± 0.040	0.1
Southern Indian Ocean^h	-	-	-	-	0.1
America Samoa (14°S, 170°W)ⁱ	-	-	-	-	0.06
Coastal Antarctica^j	-	-	-	-	0.05 - 0.17
This study, 2016	4.0 ± 2.4 (1.7 ± 0.8)	0.19 ± 0.10	0.26 ± 0.71	0.07 ± 0.01	0.03 ± 0.01
This study, 2017	3.4 ± 1.4 (1.6 ± 0.7)	0.20 ± 0.10	0.22 ± 0.12	0.07 ± 0.04	0.04 ± 0.02

^a Zorn et al. (2008); PM1 fraction, ^{aaa} calculated with respect to total sulphate

^b Quinn et al. (1998)

^c Ayers et al. (1986)

^d Andreae et al. (1995)

^e Zhang et al. (2010); total suspended particulates fraction

^f Huang et al. (2017)

^g Prodi et al. (2009)

^h Sciare et al. (2000)

ⁱ Savoie et al. (1994)

^j Chen et al. (2012)

Figure 5-8 illustrates the $\text{NH}_4^+/\text{nss-SO}_4^{2-}$ mass ratio as a function of nss-SO_4^{2-} mass concentrations. Both in 2016 and 2017, the $\text{NH}_4^+/\text{nss-SO}_4^{2-}$ mass ratios were less variable than for $\text{MSA}/\text{nss-SO}_4^{2-}$. The annual mean $\text{NH}_4^+/\text{nss-SO}_4^{2-}$ were 0.13 ± 0.10 in 2016, 0.14 ± 0.08 in 2017 and 0.15 ± 0.01 in 2017. These values are consistent with the mass ratio of 0.18 corresponding to ammonium bisulphate $((\text{NH}_4)\text{HSO}_4)$. Although some losses of NH_4^+ due to conservation on-site and transport to the laboratory in France cannot be excluded, the measured ratios are consistent with previous investigations in remote marine environments reported in Table 5-4, including offshore southern Africa (Andreae et al., 1995; Quinn et al., 1998).

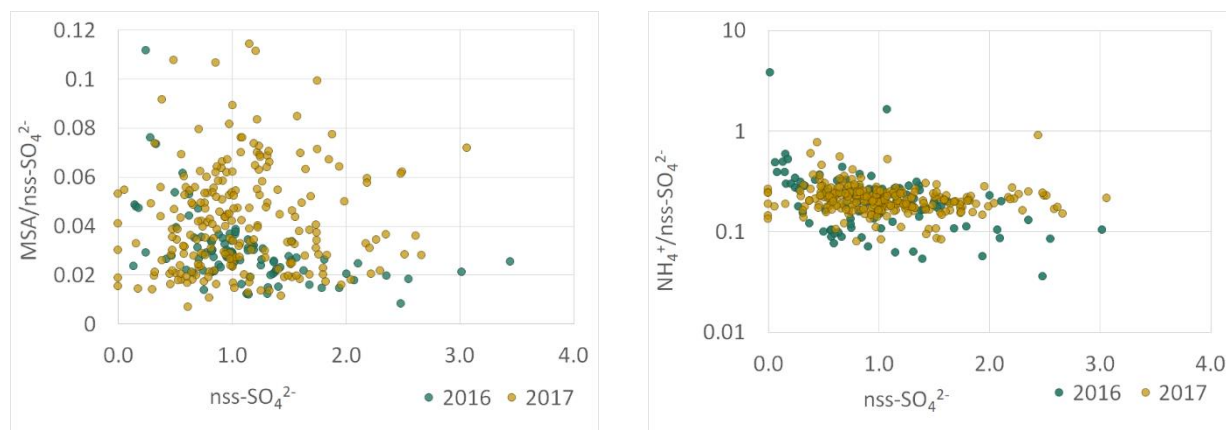


Figure 5-8. Scatterplots for ratios of MSA (left) and NH_4^+ (right) to nss-SO_4^{2-} for 2016 (blue) and 2017 (orange). Concentrations are expressed in $\mu\text{g m}^{-3}$. Note the logarithmic y-axis of the figure on the right.

The average $\text{NO}_3^-/\text{nss-SO}_4^{2-}$ ratio at HBAO was of the order of 0.14, significantly smaller than reported by Zhang et al. (2010) over the southeast Atlantic. Poor correlation between nss-SO_4^{2-} and nss-Ca^{2+} (not shown) suggests that very little of the sulphate is present as CaSO_4 , either formed by heterogeneous deposition of SO_2 on calcite mineral particles or liberated from the soils as mineral gypsum (Annegarn et al., 1983).

Finally, the mean annual concentration of oxalate at HBAO was $72 \pm 80 \text{ ng m}^{-3}$ in 2016 and $141 \pm 50 \text{ ng m}^{-3}$ in 2017. Values at HBAO are consistent with those reported by Zhang et al. (2010) over the southeast Atlantic ($200 \pm 140 \text{ ng m}^{-3}$). Oxalate aerosols in the atmosphere are due to marine biogenic activity and anthropogenic emissions including heavy-oil combustion and biomass burning (Gillett et al., 2007, and references therein). It is also formed by in-cloud processes and oxidation of gaseous precursors followed by condensation (Baboukas et al., 2000). The moderate correlation with NO_3^- , nss-SO_4^{2-} and nss-K^+ , particularly in 2017, could suggest a common origin and possible influence of occasional biomass burning.

5.5. Conclusions and significance of results

This paper presented the first long-term characterisation of the elemental and ionic composition of atmospheric aerosols and the source apportionment of the PM_{10} mass fraction at the Henties Bay Aerosol Observatory on the west coast of southern Africa, an under-explored region of the world to date.

The study was based on semi-continuous filter sampling at the HBAO site in Namibia in 2016 and 2017, laboratory analysis of the collected samples by X-ray fluorescence and ion chromatography, and PMF apportionment, supported by back-trajectory calculations and the analysis of local winds.

Trajectory analysis for the sampling period from 2016 to 2017 shows four distinct patterns of atmospheric transport to HBAO. Two transport pathways are from the South Atlantic Ocean, directly from the east and the south and south-east. A third transport pathway shows air masses reaching Henties bay from the north-west. This pathway will likely include constituents that originated over the continent. The fourth more common transport pathway is from central southern Africa. Local wind circulation is influenced by the overlying synoptic circulation patterns as well as local sea breeze mechanisms. Surface flow to HBAO is predominantly from the south and south-west. Southwesterly flow is likely to be linked to sea breeze circulation as a result of thermal gradients in the daytime between the arid surfaces and the ocean. Land and sea breezes are not common at HBAO due to a weak thermal gradient at night between the ocean and desert surface.

In general terms, the results presented in this paper are in agreement with the expectations for remote marine regions of the world, and previous observations in the area (Andreae et al., 1995; Zhang et al., 2010). Chemical and PMF apportionments showed that the PM₁₀ aerosol load is dominated by natural species such as sea salt, mineral dust and marine biogenic emissions, accounting for more than 90% of the mass. As a consequence of the proximity to the seashore of the HBAO sampling station, the majority of the PM₁₀ mass concentration (around 75%) is due to sea spray, which is persistent at the diurnal and seasonal time scales.

Our analysis provides with the first-time investigation of the frequency, intensity, and elemental composition of Namibian mineral dust aerosols. Nineteen episodes of increased Al and nss-Ca²⁺ concentrations, lasting from one to a maximum of four days, were detected during the entire sampling period. This corresponds well to the frequency of emission of dust plumes from river valleys, coastal sabkhas, and paleo-lacustrine sources (Etosha and Makgadikgadi pans) observed by various authors (Eckardt and Kuring, 2005; Vickery et al., 2013; Dansie et al., 2017). Our data series does not show any particular time dependence of the frequency nor duration of the detected episodes. This is in contrast with the observation by Dansie et al. (2017) that windblown dust derived from the ephemeral river valleys is transported offshore during large easterly wind events, and indicative of the fact that HBAO is the receptor of mineral dust emitted by various sources.

One of the striking findings of this paper was the level of anthropogenic contamination and the concentrations of various pollutants, including heavy metals and fluoride. Formenti et al. (2018) already demonstrated a seasonal increase in the light-absorbing carbon particulate between May and late July, indicative of the surface transport of biomass burning aerosols, and episodically throughout the year, attributed to pollution by ship traffic along the Cape of Good Hope sea route.

While the coarse resolution of air mass back-trajectories and the dominance of marine air masses does not allow to distinguish sources at the country scale, the PMF analysis performed in this paper was able to identify the specific and distinct contribution of mining activities, including for road construction for the majority of the heavy metals (ex., V). Our results shown that mining activities severely affect the air quality and contribute to concentrations as high as, or even higher than in well-known polluted regions of the world, such as the Venice lagoon (Prodi et al., 2009). The persistence of these high concentrations over the two years of sampling is extremely worrying for the affected populations and needs to be addressed by dedicated investigations and decision-making procedures. We suspect that some of that contamination, contributing to the highest heavy metal concentrations in October 2016, might be due to fugitive dust released by the major road construction between Walvis Bay, past Henties Bay and towards Angola, that started in the second half of 2016. Having said this, that specific week discarded, there is no significant difference between the concentration levels in 2016 (before road works) and 2017 (during the road works), suggesting that the pollution by heavy metals is a specific feature in the region, with likely implications on weather and climate. One such effect could be the deposition of these metals in the ocean. The deposition of macronutrients (P, Fe) from the outflow of mineral dust is not expected to be relevant for the BUS region, one of the most productive marine environments in the world, while it could be important in fertilising waters near the coast (Dansie et al., 2017) and in the Southern Ocean (Okin et al., 2011). On the other hand, the atmospheric deposition of trace metals (Cr, Cu, Ni, Mn, or Zn) in the aerosols, which play a biological role in enzymes and as structural elements in proteins (Morel and Price, 2003), could affect the marine productivity of the BUS and should be explored in future work. The complexity and diversity of sources that might contribute to the aerosol population at HBAO, deserve further dedicated investigation.

The long-term time series of aerosol composition at HBAO also provides new and important insights on the contribution of marine emission to the regional aerosol load. Our sampling provides the first long-term measurements of the mass concentrations of MSA in the south Atlantic, and the apportionment of sulphate aerosols, which are important for light scattering and cloud formation. Our data show that sea salt contributes, on average, to around 57% of the total sulphate mass. The non-sea salt fraction (nss- SO_4^{2-}), of the order of 43%, is partly attributed to the oxidation of sulphur-containing gaseous emissions (DMS, SO_2 , H_2S) during the marine phytoplankton life cycle, likely favoured by night-time fog and overall elevated relative humidity, typical along the coast. However, nss- SO_4^{2-} mass concentrations over $2 \mu\text{g m}^{-3}$ could be contributed by heavy-oil combustion by commercial ships and industrial processes such as power generation or copper smelting, as well as by episodic biomass burning. Ammonium bisulfate ($(\text{NH}_4)\text{HSO}_4$) was found to be the predominant sulphate forms at HBAO, where, incidentally, we observed dramatic rusting and corrosion of materials through the years. The ongoing data analysis of the AEROCLO-sa field campaign will provide with further insights on the size-dependent apportionment, chemical composition and hygroscopicity of sulphate aerosols, and its relevance as cloud condensation nuclei.

Data availability. Original and analysed data can be obtained by email request to the corresponding author. The SplitR package is found in Iannone (2018). The openair package for R is found in Carslaw and Ropkins (2017). The EPA (Environmental Protection Agency) PMF version 5.0 software is available from <https://www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses>. The NOAA Air Resources Laboratory (ARL) provides the HYSPLIT transport and dispersion model and/or READY website (<http://www.ready.noaa.gov>).

Author contributions. DK, PF, SJP, AN, MC, and AF performed the filter sampling and operated the wind sensor. PH, SC, FL, CMB, ST, and ZZ performed the XRF and IC analysis of the collected samples. DK performed the back-trajectory calculations, analysis of wind data and PMF. DK and PF performed the analysis of the chemical analysis and integration of the dataset. DK and PF wrote the paper with contributions from SJP.

Competing interests. PF is guest editor for the ACP Special Issue “New observations and related modelling studies of the aerosol–cloud–climate system in the Southeast Atlantic and southern Africa regions”. The remaining authors declare that they have no conflicts of interests.

Special issue statement. This article is part of the special issue “New observations and related modelling studies of the aerosol–cloud–climate system in the Southeast Atlantic and southern Africa regions (ACP/AMT inter-journal SI)”. It is not associated with a conference.

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The research article presented in this chapter characterised the elemental and water-soluble ionic aerosol composition of the PM₁₀ aerosols at HBAO, apportioned these species to aerosol sources using receptor models and investigated the geostatistical correlations to local and long-range air mass transport.

Chapter 6

Summary and conclusions

Air mass transport in the atmosphere is modulated by complex interactions at various spatial and temporal scales. On the Namibian coast, macroscale circulation is mainly influenced by the high-pressure belt in the south and transient easterly waves in the north. Meso and microscale circulations in the region are influenced by complex topography and warm semi-arid landscapes of Namibia and cold sea surfaces offshore. Macroscale high-pressure systems produce subsidence in the atmosphere below 500 hPa and near the surface stability is common over cold surfaces over the ocean or at night. The subsequent stratification of the atmosphere has implications for vertical mixing of air and the direction and distance of aerosol transport towards the Namibian coast. Despite ongoing research into atmospheric aerosols our understanding of their role in climate remains fraught with uncertainties due to the high variability in physical and chemical properties and distribution thereof in the atmosphere. Interactions between aerosols, radiation and clouds make the Namibian coast a region of particular interest due to the presence of the Sc deck and its role in modulating regional and global climate.

This study aimed to describe the transport of atmospheric constituents to a site on the Namibian coast by studying the thermodynamic structure of the atmosphere, the transport pathways to the site and the chemical character of constituents in the atmosphere. This was achieved by the following research objectives:

- (1.) Analyse the vertical structure of the atmosphere over the Namibian coast and evaluate the implications for air mass transport,
- (2.) evaluate the seasonality in black carbon at Henties Bay Aerosol Observatory (HBAO) and create a conceptual model of predominant circulation patterns and atmospheric transport pathways over the Namibian coast, and
- (3.) characterise the chemical composition of the aerosols at a long-term surface observatory and determine a transport climatology to assist in understanding the aerosol composition.

