Nutritional contribution of atmospheric deposition to the Strandveld vegetation of West Coast South Africa

Justine Muhoro Nyaga

July 2013

Thesis presented for the degree of

DOCTOR OF PHILOSOPHY

in the

Department of Biological Sciences,

UNIVERSITY OF CAPE TOWN

Supervisors:

Michael D. Cramer

Department of Biological Sciences, University of Cape Town

Jason C. Neff

Department of Environmental Studies and Geological sciences,
University of Colorado, Boulder

John Compton

Department of Geological Sciences, University of Cape Town

To Edmund and Divine, for their love and patience

Declaration

I, Justine Muhoro Nyaga, hereby declare that this thesis, “Nutritional contribution of atmospheric deposition to the Strandveld vegetation of West Coast South Africa” is my own work except where stated otherwise in the text, and that no part of this thesis has previously been submitted for a degree award at this university or at any other university.

Justine Nyaga, July 2013

Acknowledgements

I am very grateful for the support and guidance of all my supervisors without whom this thesis would never have been possible. I wish to thank Jason Neff and Michael Cramer for their constant engagement, inspiration and encouragement which ensured successful completion of this thesis. I very much appreciate your efforts to ensure that I had adequate funds throughout the entire period of my studies. I am grateful that you always committed time to discuss and find solutions to the numerous problems that I brought to you. Thank you for the opportunity to visit the University of Colorado, Boulder where I had the best environment anyone could wish for while writing a thesis.

To John Compton, thank you for your contributions and guidance, especially during the initial stages of my project work. Your feedback on all aspects of the project and particularly on my draft chapters was invaluable.

Special thanks go to my colleagues at the (former) Department of Botany. To my office mates, Taryn, Ignatious and Simon, thank you so much for all your support, in the field, laboratory and office. Your constant willingness to engage on issues, offer opinions and insights on my work is greatly appreciated. I will always miss your friendship and company. I wish you all the best in your studies and careers.

To Edward Chirwa, thank you for your support and company in the field every month throughout the course of my fieldwork. I greatly appreciate your help with sample preparation and other laboratory work. To Zama, your help with field work during the project start-up period are greatly appreciated.

Many thanks to Daniel Fernandez of Geological Sciences Department at CU, Boulder and Ian Newton of Archeology Department at UCT for your help with sample analysis. Thanks Dan for your warm company in the office during my time at CU.

To Sandy Smuts, I am very grateful for your kind and generous logistical and administrative support throughout my time at UCT. Your support was invaluable in ensuring successful completion of this work.

I am very grateful to the funding organizations that supported me during my study period. I thank the Andrew Mellon Foundation for supporting all aspects of my work including paying my fees, field work and upkeep. I also thank the Oppenheimer Memorial Trust for providing me with additional bursary support. Your timely contribution during my last months of stay in Boulder made this work a reality.

I thank the South Africa National Parks and the management of West Coast National Park for allowing me to carry out my study within the park. I am grateful to the park manager, Pier Neil for arranging field transport for me during the initial period of the project. Thank you very much especially for availing to me, and allowing me to use meteorological data collected within the park.

Finally, I wish to thank my family for their moral support throughout the course of my studies. Thank you for your constant words of encouragement and advice.

Abstract

Ecosystem nutrient availability depends on the balance between rates of nutrient inputs and losses. Nutrients may be lost through fire and displacement of ash, herbivory, leaching and volatilization. The main pathways through which nutrients may be acquired are weathering of rock and atmospheric deposition. Symbiotic and free-living diazotrophic bacteria and blue green algae also contribute N. In ecosystems with limited occurrence of N_2-fixation and occurring on low-nutrient bedrock, atmospheric deposition is the most significant source of nutrients. Nutrients from atmospheric deposition may be of natural or anthropogenic origin, and can be "wet-deposited" dissolved in precipitation and "dry-deposited" when aerosols settle out of the atmosphere onto plant and soil surfaces. Studies on nutrient cycling around the world suggest that nutrient deposition can provide substantial amounts of nutrients to coastal ecosystems, although mineral weathering of rocks can also a significant source. Limited prior work on deposition in coastal areas of South Africa suggests that nutrient deposition could be an important component of nutrient budgets in the Cape Floristic Region. The west coast of South Africa borders a section of the Atlantic Ocean that is highly productive and characterized by strong seasonal winds, rough waters and strong wave action. This area is home to the Strandveld vegetation, which grows on marine-derived soils. Based on this, I hypothesized that marine aerosol deposition is a significant source of nutrients for the vegetation in west coast South Africa. To test this hypothesis, I examined the spatial and temporal characteristics of atmospheric deposition as well as the climatic and ecological characteristics of the area. I measured deposition rates and concentrations of essential plant nutrients (N, P, Na, Ca, Mg, and K) delivered in rain and horizontal precipitation. Horizontal precipitation was used to refer to all forms of precipitation deposited horizontally and included fog, windblown aerosols, and horizontal rainfall. I then estimated annual demand for these nutrients in 8 plant species growing in the area and compared them to the deposition rates measured in rain. I also compared nutrients deposited in rain water with those deposited in horizontal precipitation, measured the amounts of NO_3^-, NH_4^+ and PO_4^{3-} held in canopies of the 8 plant species during summer, and estimated the species' capacity for foliar nutrient uptake.

The Strandveld vegetation was found to have relatively high soil and plant nutrient concentrations compared to the rest of the CFR, despite its soils originating as nutrient-poor marine derived aeolian sands. Although N and P fluxes deposited in rain were lower than those measured in other pristine sites around the world, a large proportion of TN (84%) and TP (51%) was organic, pointing to a strong marine influence. The marine origin of N and P is supported by the high base cation fluxes compared to those reported globally. The high proportion of organic N and P, and the high base cation contents was also observed in horizontal precipitation. In this form of deposition, base cation concentrations were highest at the coast and contents declined with distance from the ocean, further supporting a possible marine source. This study also suggests that dust may be an important contributor to the deposition of some nutrients during the winter months, and both marine and terrestrial areas could therefore be important sources of nutrient deposition to this area. Based on leaf litter nutrient losses it was estimated that atmospheric deposition through rain alone could potentially supply 36% and 64% of N and P annual demand, respectively, and over 100% of the annual demand for K and Ca. This suggests a strong marine influence in the supply of these nutrients to the Strandveld soils and vegetation. In addition, plants within the Strandveld vegetation intercepted substantial amounts of moisture and nutrients in their canopies. Species with small leaves intercepted significantly greater quantities of water and nutrients than those with larger leaves. It was also established that all the studied Strandveld plants could take up NO_3^-, NH_4^+, glycine (as a form of organic N) and Li (a proxy for K) through their leaves.

Taken together, these results show that the Strandveld ecosystem of West Coast National Park receives substantial inputs of nutrients from marine aerosols, both in rain and horizontal precipitation. This deposition appears to be a critical source of nutrients in an ecosystem with limited bedrock nutrient supplies. Over the time scale of ecosystem development, atmospheric nutrient deposition combined with other ecological characteristics, such as strong moisture-laden winds, may help explain the unique biogeochemical and biogeographical characteristics of the Strandveld.

Table of Contents

List of tables

List of Figures

1 General introduction

Nutrient availability in ecosystems is important for plant growth and maintenance of ecological processes. Over monthly to annual time scales, nutrients in ecosystems are normally available in soil and plant pools from which they are recycled (Odum, 1969). Over the timescale of ecosystem development, nutrient availability is dependent on a balance between their rates of inputs and outputs from the ecosystem (Vitousek and Reiners, 1975; De Villiers et al., 2005). Nutrients can be lost from ecosystems during fire and displacement of ash, herbivory, leaching and volatilization (Chapin et al., 2002; Laclau, et al., 2005). For nutrient stocks to be in balance, nutrients lost from ecosystems must be replaced by additions from external sources. These include natural processes like rock weathering, N_2-fixation and atmospheric deposition. In natural ecosystems the major pathways for nutrient input are nitrogen fixation, rock weathering and atmospheric deposition (Vitousek et al., 1998). In some locations, and particularly in absence of N_2-fixing plant species and on nutrient depleted bedrock, atmospheric deposition becomes the most significant nutrient source (Chadwick et al, 1999).

Atmospheric deposition of nutrients is a crucial source of nutrients to ecosystems around the world (Kennedy et al., 1998; Weathers et al., 2000; Derry and Chadwick, 2007). Nutrients can be deposited in wet forms dissolved in rainfall and in dry forms when gases or aerosols settle out of the atmosphere onto plant and soil surfaces (Chen et al., 1985; Kaya and Tuncel, 1997; Ochoa-hueso et al., 2011). There are a range of natural (e.g. non-anthropogenic) atmospheric nutrient sources including wildfires, lightening, volcanic activity, wind-blown dust, pollen, sea sprays. However, humans have greatly modified the atmosphere through the emission of nutrients from the combustion of fossil fuels and the use of fertilizers and disturbance of soils during agricultural activities (Matson et al., 1999; Tost et al., 2007). In the northern hemisphere, high rates of nitrogen and sulfur deposition associated with these activities has led to a wide range of problems including acid rain (Gustafsson and Franzen, 1996), plant damage (e.g. Franzen, 1990) and impacts on human health (Pöschl, 2005), changes in nutrient limitation patterns (Crowley et al., 2012), and even nutrient induced declines in biological diversity (Phoenix et al., 2006; Ochoa-hueso et al., 2011). In contrast to the high rates of nutrient deposition over much of the northern hemisphere, the southern hemisphere has been comparatively less affected by human activity (e.g. Likens, et al., 1987). Studies of deposition and nutrient cycling in these locations can offer insight into the long-term controls of ecosystem nutrient balance and studies of how ecosystems function in the absence of intensive anthropogenic modification of nutrient cycles (e.g. Hedin et al., 1995).

Nutrient deposition to ecosystems in the coastal and interior regions of South Africa have received relatively little attention compared to many locations around the world. However, studies to date suggest that nutrient deposition could be an important component of nutrient budgets in the Cape Floristic Province (e.g. Olivier, 2002). Work in the Fynbos suggests that dust inputs from interior continental regions of Africa may be an important aspect of ecosystem nutrient cycling (Soderberg and Compton, 2007) and on the coasts, it appears that nutrient deposition in rainfall and fog might be an important aspect of nutrient delivery to coastal ecosystems such as the Strandveld (Olivier, 2002). A particularly intriguing aspect of nutrient cycling in near coastal settings is the potential for nutrients to move from the ocean to land through the production of marine aerosols. Aerosols are small particulates suspended for a period of time in the atmosphere and in coastal regions, these aerosols can contain elevated concentrations of N, P, and base cations that could influence terrestrial ecosystems once deposited on land (Azevedo and Morgan, 1974; Dawson, 1998; Weathers et al, 2000). In this thesis, I examine the composition and fluxes of nutrients in deposition to a Strandveld ecosystem on the west coast of South Africa. The characteristics of this site are detailed in section 1.5. In particular, I evaluate whether marine nutrient sources could be playing a key role in the maintenance of productivity and nutrient cycling in these ecosystems.

1.1 Wet versus dry deposition

Nutrients in atmospheric aerosols can be deposited either in solution as wet deposition or as dry atmospheric fallout (dry deposition) depending on availability of precipitation (Al-Momani et al., 1995). Wet deposition thus includes nutrients deposited in precipitation (including rain, fog, cloud and drizzle) while dry deposition includes particulates, aerosols and gases deposited in complete absence of precipitation (Shepard, et al., 1989). This distinguishing characteristic means that wet precipitation is common during wet seasons while dry deposition is expected during dry seasons, suggesting a strong influence of seasonality on the forms of deposition (Ochoa-Hueso et al., 2011). Most studies on atmospheric deposition have focused on rainwater for analysis of nutrients in wet deposition due to its ease of measurement. In some cases, deposition in precipitation includes both wet and dry forms, commonly referred to as “bulk deposition”. Although this bulk deposition may contain about 20% of dry deposition during the wet season and 80% during the dry season (e.g. Kaya and Tuncel, 1997; Shepard, et al., 1989), it is commonly categorized as wet deposition. Bulk deposition is common during precipitation events that are separated by periods of dry weather. During these periods, precipitation may wash out aerosols and particulates that have been suspended in the atmosphere since the previous precipitation event (Bergametti et al., 1989) and also those that have accumulated on vegetation and soils over such period.

Quantification of annual atmospheric deposition, both vertical and horizontal, is necessary for assessment of ecological effects of deposition and also for better understanding of nutrient cycling within the ecosystem (Balestrini, 2007; Kaya and Tuncel, 1997;Shepard et al., 1989). In doing this, most studies around the world have relied on measurements of bulk deposition. Measurement of bulk deposition is preferred not only because of the relative ease of field sampling but also because of the difficulties associated with separating dry deposition from wet deposition during precipitation events, particularly in dry seasons (Balestrini, 2007). While measurement of wet deposition involves mainly trapping of precipitation from the atmosphere, exclusive dry deposition measurement is complicated and uncertain (Kaya and Tuncel, 1997;Shepard et al., 1989). The few measurements of dry deposition which have involved use of petri-dishes, teflon plates, dust buskets etc (e.g. Davidson et al., 1985; Kaya and Tuncel, 1997) are highly uncertain Estimations of dry deposition have also been made by modeling of deposition velocities with meteorological measurements and air concentration data (Hicks, 1987) and by regression analysis of throughfall data and other event characteristics (Lovett and Lindberg, 1984). However, data obtained from these methods are only estimates, and are subject to the predetermined assumptions. Whereas dry deposition is recognized as a major source of nutrient input to ecosystems, its measurement in the field remains a challenge (Hicks, 1986; Balestrini, 2007). Meanwhile, assessment of horizontal and vertical precipitation (dry and wet deposition) enables reliable quantification of overall nutrient input to ecosystems from atmospheric deposition.

1.2 Deposition in rain precipitation

The main distinguishing feature between rain and other forms of precipitation (e.g. cloud, drizzle and fog) is the relatively large size of its droplets (Aston, 1979) which, due to the effect of gravity (Meira et al., 2006), results in it being deposited vertically. Cloud, drizzle and fog are more susceptible to horizontal wind transport, although rain may also be deposited horizontally when it’s accompanied by strong winds. This varies between geographical locations and depends on prevailing weather conditions. Scavenging of elements from atmosphere by rain depends on a number of factors including sizes and hydroscopic properties of particles in which elements are carried (Galloway et al., 1993). Elements from different sources may therefore be correlated due to the similar physical properties of the particles in which they are contained (Kaya and Tuncell, 1997). Large size particles (>5 µm) may be deposited by sedimentation (dry deposition fallout) due to their short residence times (Ménégoz, 2012). Small size particles however can remain suspended in the atmosphere for long and even transported over long distances by wind. Smaller size particles have longer atmospheric residence times and are mainly deposited by rainfall scavenging in the atmosphere (Fitzgerald, 1991). Dust particles can also be deposited in rainfall. For example, dust particles (<2.5 µm) from the Sahara desert are routinely carried across the Atlantic to the Caribbean and to the southern and eastern United States (Prospero, 2007). Presence of aerosols in the atmosphere that can be scavenged by rain depends on the time of year and proximity to sources. Dust concentrations tend to be elevated in many locations during dry periods when soils are easily eroded and vegetation is absent or senesced and concentrations are lower in winter when soils are damp or frozen (Kaya and Tuncell, 1997; Prospero, 2007). Similarly, in some locations, aerosol concentrations can be influenced by biomass burning (Piketh et al., 2002).