The long-term study of the statistical variability in temperature inversions and boundary layer height over Namibia and the southeast Atlantic Ocean was done using radiosonde (2015) and global positioning system radio occultation (2007 to 2017) data. The seasonality, and importance, of the mass concentrations of equivalent black carbon (eBC) were analysed. Measurements were made between July 2012 and December 2015 in the marine boundary layer below the stratocumulus deck. Air mass back-trajectories were used to identify the dominant transport patterns and quantify their contributions to eBC concentrations. A comparison to the MERRA-2 model reanalysis was also performed. Finally, long-term measurements were made of aerosol elemental and water-soluble ionic composition from the analysis of PM₁₀ filter samples collected during 26 non-consecutive sampling weeks in 2016 and 2017. These were analysed for temporal variability and sources were apportioned by Positive Matrix

Factorisation. This chapter presents a summary of the findings for these studies along with a review of the relevant successes and shortcomings at the end.

6.1. Vertical atmospheric structures

1. Comparisons of temperature profiles measured by global positioning system (GPS) and radiosonde data showed an average underestimation of $1.86 \pm 0.95^{\circ}\text{C}$ and overestimation of $2.68 \pm 2.10^{\circ}\text{C}$ (overall average of $0.23 \pm 2.80^{\circ}\text{C}$).
2. The point of minimum gradient (MG) of refractivity in GPS measurements were not consistent with boundary layer height (BLH) calculated by bulk Richardson number(Rn) from radiosonde data.
3. The top of a surface-based inversion at Walvis Bay remained stable around 562 ± 90 m.
4. BLHs calculated by the bulk Rn method from radiosonde data was more useful at identifying real and physical processes than the point of MG of refractivity. The wintertime maximum in BLHs estimated by Rn at Walvis Bay (1023 ± 487 m) was attributed to surface heating effects. In the winter, cloud cover was at a minimum, and easterly wind components in near-surface flows, measured by radiosondes, resulted in increased inflow of warm continental air masses into the BL.
5. Under conditions of high cloud fractions in the Sc deck, BLHs varied least.
6. Low-level inversions (below 2.5 km) were influenced by macroscale circulation and enhanced stability at these low levels corresponded to regions where anticyclones exert the greatest influence. These areas of enhanced stability were associated with increased frequency in inversion formation and higher inversion strengths and depths.
7. Transient easterly waves disturbed the winter mean circulation and reached their zonal maximum over the subcontinent in the summer. This was evident in an overall lower frequency of inversion formation and lower strengths over the subcontinent and a steep gradient between inversion strength over land and the ocean.
8. Strong night-time low-level inversions along the coast corresponded to the formation of both the weak and strong counterparts of the Benguela jet stream.
9. The base heights of elevated temperature inversions (2.5 –10 km) increased towards the ocean (our study area extended only as far as the prime meridian).
10. The variable character of elevated inversions towards higher latitudes was mainly influenced by the migration of the high-pressure belt.
11. Towards lower latitudes and over the subcontinent, the seasonal variability in the character of elevated inversions between 2.5–7 km was linked to the maximum biomass burning (BB) season over southern Africa. In addition, the gradient of increasing depths and strengths were in agreement with an optically thicker BB pollution plume further north.

12. Elevated inversions between 2.5–10 km also varied on diurnal scales, although the variability was greatest nearer to the surface. Deeper elevated inversions were measured during the day over the subcontinent.
13. On average, one in five to one in ten inversions (0.5 to 10 km) co-occurred with another in the same atmospheric profile.
14. Maximum instances of co-occurring inversions were recorded across the region of interest in September and October coinciding with the previously reported seasonal maximums in radiation-absorbing aerosols from BB in the elevated layers over southern Africa.

6.2. Transport pathways

15. The transport of marine air masses from the southeast Atlantic coincided with ubiquitous southerly and westerly surface winds and was seen throughout the year.
16. Slow-moving ($<4 \text{ m s}^{-1}$) easterly surface winds at HBAO were only seen in the warmer months (January to March and September to December of 2015 and 2016) and during the night-time sampling periods (21h00 to 09h00 UTC). This finding only refers to local surface winds at HBAO and does not exclude easterly winds from contributing to transport in the MBLH at other times of the year.
17. In the summer, the main mechanism of transport from the south and south-east over the South Atlantic Ocean was the position of the southeast Atlantic anticyclone centre.
18. In the winter this transport pathway was sustained by the fast-moving westerly wave and the redevelopment of anti-cyclonic circulations along the high-pressure belt, forming in the wake of the peak in the amplitude of the westerly wave. These air masses deflect at the escarpment and flow southerly along the coast towards HBAO.
19. Transport was further influenced by the position and length of the easterly wave's trough line and specifically the alignment of the west coast trough enabling transport along the coast. Troughs extending as far as the south coast contributes to the transport of marine air masses from the Southern Ocean. Easterly transport from central and western southern Africa was also significantly affected by the position of the easterly wave resulting in offshore transport to the north of HBAO in the Angolan plume.
20. Shallow, localised low-pressure systems redirected transport from the Angolan plume and facilitated local recirculation around the Namibian coast. The coastal low-pressure cells were mainly seen in the winter and the continental heat cell, mainly centred at about the latitude of Henties Bay, was only seen in the second half of each year. These low-pressure systems are integral to the mesoscale circulation and transport to HBAO by enhancing (in June) or preventing (after September) the mixing of continental air masses into the local boundary layer.

6.3. Equivalent black carbon

21. Higher equivalent black carbon (eBC) concentrations were measured in the MBLH at HBAO between April and July and were linked to the easterly transport of continental air masses.
22. Continental sources of black carbon are primarily from biomass burning over central and southern Africa.
23. Isolated episodes of increased eBC transported over long-distances from the south and south-west may be attributed to commercial ship traffic along the Cape of Good Hope sea route, but could not be confirmed.
24. Our daily concentrations were seldom higher than 200 ng m^{-3} (maximum of 800 ng m^{-3}) but remained lower than those measured at Ascension Island, which is impacted by a major outflow pathway for BB plumes from the subcontinent.
25. The comparison of results with MERRA-2 satellite imagery also shows some discrepancies in the timing and concentrations of absorbing aerosols over the region. This could be due to the shift in mesoscale circulations, that limit the inflow of eBC in BB plumes into the MBL after September. The difference may also be due to uncertainties in the correction factor that was applied to convert the attenuation into eBC concentrations. The assumption for the correction factors was that biomass burning was the only contributing source and did not consider the potential changes in the aerosol properties due to ageing of these aerosols either.

6.4. Chemical character and aerosol sources

26. The continued inflow of marine air masses from the ocean was responsible for the regional background composition containing sea salt elements and ions: Cl^- , Na^+ , Mg^{2+} , ss-K^+ , ss-Ca^{2+} , F^- and ss-SO_4^{2-} , that contributed $\sim 70\%$ of the aerosol mass concentrations, estimated by comparing mass ratios to unique tracers for known sources, and positive matrix factorisation (PMF).
27. Sea salts contributed to an average of 57% of the total sulphate mass.
28. Nss-Sulphates were apportioned to several possible sources in the region. The first was biogenic sources such as marine phytoplankton in the Benguela upwelling current, whose life cycle includes the oxidation of sulphur-containing gaseous emissions (DMS , SO_2 , H_2S).
29. Marine biogenic aerosols characterised by methanesulfonic acid (MSA), As, oxalate and propionate, contributed to $2.9 \pm 0.3\%$ of the aerosol mass, as estimated by PMF.
30. Other potential sources of nss-sulphates may be combustion sources, such as biomass burning over southern Africa or exhaust emissions from commercial ships along the Cape of Good Hope sea route.

31. There was evidence for ammonium neutralisation and ammonium bisulfate ((NH₄)HSO₄) was found to be the predominant sulphate forms at HBAO, where, incidentally, we observed dramatic rusting and corrosion of materials through the years
32. Heavy metals contributed $1.6 \pm 0.1\%$ of the aerosol mass. Concentrations were in the order of that measured in the ambient air at Mediterranean harbours.
33. Mineral dust elements, characterised by Al, nss-Ca²⁺, nss-K⁺, Fe, Si, Ti, P and V, were seen in episodic peaks above the moving background that lasted between one and four days.
34. Mineral dust contributed ~10% of the aerosol mass concentration measured at the HBAO and was attributed to windblown mineral dust from untarred roads and mining.
35. Continental air masses transported over arid regions, with known mineral deposits and active mining, were linked to extremely high (25 µg m⁻³) concentrations of a fluoride source, which could pose a serious health problem to the affected populations.
36. No seasonal trends nor source dependence in mineral dust composition could be identified based on transport regimes or surface winds measured at HBAO. Mean concentrations of these elements were; however, higher during sampling at night when easterly winds at the surface were most common.

These findings validate previous hypotheses and make significant contributions to our understanding about the role of vertical structure, atmospheric circulation and aerosol transport over southern Africa and Namibia in particular. Besides the known influence of macroscale circulation on subsidence formation, we now also have some evidence that plumes of biomass burning aerosols affect atmospheric stability in the mid to lower troposphere. Additional investigation with the use of vertical atmospheric profiles of aerosol distribution could further these findings. Furthermore, cloud fractions along the coast have proven to be a major determinant of MBLHs estimated by Rn method at Walvis Bay. This study would benefit from additional long-term analyses with daily radiosonde profiles taken at the same time of day. The chemical characterisation and quantification of the relative contribution of natural and anthropogenic aerosol sources illustrated how, despite the remoteness of the HBAO, the local atmosphere cannot be considered pristine due to the influx of long-range transported air masses to the site. The analyses of corresponding transport pathways were limited by the resolution of the data and ability of models to precisely simulate atmospheric circulation. From the analyses of stratified layers, clean air slots formed most frequently over Namibia in September and, considering that they are known to inhibit vertical mixing, it is not surprising that eBC measurements at coastal Namibia were low in comparison to that measured by satellite imagery and previously reported near Ascension Island. The combined interdisciplinary methods used in this study, have proven useful in investigating the influence of vertical structures in the atmosphere and local- and long-range transport of air masses on the aerosol character and load at HBAO.

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Chapter 7

Appendices

Appendix A: Additional published works

The Aerosols, Radiation and Clouds in southern Africa (AEROCLO-sA) field campaign in Namibia: overview, illustrative observations and way forward

Paola Formenti^{1,*}, Barbara D'Anna^{2,3}, Cyrille Flamant⁴, Marc Mallet⁵, Stuart John Piketh⁶, Kerstin Schepanski⁷, Fabien Waquet⁸, Frédérique Auriol⁸, Gerard Brogniez⁸, Frédéric Burnet⁵, Jean-Pierre Chaboureau⁹, Aurélien Chauvigné⁸, Patrick Chazette¹⁰, Cyrielle Denjean⁵, Karine Desboeufs¹, Jean-François Doussin¹, Nellie Enguidi⁹, Stefanie Feuerstein⁷, Marco Gaetani^{1,4}, Chiara Giorio¹¹, Danitza Klopper⁶, Marc Daniel Mallet^{1,2}, Pierre Nabat⁵, Anne Monod³, Fabien Solmon⁹, Andreas Namwoonde¹², Chibo Chikwililwa¹², Roland Mushi¹³, Ellsworth Judd Welton¹⁴, and Brent Holben¹⁴

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Abstract. Continuous measurements between July 2012 and December 2015 at the Henties Bay Aerosol Observatory (HBAO; 22°S, 14°05'E), Namibia, show that, during the austral wintertime, transport of light-absorbing black carbon aerosols occurs at low level into the marine boundary layer. The average of daily concentrations of equivalent black carbon (eBC) over the whole sampling period is 53 ($\pm$ 55) ng m⁻³. Peak values above 200 ng m⁻³ and up to 800 ng m⁻³ occur seasonally from May to

August, ahead of the dry season peak of biomass burning in southern Africa (August to October). Analysis of 3-day air mass back-trajectories show that air masses from the South Atlantic Ocean south of Henties Bay are generally cleaner than air having originated over the ocean north of Henties Bay, influenced by the outflow of the major biomass burning plume, and from the continent, where wildfires occur. Additional episodic peak concentrations, even for oceanic transport, indicate that pollution from distant sources in South Africa and maritime traffic along the Atlantic ship tracks could be important. While we expect the direct radiative effect to be negligible, the indirect effect on the microphysical properties of the stratocumulus clouds and the deposition to the ocean could be significant and deserve further investigation, specifically ahead of the dry season.

Appendix B: Consent from co-authors for published articles

B-1. Three years of light-absorbing measurements

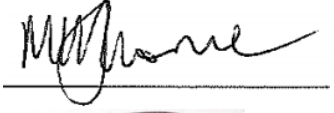
By signing below co-authors agree to the listed publication being included as part of the body of work for Danitza Klopper's thesis.

Publication details

Full title	Three years of measurements of light-absorbing aerosols over coastal Namibia: seasonality, origin, and transport
Authors	Paola Formenti, Stuart John Piketh, Andreas Namwoonde, Danitza Klopper, Roelof Burger, Mathieu Cazaunau, Anaïs Feron, Cécile Gaimoz, Stephen Broccardo, Nicola Walton, Karine Desboeufs, Guillaume Siour, Mattheus Hanghome, Samuel Mafwila, Edosa Omoregie, Wolfgang Junkermann, and Willy Maenhaut
Journal name	Atmospheric Chemistry and Physics
Volume/page numbers	Issue 18, pp. 17003 – 17016
Status	☐ In progress ☐ Accepted & in-press ☒ Published
Date published	30 November 2018

Co-author's declaration

I authorise the inclusion of this publication in the student's thesis and certify that the author contribution as included in the published article is accurate and correctly reflects the extent of the student's contribution to this work.

Co-author's name	Co-author's signature	Date (dd/mm/yyyy)
Stuart John Piketh		05/08/2019
Guillaume Siour		06/08/2019
Willy Maenhaut		06/08/2019
Karine Desboeufs		06/08/2019
Anaïs Feron		06/08/2019
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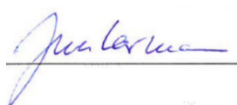
19/08/2019

Cécile Gaimoz



26/09/2019

Wolfgang Junkermann



20/11/2019

Edosa Omoregie



02/12/2019

B-2. Chemical composition and source apportionment of atmospheric aerosols on the Namibian coast

By signing below co-authors agree to the listed publication being included as part of the body of work for Danitza Klopper's thesis.

Publication details

Full title	Chemical composition and source apportionment of atmospheric aerosols on the Namibian coast
Authors	Danitza Klopper, Paola Formenti, Andreas Namwoonde, Mathieu Cazaunau, Servanne Chevaillier, Anaïs Feron, Patrick Hease, Fadi Lahmidi, Cécile Mirande-Bret, Sylvain Triquet, Zirui Zeng and Stuart J. Piketh
Journal name	Atmospheric Chemistry and Physics
Volume/page numbers	20 (24), pp. 15811-15833
Status	☐ In progress ☐ Accepted & in-press ☒ Published
Date published	18 December 2020

Co-author's declaration

I authorise the inclusion of this publication in the student's thesis and certify that the author contribution as included at the end of the article is accurate and correctly reflects the extent of the student's contribution to this work.

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11/05/2020

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Appendix C: Supplementary material for articles

C-1. Atmospheric stratification over the Namibian coast and surrounds

Table C-1.1. Marine boundary layer height (m amsl) estimated by the four different methods (described in sections 3.1 and 3.2.) from radiosonde and GPS-RO measurements made in 2015 at 9h and 10h UTC, and within two cardinal degrees from Walvis Bay airport.

Month	Bulk Richardson number	Radiosonde			GPS-RO
		Top of a surface-based inversion	Virtual potential temperature	MG of refractivity	MG of refractivity
Jan.	1090 ± 260	460 ± 190	430 ± 20	1040 ± 430	1490 ± 590
Feb.	1000 ± 190	-	430 ± 20	990 ± 270	1470 ± 530
Mar.	800 ± 170	450 ± 90	430 ± 30	720 ± 210	1430 ± 600
Apr.	810 ± 230	550 ± 210	430 ± 20	740 ± 570	1610 ± 630
May	590 ± 170	560 ± 130	430 ± 20	440 ± 250	1450 ± 680
Jun.	820 ± 520	490 ± 130	430 ± 20	670 ± 680	1360 ± 650
Jul.	950 ± 410	530 ± 150	430 ± 20	610 ± 480	1270 ± 430
Aug.	910 ± 360	510 ± 150	430 ± 20	700 ± 450	1280 ± 570
Sept.	900 ± 190	480 ± 90	440 ± 20	750 ± 190	1190 ± 460
Oct.	960 ± 200	-	430 ± 20	720 ± 270	1300 ± 520
Nov.	880 ± 230	400 ± 40	420 ± 20	870 ± 400	1350 ± 630
Dec.	900 ± 240	560 ± 250	430 ± 20	870 ± 440	810 ± 110

Table C-1.2. Mean and standard deviation of the base heights (m amsl), depths (m), strengths (°C/100 m) and strength throughout the depth (°C/depth) of low-level (0.5 – 2.5 km agl) and elevated inversions (2.5 – 10 km agl) identified in COSMIC GPS-RO data. These data are summarised by time of day where N=noon (09h00 to 13h00 UTC), A=afternoon (13h00 to 17h00), and Ni=night (17h00 to 03h00). and for the 15° to 20°S zonal band over the region of interest that is divided into ocean, coast and subcontinent. The table also shows the number of inversions measured.

		0.5 – 2.5 km			2.5 – 10 km		
		Ocean	Coast	Subcontinent	Ocean	Coast	Subcontinent
Height (km)	M.	980 ± 360	800 ± 300	1590 ± 270	5860 ± 1450	6040 ± 1370	5440 ± 1590
	N.	900 ± 320	720 ± 170	2400	6090 ± 1360	5880 ± 1460	5480 ± 1640
	A.	920 ± 330	740 ± 190	2340 ± 250	5730 ± 1290	5930 ± 1320	5400 ± 1560
	Ni.	960 ± 350	820 ± 310	1630 ± 270	6090 ± 1370	6120 ± 1240	6150 ± 1480
Depth (km)	M.	400 ± 200	400 ± 300	200 ± 100	200 ± 200	200 ± 200	200 ± 200
	N.	400 ± 200	400 ± 200	500	200 ± 300	200 ± 300	200 ± 200
	A.	400 ± 200	400 ± 200	400 ± 200	200 ± 200	200 ± 200	200 ± 200
	Ni.	400 ± 200	400 ± 200	200 ± 100	200 ± 200	200 ± 200	200 ± 200
Strength (°C/100m)	M.	0.58 ± 0.37	0.45 ± 0.28	0.38 ± 0.29	0.37 ± 0.24	0.41 ± 0.27	0.37 ± 0.25
	N.	0.62 ± 0.37	0.48 ± 0.31	0.44	0.38 ± 0.26	0.35 ± 0.27	0.33 ± 0.22
	A.	0.61 ± 0.39	0.48 ± 0.29	0.41 ± 0.17	0.35 ± 0.23	0.33 ± 0.28	0.30 ± 0.23
	Ni.	0.60 ± 0.39	0.44 ± 0.28	0.34 ± 0.19	0.35 ± 0.24	0.39 ± 0.38	0.41 ± 0.28
Strength (°C/depth)	M.	2.21 ± 2.22	1.64 ± 1.70	0.49 ± 0.56	0.69 ± 1.64	0.80 ± 1.88	0.77 ± 1.64
	N.	2.30 ± 2.06	1.75 ± 1.76	2.37	0.98 ± 2.86	0.98 ± 2.96	0.85 ± 2.63
	A.	2.30 ± 2.12	1.86 ± 1.63	1.53 ± 1.31	0.82 ± 2.08	1.04 ± 3.82	0.67 ± 1.55
	Ni.	2.25 ± 2.38	1.51 ± 1.46	0.41 ± 0.40	0.63 ± 1.59	0.90 ± 3.67	0.76 ± 1.31
Number of inversions	M.	973	160	63	276	124	273
	N.	635	92	1	151	78	153
	A.	638	99	5	130	79	126
	Ni.	1365	210	28	329	191	378

Table C-1.3. Same as for Table C-1.2., but for inversions in the 20° to 25°S zonal band.

		0.5 – 2.5 km			2.5 – 10 km		
		Ocean	Coast	Subcontinent	Ocean	Coast	Subcontinent
Height (km)	M.	1060 ± 410	920 ± 370	1740 ± 280	6160 ± 1700	6080 ± 1260	6030 ± 1390
	N.	1030 ± 400	790 ± 320	2420 ± 110	6080 ± 1750	6290 ± 1380	6100 ± 1350
	A.	990 ± 380	800 ± 300	2380 ± 100	5900 ± 1680	6070 ± 1550	5790 ± 1470
	Ni.	1040 ± 390	840 ± 320	1770 ± 320	6350 ± 1670	6170 ± 1400	5990 ± 1440
Depth (km)	M.	400 ± 200	400 ± 200	200 ± 200	200 ± 200	200 ± 200	200 ± 100
	N.	400 ± 200	400 ± 300	400 ± 400	200 ± 100	200 ± 300	200 ± 200
	A.	400 ± 200	400 ± 300	400 ± 300	200 ± 300	200 ± 200	300 ± 300
	Ni.	400 ± 200	400 ± 200	200 ± 200	200 ± 200	200 ± 200	200 ± 200
Strength (°C/100m)	M.	0.49 ± 0.34	0.36 ± 0.24	0.32 ± 0.20	0.35 ± 0.25	0.43 ± 0.30	0.43 ± 0.29
	N.	0.49 ± 0.33	0.36 ± 0.21	0.29 ± 0.13	0.34 ± 0.23	0.42 ± 0.33	0.38 ± 0.26
	A.	0.50 ± 0.35	0.34 ± 0.21	0.24 ± 0.07	0.36 ± 0.26	0.41 ± 0.26	0.40 ± 0.30
	Ni.	0.48 ± 0.33	0.37 ± 0.22	0.31 ± 0.19	0.36 ± 0.24	0.39 ± 0.26	0.44 ± 0.31
Strength (°C/depth)	M.	1.91 ± 2.27	1.30 ± 1.33	0.78 ± 1.18	0.65 ± 1.87	0.84 ± 1.91	0.68 ± 1.08
	N.	1.96 ± 2.11	1.55 ± 1.61	1.10 ± 1.32	0.50 ± 0.64	1.25 ± 3.71	0.72 ± 1.45
	A.	2.03 ± 2.31	1.31 ± 1.29	0.75 ± 0.90	1.02 ± 2.95	0.78 ± 0.98	1.30 ± 3.39
	Ni.	1.96 ± 2.20	1.45 ± 1.38	0.63 ± 0.61	0.61 ± 0.84	0.75 ± 2.62	1.00 ± 2.45
Number of inversions	M.	1472	247	63	323	189	241
	N.	993	102	5	182	103	114
	A.	903	104	6	175	77	124
	Ni.	1972	261	43	411	228	299

Table C-1.4. Same as for Table C-1.2., but for inversions in the 25° to 30°S zonal band.

		0.5 – 2.5 km			2.5 – 10 km		
		Ocean	Coast	Subcontinent	Ocean	Coast	Subcontinent
Height (km)	M.	1180 ± 470	1130 ± 490	1550 ± 350	5810 ± 1960	6120 ± 1690	5870 ± 1570
	N.	1150 ± 480	1040 ± 460	1950 ± 180	5980 ± 1830	6200 ± 1800	5830 ± 1350
	A.	1130 ± 460	1120 ± 600	2020 ± 320	6300 ± 1900	6250 ± 1780	6520 ± 1310
	Ni.	1160 ± 470	1040 ± 490	1750 ± 410	6150 ± 1880	6360 ± 1820	6210 ± 1350
Depth (km)	M.	400 ± 200	300 ± 200	300 ± 200	200 ± 200	200 ± 200	200 ± 100
	N.	400 ± 200	300 ± 200	200 ± 100	200 ± 200	200 ± 300	200 ± 100
	A.	400 ± 200	300 ± 200	200 ± 100	200 ± 200	200 ± 300	200 ± 200
	Ni.	400 ± 200	300 ± 200	300 ± 200	200 ± 100	200 ± 200	200 ± 100
Strength (°C/100m)	M.	0.44 ± 0.33	0.31 ± 0.21	0.32 ± 0.20	0.39 ± 0.35	0.47 ± 0.34	0.46 ± 0.29
	N.	0.45 ± 0.32	0.28 ± 0.23	0.29 ± 0.16	0.40 ± 0.29	0.42 ± 0.29	0.47 ± 0.27
	A.	0.46 ± 0.35	0.27 ± 0.17	0.18 ± 0.10	0.36 ± 0.26	0.40 ± 0.28	0.39 ± 0.27
	Ni.	0.44 ± 0.33	0.31 ± 0.20	0.25 ± 0.16	0.38 ± 0.35	0.39 ± 0.25	0.44 ± 0.30
Strength (°C/depth)	M.	1.79 ± 2.43	0.95 ± 0.94	0.81 ± 0.83	0.80 ± 1.87	1.07 ± 2.23	0.78 ± 1.01
	N.	1.92 ± 2.50	0.76 ± 0.89	0.52 ± 0.39	0.87 ± 2.17	1.18 ± 2.83	0.71 ± 0.90
	A.	2.01 ± 3.08	0.84 ± 0.85	0.31 ± 0.25	0.93 ± 2.07	1.02 ± 3.43	0.65 ± 1.10
	Ni.	1.83 ± 2.57	1.03 ± 1.00	0.77 ± 1.09	0.63 ± 1.10	0.69 ± 0.84	0.79 ± 1.15
Number of inversions	M.	1173	182	55	282	120	100
	N.	747	78	6	187	55	44
	A.	792	98	5	200	82	43
	Ni.	1653	247	56	387	176	124

C-2. Three years of measurements of light-absorbing aerosols over coastal Namibia: seasonality, origin, and transport

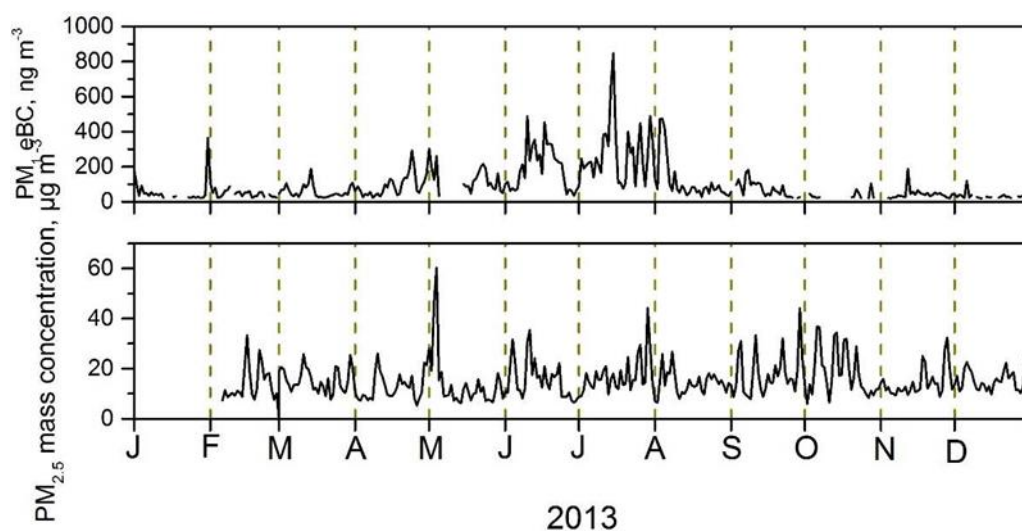


Figure C-2.1. Time series of the fine (black line) and coarse mode (grey line) aerosol optical depths obtained at HBAO between February and June 2011 (upper panel) and July to December 2015 (lower panel).

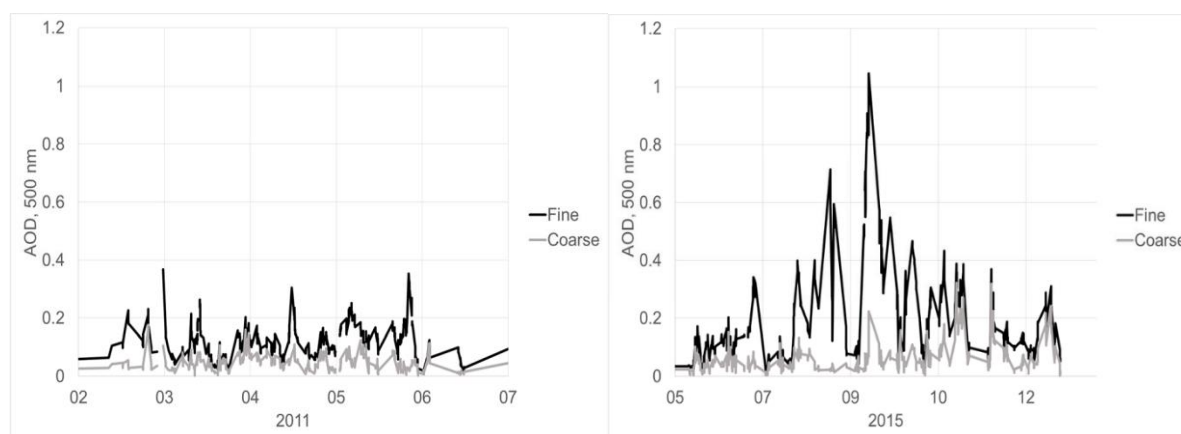


Figure C-2.2. Time series of the fine (black line) and coarse mode (grey line) aerosol optical depths obtained at HBAO between February and July 2011 (left) and July to December 2015 (right).