1.3 Deposition in horizontal precipitation

Although several forms of horizontal precipitation can be identified, the most commonly recognized are fog and cloud. Both fog and cloud precipitations are formed as a result condensation of vapor onto surfaces. Coastal areas are characterized by changes in pressure gradients that are produced due to heating and cooling of ambient air on land and sea at different times of day making them prone to fog formation (Dawson, 1998; Cereceda et al., 2002; Olivier, 2002). Fog formed within the atmospheric marine boundary layer may interact with marine aerosols produced at the sea surface enriching it with marine nutrients. Marine aerosols are formed from bursting bubbles generated during breaking waves caused by wind stress on surface ocean water and ejected into the atmosphere as sea spray aerosols (Fitzgerald., 1991; O'Dowd, 2007).

Sea spray aerosols are composed mainly of inorganic sea salts and organic matter, and constitute the greatest proportion of the particulate matter within the atmospheric marine boundary layer (O'Dowd, 2007). Fog precipitation enriched with these aerosols may be transported horizontally by onshore winds and deposited on terrestrial ecosystems inland. Globally, ecosystems bordering upwelling zones have been shown to benefit greatly from moisture and nutrient input by this precipitation (e.g. Azevedo and Morgan, 1974; Dawson, 1998; Weathers et al., 2000). Nutrients contained in horizontal precipitation formed in coastal environments are largely of marine origin. These include P which gets enriched due to fractionation during the bubble bursting process (Chen et al, 1985; Graham et al, 1979) and base cations which occur at high concentrations in ocean water (Chadwick et al., 1999). Ocean water has also been identified as an important source of organic N (Miyazaki et al. 2011; Cornell 1995) and P (Cundiff, 2001). At a coastal site in southern Chile, Weathers et al (2000) established that cloud water contained more N than rain water, 66% of which was DON. Fog may also contain nutrients of continental origin that may be intercepted and dissolved in the moist air advected inland (Cereceda, et al., 2002). Such nutrients may include mineral elements from dust, organic and inorganic forms of N and P from natural sources like biomass burning and anthropogenic sources like burning of fossil fuels and agricultural activities. Horizontal precipitation has been found to have a higher concentration of nutrients than rain precipitation (Asbury et al. 1994). In the eastern USA, cloud precipitation was found to have elemental and ionic concentrations that are 5-10 times those found in rain water (Lovett et al., 1982; Vong et al., 1991). This suggests that horizontal precipitation, mainly marine aerosols, contains substantial amounts of nutrients, which could be deposited to ecosystems by wind and possibly contribute to increased plant productivity.

Marine derived nutrients transported inland by wind may be deposited on the soil or intercepted by plant foliage. This horizontal deposition is influenced by both topography and vegetation. Topography causes lee effects behind heights and increased deposition on windward slopes (Hasselrot and Grennfelt, 1987) while vegetation increases landscape roughness and hence the surface available for deposition (Gustafsson and Franzen 1996). Canopy interception has been found to be an efficient means of moisture and nutrient acquisition from fog precipitation (Dawson, 1998) and plants have been found to be able to take up moisture (Yates and Huntley 1995) and nutrients (Peuke et al., 1998a) intercepted by the canopies through the leaves. ;. The capacity of plant canopies to intercept fog precipitation depends on the canopy structure, mainly leaf and branch sizes which determines canopy surface area (Westoby and Wright, 2003). The capacity for fog interception may also depend on pubescence and presence of wax on the leaf surface. Small and narrow leaves have been found to increase fog interception efficiency due to their large surface area (Martorell and Ezcurra 2007). They are therefore likely to also take up more moisture and nutrients compared to the big leaves

1.4 Influence of atmospheric deposition on ecosystem nutrient status

A number of studies on ecosystem nutrient dynamics around the world have identified atmospheric deposition as an important source of nutrients that contribute significant proportions of ecosystems' nutrient budgets. Deposition contribution to nutrient budgets of different elements have been studied but globally, N and P have received special attention due to their tendency to be most limiting to plants growth (Venterink et al., 2002; Pilkington et al, 2005). Weathers et al. (2000) found that the 2 and 9 kg ha^{-1} annum^{-1} of DIN and DON respectively deposited by marine aerosols through cloud precipitation in southern Chile contributed substantially to the N budgets of Chillean coastal forests. The 0.27 kg ha^{-1} $annum^{-1}$ of SRP deposited mainly from marine aerosols in the Hawaiian islands also contributes significantly to P budgets of Hawaiian coastal ecosystems (Cundiff, 2001). Globally, the 0.07-1.7 kg ha^{-1} $annum^{-1}$ TP input to terrestrial ecosystems forms an important part of ecosystems P budgets (Newman, 1995; Weathers et al. 2000; Vitousek, 2004). The proportion of nutrient budgets that atmospheric deposition in specific ecosystems may support is influenced by a number of things. These include amounts and nutritional composition of the atmospheric deposition, soil nutrient contents, and the capacity for plant foliar nutrient interception and uptake. For example, the annual average deposition fluxes of 43 kg N ha^{-1} $annum^{-1}$ and 80 kg N ha^{-1} $annum^{-1}$ for the meadows and moorland forest respectively in Europe can support approximately 63-76% of the annual ecosystem N budgets (Venterink et al., 2002; Pilkington et al, 2005). Atmospheric nutrient deposition is expected to have a greater impact on areas with low nutrient contents (Likens et al., 1996) and where nutrients have been lost from the ecosystem. Examples of such cases include the nutrient poor California chaparral shrublands where atmospheric N deposition can replace N lost annually via runoff (Schlesinger et al., 1982) and the Atacama desert in Chile where fog provides ecologically significant amounts of Ca, S and NO_3^- (Rech, et al., 2003).

Besides having the capacity to support N and P budgets in terrestrial ecosystems, atmospheric deposition can also support significant proportions of annual demands for base cations in these ecosystems apart from being able to replace those lost from the ecosystems. For example, atmospheric deposition of Ca and K can supply between 20-40% of the nutrients sequestered in plant wood in temperate forests, while atmospheric inputs of N are slightly less than hydrologic losses experienced after timber harvesting (Swank, 1984). Using strontium isotopes, Whipkey (2000) determined that deposition of sea spray aerosols provided up to 80% of base cations and Na in coastal Hawaiian ecosystems. In these ecosystems, base cation deposition can exceed their annual demands, even after nearly all have been lost from the soil through leaching during soil development (Kennedy et al., 1998). Deposition fluxes of base cations measured in the California chaparral shrublands have also been reported to exceed their annual losses (Schlesinger et al., 1982). Within the fynbos ecosystem in South Africa, Soderberg and Compton (2007) provided evidence for the potential of dust to provide significant amounts of clay and base cations to plants. Clay in dust deposition improves nutrient and water holding capacity of soils and thus their fertility. Overall, these examples suggest that atmospheric deposition has a potential to provide substantial proportions of plant and ecosystem nutrient budgets especially in areas with low nutrient contents and those impacted by high amounts of deposition. Increased nutrients in low nutrient areas would in turn lead to increased soil fertility and a significant increase in ecosystem productivity (Söderlund and Svensson, 1976; Newman, 1995).

Atmospheric deposition is a major source nutrients in the fynbos ecosystems. Other sources of nutrients in these ecosystems are mineral weathering and biological N fixation (Van Wyk et al., 1992). Studies on nutrient cycling within the fynbos have found that atmospheric deposition provides up to 0.2 kg ha^{-1} a^{-1} of P (Brown et al., 1984) and about 2 kg ha^{-1} a^{-1} of N (Stock and Lewis, 1986b) in pericoastal areas of the lowland fynbos. Within these ecosystems, nutrients are stored either within the soil or in the phytomass, and may be lost through denitrification, volatilization or streamflow and sediments (Van Wyk et al., 1992).

Although this information is known about the fynbos ecosystems, nutrient cycling within the Strandveld which has high amounts of sand with low nutrients (Cramer and Hawkins, 2009), remains largely unknown.

1.5 The study area

The study was carried out in the West Coast National Park (33^o 13’ 52.26”S, 18^o 09’ 50.96”E) which is home to a significant portion of the Langebaan dune Strandveld vegetation. The highly conserved status of this portion of Strandveld provided an environment for evaluating the effect of marine aerosol deposition in a relatively pristine setting. The park is *ca.* 100 km northwest of Cape Town on the Atlantic seaboard in the Western Cape Province of South Africa. It borders the towns of Yzerfontein and Langebaan to the southern and northern ends respectively, the Atlantic Ocean to the west and cuts across the west coast road (R27) to the east. It includes a 30 km coastal strip adjoining the sixteen mile beach marine protected area (Franceschini and Compton, 2006). The study was set on a 17 km migrating dune cordon running inland from the coast in a northerly direction. The dune cordon consists of vegetated and non-vegetated, active dunes (Franceschini and Compton, 2006).

1.5.1 Vegetation

The vegetation of the area is the Langebaan dune Strandveld consisting mainly of sclerophyllous evergreen shrubs, abundant grasses and annual herbs (Mucina and Rutherford, 2006). The immediate coastal section of the study site (*Ca.* 4 km from the sea shore) has been heavily invaded by *A. cyclops* which grow alongside the broad-leaved *Chrysanthemoides monilifera*, and a few stands of the hairy leaved *Metalasia muricata*. The intermediate section of the study site (approx. 4-10 km from the ocean) is dominated by three species of *Searsia* (*S. glauca*, *S. laevigata* and *S. lucida*). The last section of the 17 km transect is dominated by the small leaved *Morella cordifolia* and the fine leaved *Metalasia muricata* and *Agathosma imbricata.*

Acacia cyclops is an alien invasive N_2-fixing species originally from Australia with high growth rates that are supported by its ability to acquire and use resources efficiently in non-native environments (Morris et al., 2011). *Chrysanthemoides monilifera* is a native evergreen species also with high growth rates largely supported by its ability to utilize nutrients efficiently in low nutrient environments by production of large amounts of high quality litter (Lindsay and French, 2005). *Searsia glauca, S. laevigata* and *S. lucida* are sclerophyllous evergreen shrubs with relatively low growth rates. They all have medium-sized leaves that are hard and leathery. *Morella cordifolia* is an N-fixing native species with small sized leaves of serrated margins and has a relatively high growth rate compared to other native species. *Metalasia muricata* has small hairly leaves while those of *A. imbricata* are small and narrow.

1.5.2 Soils

Soils of this area are mainly aeolian dune sands deposited over a long period by wind blowing from the coast. These soils form a loose sandy surface that is sculpted into flats, dunes and hollows by the strong southerly winds (Tinley, 1985). These sands are underlaid by a calcrete geological formation (Abanda et al., 2011). The leaching of calcareous sands results in the formation of extensive pedogenic calcrete horizons throughout the region (Knox 1977).

1.5.3 Climate

The area has a semi-arid Mediterranean type climate with strong seasonal winds, predominantly southerly during summer and northerly during winter (SAWB, 1986). Winter season also experiences occasional northerly and easterly winds. Rainfall arrives mostly in winter (Jun-Aug) and has an annual average of 240 mm (Franceschini and Compton, 2006). Monthly minimum air temperatures range between 7.1^{o}C-14.9^{o}C while maximum air temperatures range between 18.4^{o}C-27.5^{o}C (SAWB, 1986).

1.5.4 Effect of the ocean

The study site borders a section of the Atlantic Ocean that is characterized by rough waters, storms and strong wave action (Franceschini and Compton, 2006). This region is also dominated by a seasonal wind cycle of predominant southeast and southwest winds in summer and northwest winds in winter (Jury, 1987; Andrews and Hutchings, 1979). The south easterly winds are associated with seasonal Benguela Upwelling and, along with the south westerly winds increase in speed as they transport moist air landward (Nelson and Hutchings, 1987). The coastal waters are also highly productive due to the seasonal upwelling (Andrews and Hutchings, 1979). Benguela Upwelling results from the deflection of the South easterly trade winds away from the coast, and occurs most prominently during the summer and spring seasons when the South Atlantic high pressure cell ridges to the south of the

African continent (Jury, 1987; Nelson and Hutchings, 1987). During these seasons, which extend from September to March, a semi-permanent plume is isolated by a pronounced oceanic front varying in position and related to wind direction leading to surface and deep water changes due to fluctuations in wind (Andrews and Hutchings, 1979). This results in nutrient-rich waters being supplied to the surface ocean. Marine air from this highly productive ocean may be transported inland by wind and eventually get deposited to ecosystems inland.

The seasonal Benguela Upwelling and southerly winds are responsible for formation of the advection sea fog that frequents the west coast Strandveld during summer and spring (Olivier, 2002). Although advection sea fog is known to be most dominant (Heydoorn and Tinley, 1980; Bailey and Chapman, 1991), other types of fog may occur. Such fog types may include radiation fog, inversion fog and cloud interception (Olivier, 2002). Sea fog may be advected inland to form radiation fog in the early hours of the day (Cereceda, et al., 2002). During such times, moist air from the sea that is advected inland may be trapped below a surface inversion in valleys and cooled to form valley fog (Olivier, 2002). In higher elevations, clouds transported inland by the westerly winds may be intercepted and engulfed at high elevation sites resulting in fog (Olivier, 2002). Together, these characteristics provide favorable conditions for production, transport and deposition of marine aerosols, which may influence the adjacent terrestrial vegetation.

1.5.5 Nutrient status of the Strandveld ecosystem

The Strandveld ecosystem is part of the fynbos biome within the Cape Floristic Region. The CFR is known to be nutrient poor especially in N and P (Kruger, 1983).