C-3. Chemical composition and source apportionment of atmospheric aerosols on the Namibian coast

Table C-3.1. Correction factor used to scale up the elemental concentrations measured by XRF to account for the X-ray self-attenuation effects in the individual particle grains. A mean diameter of 4.5 μm is chosen to represent the average coarse particle size.

	Na	Mg	Al	Si	P	S	Cl	K	Ca
Correction factor	0.53	0.67	0.77	0.76	0.88	0.9	0.9	0.91	1

Table C-3.2. List of mineral dust episodes identified by peaks in Al and nssCa^{2+} above background concentrations. The start and end dates and times of measurements are provided in UTC.

Episode identifier	Start and end date (UTC)
Dust_2016_01	28/02/2016 04h – 01/03/2016 16h
Dust_2016_02	21/03/2016 07h – 23/03/2016 16h
Dust_2016_03	05/04/2016 20h – 09/04/2016 05h
Dust_2016_04	23/07/2016 08h – 25/07/2016 17h
Dust_2016_05	27/08/2016 20h – 30/08/2016 05h
Dust_2016_06	16/09/2016 19h – 19/09/2016 16h
Dust_2016_07	07/10/2016 07h – 10/10/2016 16h
Dust_2017_01	25/02/2017 19h – 27/02/2017 04h
Dust_2017_02	25/03/2017 19h – 27/03/2017 16h
Dust_2017_03	29/03/2017 19h – 01/04/2017 16h
Dust_2017_04	19/05/2017 08h – 20/05/2017 17h
Dust_2017_05	24/05/2017 20h – 26/05/2017 05h
Dust_2017_06	11/07/2017 08h – 13/07/2017 05h
Dust_2017_07	04/08/2017 20h – 06/08/2017 05h
Dust_2017_08	03/09/2017 09h – 05/09/2017 18h
Dust_2017_09	23/09/2017 21h – 24/09/2017 18h
Dust_2017_10	05/10/2017 21h – 08/10/2017 06h
Dust_2017_11	15/11/2017 09h – 18/11/2017 06h
Dust_2017_12	30/11/2017 09h – 01/12/2017 18h
Dust_2017_13	15/12/2017 09h – 19/12/2017 06h

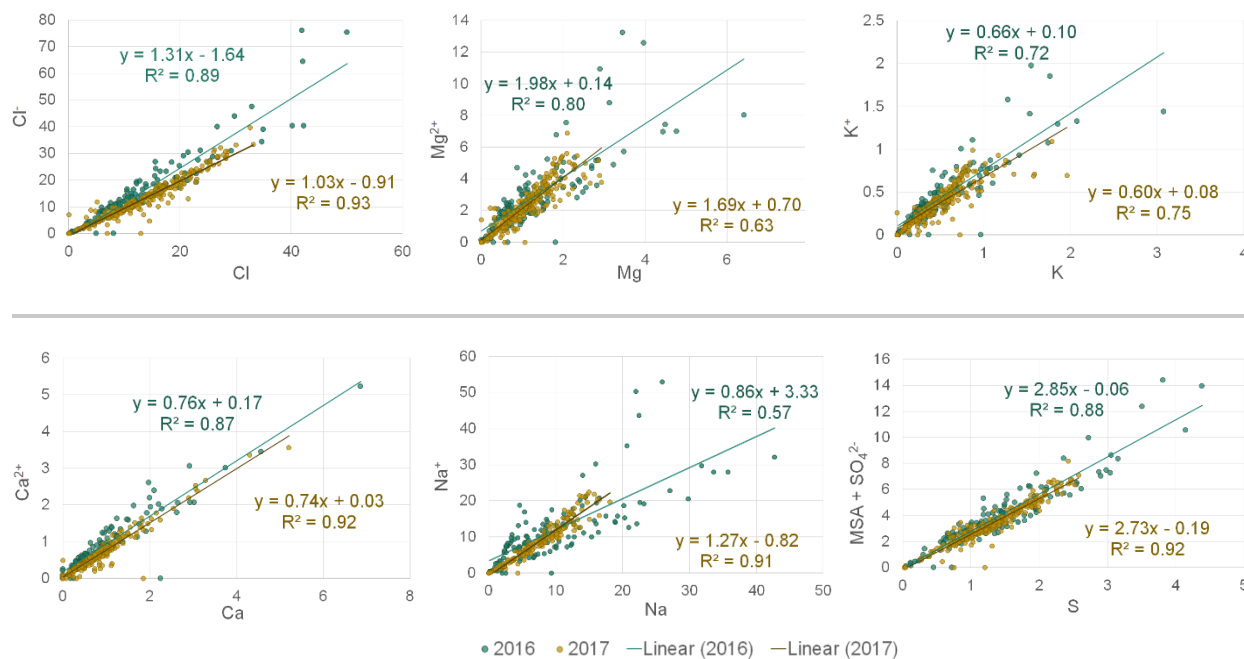


Figure C-3.1. Scatterplots of Cl, Mg, K, Ca, Na and SO₄²⁻/S concentrations (in $\mu\text{g m}^{-3}$) obtained by ion chromatography and XRF analysis showing the slope and distribution of data as well as the Pearson correlation coefficient (R^2).

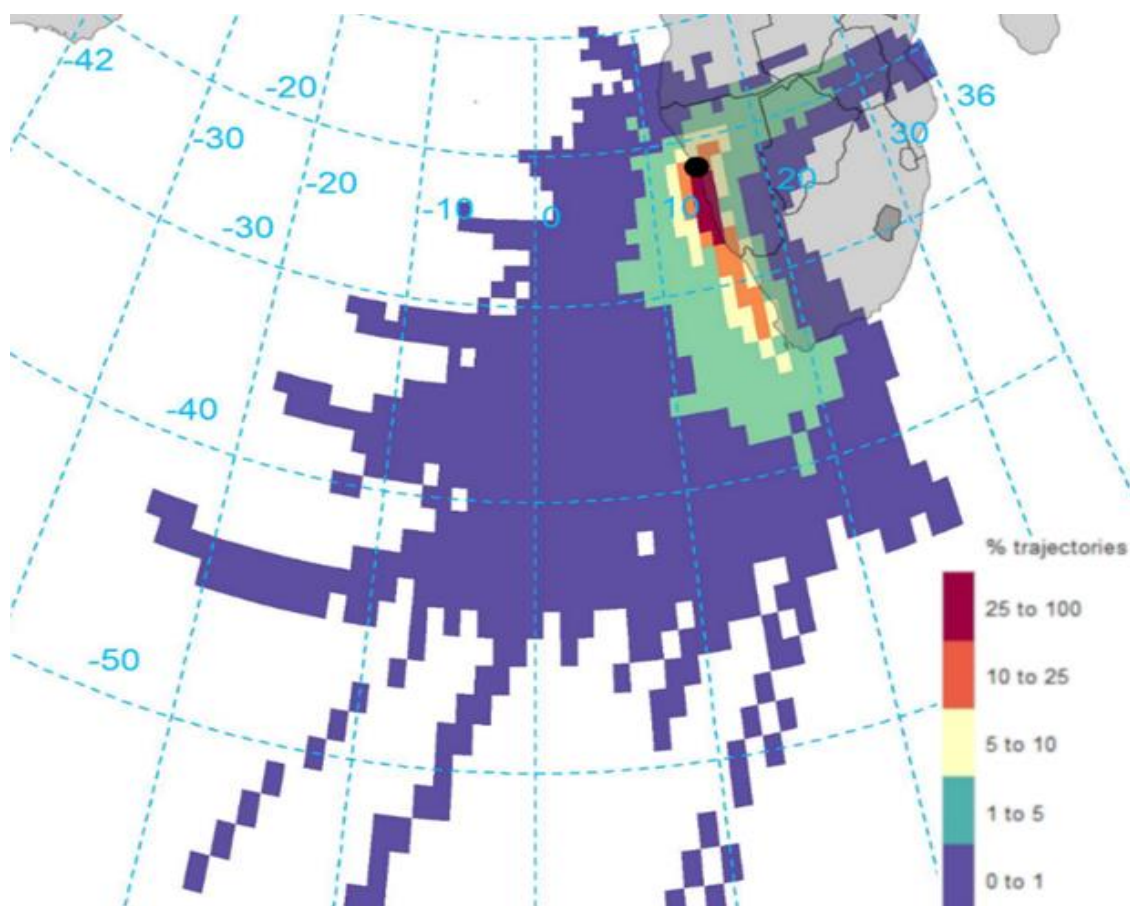


Figure C-3.2. Gridded frequency plot of the variability of the 72-h air mass back-trajectories run for sampling periods in 2016 and 2017 (except the long-range transported air masses in September 2016 and November 2017, which show air masses arriving from as far south as 74°S) run for 21 of the 26 filter sampling periods. Back-trajectories were initiated at 250 m agl. The grid colour indicates the percentage of trajectories of the total trajectories run for all sampling periods, passing the over the 1° x 1° grid.

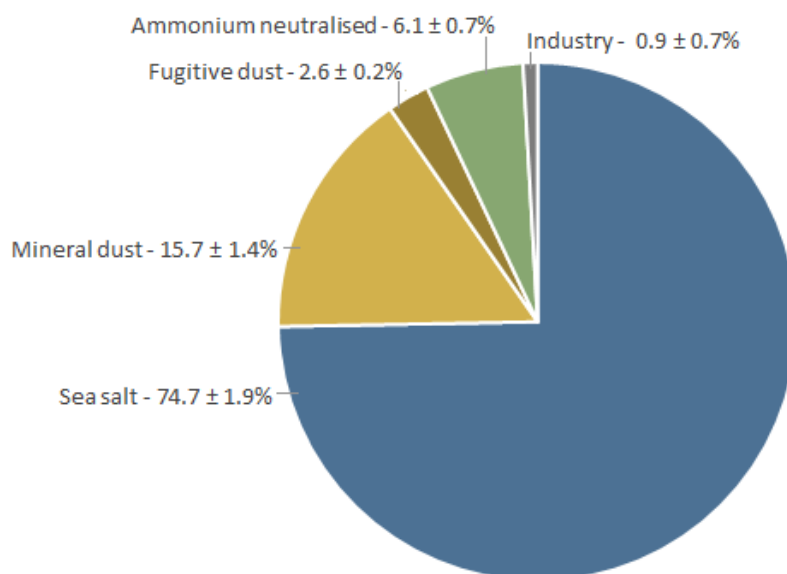


Figure C-3.3. PMF mass apportionment for the five component solution.

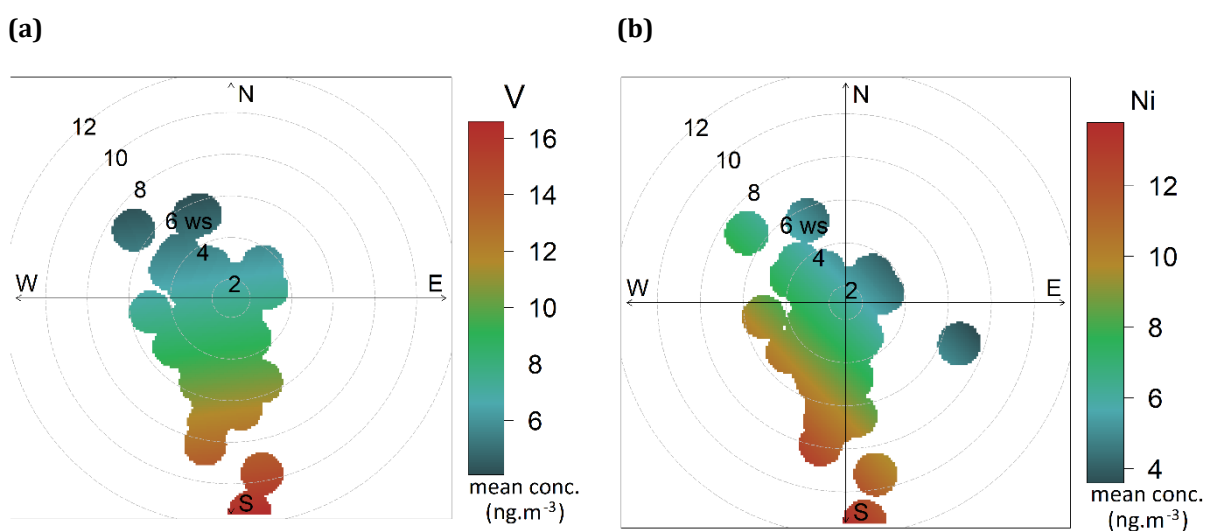


Figure C-3.4. Bivariate polar plots for (a) vanadium and (b) nickel, showing the variability in mean concentrations with changes in wind speed and -direction. Wind direction is indicated by the cardinal point in the four quadrants, mean wind speed (m s⁻¹) is indicated by the concentric circles from the centre of the plot and the mean concentrations are measured in ng m⁻³, and given by the gradient colour scale.

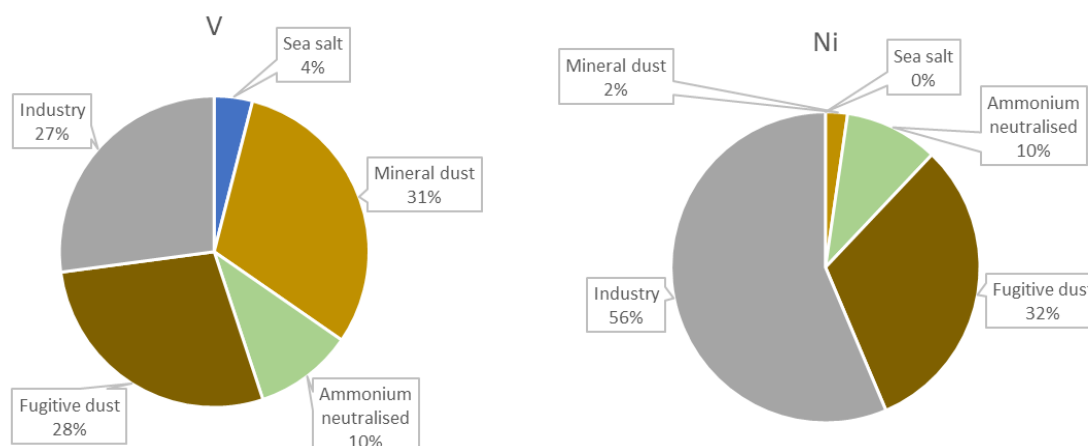


Figure C-3.5. Pie charts of the PMF mass apportionment of V and Ni measured at HBAO. Legends provide with the name of the source component and the fraction of the contributed mass elemental concentration.