Soils of the Strandveld have however been shown to have higher nutrient contents than those of the rest of the CFR despite having higher amounts of sand (Witkoski and Mitchell, 1987). The high amounts of sand in the Strandveld soils are due to deposition of marine derived sands in the area for the last 1 million years (Abanda et al., 2011). The marine sands are however known to be very low in nutrients (Cramer and Hawkins, 2009), suggesting that other nutrients sources are responsible for the relative nutrient richness of the Strandveld soils. The granitic bedrock substrate of this area is rich in N and P and may be partly responsible for the elevated nutrient contents. However the high amounts of sand which has overlaid it for many years makes this possibility less likely. The relative nutrient richness in the Strandveld therefore points to an external nutrient source whose input is higher than in the CFR. It may also suggest that nutrient loss within the Strandveld is lower than the rest of the CFR. Previous studies on nutrient dynamics within the West Coast Strandveld have suggested that deposition of marine aerosols is a possible nutrient source to this ecosystem (e.g. Brown et al., 1984; Stock and Lewis, 1986b; Witkoski and Mitchell, 1987; Olivier, 2002; Smith and Compton, 2004; Abanda et al, 2011;). Other possible nutrient sources to this ecosystem may include N_2-fixation by the alien invasive *A. cyclops* and other indigenous N_2-fixing species like *M. cordifolia* common in the area. However, the invasive *Acacia cyclops* within the Strandveld has been shown to depend on less than 50% of N from fixation (Stock et al., 1995). *A. cyclops* also occurs very close to the ocean, which limits the potential impact on N_2-fixation across the broader Strandveld region. Nitrogen fixed by the legumes is also unlikely to benefit plants growing further from where they occur.

Data from past studies in this area provide some potential evidence for deposition of marine aerosols. For example, Fog water collected by Olivier (2002) in the area had Cl to Na and Mg ratios similar to sea water, and high concentrations of Na and base cations. Base cations are known to have high concentrations in sea water, and Na Mg are frequently used as a sea water index (Schlesinger, 1982; Keen et al., 1986). These points suggest a strong marine influence in nutrient supply to the Strandveld ecosystem. This is mainly through deposition of marine derived aerosols blown inland by the southerly winds. Although topography is known to influence deposition of aerosols transported by wind (Hasselrot and Grennfelt, 1987), the uniform topography of this area makes marked orographic influences less likely (Jury, 1987). The shrubby vegetation that dominates the area may however significantly influence deposition of these aerosols through canopy interception and could possibly benefit from the nutrients carried in the aerosols. Most plants have small, hairy and narrow leaved canopy structures. The small leaf sizes of these plants are likely to facilitate moisture and nutrient interception from fog precipitation, and possible uptake.

Nutrients contained within the Strandveld can also be lost from the ecosystem in a number of ways. These may include herbivory, soil erosion and nutrient leaching, fire and ash displacement, nutrient volatilization and tissue senescence. In this ecosystem, herbivory has been reported to be relatively low (Radloff, 2008). The dense vegetation in the area (Mills et al 2012) and the undulating topography are unfavorable conditions for both wind and water erosion. Fire, and the resultant ash displacement and nutrient volatilization are common occurrences within the fynbos biome (Govender et al., 2006). However, within the Strandveld ecosystem, fire occurs less frequently than the 18 year average of the CFR (Kruger, 1983), and therefore unlikely to be a major cause for nutrient loss. In the absence high herbivory and frequent fires, tissue senescence is likely to be the most significant way through which nutrients may be lost from plants in this ecosystem.

1.6 Hypothesis

The proximity of the west coast South Africa to a highly productive ocean that is characterized by strong seasonal winds suggests a possible influence of marine aerosol deposition. This is further supported by the relatively high nutrient contents in the soils of the area compared to the rest of the fynbos, despite having higher sand contents and being developed from nutrient poor aeolian sands. Thus atmospheric deposition may significantly influence nutritional supply to the Strandveld ecosystem. Based on this, I hypothesized that marine aerosol deposition is a significant source of nutrients for the vegetation in west coast South Africa. To test this hypothesis, I examined the spatial and temporal characteristics of atmospheric deposition within the study area. I also examined the climatic and ecological characteristics of the area. The climatic characteristics were examined in the context of their possible influence on deposition while ecological characteristics were studied on the basis of the possibility that they could be influenced by deposition. The climatic characteristics I studied include rainfall and horizontal precipitation, wind direction and speed, and their seasonal patterns. Ecological characteristics included plant and soil chemical properties, vegetation composition and structure. To be able to examine these characteristics in detail, I developed 3 sub-hypotheses focusing on different aspects of the major hypothesis and tested them independently. The first sub-hypothesis was that deposition of atmospheric aerosols in a coastal dune Strandveld vary seasonally and with distance from the ocean (Chapter 2); the second was that atmospheric nutrient deposition potentially supports a significant proportion of annual nutrient demands for the Strandveld fynbos vegetation (Chapter 3); and the third was horizontal precipitation, mainly coastal sea fog, has a significant potential to supply moisture and nutrients to vegetation of the west coast Strandveld (Chapter 4).

To test these hypotheses, I measured deposition, soil and plant nutrients within the West Coast National Park, and also carried out a number of supporting laboratory experiments. The conservation status of the park enabled sample collection in an environment with minimal human interference. To test the first sub-hypothesis, I measured deposition rates and concentrations of essential plant nutrients (N, P, Na, Ca, Mg, and K) delivered in rain precipitation. For the second sub-hypothesis, I estimated annual demand for these nutrients in 8 plant species growing in the area and compared them to the measured deposition rates. And finally, to test the third sub-hypothesis, I compared nutrients deposited in rain water with those deposited in horizontal precipitation and measured the amounts of NO_3^-, NH_4^+ and PO_4^{3-} held in canopies of the 8 plant species during summer, and estimated their capability of foliar nutrient uptake.

1.7 References

Abanda, P.A., Compton, J.S., Hannigan, R.E., 2011. Soil nutrient content, above-ground biomass and litter in a semi-arid shrubland, South Africa. Geoderma 164, 128-137

Al-Momani, I.F., Tuncel, S., Eler, Ü., Ortel, E., Sirin, G., Tuncel, G., 1995. Major ion composition of wet and dry deposition in the eastern Mediterranean basin. The Science of the Total Environment 164, 75-85.

Andrews, W.R.H., Hutchings, L., 1979. Upwelling in the Southern Benguela Current. Progress in Oceanography 9, 1-81.

Asbury, C.E, McDowell, W.H., Trinidad-Pizarro, R., Berrios, S., 1994. Solute deposition from cloud water to the canopy of a Puerto Rican montane forest. Atmospheric Environment 28,1773–1780.

Aston, A.R., 1979. Rainfall interception by eight small trees. Journal of Hydrology 42 (3/4), 383–396.

Azevedo, J., Morgan, D.L., 1974. Fog precipitation in coastal California forests. Ecology 55, 1135-1141

Bailey, G.W., Chapman, P., 1991. Short-term variability during an anchor station study in the southern Benguela upwelling system: Chemical and physical oceanography. Progress in Oceanography 28, 9-37.

Balestrini, R., Arisci, S., Cristina, M., Masello, R., Rogora, M., Tagliaferri, A., 2007. Dry deposition of particles and canopy exchange: Comparison of wet, bulk and throughfall deposition at five forest sites in Italy 41 (4), 745–756

Bergametti, G., Dutot, A.L., Buat-Mènard, P., Losno, R., and Remoudaki, E., 1989. Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean. Tellus 41 (B), 353-361.

Brown, G., Mitchell, D.T., Stock, W.D., 1984. Atmospheric deposition of phosphorus in a coastal fynbos ecosystem in the south western cape South Africa. Journal of Ecology 72 (2), 547-551

Cereceda, P., Osses, P., Larrain, H., Farías, M., Lagos, M., Pinto, R., Schemenauer, R.S., 2002. Advective, orographic and radiation fog in the Tarapacá region, Chile. Atmospheric Research 64, 261–271.

Chadwick, O.A., Derry, L.A., Vitousek, P.M., Huebert, B.J., Hedin, L.O., 1999. Changing sources of nutrients during four million years of ecosystem development. Nature 397, 491-497.

Chapin, F.S., Matson, P.A., Mooney, H., 2002. Principles of terrestrial ecosystem ecology. Springer-Verlag, New York, New York, USA.

Chen, L., Arimoto, R., Duce, R.A., 1985. The sources and forms of phosphorus in marine aerosol particles and rain from the Northern New Zealand. Atmospheric Environment 19 (5), 779-787.

Cramer, M.D., Hawkins, H.J., 2009. A physiological mechanism for the formation of root casts. Palaeogeography, Palaeoclimatology, Palaeoecology. 274, 125-133.

Cornell, S.E., Rendel, A., Jickells, T.D., 1995. Atmospheric inputs of dissolved organic nitrogen to the oceans. Nature 376, 243-246

Crowley, K.F., McNeil, B.E., Lovett, G.M., Canham, C.D., Driscoll, C.T., Rustad, L.E., Denny, E., Hallett, R.A., Arthur, M.A., Boggs, J.L., Goodale, C.L., Kahl, J.S., McNulty, S.G., Ollinger, S.V., Pardo, L.H., Schaberg, P.G., Stoddard, J.L., Weand, M.P., Weathers, K.C., 2012. Do nutrient limitation patterns shift from nitrogen toward phosphorus with increasing nitrogen deposition across the northeastern United States? Ecosystems 15, 940–957.

Cundiff, A., 2001. BerkeleyPhosphorus Deposition to Hawaii via Precipitation. University of California. http://www.soest.hawaii.edu/PubServices/REU_2000_2001/Cundiff.pdf

Dawson, T.E., 1998. Fog in the California redwood forest: ecosystem inputs and use by plants. Oecologia 117, 476-485.

Derry, L.A., Chadwick, O.A., 2007. Contributions from earth's atmosphere to soil. Elements 3, 333–338.

De Villiers, C.C., Driver, A., Clark, B., Euston-Brown, D.I.W., Day, E.G., Job, N., Helme, N.A., Holmes, P.M., Brownlie, S., Rebelo , A.B., 2005. Fynbos Forum Ecosystem Guidelines for Environmental Assessment in the Western Cape. Fynbos Forum and Botanical Society of South Africa, Kirstenbosch.

Fitzgerald, J.W., 1991. Marine Aerosols. Atmospheric Environment. 25A (3/4), 533-545.

Franceschini, G., Compton, J.S., 2006. Holocene evolution of the sixteen mile beach, Western Cape, South Africa. Journal of Coastal Research 22 (5), 1158–1166.

Franzen, L.G., 1990. Transport, Deposition and Distribution of Marine Aerosols over Southern Sweden during Dry Westerly Storms. Ambio. 19 (4), 180-188.

Galloway J.N., Savoie, D.L., Keene, W.C, Prospero, J.M., 1993.The temporal and spatial variability of scavenging ratios for NSS sulfate, nitrate, methanesulfonate and sodium in the Atmosphere over the North Atalantic Ocean. Atmospheric Environment 27 (2), 235–250.

Govender, N.W., Trollope S.W., van Wilgen, B.W., 2006. The effect of fire season, fire frequency, rainfall and management on fire intensity in savanna vegetation in South Africa. Journal of Applied Ecology 43, 748-758.

Graham, W.F., Piotrowicz, S.R., Duce, R.A., 1979. The seas as a source of atmospheric phosphorus. Marine chemistry 7, 325-342

Gustafsson, M.E.R., Franzen, L.G., 1996. Dry deposition and concentration of marine aerosols in a coastal area, SW Sweden. Atmospheric Environment. 30 (6), 977-989.

Hasselrot, B., Grennfelt, P., 1987. Deposition of air pollutants in a wind-exposed forest edge. Water, Air and Soil Pollution 34, 135-143.

Hedin, L.O., Armesto, J.J., Johnson, A.H., 1995. Patterns of nutrient loss from unpolluted, old-growth temperate forests: Evaluation of biogeochemical theory. Ecology 76, 493-509.

Heydoorn, A.E., Tinley, K.L., 1980. Estuaries of the Cape. Part 1: Synopsis of the Cape Coast. CSIR Research Report 380.

Hicks, B.B., Wesely, M.L., Lindberg, S.E., Bormberg, S.M., 1986. Proceedings of the dry deposition workshop of the National Acid precipitation Assesment Program. NOAA/Atmospheric Transport and Diffusion Division, Oak Ridge, Tennessee, USA.

Hicks, B.B., Matt, D.R., 1987. Combining biology, chemistry and meteorology in modeling and measuring dry deposition. Journal of Atmospheric Chemistry 6, 117-131.

Jury, M.R., 1987. Aircraft observations of meteorological conditions along Africa's west coast between 30^{o}-35^{o} south. Journal of climate and applied meteorology. 26, 1540-1552.

Kaya, G., Tuncel, G., 1997. Trace element and major ion composition of wet and dry deposition in Ankara, Turkey. Atmospheric Environment. 31 (23), 3985-3998.

Keene, W.C., Pszenny, A.A.P., Galloway, J. Hawley, M.E., 1986. Sea-salt corrections and interpretations of constituent ratios in marine precipitation. Journal of Geophysical Research, 91, 6647-6658.

Kennedy, M.J., Chadwick, O.A., Vitousek, P. M., Derry, L. A., Hendricks, D. M., 1998. Changing sources of base cations during ecosystem development, Hawaiian islands. Geology 26, 1015-1018.

Knox, G.F., 1977. Caliche profile formation, Saldanha Bay (South Africa). Sedimentology 24, 657–674.

Kruger, F.J., 1983. Plant community diversity and dynamics in relation to fire, in: Kruger F.J. (Eds.), Mediterranean-type ecosystems. The role of nutrients, Springer, New York, pp. 446-472.

Laclau, J-P., Ranger, J., Deleporte, P., Nouvellon, Y., Saint-André., L., Marlet, S., Bouillet, J-P., 2005. Nutrient cycling in a clonal stand of Eucalyptus and an adjacent savanna ecosystem in Congo 3. Input–output budgets and consequences for the sustainability of the plantations. Forest Ecology and Management 210, 375-391.

Likens, G.E., Driscoll, C.T., Buso, D.C., 1996. Long term effects of acid rain: Response and recovery of a forest ecosystem. Science. 272, 244–245.

Likens, G.E., Keene, W.C., Miller, J.M. Galloway, J.N. 1987. Chemistry of precipitation from a remote, terrestrial site in Australia. Journal of Geophysical Research: Atmospheres (1984–2012) 92(D11), 13299–13314.

Lindsay, E.A., French, K., 2005. Litterfall and nitrogen cycling following invasion by *Chrysanthemoides monilifera* ssp*. Rotundata* in coastal Australia. Journal of Applied Ecology 42, 556-566.

Lovett, G.M., Reiners, W.A., Olson, R.K., 1982. Cloud droplet deposition in subalpine Balsam fir forests: Hydrological and chemical inputs. Science 218, 1303-1304.

Lovett, G.M., Lindberg, S.E., 1984. Dry deposition and canopy exchange in a mixed oak forest as determined by analysis of throughfall. Journal of Applied Ecology 21: 1013-1028

Martorell, C., Ezcurra, E., 2007. The narrow-leaf syndrome: a functional and evolutionary approach to the form of fog-harvesting rosette plants 151, 561–573.

Matson, P.A., McDowell, W., Townsend, A.R., Vitousek, P.M., 1999.The globalization of N deposition: ecosystem consequences in tropical environments. Biogeochemistry 46, 67-83.

Meira, G.R., Andrade, M.C., Padaratz, I.J., Alonso, M.C., Borba Jr, J.C., 2006. Measurements and modelling of marine salt transportation and deposition in a tropical region in Brazil. Atmospheric Environment 40, 5596–5607.