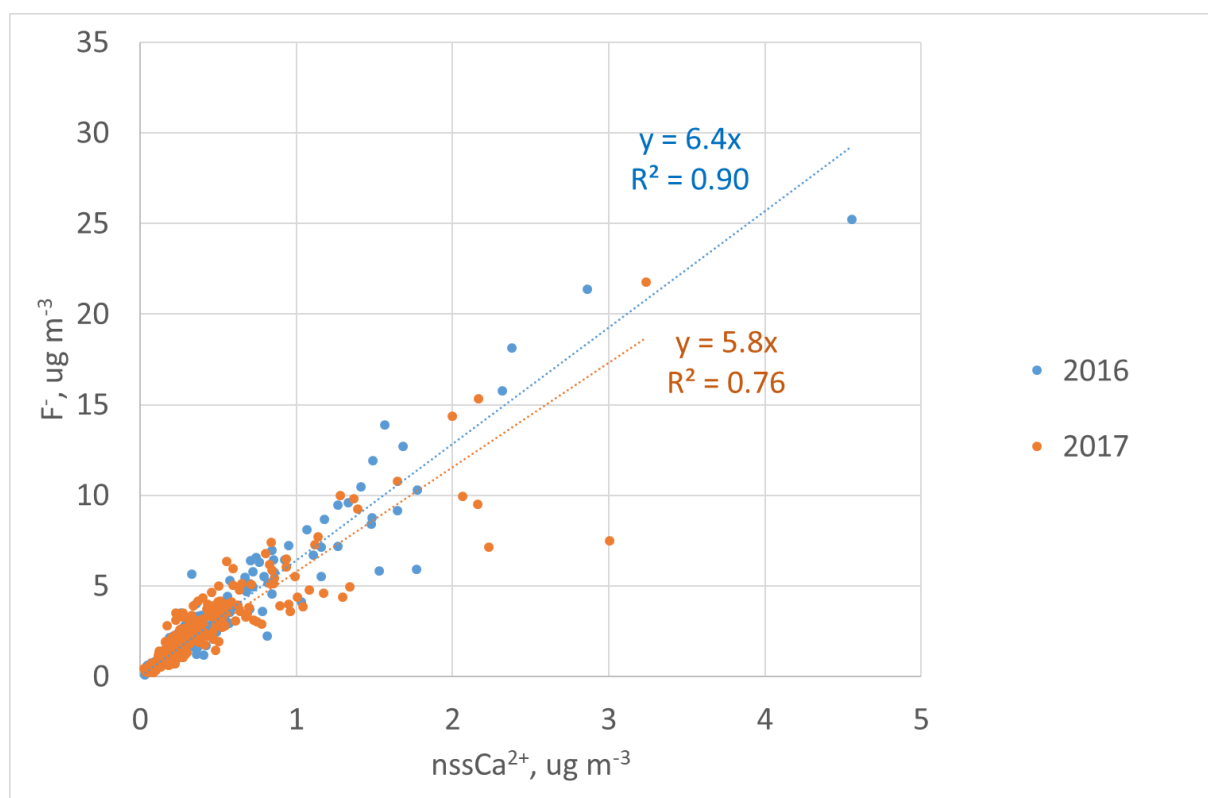


Figure C-3.6. Scatterplot of F^- with respect to nssCa^{2+} for 2016 (blue) and 2017 (orange). Concentrations are expressed in $\mu\text{g m}^{-3}$. The slope and the Pearson correlation coefficient (R^2) are indicated.

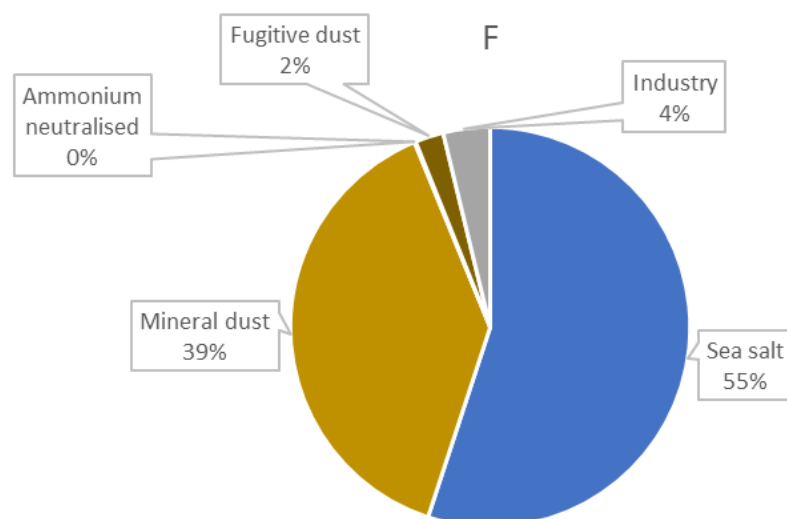
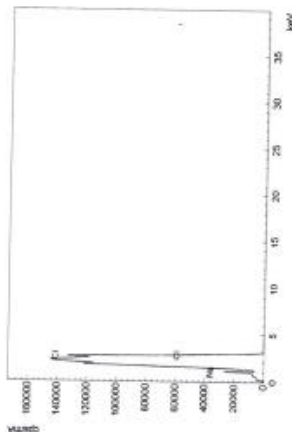


Figure C-3.7. Same as Figure C-3.5. for F⁻ concentrations.

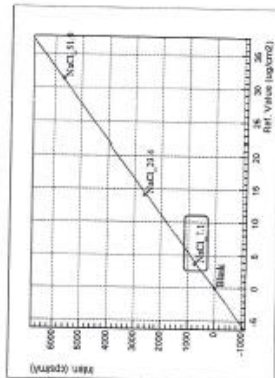
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Serial No.	Standard	Areal density ($\mu\text{g}/\text{cm}^2$)
41211	Sodium or Chlorine as NaCl	7.1 $\pm$ 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for Cl



Testing Conditions

Voltage (kV)	3	Ka (Na)	1.040
Current (mA)	2000	Ka (Cl)	2.621
Anode	Rh	Kb (Cl)	2.812
Time (s)	130		

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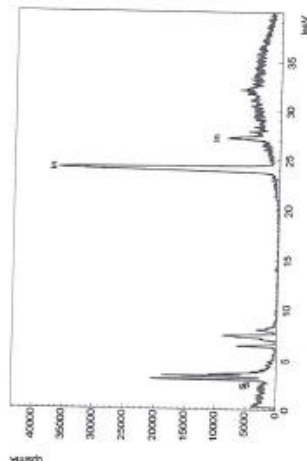
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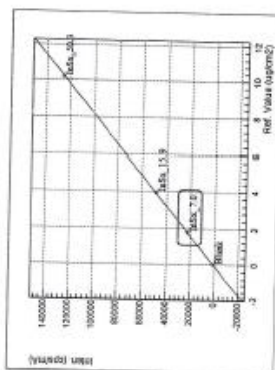
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Serial No.	Standard	Areal density ($\mu\text{g}/\text{cm}^2$)
41210	Sulfur as InSx	In = 5.2 S = 1.8 $\pm$ 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for S



Testing Conditions

Voltage (kV)	50	Ka1 (In)	24.210
Current (mA)	800	Kb (In)	27.262
Anode	Rh	Ka (S)	2.309
Time (s)	60	Kb (S)	2.465

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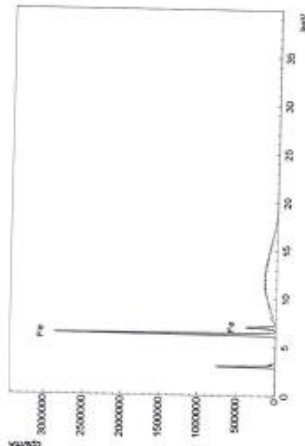
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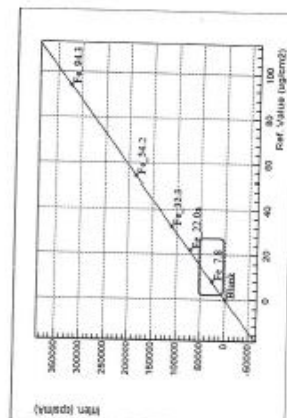
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Serial No.	Standard	Areal density (µg/cm ²)
41213	Iron as Fe metal (Will Oxidize)	7.8 ±1.5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for Fe



Testing Conditions

Voltage (kV)	20	Ka (Fe)	6.401
Current (mA)	200	Kb (Fe)	7.059
Anode	Rh		
Time (s)	30		

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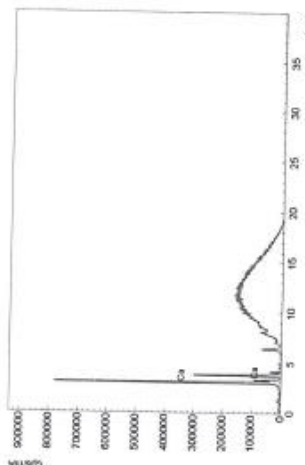
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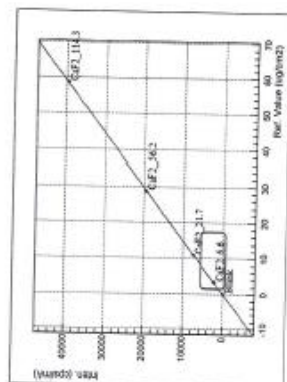
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Serial No.	Standard	Areal density (µg/cm ²)
41212	Calcium as CaF ₂	6.6 ±1.5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for Ca



Testing Conditions

Voltage (kV)	20	Ka (Ca)	3.691
Current (mA)	200	Kb (Ca)	4.013
Anode	Rh		
Time (s)	30		

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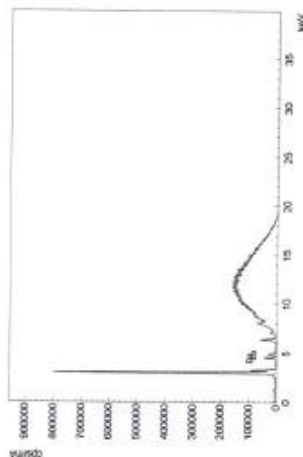
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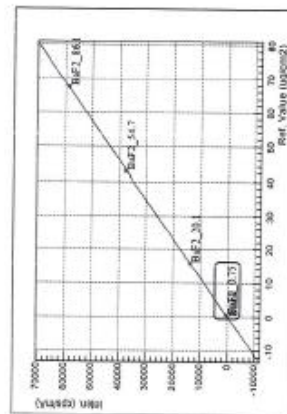
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Serial No.	Standard	Areal density ($\mu\text{g}/\text{cm}^2$)
41207	Barium as BaF2	0.75 +/- 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for Ba



Testing Conditions			
Voltage (kV)	20	La (Ba)	4.465
Current (mA)	200	Lb (Ba)	4.820
Anode	Rh		
Time (s)	30		

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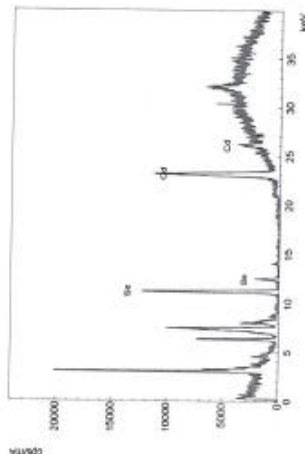
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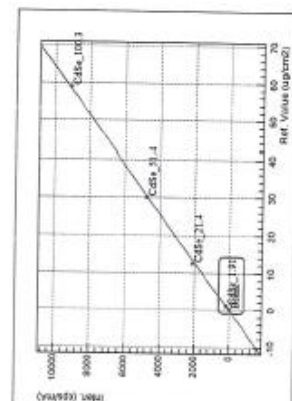
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Serial No.	Standard	Areal density ($\mu\text{g}/\text{cm}^2$)
41206	Cadmium as CdSe (May not be Stoichiometric)	1.91 +/- 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for Cd



Testing Conditions			
Voltage (kV)	50	Ka1 (Cd)	23.173
Current (mA)	800	Kb (Cd)	26.081
Anode	Rh	Ka1 (Se)	11.224
Time (s)	60	Kb (Se)	12.495

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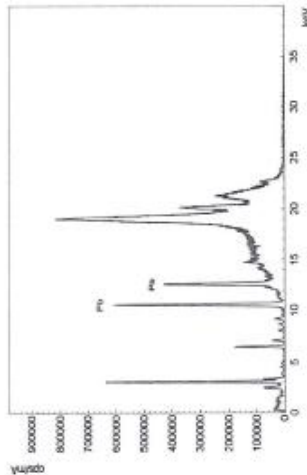
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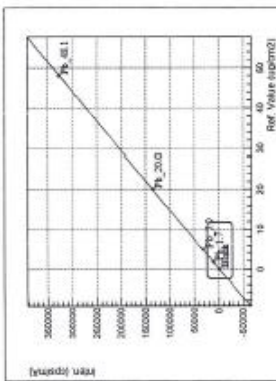
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Serial No.	Standard	Areal density (µg/cm ²)
41208	Lead as Pb metal (Will Oxidize)	1.7 +/- 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for Pb



Testing Conditions

Voltage (kV)	40	Lα1 (Pb)	10.551
Current (mA)	100	Lβ (Pb)	12.611
Anode	Rh		
Time (s)	15		

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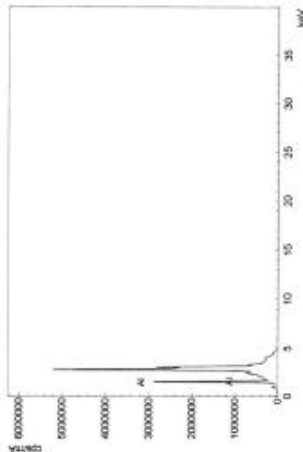
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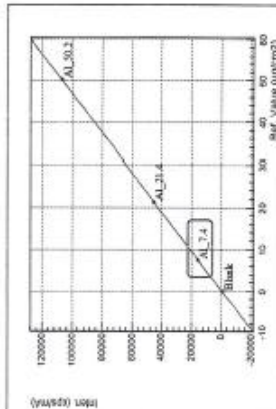
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Serial No.	Standard	Areal density (µg/cm ²)
41209	Aluminum as Al metal	7.4 +/- 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for Al



Testing Conditions

Voltage (kV)	5	Kα (Al)	1.486
Current (mA)	200	Kβ (Al)	1.557
Anode	Rh		
Time (s)	30		

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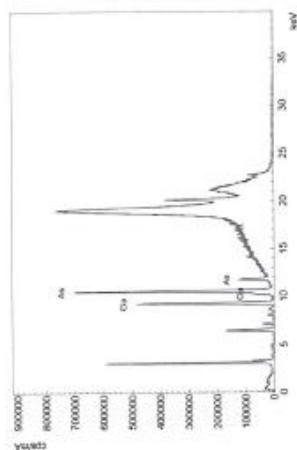
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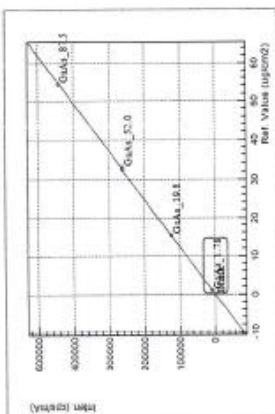


Serial No.	Standard	Areal density (µg/cm ²)
41204	Arsenic or Gallium as GaAs Ga = 0.80 As = 0.98 (May not be Stoichiometric)	1.78 +/- 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

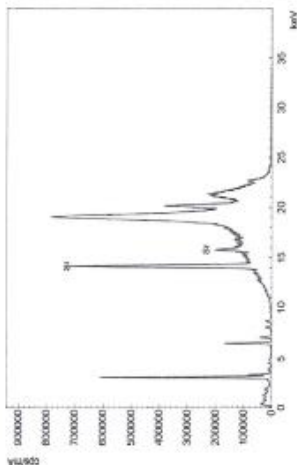
XRF Spectrum



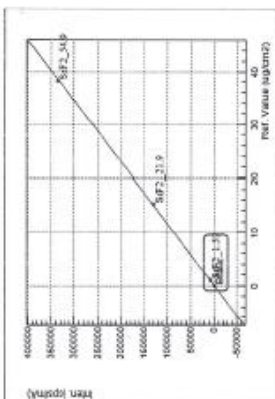
Standard Calibration Curve for As



XRF Spectrum



Standard Calibration Curve for Sr



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Serial No.	Standard	Areal density (µg/cm ²)
41205	Strontium as SrF ₂	1.53 +/- 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

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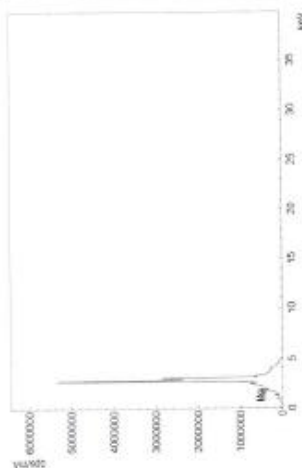
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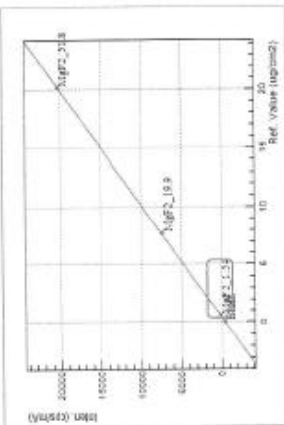
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Serial No.	Standard	Areal density ($\mu\text{g}/\text{cm}^2$)
41202	Magnesium as MgF ₂	1.54 $\pm$ 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for Mg



Testing Conditions			
Voltage (kV)	5	Ka (Mg)	1.254
Current (mA)	200	Kb (Mg)	1.302
Anode	Rh		
Time (s)	30		

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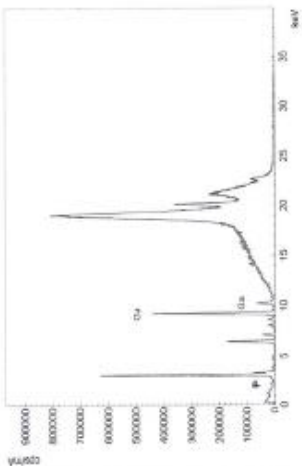
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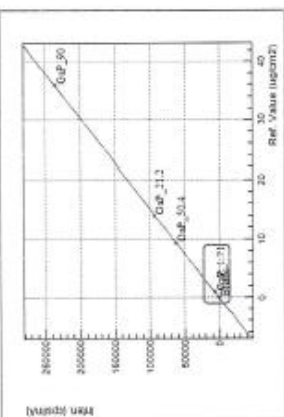
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Serial No.	Standard	Areal density ($\mu\text{g}/\text{cm}^2$)
41203	Gallium or Phosphorous as GaP Ga = 0.72 P = 0.99 (May not be Stoichiometric)	1.71 $\pm$ 5%
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for P



Testing Conditions			
Voltage (kV)	40	Ka (Ga)	9.242
Current (mA)	100	Kb (Ga)	10.266
Anode	Rh	Ka (P)	2.010
Time (s)	60	Kb (P)	2.139

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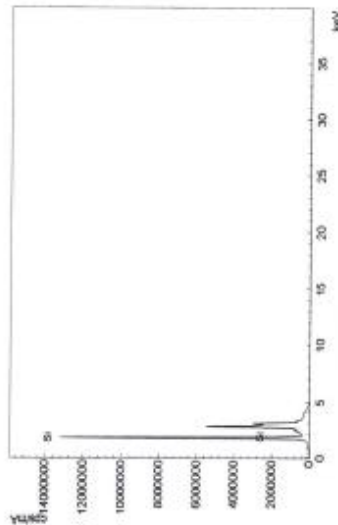
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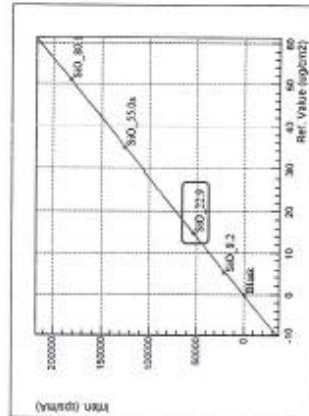
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Serial No.	Standard	Areal density ($\mu\text{g}/\text{cm}^2$)
41214	Silicon as SiO	22.9
Backing	N - Nuclepore® polycarbonate aerosol membranes	
Mount	Custom Mount	
Comments	NIST Traceable Reference Material	

XRF Spectrum



Standard Calibration Curve for Si



Testing Conditions

Voltage (kV)	5	Ka (Si)	1.740
Current (mA)	200	Kb (Si)	1.837
Anode	Rh		
Time (s)	30		

CUSTOMER: LISA Paris

P.O. # 3121L015225

P.O. DATE: Oct. 07, 2016

PREPARER'S SIGNATURE

DATE: Oct 19, 2016

MICROMATTER Technologies Inc.

Unit # 1 - 8333 130th Street

Surrey, BC, V3W 7X4, Canada

For more information

Phone 1-866-966-2286

www.micromatter.com

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Fax: +1-604-594-9726

info@micromatter.com

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SC-0902



XRF CALIBRATION STANDARD CERTIFICATION

STANDARD Magnesium as MgF₂
 SERIAL NUMBER 16868
 AREAL DENSITY COMPOUND 54.0 µg/cm² +/- 5% as MgF₂
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Aluminum as Al metal
 SERIAL NUMBER 16869
 AREAL DENSITY COMPOUND 42.4 µg/cm² +/- 5% as Al
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Silicon as SiO₂
 SERIAL NUMBER 16870
 AREAL DENSITY COMPOUND 41.8 µg/cm² +/- 5% as SiO₂
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Phosphorus or Gallium as GaP (NOT STOICHIOMETRIC)
 SERIAL NUMBER 16871
 AREAL DENSITY COMPOUND 45.9 µg/cm² +/- 5% as GaP
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Sulfur as CuS_x
 SERIAL NUMBER 16872
 AREAL DENSITY COMPOUND 54.4 µg/cm² +/- 5% as CuS_x
 AREAL DENSITY ELEMENT 1 12.9 µg/cm² - S ELEMENT 2 41.5 µg/cm² +/- 5% - Cu

STANDARD Chlorine or Sodium as NaCl
 SERIAL NUMBER 16873
 AREAL DENSITY COMPOUND 40.4 µg/cm² +/- 5% as NaCl
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Potassium or Chlorine as KCl
 SERIAL NUMBER 16874
 AREAL DENSITY COMPOUND 45.5 µg/cm² +/- 5% as KCl
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

BACKING MATERIAL Nuclepore polycarbonate aerosol membranes
 MOUNT Mounted on user supplied clipped plastic rings
 OTHER INFORMATION Deposit sides face up in clipped ring mounts

PREPARER'S SIGNATURE Joanne M. Heagney
 DATE June 19, 2006

CUSTOMER CNES-LISA, UNIV. PARIS XII
 PURCHASE ORDER NUMBER L 15487/06/FORAMT
 PURCHASE ORDER DATE May 30, 2006

MICROMATTER

TEL: (360) 652-2574
 FAX: (360) 654-0874
 Email: jheagney@micromatter.com
 ARLINGTON, WA 98223 U.S.A.

SC-0902



XRF CALIBRATION STANDARD CERTIFICATION

STANDARD Calcium as CaF₂
 SERIAL NUMBER 16875
 AREAL DENSITY COMPOUND 45.2 µg/cm² +/- 5% as CaF₂
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Titanium as Ti metal
 SERIAL NUMBER 16876
 AREAL DENSITY COMPOUND 45.9 µg/cm² +/- 5% as Ti
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Vanadium as V metal (WILL OXIDIZE)
 SERIAL NUMBER 16877
 AREAL DENSITY COMPOUND 45.7 µg/cm² +/- 5% as V
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Chromium as Cr metal
 SERIAL NUMBER 16878
 AREAL DENSITY COMPOUND 44.8 µg/cm² +/- 5% as Cr
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Manganese as Mn metal (WILL OXIDIZE)
 SERIAL NUMBER 16879
 AREAL DENSITY COMPOUND 53.8 µg/cm² +/- 5% as Mn
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Iron as Fe metal (WILL OXIDIZE)
 SERIAL NUMBER 16880
 AREAL DENSITY COMPOUND 47.7 µg/cm² +/- 5% as Fe
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Zinc as ZnTe (NOT STOICHIOMETRIC)
 SERIAL NUMBER 16881
 AREAL DENSITY COMPOUND 50.8 µg/cm² +/- 5% as ZnTe
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

BACKING MATERIAL Nuclepore polycarbonate aerosol membranes
 MOUNT Mounted on user supplied clipped plastic rings
 OTHER INFORMATION Deposit sides face up in clipped ring mounts

PREPARER'S SIGNATURE Joanne M. Heagney
 DATE June 19, 2006

CUSTOMER CNES-LISA, UNIV. PARIS XII
 PURCHASE ORDER NUMBER L 15487/06/FORAMT
 PURCHASE ORDER DATE May 30, 2006

MICROMATTER

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 ARLINGTON, WA 98223 U.S.A.

SC-0902



XRF CALIBRATION STANDARD CERTIFICATION

STANDARD Sodium or Chlorine as NaCl
 SERIAL NUMBER 19116
 AREAL DENSITY COMPOUND 17.7 µg/cm² +/- 5% as NaCl
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Magnesium as MgF₂
 SERIAL NUMBER 19117
 AREAL DENSITY COMPOUND 18.9 µg/cm² +/- 5% as MgF₂
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Aluminum as Al metal
 SERIAL NUMBER 19118
 AREAL DENSITY COMPOUND 18.7 µg/cm² +/- 5% as Al
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Silicon as SiO₂
 SERIAL NUMBER 19119
 AREAL DENSITY COMPOUND 19.5 µg/cm² +/- 5% as SiO₂
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Potassium or Chlorine as KCl
 SERIAL NUMBER 19120
 AREAL DENSITY COMPOUND 17.7 µg/cm² +/- 5% as KCl
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Calcium as CaF₂
 SERIAL NUMBER 19121
 AREAL DENSITY COMPOUND 19.1 µg/cm² +/- 5% as CaF₂
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Titanium as Ti metal
 SERIAL NUMBER 19122
 AREAL DENSITY COMPOUND 20.3 µg/cm² +/- 5% as Ti
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

BACKING MATERIAL Nuclepore polycarbonate aerosol membrane filters
 MOUNT Mounts provided by the customer
 OTHER INFORMATION Deposit slides face up in mounts. Deposit side of mounts placed face down in petri slides for easier removal from petri slides.
 PREPARER'S SIGNATURE *Servanne M. Chevallier* DATE Nov. 13, 2008

CUSTOMER LISA, UMR, CNRS (SERVANNE CHEVALLIER)
 PURCHASE ORDER NUMBER E-MAIL ORDER FROM SERVANNE CHEVALLIER
 PURCHASE ORDER DATE Nov. 7, 2008

MICROMATTER
 18218 -18th AVE. NW
 ARLINGTON, WA 98223 U.S.A.
 TEL: (360) 652-2574
 FAX: (360) 654-0874
 Email: jheagney@micromatter.com

SC-0902



XRF CALIBRATION STANDARD CERTIFICATION

STANDARD Iron as Fe metal (WILL OXIDIZE)
 SERIAL NUMBER 19123
 AREAL DENSITY COMPOUND 20.7 µg/cm² +/- 5% as Fe
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____
 SERIAL NUMBER _____
 AREAL DENSITY COMPOUND _____
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____
 SERIAL NUMBER _____
 AREAL DENSITY COMPOUND _____
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____
 SERIAL NUMBER _____
 AREAL DENSITY COMPOUND _____
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____
 SERIAL NUMBER _____
 AREAL DENSITY COMPOUND _____
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____
 SERIAL NUMBER _____
 AREAL DENSITY COMPOUND _____
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____
 SERIAL NUMBER _____
 AREAL DENSITY COMPOUND _____
 AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

BACKING MATERIAL Nuclepore polycarbonate aerosol membrane filters
 MOUNT Mounts provided by the customer
 OTHER INFORMATION Deposit slides face up in mounts. Deposit side of mounts placed face down in petri slides for easier removal from petri slides.
 PREPARER'S SIGNATURE *Servanne M. Chevallier* DATE Nov. 13, 2008

CUSTOMER LISA, UMR, CNRS (SERVANNE CHEVALLIER)
 PURCHASE ORDER NUMBER E-MAIL ORDER FROM SERVANNE CHEVALLIER
 PURCHASE ORDER DATE Nov. 7, 2008

MICROMATTER
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 TEL: (360) 652-2574
 FAX: (360) 654-0874
 Email: jheagney@micromatter.com

SC-0902



XRF CALIBRATION STANDARD CERTIFICATION

STANDARD Arsenic as GaAs (NOT STOICHIOMETRIC)SERIAL NUMBER 16882AREAL DENSITY COMPOUND 48.9 µg/cm² +/- 5% as GaAs

AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Cadmium as CdSe (NOT STOICHIOMETRIC)SERIAL NUMBER 16883AREAL DENSITY COMPOUND 49.0 µg/cm² +/- 5% as CdSe

AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD Lead as Pb metal (WILL OXIDIZE)SERIAL NUMBER 16884AREAL DENSITY COMPOUND 46.6 µg/cm² +/- 5% as Pb

AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____

SERIAL NUMBER _____

AREAL DENSITY COMPOUND _____

AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____

SERIAL NUMBER _____

AREAL DENSITY COMPOUND _____

AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____

SERIAL NUMBER _____

AREAL DENSITY COMPOUND _____

AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

STANDARD _____

SERIAL NUMBER _____

AREAL DENSITY COMPOUND _____

AREAL DENSITY ELEMENT 1 _____ ELEMENT 2 _____

BACKING MATERIAL Nuclepore polycarbonate aerosol membranesMOUNT Mounted on user supplied clipped plastic ringsOTHER INFORMATION Deposit sides face up in clipped ring mountsPREPARER'S SIGNATURE Deanne M. HeagneyDATE June 19, 2006CUSTOMER CNRS-LISA, UNIV. PARIS XIIPURCHASE ORDER NUMBER L15487/06/FORMANTPURCHASE ORDER DATE May 30, 2006**MICROMATTER**18218 -18th AVE. NW
ARLINGTON, WA 98223 U.S.A.