Ménégoz, M., Voldoire, A., Teyssédre, H., Salasymelia, D., Peuch, V.H., Gouttevin, I., 2012. How does the atmospheric variability drive the aerosol residence time in the Arctic region? Tellus B, 64, DOI: 10.3402/tellusb.v64i0.11596

Mills, A.J., Burch, S.C., Stephenson, J.D., Bailey, R.V., 2012. Carbon stocks in fynbos, pastures and vineyards on the Agulhas Plain, South Africa: a preliminary assessment. South African Journal of Plant and Soil DOI:10.1080/02571862.2012.730636.

Miyazaki, Y., Kawamura, K., Jung, J., Furutani, H., Uematsu, M., 2011. Latitudinal distributions of organic nitrogen and organic carbon in marine aerosols over the western North Pacific. Atmospheric chemistry and Physics 11, 3037-3049.

Morris, T.L., Esler, K.J., Barger, N.N., Jacobs, S.M., Cramer, M.D., 2011. Ecophysiological traits associated with the competitive ability of invasive Australian acacias. Diversity and Distributions 17, 898-910

Mucina, L., Rutherford, M.C., 2006. The Vegetation of South Africa, Lesotho and Swaziland. SANBI, Pretoria pp. 804.

Nelson, G., Hutchings, L., 1987. Passive transportation of pelagic system components in the southern Benguela area. South African Journal of Marine Science. 5 (1), 223-234.

Newman, E.I., 1995. Phosphorus input in terrestrial ecosystems. Journal of Ecology 83, 713-726.

O’Dowd, C.D., Leeuw, G.D., 2007. Marine aerosol production: a review of the current knowledge. Philosophical Transactions of the Royal Society of America 365: 1753–1774.

Ochoa-Hueso, R., Allen, E.B., Branquinho, C., Cruz, C., Dias, T., Fenn, M.E., Manrique, E., Pérez-Corona, M.E., Sheppard, L.J., Stock, W.D. 2011. Nitrogen deposition effects on Mediterranean-type ecosystems, An ecological assessment. Environmental pollution 159, 2265-2279.

Odum, E.P., 1969. The strategy of ecosystem development. Science 164, 262-270.

Olivier, J., 2002. Fog-water harvesting along the West Coast of South Africa: A feasibility study. Water South Africa 28 (4), 349-360.

Peuke, A.D., Jeschke, W.D., Hartung, W., 1998. Foliar application of nitrate or ammonium as sole nitrogen supply in *Ricinus communis*: I. Carbon and nitrogen uptake and inflows. New Phytologist 138, 675-687

Phoenix, G.K., Hicks, W.K., Cinderby, S., Kuylenstierna, J.C.I., Stock W.D., Dentener, F.J., Giller, K.E., Austin, A.T., Lefroy, R.D.B., Gimeno, B.S., Ashmore, M.R., Ineson, P., 2006. Atmospheric nitrogen deposition in world biodiversity hotspots-the need for a greater global perspective in assessing N deposition impacts. Global change Biology 12, 470–476.

Piketh, S.J., Swap, R.J., Maenhaut, W., Annegarn, H. J. Formenti, P., 2002. Chemical evidence of long-range atmospheric transport over southern Africa. Journal of Geophysical research 107 (D24), doi:10.1029/2002JD002056.

Pilkington, M.G., Caporn, S.J.M., Carroll, J.A., Cresswell, N., Lee, J.A., Reynolds, B., Emmett, B.A., 2005. Effects of increased deposition of atmospheric nitrogen on an upland moor: Nitrogen budgets and nutrient accumulation. Environmental Pollution 138, 473-484.

Pöschl, U., 2005. Atmospheric aerosols: composition, transformation, climate and health effects. Angewandte Chem-International Edition In English 44, 7520.

Prospero, J.M., 2007. African dust: Its large scale transport over the Atlantic oean and its impact on the Mediterranean region. In: Mellouki, A., Ravishankara, A.R. (eds) Regional Climate Variability and its Impacts in the Mediterranean Area, Springer, pp. 15–38.

Radloff, F.G.T., 2008. The ecology of large herbivores native to the coastal lowlands of the fynbos biome in the Western Cape, South Africa. PhD thesis. University of Stellenbosch, Stellenbosch.

Rech, J.A., Quade, J., Hart, W.S., 2003. Isotopic evidence for the source of Ca and S in soil gypsum, anhydrite and calcite in the Atacama Desert, Chile. Geochimica et Cosmochimica Acta, 67 (4), 575–586

Schlesinger, W.H., Gray, J.T., Gilliam, F.S., 1982. Atmospheric deposition processes and their importance as sources of nutrients in a chaparral ecosystem of southern California. Water Resources Research. 18 (3), 623-629.

Shepard, J.P., Mitchell, M.J., Scott, T.J., Zhang, Y.M., Raynal, D.J., 1989. Measurements of wet and dry deposition in a Northern hardwood forest. Water, Air and Soil Pollution 48, 225-238.

Smith, M., Compton, J.S., 2004. Origin and evolution of major salts in the Darling pans, Western Cape, South Africa. Applied Geochemistry 19, 645-664.

Soderberg, K., Compton, J.S., 2007. Dust as a nutrient source for fynbos ecosystems, South Africa. Ecosystems 10, 550–561.

Söderlund, R., Svensson, B.H. 1976. The Global Nitrogen Cycle. Ecological Bulletins 22 (7), 23-73.

South African Weather Bureau (SAWB)., 1986. Climate of South Africa. Climate Statistics up to 1984. WB40. Department of Environmental Affairs, Pretoria

Stock, W.D., Wienand, K.T., Baker, A.C., 1995. Impacts of invading N2-fixing Acacia species on patterns of nutrient cycling in two Cape ecosystems: evidence from soil incubation studies and ^{15}N natural abundance values. Oecologia 101, 375-382.

Stock, W.D., Lewis, O.A.M., 1986. Atmospheric input of nitrogen to a coastal fynbos ecosystem of the south-western Cape Province, South Africa. South African Journal of Botany 52 (4), 273-276.

Swank, W.T., 1984. Atmospheric contributions to forest nutrient cycling. Journal of the American Water Resources Association 20 (3), 313-321.

Tost, H., Jöckel P., Kerkweg, A., Pozzer, A., Sander, R., Lelieveld, J., 2007. Global cloud and precipitation chemistry and wet deposition:tropospheric model simulations with ECHAM5/MESSy1. Atmospheric Chemistry and Physics 7, 2733-2757

Tinley, K.L., 1985. Coastal dunes of South Africa. South African National Scientific Programmes, Council for Scientific and Industrial Research, Pretoria 109, p300

Venterink, H.O., Pieterse, N.M., Belgers, D.M., Wassen, M.J., De Ruiter, P.C., 2002. N, P, and K budgets along nutrient variability and productivity gradients. Ecological applications12 (4), 1010-1026.

Vitousek, P.M, Reiners, W.A., 1975. Succession and Nutrient Retention: A Hypothesis. BioScience 25 (6), 376-381

Vitousek, P.M., Hedin, L.O., Matson, P.A., Fownes J.H., Neff J. 1998. Within-system element cycles, input-output budgets, and nutrient limitation. In: Pace, M.L., Groffmann, P.M. (Eds.), Successes, Limitations, and Frontiers in Ecosystem Science, New York: Springer-Verlag, pp. 57-74.

Vitousek, P., 2004. Nutrient cycling and limitation: Hawaii as a model system. Princeton university Press, Princeton, New Jersey, pp. 104-106.

Vong, R.J., Sigmon, J.T., Mueller S.F., 1991. Cloud water deposition to Appalachian forests. Environmental Science and Technology 25(6), 1014-1021.

Weathers, K.C., Lovett, G.M., Likens, G.E., Caraco, N.F.M., 2000. Cloudwater inputs of nitrogen to forest ecosystems in southern Chile: forms, fluxes, and sources. Ecosystems 3, 590–595.

Westoby, M., Wright, I.J., 2003. The leaf size – twig size spectrum and its relationship to other important spectra of variation among species. Oecologia 135, 621-628.

Whipkey, C.E., Capo, R.C., Chadwick, O.A., Stewart, B.W., 2000. The importance of sea spray to the cation budget of a coastal Hawaiian soil: a strontium isotope approach. Chemical Geology 168, 37–48

Witkoski, E.T.F., Mitchell, D.T.1987. Variation in Soil phosphorus in the fynbos biome, South Africa. Journal of Ecology 75, 1159-1171.

Yates, D.J., Huntley, L.B., 1995. Foliar uptake of water by wet leaves of Sloanea woollsii, an Australian subtropical rainforest tree. Australian Journal of Botany 43, 157-167.

2 Atmospheric nutrient deposition to the west coast of South Africa

2.1 Abstract

Atmospheric deposition is an important source of nutrients to many ecosystems, but is of particular importance to plant nutrition in areas where nutrients are scarce. Nutrient containing aerosols enter the atmosphere through industrial and agricultural activities, wildfires, and the production of terrigenous and marine aerosols. In this study, I collected bulk rain precipitation along the Atlantic coast of South Africa in a coastal “Strandveld” vegetation region. This region is relatively remote from significant anthropogenic influences and is downwind of a highly productive and stormy portion of the Atlantic. I therefore hypothesized that strong seasonal onshore winds are a potential source of marine aerosols to the terrestrial coastal areas and should decline with distance from the ocean. Samples were collected over 12 months at sites along a 17 km downwind transect from the shoreline and analyzed for N, P, Na, Ca, Mg and K. Annual total N and total P fluxes of 4.8 kg ha-1 yr-1 and 0.16 kg ha-1 yr-1 are amongst the lowest fluxes measured globally. In contrast, fluxes of Na were 88.7 kg ha-1 yr-1, 16.2 kg ha-1 yr-1 for Ca, 12.1 kg ha-1 yr-1 for Mg and 5.2 kg ha-1 yr-1 for K; rates that are higher than most other measurements elsewhere in the world. Dissolved organic nitrogen represented ca. 70.7% of the N flux and 43% of the P flux was in the form of soluble reactive P (SRP). These results combined with the high fluxes of Na and Mg strongly suggest that marine aerosols are important contributors to nutrient deposition at this site.

2.2 Introduction

Atmospheric deposition is an important source of nutrients for terrestrial ecosystems (Kennedy et al., 1998; Weathers et al., 2000; Whipkey et al., 2000; Derry and Chadwick, 2007). Nutrients enter the atmosphere through a variety of natural processes and human activities. Natural sources include wildfire, and the production of mineral and marine aerosols (Vicars et al., 2010). The combustion of fossil fuels and the application of agricultural fertilizers are also major sources of atmospheric N (Galloway et al., 2008). Industrial activity also results in direct emission of some base cations, such as Ca (Keller et al., 2003). Phosphorus and other rock-derived nutrient concentrations can also be elevated by agricultural activities, especially those that increase wind erosion (Neff et al., 2008). Ecosystem eutrophication as a consequence of anthropogenic sources of nutrient deposition is a major worldwide ecological problem (Matson et al., 1997). Despite this, natural deposition remains an important component of nutrient cycling in areas where anthropogenic influences are small.

Natural deposition can be a critical contributor to ecosystem nutrient budgets, particularly in nutrient-poor ecosystems and areas where losses of nutrients from the soil are more rapid than replacement by weathering of the parent bedrock (Likens et al., 1996). In these contexts the sources of nutrients in deposition may include both the ocean and land. For example, the marine to terrestrial flux of cloud water substantially contributes to Chilean coastal forest N budgets (Weathers et al., 2000) and marine aerosols are an important component of Hawaiian Islands ecosystem nutrient supply (Derry and Chadwick, 2007, Kennedy et al., 1998). In other areas, terrigenous aerosols dominate depositional fluxes. For example, Saharan dust provides a constant source of N and P (Bergametti et al., 1992; Rodá et al., 2002;

Markaki et al., 2010) and other nutrients (Goudie and Middleton, 2001) to Mediterranean-basin ecosystems.

The west coast Strandveld vegetation of the Cape Floristic Region (CFR) of South Africa is adjacent to the Atlantic Ocean in an area that is not immediately downwind of densely populated areas (e.g. Cape Town, Atlantis). The CFR contains a variety of mediterranean-type biomes (including the Fynbos and Succulent Karoo biomes) that are characterized by hot, dry summers and mild, wet winters (Mucina and Rutherford, 2006). Although the area of CFR is small (*ca.* 90 000 km^2), the species diversity is very high with 9 000 vascular species, 69% of which are endemic (Goldblatt and Manning, 2000). The vegetation of the study area consists mainly of evergreen shrubs, grasses and annual herbs (Mucina and Rutherford, 2006). Although the soils of the Fynbos biome are generally low in nutrients, especially N and P (Kruger et al., 1983), some areas, including the coastal ecosystems known as 'Strandveld' that are the focus of this study have higher soil nutrient contents (Witkowski and Mitchell, 1987). The Strandveld occurs on marine derived aeolian sands (Cowling et al., 2009) that have low nutrient content early in soil development (e.g. Cramer and Hawkins, 2009), but increase over time during pedogenesis (Abanda et al., 2011).

A number of studies have investigated the possible role of atmospheric deposition in nutrient provision to fynbos ecosystems and found ecologically significant rates of P (0.2 kg ha^{-1} a^{-1}) and N deposition (2 kg ha^{-1} a^{-1}) in pericoastal areas of the lowland fynbos (Brown et al., 1984; Stock and Lewis, 1986b). However, the Fynbos Biome as a whole is also adjacent to the inland arid and semi-arid Kalahari desert and Karoo. Inland derived atmospheric dust may provide an important source of clay and rock-derived nutrients (i.e. Ca, K, Fe, Mn and Zn) to the fynbos ecosystems (Soderberg and Compton, 2007). Despite these intriguing examples of the potential importance of marine and terrigenous derived atmospheric deposition, there have been few systematic studies of annual patterns in nutrient deposition of elements important for plant growth. Similarly, there is limited information on the relative importance of marine versus terrigenous aerosols as the source of nutrients to these ecosystems.

This study examines the annual rates and patterns of atmospheric bulk deposition in a coastal dune Strandveld ecosystem located adjacent to the Atlantic Ocean. The highly productive Benguela Upwelling System occurs offshore where seasonal coastal upwelling supplies nutrient-rich waters to the surface ocean (Andrews and Hutchings, 1979). I hypothesized that strong seasonal onshore winds are a potential major source of marine aerosols to the terrestrial coastal areas and should decline with distance from the ocean. I therefore measured concentrations and wet deposition rates of N, P, Na, Ca, Mg, and K delivered in the West Coast National Park located 90 km north of city of Cape Town to determine the source and flux of these nutrients.

2.3 Methods

2.3.1 Description of study site

The study area is located in the West Coast National Park (33^{o}13’52.26”S, 18^{o}09’50.96”E) along a 17 km long transect of a migrating dune cordon running inland from the coast in a northerly direction (Figure 2.1). The dune cordon consists of vegetated and non-vegetated, active dunes (Franceschini and Compton, 2006). The central location of the site is approximately 10 km north and 20 km south of the nearest non-industrial towns of Yzerfointen and Langebaan, respectively. The area has a semi-arid Mediterranean type climate with strong seasonal winds, predominantly southerly during summer and northerly during winter (SAWB, 1986). Winter season also experiences occasional northerly and easterly winds. Rainfall arrives mostly in winter (Jun-Aug) and has an annual average of 240 mm (49 mm-440 mm) (Franceschini and Compton, 2006) (Figure 2). Monthly minimum air temperatures range between 7.1^{o}C-14.9 ^{o}C while maximum air temperatures range between 18.4^{o}C-27.5^{o}C (SAWB, 1986) (Figure 2).

The geology of the area consists of basement rocks of the Malmesbury group and cape granite overlaid by quaternary coastal calcareous to quartzose sands (Tinley, 1985). The aeolian sands are marine-derived and contain a large proportion of calcareous material (Franceschini and Compton, 2006). The leaching of calcareous sands results in the formation of extensive pedogenic calcrete horizons throughout the region (Knox 1977). The main vegetation type in the area is formally Langebaan dune Strandveld, which dominates most of the deep calcareous sands and consists mainly of sclerophyllous shrubs and annual herbs (Mucina and Rutherford, 2006).

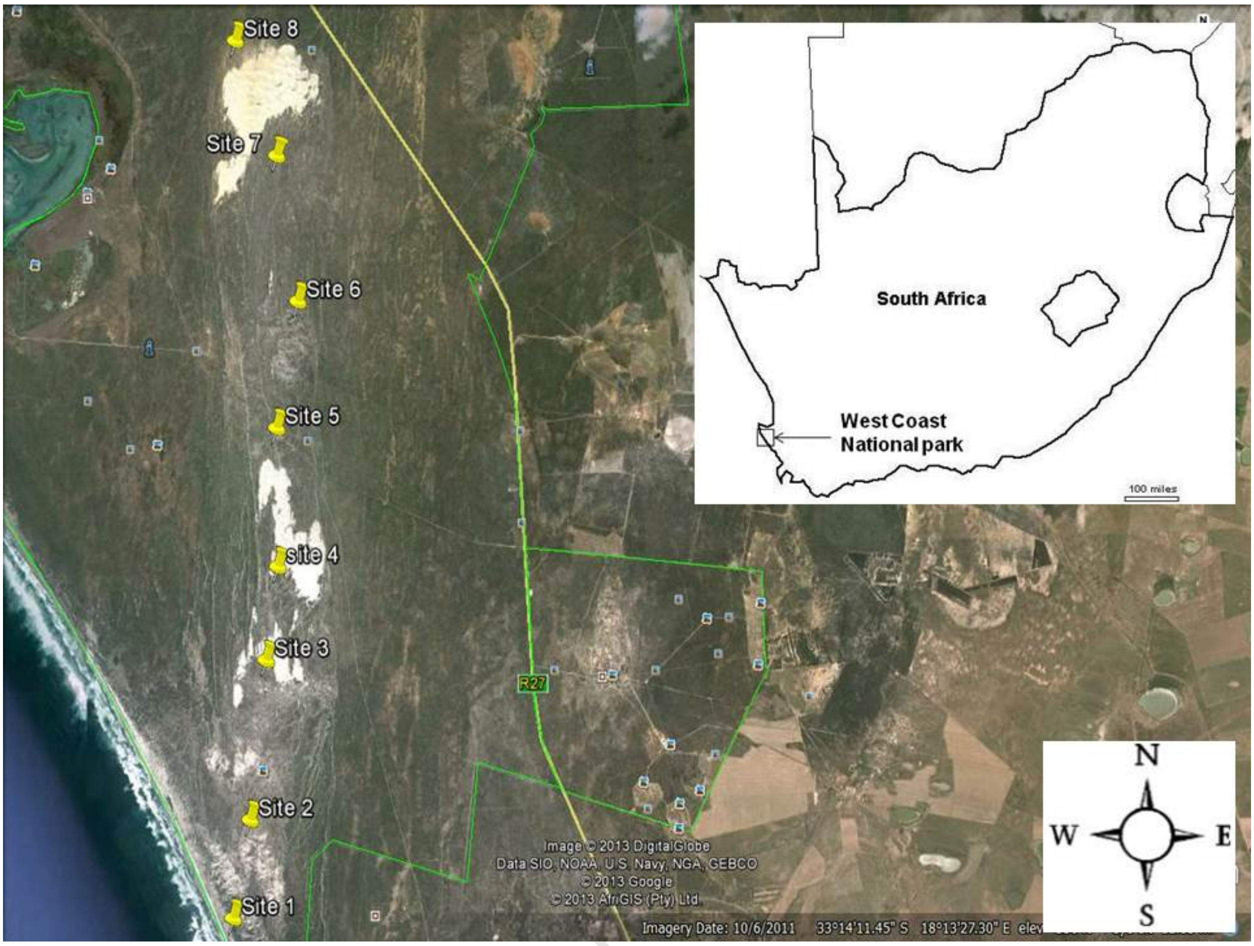

Fig. 2.1: Location of the study area and the eight sampling sites within the West Coast National Park, South Africa. The green line marks the park boundary and the yellow line is R27 road from Cape Town to Langebaan.

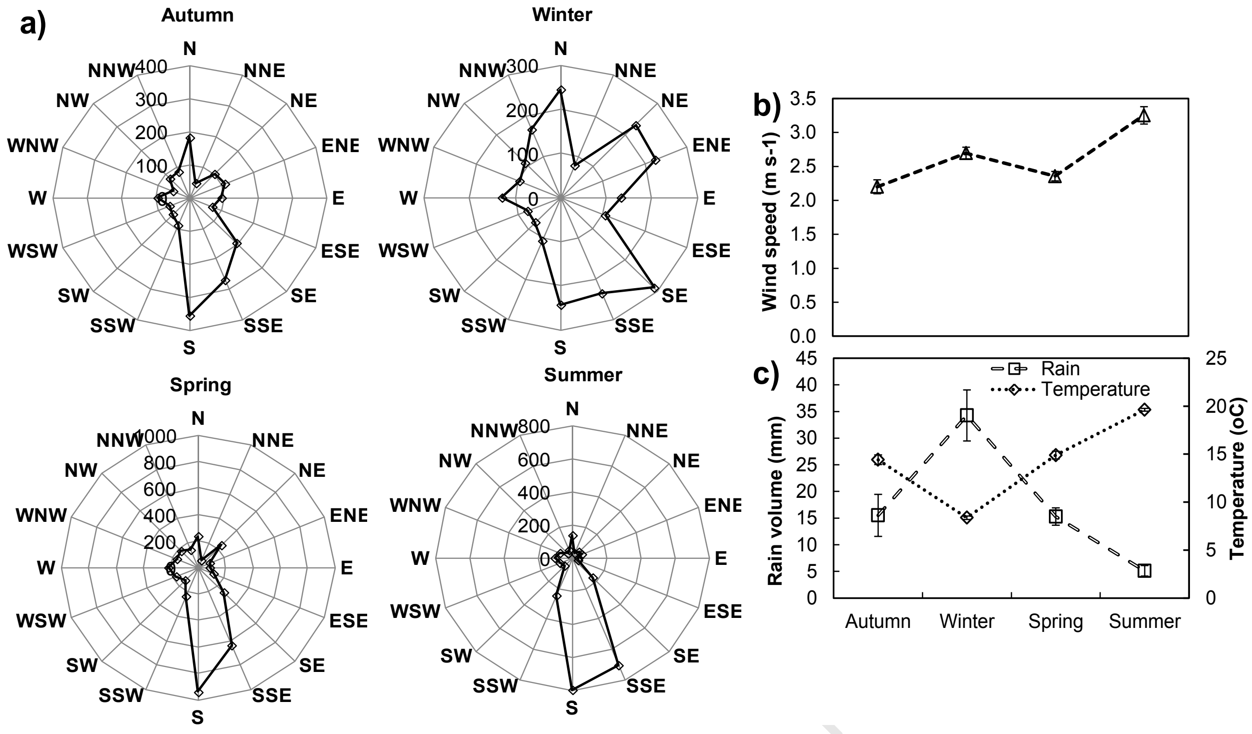

Fig. 2.2: Field patterns of climatic variables within the West Coast National Park including (a) Seasonal wind directions represented as wind roses of hourly wind directions. The wind roses represent the number of hours of wind in all cardinal and inter-cardinal directions (hourly frequencies) for each season from Jan-Dec 2011; (b) Seasonal average wind speeds and (c) Seasonal average temperature and rainfall volumes.

2.3.2 Precipitation sampling

Eight sites were selected at varying distances from the ocean (0.10, 3.54, 6.09, 7.99, 10.65, 12.53, 14.59 and 16.82 km) along the dune cordon running northwards from the coast (Fig. 1). The apparatus used to collect rain water consisted of a 12 cm diameter plastic funnel positioned at 1.5 m above the ground (i.e. height of dominant vegetation). A circular stainless steel wire bird guard was fitted outside the rim of the funnel and the funnel covered with a 2 mm nylon mesh to exclude insects and other large wind-blown debris. Samples were discarded if there was any evidence of contamination (e.g. bird faeces or insects) on the collectors. A total of three samples were found to be contaminated during the sampling period. The funnels were connected to 2L Schott bottles by a 6 mm ID tube (1 m long) that was looped to form a moisture trap and thus reduce sample evaporation. These sampling bottles were thoroughly cleaned and multiple-rinsed with Millipore water. A biocide (200 mg of 2-isopropyl-5-methylphenol) was added to each of the bottles to minimize microbial degradation of the sample (Cape et al., 2010).

The sampling bottles were changed monthly for 12 consecutive months (Jan 2011 to Dec 2011). Prior to sample removal, the plastic mesh covering the funnel was washed with 50 ml Millipore water that was included in the rainwater sample to flush dried deposition into the collector. Separate samples of this rinse water were collected in bottles also containing the biocide for determination of analytical blanks and all values were below detection limits. All sample concentrations were back corrected to remove the dilution effect of the rinse. The volume of the collected water was measured using a volumetric flask and new clean plastic containers pre-rinsed with Millipore water used in sampling and storing the water. All samples were stored in at 4 ^{o}C for a maximum of 2 days prior to transfer to 50 ml centrifuge tubes and storage at -20 ^{o}C.

2.3.3 Environmental variables

Daily rainfall, temperature, wind direction and wind speed data were obtained from the Geelbek weather station located within the study area, and supplied by the West Coast National Park management. Wind speed and direction was summed cumulatively for cardinal and intercardinal directions for the seasonal wind roses (Figure 2a).

2.3.4 ICP analysis

Samples were analyzed for total P (TP), Na, Mg, Ca and K using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and total N was analyzed with a Shimadzu TOC/TN high temperature combustion analyzer. These analyses were done at the Environmental biochemistry laboratory at the Geological sciences department of the University of Colorado, Boulder. The detection limits for the various elements (in mg L^{-1}) were 0.05 for dissolved TN, 0.008 for dissolved TP, 0.095 for Na, 0.005 for Mg, 0.052 for Ca, 0.141 for K, 0.04 for Fe, and 0.35 for Al. Values that were below the detection limits were assigned a value of one half the detection limit for all subsequent calculations. A standard sample was analyzed alongside the water samples for up to six duplicate runs and gave analytical variances of 2% for Total N, 0.5% for dissolved total P, 3.37% for Mg, 1.43% for Ca, 3.19% for Na, 1.74% for K, 2.43% for Fe, 1.19% for Al.

2.3.5 Colorimetric procedures

Analysis for NH_4^+ followed the method by Weatherburn, (1967) while NO_3^- analysis was according to the method of Doanea and Horwáth (2003). Dissolved organic nitrogen (DON) was calculated as the difference between TN and the sum of NH_4^+ and NO_3^-. The malachite green oxalate method (Motomizu et al., 1983) was used to determine the concentration of PO_4^-, but other phosphates can be hydrolyzed to orthophosphate during this analysis (Motomizu et al., 1983). The measured PO_4^- is thus reported as soluble reactive P (SRP). Other forms of phosphate not determined in this method are referred to as the soluble non-reactive phosphate (SNP=TP-SRP). A 1500 Multiskan spectrum plate reader (Thermo electron corporation, Vantaa, Finland) was used to determine sample absorbencies. The detection limit for each analysis was determined by dividing the standard error of the standard sample absorbencies by the slope of the standard curve (Doyle et al., 2004). Samples whose concentration fell below the detection limit were assigned a value of one half the detection limit. The detection limits for NH_4^+, NO_3^- and SRP were determined to be (mg L^{-1}) 0.0458, 0.0251 and 0.0095, respectively. Most NH_4^+ values were found to be below the detection limit. Five duplicate runs of a randomly selected sample produced analytical variance of 7.8%, 5.0% and 4.3% for NH_4^+, NO_3^- and SRP analysis, respectively. Colorimetric analysis was done at the Ecophysiology laboratory of Botany department at the University of Cape Town.

2.3.6 Data analysis

Monthly deposition rates for each site were calculated by multiplying precipitation volume (determined for each sample site), by the concentration of the nutrient in the sample and dividing the product by the number of days in the sampling period. The monthly data were grouped into four climatically distinct seasons of three months each: Autumn (Mar, Apr and May), winter (Jun, Jul and Aug), spring (Sep, Oct and Nov) and summer (Dec, Jan and Feb). The effect of seasonality and distance from the ocean on concentration and flux was evaluated by comparing across the four seasons and the various distances from the ocean. Cumulative annual fluxes (in kg ha^{-1} yr^{-1}) fluxes for the entire study for base cations, N and P were calculated to allow comparison with other parts of the world.

To evaluate the effects of distance and seasonality on the concentration and fluxes of nutrients, analysis of co-variance (ANCOVA) was used with season as a categorical variable and distance as a continuous variable. Analysis of variance

(ANOVA) was used to test the seasonal variability of the fluxes for each of the nutrients. Sodium and Mg are commonly used as tracers of marine nutrient sources because both are present in high concentrations in seawater with lower contributions from terrestrial sources (e.g. Keene et al., 1986, Freydier et al., 2002). At this site, both Na and Mg appear to be equally strong predictors of marine inputs and subsequent analyses are based on the ratio of elemental concentrations to Na (results presented below). All statistical analyses were performed with STATISTICA ver. 8 (StatSoft, Inc., Tulsa, OK, USA). Statistical significance was determined at the $p<0.05$ level unless otherwise noted.