TEL: (360) 652-2574

FAX: (360) 654-0874

Email: jhcagney@micromatter.com

D-2.

Certified mono- and multi-ionic solutions

1. CONCEPT OF CERTIFICATION

The certified concentrations and expanded uncertainties of the analyte are based on the results obtained from gravimetric production and from the analytical results determined using high-resolution quantitative NMR, which is recognized as primary measurement method.

Gravimetric preparation using well defined and pure materials is a practical realization of concentration units, through conversion of mass to amount of substance^[1]. All high-precision balances are periodically calibrated by a third party and certified according to DAkkS guidelines (DAkkS = Deutsche Akkreditierungsstelle GmbH, which is the national accreditation body for the Federal Republic of Germany).

Production and certification of this CRM are performed under double-accreditation in accordance with ISO/IEC 17025^[2] and also ISO Guide 34^[3]. Storage stability, leaching and homogeneity tests are also considered for certification.

2. STARTING MATERIAL CONTENT BY qNMR

The absolute content of starting material is measured by high-resolution quantitative NMR measurements on a Bruker 600 MHz Avance III NMR spectrometer.

The certification of the content is performed using 7 separate samples which are each spiked with an adequate amount of internal reference and then immediately dissolved in deuterated solvent. In most cases 16 scans are recorded for every sample with a 1H relaxation time of $t_1 = 60$ seconds. Quantification of the content is directly calculated from the 1H-NMR peak areas and the initial weights of the sample and reference substance. After ANOVA the resulting standard deviation is included into the uncertainty calculation of the certified value.

Extensive stability and homogeneity tests are considered for certification.

Stability stress test is performed with samples which are stored above the recommended storing temperature (mostly at 45 °C) and q-NMR double determinations after 1 and 3 months.

Long term stability test is performed with samples which are stored at the recommended storing temperature and q-NMR double determination after 3, 9 and 24 or 36 months.

Homogeneity of the material is tested by q-NMR measurements using 7 subsamples which are taken from different positions in the entire bulk material. The recommended minimal sample size is taken for all the homogeneity test samples. Analysis of variance (ANOVA) results are included into the calculation of content uncertainty of this CRM.

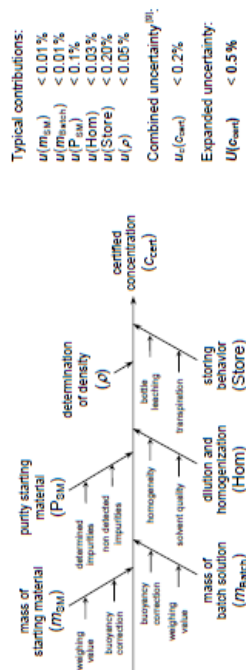
Starting material	Starting material content with expanded uncertainty	Traceable to
Sodium propionate PIN 493804 Lot BC8BM0051V	99.4 % ± 0.2 %	NIST SRM 84i potassium hydrogen phthalate

3. DENSITY MEASUREMENT

The density measurement is carried out according to ISO 15212-1^[1] and using the digital density meter DMA 4500M from Anton Paar with an oscillating U-tube installed. The measurement uncertainty is calculated according to Eurachem/CITAC Guide and reported as combined expanded uncertainty at the 95% confidence level.

4. UNCERTAINTY EVALUATION

All uncertainties are calculated according to Eurachem/CITAC Guide^[2] and reported as combined expanded uncertainties at the 95% confidence level. For gravimetric preparation the uncertainty contributions are illustrated by the following cause-effect diagram^[3].



References

- [1] ISO Guide 31:2000, "Reference materials - Contents of certificates and labels"
- [2] ISO Guide 35:2005, "Reference materials - General and statistical principles for certification"
- [3] Eurachem/CITAC Guide, 4th Ed. (2003), "Uncertainty in analytical measurement"
- [4] Eurachem/CITAC Guide, 4th Ed. (2003), "Traceability in chemical measurement"
- [5] ISO/IEC 17025, 2nd Ed. (2005), "General requirements for the competence of testing and calibration laboratories"
- [6] ISO Guide 34:2003, "General requirements for the competence of reference material producers"
- [7] DIN EN ISO 15212-1:1998, "Oscillation-type density meters - Part 1: Laboratory instruments"
- [8] Meschum, A. (Herausg.), 1998, "Oscillation-type density meters - Part 1: Laboratory instruments"
- [9] Meschum, A. (Herausg.), 1998, "Oscillation-type density meters - Part 1: Laboratory instruments"

TraceCERT®
Traceable Certified Reference Materials

SIGMA-ALDRICH®

Certificate

produced in accordance with
ISO/IEC 17025 and
ISO Guide 34

This certificate is designed in accordance with ISO Guide 31^[1].

Object of certification: **Propionate standard for IC**

Product no.: **51716**

Lot no.: **BCBP4264V**

Composition: Sodium propionate (high purity quality) in high-purity water (19.2 MΩ·cm, 0.22 µm filtered). The bottled solution is stabilized with sodium azide (about 5 mg/L) and additionally filtered through a 0.2 µm membrane.

Intended use: Calibration of ion chromatography or any other analytical technique.

Storing and handling: This reference material shall be stored between 5 °C and 30 °C whereas the certified value is guaranteed when the long-term storage temperature will not exceed 25 °C. Before every use of the material the bottle must be shaken well and its temperature has to be 20 °C. If storage of a partially used bottle is necessary, the cap should be tightly sealed and the bottle should be stored at reduced temperature (e.g. refrigerator) to minimize transpiration rate.

Expiry date: **JAN 2018**

Certificate issue date: **10 APR 2015**

Bottle opening date:

The certified values and uncertainties are according to ISO Guide 35^[2] and Eurachem/CITAC Guide^[3]

Constituent	Certified value at 20 °C and expanded uncertainty [U = k·u; k = 2]
Propionate	1'001 mg kg⁻¹ ± 5 mg kg⁻¹
Traceability ^[4]	NIST SRM 84i Potassium Hydrogen Phthalate

Measurand	Certified value and expanded uncertainty [U = k·u; k = 2]
Density at 20 °C	0.9989 g mL⁻¹ ± 0.0005 g mL⁻¹

CRM operations: *S. Mat*
S. Mat
Certification body: *Anna R. Schmid*
K.-S. Schmid, Ph.D.

ISO Guide 34 ISO/IEC 17025 ISO 9001

Certificate page 1 of 3 Sigma-Aldrich Production GmbH, Industriestraße 25, 6471, Buchs/Schweiz, Switzerland
Tel +41-61-7165-5511, Fax +41-61-7165-5449 **SIGMA-ALDRICH®**

CERTIFIED REFERENCE MATERIAL

This document OF 6.17-1/1 version 1 is designed and the certified value(s) and uncertainty(ies) are determined in accordance with ISO Guide 31/11, ISO Guide 38/1 and Eurachem / CITAC Guides/II

Lot N: 213385 Barcode: 83095207 Certification Date: 10.10.2017 Date of Stability last check:

Description of the Reference Material (CRM): Solution of Acetates (CH₃COO-) concentration 1.000 g/l in Water (H₂O)

Material Number: 84951.180 Certified Value and Uncertainty: [mg/l]: Metrological traceability:

CH₃COO- 1000.1 ± 2.7 (M) BAM CRM No 60357 Lot BCBP3137V, BAM CRM No 60357 Lot BCBP3137V

Method(s) of certification used: CRM's calibration procedure(s): Notes: (Y) WQP 5.15.1.24 The certified value was obtained by a weighted mean of the results of two independent methods among: Classical Volumetric, Primary Gravimetric, Instrumental (ICP/OES, ICP/MS or IC)

Concept of Certification and traceability statement: This certified reference material is produced using a high-purity starting material, acid from sub-boiling and 18 MΩcm deionized water. The reported expanded uncertainty of measurement is stated as the standard uncertainty of measurement multiplied by the coverage factor k = 2, which for a normal distribution corresponds to a coverage probability of approximately 95%. The standard uncertainty of measurement has been determined in accordance with ISO Guide 31/11. The procedure with which the uncertainty is evaluated is described in the Eurachem / CITAC Guide 5.15.1.24. The metrological traceability is assured through calibration on Ion Chromatography. The calibration curve is drawn using a series of standard solutions prepared from a certified reference material traceable to SI of NIST (SRM) and of accredited according to ISO/IEC 17025/4 and/or ISO Guide 34/4 laboratories/producers. All contributions in relation to the certification of standard solutions are considered when evaluating the uncertainty. The measurement results are traceable to SI. All analytical balances used for the preparation of the solution are calibrated yearly under an in-house procedure with analytical weights, traceable to DND and are checked daily. The results from temperature measurement are traceable to SI. The thermometers used for solution's calibration are calibrated from an ISO 17025 accredited laboratory. The ambient conditions are controlled with a hygrometer calibrated from an ISO 17025 accredited laboratory.

Starting material, purity *: CH₃COOH 99.9% CH₃COOH - 83095207 Density *: 0.996 g/cm³ at 20 °C Minimum shelf-life: 11.2019 (unopened bottle in aluminized bag) Date of opening: (Recommended period of use should not exceed 12 months from date of opening)

* These values are not certified Intended use: For Laboratory Use Only Calibration of Ion Chromatographs Preparation of working reference samples* This statement is not intended to restrict the use for other purposes. Validation of analytical methods Detection limit and linearity studies Instructions for the correct use of this reference material: This certified reference material can be used directly or can be diluted in an appropriate high-purity matrix. Only a clean glassware should be used. Do not pipet from container. Obtained concentration (in mg/l) after dilution is a result from the multiplication of certified value of CRM concentration and the CRM's volume used for dilution and divided into the flask's volume used for dilution.

Stability and storage: Storage conditions: Long-term stability: Store in a refrigerator. Shipping: at room temp. This CRM is with a guaranteed stability until ±0.5% of the certified concentration within its shelf-life. Stability is guaranteed provided that the solution is kept in its original packaging, tightly closed as written in Storage conditions. The original packaging consists of the bottle & its aluminized bag. The aluminized bag is an inseparable part of the unit packing of the CRM. Hazardous situation: The normal laboratory safety precautions should be observed when working with this RM. Further details for the handling of this RM are available as safety data sheet.

Level of homogeneity: This solution was mixed according to an in-house procedure and is guaranteed to be homogeneous. To ensure sufficient homogeneity of the sample prior to use thoroughly mix by inversion.

Name of certifying officer:

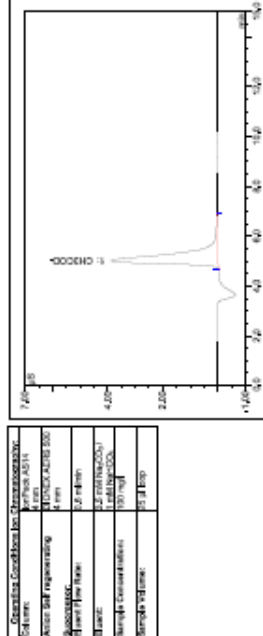
Manager: Taralova Krassimira Taralova

- [1] ISO Guide 31: Reference materials - Contents of certificates and labels
- [2] ISO Guide 35: Reference materials - General and statistical principles for certification
- [3] EURACHEM/CITAC Guide: Quantifying Uncertainty in Analytical Measurement
- [4] ISO/IEC 17025: General requirements for the competence of testing and calibration laboratories
- [5] ISO Guide 34: General requirements for the competence of Reference Material Producers

This certificate relates solely to the lot number given above. All processes (including generating of this certificate) are completely controlled by the specialized Computer-Aided-Manufacturing (CAM) software. This Certified Reference Material was produced under a quality management system that is: - Registered to ISO 9001 Quality Management System (Joyce's Register Quality Assurance Ltd Cert No. S0F0368072) - Accredited according to ISO/IEC 17025 - Testing (ANAB Cert No. AT-1835) - Accredited according to ISO Guide 34 - Reference Material Producer (ANAB Cert No. AP-1836)

Additional Information (all values below are minimal and not certified)

Trace Impurities in the actual solution reported in ppm:	
F ⁻	<0.004
NO ₃ ⁻	0.051
Cl ⁻	0.202
NO ₂ ⁻	<0.003
Br ⁻	<0.002
PO ₄ ³⁻	<0.005
SO ₄ ²⁻	<0.005





CERTIFIED REFERENCE MATERIAL

This document is designed and the certified value(s) and uncertainty(ies) are determined in accordance with ISO Guide 31¹⁾ (ISO Guide 35²⁾ and Eurachem / CITAC Guides³⁾

Lot N°: 188705	Barcode: 83096808	Certification Date: 06.04.2017
		Date of Stability last check:
Description of the Reference Material (CRM):	Solution of: Formates (HCOO-) concentration 1.000 g/l in Water (H₂O)	
Material Number:	84957.180	
Certified value/ Uncertainty:	Element	Metrological traceability:
	Certified Value and Uncertainty [mg/l]:	
	HCOO ⁻	BAM CRM No 60357 Lot BCBP3137V; BAM CRM No 60357 Lot BCBP3137V

Method(s) of certification used:
(V) WQP 5.1.5.1.24

Notes:
The certified value was obtained by a weighted mean of the results of two independent methods among: Classical Volumetric, Primary Gravimetric, Instrumental (ICP/OES, ICP/MS or IC)

Concept of Certification and traceability statement:
This certified reference material is produced using a high-purity starting material, acid from sub-boiling and 18 MΩcm deionized water. The reported expanded uncertainty of measurement is stated as the standard uncertainty multiplied by the coverage factor $k = 2$, which for a normal distribution corresponds to a coverage probability of approximately 95%. The standard uncertainty of measurement has been determined in accordance with EA 402.
Property of the result of a measurement whereby it can be related to stated references, usually national or international standards, through an unbroken chain of calibrations, each having a stated uncertainty (traceability).
The metrological traceability is assured through calibration on Ion Chromatographs. The calibration curve is drawn using a series of standard solutions prepared from a certified reference material traceable to SI of NIST (SRM) and of accredited according to ISO/IEC 17025:04 and/or ISO Guide 34 R laboratories/producers. All contributions in relation to the certification of standard solutions are considered when evaluating the uncertainty. The measurement results are traceable to SI. All analytical balances used for the preparation of the solution are calibrated yearly under an in-house procedure with analytical weights, traceable to DKD and are checked daily.
Class A laboratory glassware is used.
The ambient conditions are controlled with a hygrothermostat used for solution's calibration are calibrated from an ISO 17025 accredited laboratory. The ambient conditions are controlled with a hygrothermostat calibrated from an ISO 17025 accredited laboratory.