2.4 Results

Winds were predominant southerly in autumn, spring and summer while in winter there was an additional northerly, northeasterly and southeasterly component (Fig. 2.2a). Annual wind speed averaged 2.6 m s^{-1}, but was somewhat stronger in summer (3.3 m s^{-1}) and winter (2.7 m s^{-1}) relative to autumn (2.2 m s^{-1}) and spring (2.4 m s^{-1}) (Fig.2.2b). Although these wind speeds are moderate relative to global averages (3.3 m s^{-1}; Archer and Jacobson, 2005), winds at Dassen island (14 km south west of our coastal site) are considerably higher, averaging 6 m s^{-1} (www.windfinder.com). Rain was strongly seasonal with 48.8% of total precipitation measured in the entire period falling during winter (Fig. 2.2c).

Distance from the ocean was an important determinant of element fluxes for Na, Mg, K, NO_3^- and TP (Table 2.1). The fluxes of Na, Mg, and K all declined from the point closest to the ocean to the further inland sites (Fig. 2.3a). Total P fluxes were high near the ocean and at the furthest inland sites. Nitrate fluxes followed a different pattern and increased with distance from the ocean. Of the remaining elements, most followed a pattern of high fluxes immediately adjacent to the ocean with variable fluxes with distance inland (Table 2.1, Fig. 2.3).

Table 2.1: Effects of seasonality and distance from the ocean on the concentration and fluxes of the various nutrients measured in rainwater collected in the West Coast National Park. *P* indicates significant differences between seasons and between distances determined using ANCOVA. Values in bold indicate significant differences at $P \leq 0.05$ confidence interval, (n = 8 sampling sites). F is the value of the F statistic from the analysis of covariance. Data were collected between Jan-Dec 2011.

		Season		Distance	
		F	*p*	F	*p*
NO_3^-	Conc	2.26	0.089	6.68	**0.012**
	Flux	1.40	0.251	6.51	**0.013**
Total N	Conc	7.67	**<0.001**	0.16	0.694
	Flux	10.11	**<0.001**	0.19	0.661
DON	Conc	2.82	**0.050**	0.12	0.732
	Flux	9.98	**<0.001**	1.43	0.518
SRP	Conc	3.42	**0.022**	9.97	**0.002**
	Flux	1.59	0.200	1.57	0.214
Total P	Conc	2.68	0.054	1.68	0.199
	Flux	2.54	0.064	18.16	**<0.001**
Mg	Conc	1.27	0.293	5.36	**0.023**
	Flux	2.12	0.105	11.50	**0.001**
Ca	Conc	1.02	0.389	4.64	**0.035**
	Flux	2.56	0.062	1.87	0.175
Na	Conc	1.11	0.349	7.30	**0.009**
	Flux	1.65	0.186	9.62	**0.003**
K	Conc	1.52	0.217	5.45	**0.023**
	Flux	1.64	0.187	12.47	**0.001**
Mn	Conc	1.43	0.241	5.92	**0.017**
	Flux	1.08	0.365	0.20	0.655
Fe	Conc	1.21	0.312	3.51	0.065
	Flux	0.60	0.619	0.60	0.440
Al	Conc	1.72	0.171	4.46	**0.038**
	Flux	2.06	0.113	1.97	0.164

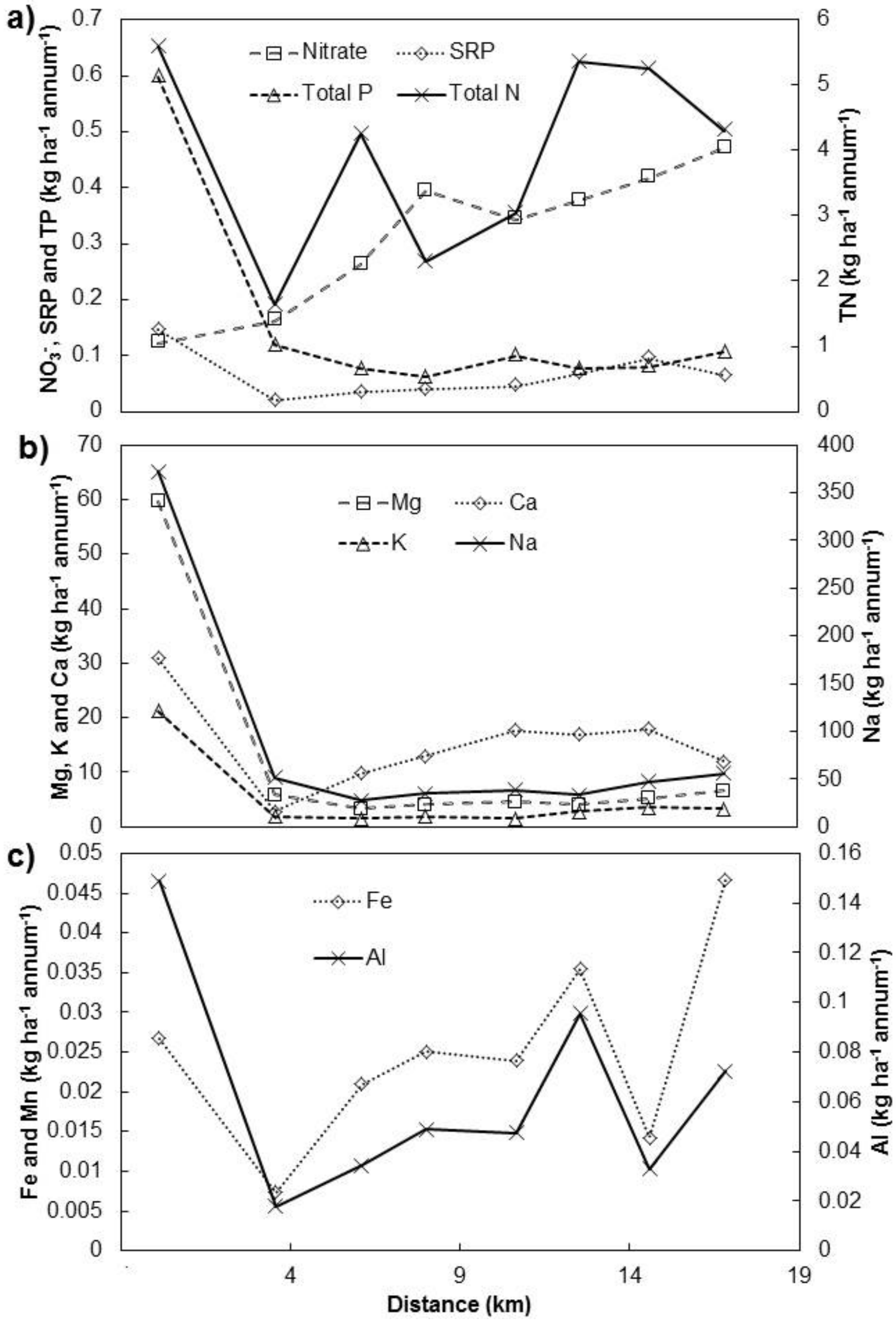

Figure 2.3: Fluxes of dissolved nutrients along the West Coast National Park study transect. Sites are shown from left (proximate to ocean) to right (inland) along the ~17 km transect. Fluxes are annual means for each sampling site along the transect.

Deposition fluxes for TN and TP varied significantly throughout the year, driven by high fluxes in winter and spring, respectively (Table 2.1; Fig. 2.4, TP significant at the $p<0.1$ level). The magnitude of these differences was driven by the seasonal variation in precipitation and, in the case of TN, higher winter and spring concentrations when compared to autumn (Table 2.1; Table 2.2). Both TN and TP exhibited different deposition patterns inland from the ocean and across seasons compared to their respective constituent inorganic forms, NO_3^- and SRP (Table 2.1; Fig. 2.3, Fig. 2.4). Nitrate concentrations in deposition were also significantly affected by season, but with the highest concentrations in autumn. Deposition of SRP was not significantly affected by season. There were no significant seasonal differences in flux and concentrations for the remaining elements (Table 2.1, Fig. 2.4).

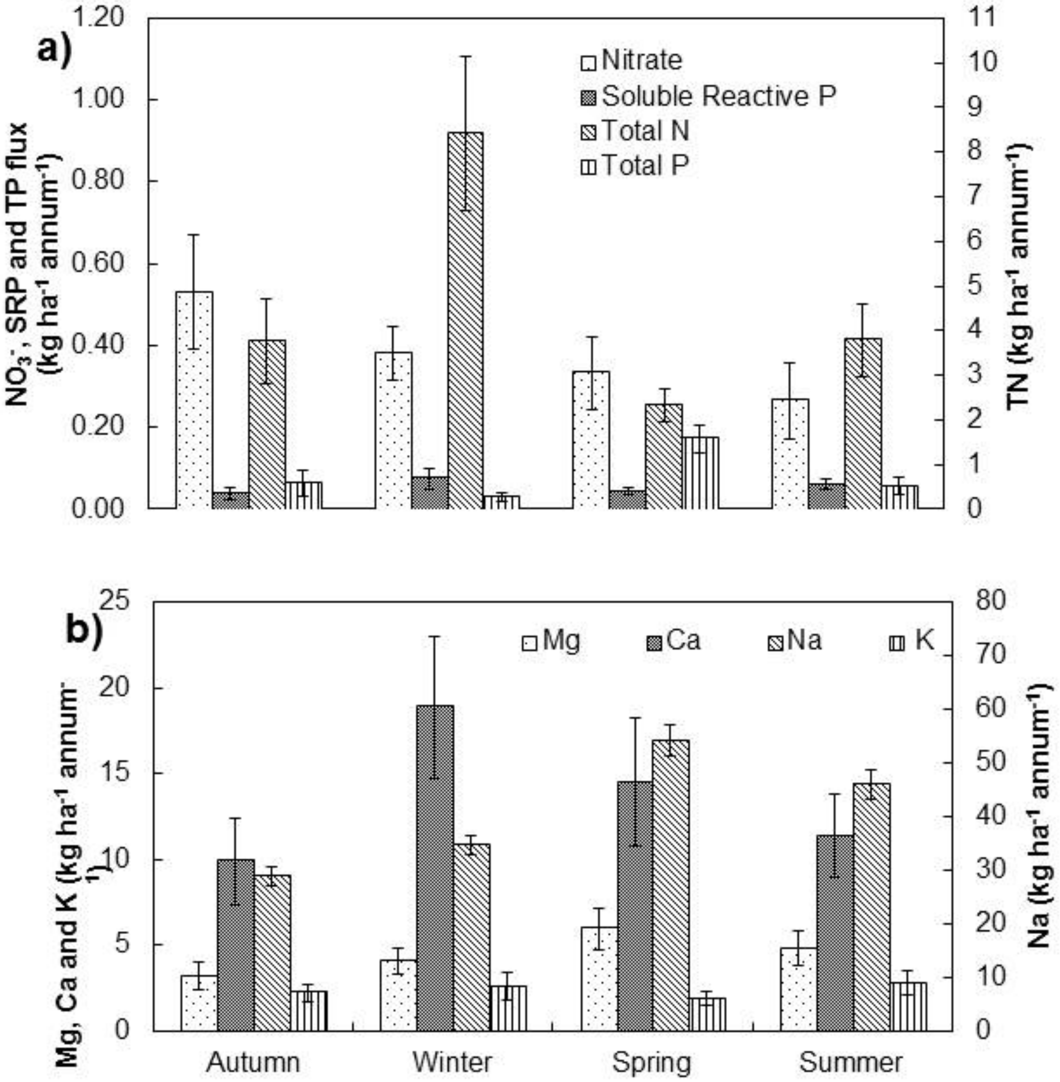

Figure 2.4: Seasonal deposition fluxes (kg ha^{-1} annum^{-1}) of dissolved nutrients measured in rain water at the West Coast National Park. Fluxes are averaged across all sampling sites for 12 consecutive months (Jan-Dec 2011). Symbols and bars represent means ± SE (*n* = 8 sampling sites).

Table 2.2: Seasonal concentrations and annual fluxes in rainfall. Concentrations are presented as mean (± SE) seasonal concentrations (mg L^{-1}) measured in rain water collected from the West Coast National Park (*n* = 8 sites) for 12 consecutive months (Jan-Dec 2011). Fluxes (kg m^{-2} $annum^{-1}$) are presented as an average of monthly fluxes for the one-year sampling period.

	Concentration (mg L^{-1})				Annual Flux (kg ha^{-1} $annum^{-1}$)
	Autumn	Winter	Spring	Summer	
NO_3^-	1.1±0.030	0.20±0.061	0.37±0.08	0.73±0.25	0.35±0.077
SRP	0.082±0.030	0.04±0.01	0.32±0.18	0.26±0.06	0.07±0.018
DON	1.32±0.54	0.64±0.28	1.17±0.22	1.74±1.14	3.4±0.82
Total N	2.6±0.66	0.68±0.29	1.5±0.22	2.4±1.1	4.8±1.0
Total P	0.082±0.033	0.006±0.0009	0.17±0.021	2.1±2.3	0.16±0.04
Mg	5.9±1.5	1.2±0.21	130±116	57±34	12±3.3
Ca	18±4.3	3.7±0.73	289±256	37±6.6	16±2.6
Na	53±14	9.7±1.1	1194±1066	234±47	89±25
K	4.6±1.2	0.56±0.14	5.2±3.2	10±2.0	5.1±1.0
Fe	0.024±0.007	0.008±0.001	0.014±0.009	0.044±0.012	0.030±0.010
Al	0.066±0.012	0.020±0.005	0.084±0.037	0.08±0.02	0.074±0.023

To evaluate the potential contribution of marine nutrients to deposition, I compared the ratio of N and P forms to Na. Both Mg and Na can be used as tracers of marine nutrients inputs (Keene et al., 1986). An analysis of data across all sampling points and dates illustrates that Mg and Na concentrations are highly correlated (r^2=0.997, $p < 0.001$) and are nearly identical to the ratios expected for sea water (Fig. 5). Calcium and Na concentrations are correlated ($r^2 = 0.6507$, $p < 0.001$) but Ca is present in excess relative to expectations for seawater contributions to precipitation. Similarly K and Na concentrations are correlated ($r^2 = 0.92$, $p < 0.001$) but K is also present well in excess of concentrations for seawater. There were seasonal variations in the nutrient:Na ratios for several nutrients (Table 2.3). Both TN and NO_3^- were elevated relative to Na in autumn and winter when compared to spring and summer. A similar pattern of elevated ratios in autumn and/or winter occurred for SRP:Na, K:Na, Fe:Na, and Al:Na though not all these seasonal differences were statistically significant (Table 2.3). The ratio of TP:Na followed a different pattern with a trend toward elevated ratios in spring and summer compared to autumn and spring.

§Table 2.3: Seasonal variations of concentration ratios of N and P forms and base cations to Na measured in rain water at the West Coast National Park as an indication of their putative marine source. The seasonal variations were determined using one way ANOVA on data collected from the study area (n = 8 sites) for 12 consecutive months (Jan-Dec 2011). Different letters in each row represent significant differences from a Tukey post-hoc analysis at p≤0.05.

	Autumn	Winter	Spring	Summer
NO_3^-:Na	0.013b	0.009ab	0.004a	0.008ab
Total N:Na	0.067ab	0.074b	0.031a	0.044ab
DON:Na	0.030ab	0.065b	0.026a	0.025ab
SRP:Na	0.002a	0.006a	0.003a	0.004a
Total P:Na	0.003ab	0.002a	0.006b	0.007ab
Mg:Na	0.123a	0.125a	0.129a	0.126a
Ca:Na	0.686a	0.955a	0.648a	0.818a
K:Na	0.147b	0.101ab	0.087a	0.106ab
Fe:Na	0.003a	0.003a	0.001a	0.002a
Al:Na	0.003ab	0.003b	0.001a	0.002ab

2.5 Discussion

The West Coast National Park borders a turbulent section of the Atlantic Ocean that is well known for rough seas, storms and strong onshore winds. These coastal waters are highly productive due to the seasonal Benguela nutrient upwelling (Andrews and Hutchings, 1979). In spring and summer the prevailing wind direction at this site is dominated by southerly winds that blow off of the Atlantic Ocean. Southerly winds are also important in winter but during this season there are also strong northeasterly winds that come from the direction of arid inland areas. These wind patterns and their associated maritime and terrestrial nutrient sources appear to play an important role in the delivery of nutrients to this portion of west coast South Africa.

The fluxes of Na and Mg at this site are very large compared to other deposition studies around the world (Table 2.4). Both of these elements are commonly used as tracers for marine contributions to precipitation chemistry (c.f. Négrel and Roy, 1998). Mg and Na concentrations are strongly correlated in precipitation and have the highest rates of deposition during the spring and summer when winds are predominantly from a southerly (maritime) direction. Fluxes of both these elements were also considerably higher than those observed at an inland site in Citrusdal (*ca.* 100 km inland from this study) (Soderberg and Compton, 2007) further suggestive of the importance of marine nutrient inputs to these pericoastal settings. The quantitative proportion of Na originating from marine and terrestrial sources can be estimated by reference to Al concentrations in precipitation following Négrel and Roy (1998) and Lostno et al. (1988) using $Na_t = Al_{rw}\left(\frac{Na}{Al}\right)_t$, where Na_t is the concentration of terrestrial Na, Al_{rw} is the concentration of Al in rainwater and $\left(\frac{Na}{Al}\right)_t$ is the common ratio of Na to Al in terrestrial material (dust) assumed to be 0.11 based on values for terrestrial shales (Condie, 1993). Application of this equation to the data from this study indicates that, on average, 98% of the Na found in precipitation samples can be attributed to marine sources. This estimate is close to 100% for most of the year but averages 96% during the winter and autumn when winds have a more northerly (inland) origin. A similar calculation for Mg using Na as a seawater reference with the expected seawater reference line shown in Figure 5 from Keene et al., 1986 indicates that 86% of the Mg deposited to this site on an annual basis is derived from marine sources.

Table 2.4: Average deposition fluxes (kg ha-1 yr-1) of Na, Mg, Ca, and K in different remote coastal and non-coastal ecosystems from other parts of the world in comparison to the study site.

Location	Na	Mg	Ca	K	Reference
Woodland savanna, Belize	9.30	0.28	1.96	3.40	Kellman and Carty, 1986
Changwon forest, Korea	3.50	0.08	7.00	1.40	Lee et al., 2000
Longan forest, China	18.10	1.99	28.00	6.14	Shen et al., 2013
Coper lake, Washington	10.30	1.30	3.50	3.50	Dethier, 1979
Coastal inland, La Selva, Costa Rica	27.8	3.93	5.73	3.20	Eklund and McDowell, 1997
Coastal range, British Columbia	13.20	2.20	7.20	0.90	Zeman, 1975
Ullung Island, korea	18.00	0.33	5.70	1.20	Lee et al., 2000
West Coast South Africa	**56.24**	**6.30**	**15.76**	**2.80**	**This study**

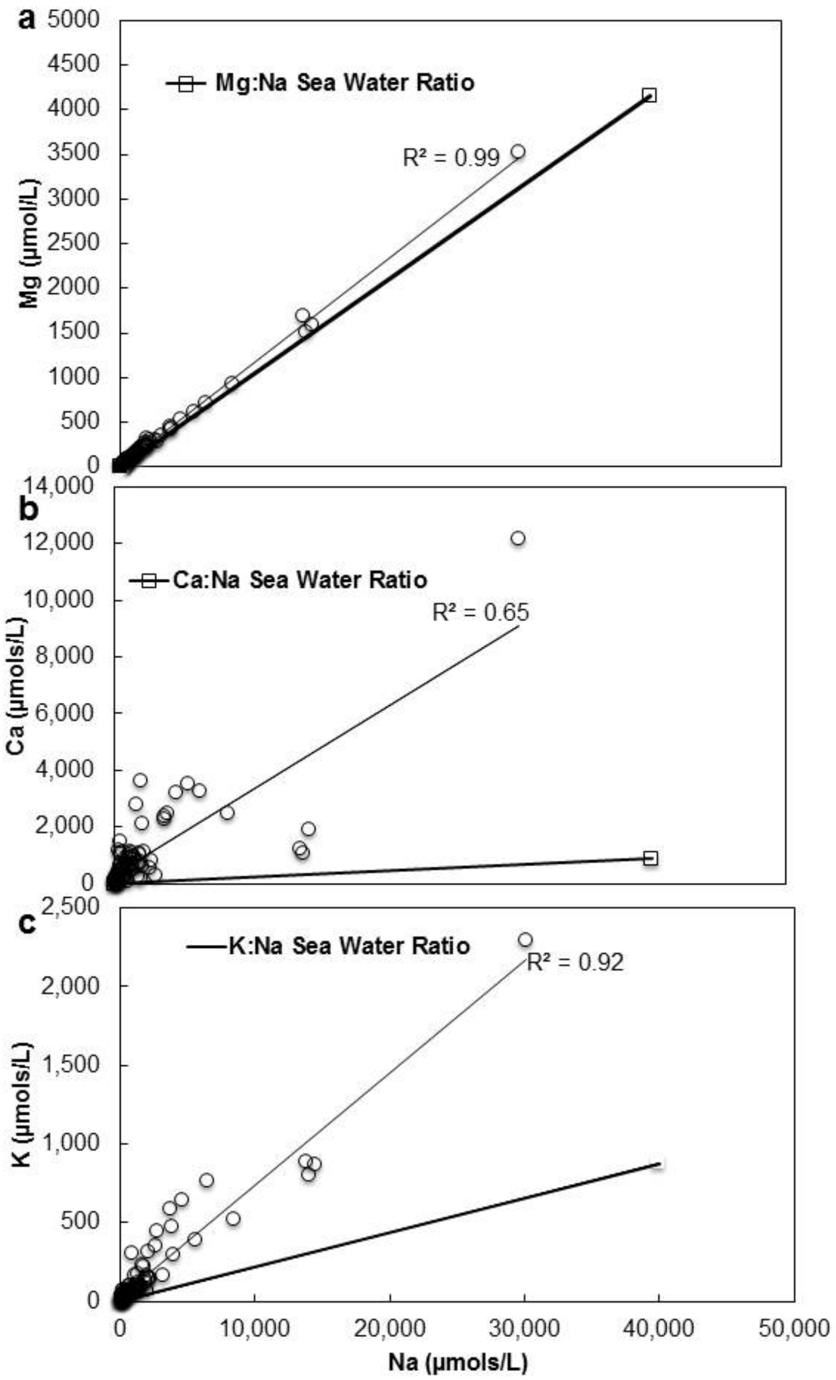

Figure 2.5: Molar ratios of nutrients in precipitation collected at the West Coast National Park. Molar ratios of total element concentration in precipitation including Mg:Na (Panel A), Ca:Na (Panel B), and K:Na (Panel C). Data points include all rainfall collections. The sea water ratio line is determined from an average of sea water concentrations presented in Keene et al., 1986.

In contrast to Mg and Na, there are a number of elements deposited to this site that appear to be more strongly influence by terrestrial sources. The deposition of K and Ca, although higher than many other locations (Table 2.4) around the world, are much larger than would be expected given ratios in marine water as indicated in Figure 5. Using Na as a reference for seawater and the ratios from Keene et al., 1986, the estimated average proportion of K from seawater is 51% and for Ca is 14%. The presence of detectable aluminum in a number of samples is unambiguous evidence of terrestrial dust contributions to deposition at this site and it is likely that dust also contributes to the fluxes of both Ca and K. The ratios of Fe:Na and Al:Na both are higher in autumn and winter compared to spring and summer. In general, mineral aerosols dominate the concentration of tropospheric aerosols in interior regions of South Africa while marine aerosols can be the major contributor to lower atmosphere aerosol loads (Piketh et al., 1999). The seasonal variation in Fe and Al ratios to Na combined with a suggestion of some terrestrial contribution of Na during the winter months, suggest that that winds of northerly origin likely bring terrestrial aerosols off the continent and contribute to nutrient deposition in rainfall during the winter season. It is also possible that local sources of dust contribute to the flux of both K and Ca, which are present in relatively high concentrations in the soils at this site (Abanda et al., 2011)

Nitrogen fluxes at West Coast National Park are low and appear to be relatively little affected by industrial pollution. N deposition fluxes in the urban area around Cape Town (*ca.* 90 km south east) are estimated at 6-13 kg ha^{-1} annum^{-1} (Wilson et al., 2009) in comparison to the measured TN flux of 4.8 kg ha^{-1} yr^{-1} at West Coast National Park. The N flux at the site is similar to a nearby coastal site at Pella (*ca*. 2 kg ha^{-1} yr^{-1}) south of our study site, and located at approximately the same distance from the ocean as this site (Stock and Lewis, 1986b). Both of these flux estimates are lower than those measured in many pristine and disturbed areas around the world (Table 2.5) and in the range of 3.5 kg ha^{-1} yr^{-1} (Phoenix et al., 2006; Ochoa-Hueso et al., 2011) that is heavily influenced by estimates of deposition in marine locations.

Table 2.5: Average deposition fluxes of NO3- and TN (kg ha-1 annum-1) in selected pristine and disturbed areas around the world in comparison to the study site.

Location	NO_3^-	Total N	Reference
La Selva, Costa Rica	2.5	9.6	Eklund and McDowell, 1997
Ullung Island, korea	10.0		Lee et al, 2000
Coastal site, Central Chile	1.8		Prado-Fiedler and Fuenzalida 1996
Coastal site, Southern Chile	1.1	11.0	Weathers et al, 2000
Coastal sage, California		7.8-1	Fenn et al, 2010
Sierra Nevada forest, California		1.2-18.4	Fenn et al, 2008
San Bernadino forest, California		6.1-71.1	Fenn et al, 2008
Chaparral shrubland, California		12-14	Fenn et al, 2010
Grassland forest site, California		6.0	Fenn et al, 2010
Changwon forest, Korea	14.0		Lee et al, 2000
Longan forest, China	4.1	25.2	Shen et al, 2013
Urban area, Thesaloniki, Greece		15.0	Anatolaki and Tsitouridou, 2007
Hawaii and Kauai		17.0	Carrillo et al, 2002
West Coast, South Africa		2	Stock and Lewis, 1986b
West Coast, South Africa	**0.4**	**3.3**	**This study**

Nitrogen deposition fluxes are sensitive to industrial and agricultural activity due to the multiple sources of reactive N released during fossil fuel combustion and fertilizer use (Galloway et al., 2004). For example, If industrial or agricultural N sources were important to total N fluxes at this site, It would be expected that inorganic N fluxes (NO_3^- and NH_4^+) are elevated, but instead NH_4^+ concentrations at West Coast National Park were typically below detection limits and 70.7% of TN deposition was in organic forms; a value that is at the upper limit of the global range

(7-80%; Neff et al., 2002; Cornell et al., 2003; Cornell, 2011) suggesting that non-industrial sources of N dominate N deposition in this region.

Total P deposition, like N, is low relative to global average fluxes (Table 2.6). The average TP flux of 0.16 kg ha^{-1} yr^{-1} is lower than a number of fluxes in similar maritime influenced sites around the world (Table 2.6), and at the lower end of global terrestrial and maritime deposition ranges of 0.07-1.17 and 0.03-0.55 kg ha^{-1} annum^{-1}, respectively (Graham and Duce, 1979; Newman, 1995; Mahowald et al., 2009). Phosphorus deposition can be affected by erosion of soils and subsequent deposition of dust and can become elevated in areas influenced by agricultural activity and some types of industrial activity (Mahowald et al., 2005). The dominant source of TP in rainfall in many remote regions is mineral dust deposition. However, at this site, TP fluxes peak in spring when winds are southerly (onshore) and TP:Na ratios are also higher in spring and summer than during the autumn and winter when winds have a more northerly (offshore) component. Also notable is the relatively high fraction of SRP in TP (43%) compared to an average of less than 20% in global P deposition (Mahowald et al., 2009). These patterns are not easily explained but could be related to elevated nutrients in upwelling seawater associated with the Benguela current (Andrews and Hutchings, 1979). Alternatively, it is possible that some P in rainfall is associated marine sedimentary phosphate deposits found in the region around West Coast National Park (Roux et al., 1989). There were a number of historical P mining operations in the region and exploratory mining activity has increased in the area since 2010. Although P deposition rates are currently low relative to global averages, it is possible that this will change in the future if phosphate mining activity increases in the region.

Table 2.6: Average deposition fluxes of SRP and TP (kg ha^{-1} $annum^{-1}$) in selected pristine sites around the world in comparison to the study site.

Location	SRP	TP	Reference
Caura river watershed, Venezuela	0.31	0.51	Lewis Jr 1986
Mountanous watershed, Plynlimon, UK	0.17		Neal, et al, 2003
Chamela forest Biological Station, Pacific coast, Mexico	0.16		Campo et al, 2001
Turrialba, Florencia forest Costa Rica	0.09	0.20	Hendry et al, 1984
Waksmundzka valley,Tatra mountains Poland	0.05		Grodzinska-Jurczak I995
Fir, Pine and oak forest,Central Netherlands	0.04		Vanek and Draaijers I994
Hitsukura, Ashiu Experimental Forest, Japan	0.06	0.08	Tsukuda et al, 2005
Upland lake catchment, Antrim Plateau, Northern Ireland.	0.11	0.14	Gibson et al, 1995
Coastal inland, Chesapeake Bay, USA	0.21		Jordan et al, 1995
Mediterranean basin, Crete Island, Finokalia	0.19		Markaki et al, 2003
Mediterranean basin, Israeli coast	0.09		Herut et al, 1999
Windward coastal tower		0.03	Graham and Duce, 1981
Hawaiian Island Chain	0.27		Cundiff, 2001
West Coast, South Africa		1.0	Witkowski and Mitchell, 1987
West Coast, South Africa	**0.06**	**0.11**	**This study**

Taken as a whole, the results from this study suggest that both marine and terrestrial nutrients are transported into pericoastal terrestrial environments and may provide an important source of nutrients to the coastal ecosystems that develop on very low nutrient content coastal sand dunes (Mucina and Rutherford, 2006). The continued input of these nutrients to these aoelian sands over millennia and a relative lack of fire (Kruger, 1983) may have contributed to the conversion of nutrient impoverished aeolian sand into the relatively fertile sands associated with the Strandveld (coastal) vegetation type. Deposition of N and P in the region is low at present but with an expansion of urban areas, agricultural activities, and the potential for regional phosphate mining, deposition of these elements may increase in the future.