Starting material, purity : HCOOH 99.5% HCOOH - 83096808
0.997 g/cm³ at 20 °C

Density :

Minimum shelf-life: 10.2019 (unopened bottle in aluminized bag)

Date of opening:
(Recommended period of use should not exceed 12 months from date of opening.)

* These values are not certified

Intended use: For Laboratory Use Only
Calibration of Ion Chromatographs
Preparation of "working reference samples"
This statement is not intended to restrict the use for other purposes.

Validation of analytical methods
Detection limit and linearity studies

Instructions for the correct use of this reference material:

This certified reference material can be used directly or can be diluted in an appropriate high-purity matrix. Only a clean class A glassware should be used. Do not pipette from container. Obtained concentration (in mg/l) after dilution is a result from the multiplication of certified value of CRM concentration and the CRM's volume used for dilution and divided into the final's volume used for dilution.

Stability and storage:

Storage conditions: To be stored under normal laboratory conditions
This CRM is with a guaranteed stability until 40.5% of the certified concentration within its shelf-life. Stability is guaranteed provided that the solution is kept in its original packaging, tightly closed as written in Storage conditions. According to an in-house procedure the producer will monitor this CRM at appropriate intervals and the purchasers will be notified of any significant changes resulting in recertification or with withdrawal of the CRM during the stable period of the validity of the certificate.
The original packaging consists of the bottle & its aluminized bag. The aluminized bag is an inseparable part of the unit packing of the CRM.

Hazardous situation:

The normal laboratory safety precautions should be observed when working with this RM. Further details for the handling of this RM are available as safety data sheet.

Level of homogeneity:

The material was tested for homogeneity by analyzing randomly selected samples according to an in-house procedure. The level of homogeneity proved satisfactory for a sample volume of 20 ml. The uncertainty incorporates the sample standard deviation combined with the uncertainty calculated from heterogeneity and standard uncertainty.
To ensure sufficient homogeneity of the sample prior to use thoroughly mix by inversion.

Names of certifying officer:

Manager: *Sarabou* Krassimira Tarsiova

- 1) ISO Guide 31: Reference materials - Contents of certificates and labels
- 2) ISO Guide 35: Reference materials - General and statistical principles for certification
- 3) Eurachem / CITAC Guides: General principles for the production, certification and use of reference materials
- 4) ISO/IEC 17025: General requirements for the competence of testing and calibration laboratories
- 5) ISO Guide 34: General Requirements for the Competence of Reference Material Producers

This certificate relates solely to the lot number given above.

All processes (including generating of this certificate) are completely controlled by the specialized Computer-Aided-Manufacturing (CAM) software.

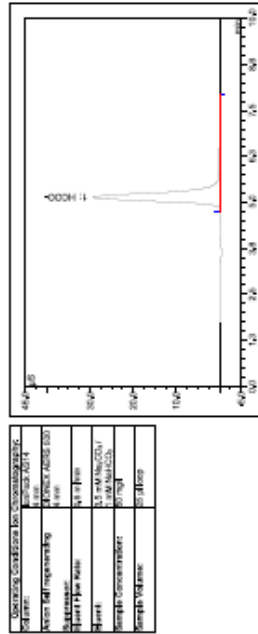
This Certified Reference Material was produced under a quality management system that is:

- Registered to ISO 9001 Quality Management System (Lloyd's Register Quality Assurance Ltd Cert No SGP0386072)
- Accredited according to ISO/IEC 17025 - Testing (ANAB Cert No AT-1838)
- Accredited according to ISO Guide 34 - Reference Material Producer (ANAB Cert No AP-1835)

Additional Information

(all values below are nominal and not certified)

Trace Impurities in the actual solution reported in ppm:	
F ⁻	<0.004
NO ₃ ⁻	<0.002
Cl ⁻	<0.003
NO ₂ ⁻	<0.003
Br ⁻	<0.002
PO ₄ ³⁻	<0.005
SO ₄ ²⁻	<0.005



CERTIFIED REFERENCE MATERIAL

This document QF.6.17-1/1 version 1 is designed and the certified value(s) and uncertainty(ies) are determined in accordance with ISO Guide 31/1, ISO Guide 38/1 and Eurachem / CITAC Guide 5/1

Lot N: 249155	Barcode: 83097614	Certification Date: 01.11.2017 Date of Stability last check:
Description of the Reference Material (CRM):	Solution of: Methanesulphonates (CH ₃ SO ₃ -) concentration: 1.000 g/l in Water (H ₂ O)	
Material Number:	84977.180	
Certified value/ Uncertainty:	Certified Value and Uncertainty [mol/l]	Metrological traceability:

Method(s) of certification used:	CRM's calibration procedure(s):	Notes:
	CH ₃ SO ₃ ⁻ : 1001.0 ± 4.0 (%)	
	(n) WQP 5.15.1/13	The certified value was obtained using calibration
		BAM CRM 60357 LotN BC8P3137V

Concept of Certification and traceability statement: The results of the measurement are traceable to the SI through the use of a certified reference material, an ISO 17025 accredited calibration laboratory and a certified reference material traceable to SI of NIST (SRM) and of accredited according to ISO/IEC 17025-1 and/or ISO Guide 34 in accordance with the requirements of the standard. The reported expanded uncertainty of measurement is stated as the standard uncertainty of measurement multiplied by the coverage factor $k = 2$, which for a normal distribution corresponds to a coverage probability of approximately 95%. The standard uncertainty of measurement has been determined in accordance with EN 4502.

Traceability of the result of a measurement whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties (ISO VIM).

The metrological traceability is assured through calibration on Ion Chromatographs. The calibration curve is drawn using a series of standard solutions prepared from a certified reference material traceable to SI of NIST (SRM) and of accredited according to ISO/IEC 17025-1 and/or ISO Guide 34 in accordance with the requirements of the standard. All contributions in relation to the certification of standard solutions are considered when evaluating the uncertainty.

The measurement results are traceable to SI. All analytical balances used for the preparation of the solution are calibrated yearly under an in-house process with analytical weights, traceable to SI, and are checked daily.

The results from the preparation measurement are traceable to SI. The thermometers used for solution's calibration are calibrated from an ISO 17025 accredited laboratory. The ambient conditions are controlled with a thermometer calibrated from an ISO 17025 accredited laboratory.

Starting material, purity *	CH ₃ SO ₃ H 99.9% 0.996 g/cm ³ at 20 °C	CH ₃ SO ₃ H - 83007814
Density *		
Minimum shelf-life:	12.2019 (unopened bottle in aluminized bag)	
Date of opening:	*****	
		(Recommended period of use should not exceed 12 months from date of opening)

Intended use: For Laboratory Use Only
Calibration of Ion Chromatographs
Preparation of "working reference samples"
This statement is not intended to restrict the use for other purposes.

Instructions for the correct use of this reference material:
This certified reference material can be used directly or can be diluted in an appropriate high-purity matrix. Only a clean class A glassware should be used. Do not pipet from container. Obtained concentration (in mg/l) after dilution is a result from the multiplication of certified value of CRM concentration and the sample's volume used for dilution and divided into the flask's volume used for dilution.

Stability and storage:
Storage conditions: To be stored under normal laboratory conditions.
This CRM is with a guaranteed stability until ± 0.5% of the certified concentration within its shelf-life. Stability is guaranteed provided that the solution is kept in

AWR International LLC, Radnor Corporate Center, Building One, Suite 200, 100 Maissonford Road, Radnor, PA 19087, USA
AWR International bvba, Hasselode Research Park Zone 2020, Gelleraaksebaan 464, 3001 Leuven, Belgium

its original packaging, tightly closed as written in Storage conditions. The original packaging consists of the bottle & its aluminized bag. The aluminized bag is inseparable part of the unit packing of the CRM

Hazardous situation:
The normal laboratory safety precautions should be observed when working with this RM. Further details for the handling of this RM are available as safety data sheet.

Level of homogeneity:
This solution was mixed according to an in-house procedure and is guaranteed to be homogeneous. To ensure sufficient homogeneity of the sample prior to use thoroughly mix by inversion.

Names of certifying officer:

Manager: **Krassimira Taralova**

- 1) ISO Guide 31: Reference materials - Contents of certificates and labels
- 2) ISO Guide 35: Reference materials - General and statistical principles for certification
- 3) EURACHEM/CITAC Guide: Quantifying Uncertainty in Analytical Measurement
- 4) ISO/IEC 17025: General requirements for the competence of testing and calibration laboratories
- 5) ISO Guide 34: General Requirements for the Competence of Reference Material Producers

This certificate relates solely to the lot number given above.
All processes (including generating of this certificate) are completely controlled by the specialized Computer-Aided-Manufacturing (CAM) software.

This Certified Reference Material was produced under a quality management system that is Registered to ISO 9001 Quality Management System (Lloyd's Register Quality Assurance Ltd Cert No SOF368072)
Accredited according to ISO/IEC 17025 - Testing (ANAB Cert No AT-1638)
Accredited according to ISO Guide 34 - Reference Material Producer (ANAB Cert No AR-1638)

Additional Information

(all values below are nominal and not certified)

Trace Impurities in the actual solution reported in ppm:	
F ⁻	<0.004
NO ₃ ⁻	0.07
Cl ⁻	0.021
NO ₂ ⁻	<0.003
Br ⁻	<0.002
PO ₄ ³⁻	<0.005
CO ₃ ²⁻	<0.005



Certificate of Analysis

1.11437.0500 Anion multi-element standard I 1000 mg/l; F⁻, PO₄³⁻, Br⁻ in H₂O CertiPUR®
Batch HC61282237

Spec. Values		Batch Values
Concentration	β (PO ₄ ³⁻)	990 - 1010 mg/l 1001 mg/l
Determination method: alkalimetric titration. Accuracy of the method: ± 0.5 % (traceable to NIST SRM 723e)		
Spec. Values		Batch Values
Concentration	β (Br ⁻)	990 - 1010 mg/l 1002 mg/l
Determination method: argentometric titration. Accuracy of the method: ± 0.5 % (traceable to NIST SRM 990c)		
Spec. Values		Batch Values
Concentration	β (F ⁻)	990 - 1010 mg/l 1003 mg/l
Determination method: ion chromatography Accuracy of the method: F ± 2%		
Date of release (DD.MM.YYYY) 11.01.2017		
Minimum shelf life (DD.MM.YYYY) 31.12.2019		

Ayfer Yildirim

Responsible laboratory manager quality control

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Merck KGaA, Frankfurter Straße 250, 64293 Darmstadt (Germany): +49 6151 72-0
END Millipore Corporation - a subsidiary of Merck KGaA, Darmstadt, Germany
400 Summit Drive, Burlington, MA 01803, USA, Phone +1 (781) 533-6000
SAL/SA, Version 030305 19100503060071 Date: 12.10.2017

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Certificate of Analysis

Certipur® Reference Material

Multi-Element Standard VII
for cation chromatography

1.10322.0100

Batch No.: HC69087422

This product is a suitable reference material in ion chromatography. It is produced from high-purity salts. The test is performed by cation chromatography (accuracy of the method: ± 5%) against single-element standard solutions manufactured by Merck, Darmstadt, Germany. The concentrations of these single-element standard solutions are checked with an accuracy of 0.2 % by means of titration. The titrant used is traceable to NIST standard reference materials.

Ions and concentrations:

NH ₄	(Ammonium)	100 ± 5 mg/l
Ba	(Barium)	100 ± 5 mg/l
Ca	(Calcium)	100 ± 5 mg/l
K	(Potassium)	100 ± 5 mg/l
Li	(Lithium)	100 ± 5 mg/l
Mg	(Magnesium)	100 ± 5 mg/l
Mn	(Manganese)	100 ± 5 mg/l
Na	(Sodium)	100 ± 5 mg/l
Sr	(Strontium)	100 ± 5 mg/l

Matrix: 0.001 mol/l nitric acid
Package: 100-ml PE bottles

Before use, mix the solution thoroughly. Never pipet directly from the bottle. Prepare working solutions, as required, by dilution with 0.001 mol/l nitric acid.

Minimum shelf-life: 2019/04/30
Date of release: 2016/05/10

A. Yildirim

Dipl.-Ing. Ayfer Yildirim
(responsible laboratory manager quality control)

Merck KGaA - Frankfurter Straße 250, 64293 Darmstadt, Germany: +49 6151 72-0

EMD Millipore Corp. - 290 Concord Road, Billerica, MA 01821, USA: +1-781-533-6000



Certificate of Analysis

1.11448.0500 Anion multi-element standard II 1000 mg/l: Cl⁻, NO₃⁻, SO₄²⁻ in H₂O
Certipur®
Batch HC69799848

Spec. Values		Batch Values
Determination method: titrimetric		
Accuracy of the Method: Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ +/- 0.5 %		
Concentration	β (Cl ⁻)	995 - 1005 mg/l
		1001 mg/l
Determination method: argentometric titration. (traceable to NIST - SRM 999b)		
Spec. Values		Batch Values
Concentration	β (NO ₃ ⁻)	995 - 1005 mg/l
		1002 mg/l
Determination method: alkalimetric titration. (traceable to NIST - SRM 723a)		
Spec. Values		Batch Values
Concentration	β (SO ₄ ²⁻)	995 - 1005 mg/l
		1000 mg/l
Determination method: titration with lead(II)perchlorate solution. (traceable to NIST - SRM 682)		
Date of release (DD.MM.YYYY) 06.07.2016		
Minimum shelf life (DD.MM.YYYY) 30.06.2019		

Ayfer Yildirim
Responsible laboratory manager quality control

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