2.6 References

Abanda PA, Compton JS, Hannigan RE. 2011. Soil nutrient content, above-ground biomass and litter in a semi-arid shrubland, South Africa. Geoderma 164, 128-137

Anatolaki, Ch., Tsitouridou, R., 2007. Relationship between acidity and ionic composition of wet precipitation: A two years study at an urban site, Thessaloniki, Greece. Atmospheric Research 92, 100–113.

Anatolaki, Ch., Tsitouridou, R., 2007. Relationship between acidity and ionic composition of wet precipitation: A two years study at an urban site, Thessaloniki, Greece. Atmospheric Research 92, 100–113.

Andrews, W.R.H., Hutchings, L., 1979. Upwelling in the southern benguela current. Progress in Oceanography 9, 1-81.

Archer, C.L., Jacobson, M.Z., 2005. Evaluation of global wind power. Journal of Geophysical Research 110 (D12), D12110.

Bergametti, G., Remoudaki, E., Losno, R., Steiner, E., Chatenet, B., Buat-Menard, P., 1992. Source, transport and deposition of atmospheric phosphorus over the Northwestern Mediterranean. Journal of Atmospheric Chemistry 14, 501–513.

Brown, G., Mitchell, D.T., Stock, W.D., 1984. Atmospheric deposition of phosphorus in a coastal fynbos ecosystem in the south western cape South Africa. Journal of Ecology 72 (2), 547-551

Campo, J., Maass, M., Jarammillo, V.J., Martinez-Yrizar, A., Sarukhan, J., 2001. Phosphorus cycling in a Mexican tropical dry forest ecosystem. Biogeochemistry 53, 161–179.

Cape, J.N., Sheppard, L.J., Crossley, van Dijk, A.,N., Tang, Y.S., 2010. Experimental field estimation of organic nitrogen formation in tree canopies. Environmental Pollution 158, 2926-2933

Carrillo, J. H., Hastings, M.G., Sigman, D.M., 2002. Atmospheric deposition of inorganic and organic nitrogen and base cations in Hawaii. Global Biogeochemical Cycles. Vol. 16, NO. 4, 1076, doi: 10.1029/2002GB001892

Condie K.C., 1993. Chemical composition and evolution of the upper continental crust, contrasting results from surface samples and shales. Chemical Geology 104, 1-37.

Cornell, S.E., 2011. Atmospheric nitrogen deposition: Revisiting the question of the importance of the organic component. Environmental Pollution 159, 2214-2222.

Cornell, S.E., Jickells, T.D., Cape, J.N., Rowland, A.P., Duce, R.A., 2003. Organic deposition on land and coastal environments: a review of methods and data. Atmospheric Environment 37, 2173–2191.

Cowling, R.M., Knight , A.T., Privett, S.D.J., Sharma G., 2009. Invest in opportunity, not inventory of hotspots. Conservation Biology 24 (2), 633-635.

Cramer, M.D., Hawkins, H.J., 2009. A physiological mechanism for the formation of root casts. Palaeogeography, Palaeoclimatology, Palaeoecology 274, 125–133.

Cundiff, A., 2001. BerkeleyPhosphorus Deposition to Hawaii via Precipitation. University of California. http://www.soest.hawaii.edu/PubServices/REU_2000_2001/Cundiff.pdf

Derry, L.A., Chadwick, O.A., 2007. Contributions from earth's atmosphere to soil. Elements 3, 333–338.

Dethier, D.P., 1979. Atmospheric contributions to stream water chemistry in the Northern Cascade Range, Washington. Water Resources research 15(4), 787-794.

Doanea, T.A., Horwátha, W.R., 2003. Spectrophotometric determination of nitrate with a single reagent. Analytical Letters 36 (12), 2713-2722.

Doyle, A., Weintraub, M.N., Schimel, J.P., 2004. Persulfate digestion and simultaneous colorimetric analysis of carbon and nitrogen in Soil Extracts. Soil science society of America Journal 68 (2), 669-676.

Eklund, T.J., Dowell, M.C., 1997. Seasonal variation of tropical precipitation chemistry-Costa Rica. Atmospheric environment 31 (23), 3903-3910.

Fenn, M.E., Allen, E.B., Weiss, S.B., Jovan, S., Geiser, L.H., Tonnesen, G.S., Johnson, R.F., Rao, L.E., Gimeno, B.S., Yuani, F., Meixner, T., Bytnerowicz, A., 2010. Nitrogen critical loads and management alternatives for N-impacted ecosystems in California. Journal of Environmental Management 91, 2404-2423.

Fenn, M.E., Jovan, S., Yuan, S., Geiser, L., Meixner, T., Gimeno, B.S., 2008. Empirical and Simulated critical loads for nitrogen deposition in California mixed conifer forests. Environmental pollution 155, 492-511.

Franceschini, G., Compton, J.S., 2006. Holocene evolution of the sixteen mile beach, Western Cape, South Africa. Journal of Coastal Research 22 (5), 1158–1166.

Freydier, R., Dupré, B., Dandurand, J-L., Fortune, J-P., Sigha-Nkamdjou. L., Trace elements and major species in precipitation at African stations: concentrations and sources. Société géologique de France Éditeur, Paris, 173(2), 129-146.

Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.H., Seitzinger, S.P., Asner, G.P., Cleveland, C., Green, P., Holland, E., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A., Vörösmarty, C., 2004. Nitrogen cycles: past, present, and future. Biogeochemistry 70, 153-226.

Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., Sutton, M.A., 2008. Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions. Science 320, 889-892.

Gibson, C.E., Wu, Y., Pinkerton, D., 1995. Substance budgets of an upland catchment: the significance of atmospheric phosphorus inputs. Freshwater Biology 33, 385–392.

Goldblatt, P., Manning, J., 2000. Cape plants: a conspectus of the Cape flora of South Africa. Cape Town, pp. 743.

Goudie, A.S., Middleton, N.J., 2001. Saharan dust storms: nature and consequences. Earth-Science Reviews 56,179–204

Graham, W.F., Duce, R.A., 1979. Graham et al, 1979. The seas as a source of atmospheric phosphorus. Marine chemistry 7, 325–342

Graham, W.F., Duce, R.A., 1981. The atmospheric transport of phosphorus to the western North Atlantic. Atmospheric Environment 16 (5), 1089-1097.

Grodzinska-Jurczak, M., 1995. Acidity of atmospheric precipitation in Polish Tatra Mountains. Water, Air, and Soil Pollution 85, 773–778.

Hendry, C.D., Berish, C.W., Edgerton, E.S., 1984. Precipitation chemistry of Turrialba, Costa Rica. Water Resources Research 20, 1677–1684.

Herut B., Krom, M.D., Pan, G., Mortimer, R., 1999. Atmospheric input of nitrogen and phosphorus to the southeast Mediterranean. Limnology and Oceanography. 44 (7), 1683-1692.

Jordan, T.E., Correll, D.L., Weller, D.E., Goff, N.M., 1995. Temporal variation in precipitation chemistry on the shore of the Chesapeake Bay. Water, Air, and Soil Pollution 83, 263–284.

Keene, W.C., Pszenny, A.A.P., Galloway, J. Hawley, M.E., 1986. Sea-salt corrections and interpretations of constituent ratios in marine precipitation. Journal of Geophysical Research, 91, 6647-6658.

Keller, W.B., Heneberry, J.H., Dixit, S.S., 2003. Decreased acid deposition and the chemical recovery of Killarney, Ontario, Lakes. Ambio 32 (3), 183-189.

Kellman, M., Carty, A., 1986. Magnitude of nutrient influxes from atmospheric sources to a Central American Pinus Caribbean woodland. Journal of Applied Ecology 23 (1), 211-226.

Kennedy, M.J., Chadwick, O.A., Vitousek, P. M., Derry, L. A., Hendricks, D. M., 1998. Changing sources of base cations during ecosystem development, Hawaiian islands. Geology 26, 1015-1018.

Kruger, F.J. 1983., Plant community diversity and dynamics in relation to fire. In: Kruger F.J. (Eds.), Mediterranean-type ecosystems. The role of nutrients, Springer, New York, pp. 446-472.

Lee, B.K., Hong, S.H., Lee, D.S., 2000. Chemical composition of precipitation and wet deposition of major ions on the Korean Peninsula. Atmospheric environment 34, 563-575.

Lewis Jr., W.M., 1986. Nitrogen and phosphorus runoff losses from a nutrient-poor tropical moist forest. Ecology 67, 1275–1282.

Likens, G.E., Driscoll, C.T., Buso, D.C., 1996. Long term effects of acid rain: Response and recovery of a forest ecosystem. Science 272, 244–245.

Losno R., Bergametti G., Carlier P., Mouvier G., 1991. Major ions in marine rainwater with attention to sources of alkaline and acidic species. Atmospheric Environment 25 (A), 763-770.

Mahowald, N., Jickells, T.D., Baker, A.R., Artaxo, P., Benitez-Nelson, C.R., Bergametti, G., Bond, T.C., Chen, Y., Cohen, D.D., Herut, B., Kubilay, N., Losno, R., Luo, C., Maenhaut, W., McGee, K.A., Okin, G.S., Siefert,R.L., Tsukuda, S., 2009. Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts. Global Biogeochemical Cycles doi:10.1029:2008GB003240.

Mahowald, N.M., Artaxo, P., Baker, A.R., Jickells, T.D., Okin, G.S., Randerson, J.T., Townsend, A.R., 2005. Impacts of biomass burning emissions and land use change on Amazonian atmospheric phosphorus cycling and deposition. Global Biogeochemical Cycles 19, 1944-9224.

Markaki, Z., Loÿe-Pilot, M.D., Violaki, K., Benyahya, L., Mihalopoulos, N., 2010. Variability of atmospheric deposition of dissolved nitrogen and phosphorus in the Mediterranean and possible link to the anomalous seawater N:P ratio. Marine Chemistry 120,187-194.

Markaki, Z., Oikonomou ,K., Kocak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., Mihalopoulo, N., 2003. Atmospheric deposition of inorganic phosphorus in the levantine basin, eatern mediterranean. Limnology and Oceanography 48 (4), 1557-1568.

Matson, P.A., Parton, W.J., Power, A.G., Swift, M.J., 1997. Agricultural Intensification and Ecosystem Properties. Science 277, 504-509.

Motomizu, S., Wakimoto, T., Toi, K., 1983. Spectrophotometric Determination of Phosphate in River Waters with Molybdate and Malachite Green. Analyst. 108, 361-367

Mucina, L., Rutherford, M.C., 2006. The Vegetation of South Africa, Lesotho and Swaziland. SANBI, Pretoria pp. 804.

Neal, C., Reynolds, B., Neal, M., Hughes, S., Wickham, H., Hill, L., Rowland, P., Pugh, B., 2003. Soluble reactive phosphorus levels in rainfall, cloud water, throughfall, stemflow, soil waters, stream waters and groundwaters for the Upper River Severn area, Plynlimon, mid Wales. The Science of the Total Environment. 314–316, 99–120.

Neff, C.N., Ballantyne, A.P., Farmer, G.L., Mahowald, N.M., Conroy J.L., Landry,C.C., Overpeck, J.T., Painter, T.H., Lawrence, C.R., Reynolds, R.L.,

2008. Increasing aeolian dust deposition in the western United States linked to human activity. Nature Geoscience 1, 189-195.

Neff, C.N., McDowell, W.H., Russell, K.M., 2002. The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle? Biogeochemistry 58, 99–136.

Négrel, P., Roy, S., 1998. Chemistry of rainwater in the Massif Central (France): a strontium isotope and major element study. Applied Geochemistry, 13(9), 941-952.

Newman, E.I., 1995. Phosphorus input in terrestrial ecosystems. Journal of Ecology 83, 713-726.

Ochoa-Hueso, R., Allen, E.B., Branquinho, C., Cruz, C., Dias, T., Fenn, ME., Manrique, E., Pérez-Corona, M.E., Sheppard, L.J., Stock, W.D., 2011. Nitrogen deposition effects on mediterranean-type ecosystems, an ecological assessment. Environmental pollution doi:10.1016:j.envpol.2010.12.019.

Phoenix, G.K., Hicks, W.K., Cinderby, S., Kuylenstierna, J.C.I., Stock W.D., Dentener, F.J., Giller, K.E., Austin, A.T., Lefroy, R.D.B., Gimeno, B.S., Ashmore, M.R., Ineson, P., 2006. Atmospheric nitrogen deposition in world biodiversity hotspots-the need for a greater global perspective in assessing N deposition impacts. Global change Biology 12, 470–476.

Piketh, S.J., H.J. Annegarn, P.D. Tyson., 1999. Lower tropospheric aerosol loadings over South Africa: The relative contribution of Aeolian dust, industrial emissions, and biomass burning. Journal of Geophysical Research, 104(D1), 1597-1607.

Prado-Fiedler, R., Fuenzalida, A., 1996. Wet and dry deposition of nitrogen compounds in the southeast Pacific coast: Montemar, central Chile. Journal of Geophysical

Rodá, F., Avila, A., Rodrigo, A., 2002. Nitrogen deposition in the Mediterranean forests. Environmental pollution 118, 205–213

Roux E.H., De Jager, D.H., Du Plooy, J.H., Nicotra, A., Van Der Linde, G.J., De Waal, P., 1989. Phosphate in South Africa. Journal of South Africa Institute of Mineralogy and Metallurgy. 89(5), 129-139.

Shen, W., Ren, H., Janerette, D., Hui,D., Ren, H., 2013. Atmospheric deposition and canopy exchanges of anions and cations in two plantations under acid rain influence. Atmospheric Environment 64, 242-250.

Soderberg, K., Compton, J.S., 2007. Dust as a nutrient source for fynbos ecosystems, South Africa. Ecosystems 10, 550–561.

South Africa National Parks, 2006. West coast National Park, park management plant, October, SANParks, Pretoria, p. 4.

South African Weather Bureau (SAWB). 1986. Climate of South Africa. Climate Statistics up to 1984. WB40. Department of Environmental Affairs, Pretoria.

Stock, W.D., Lewis, O.A.M., 1986. Atmospheric input of nitrogen to a coastal fynbos ecosystem of the south-western Cape Province, South Africa. South African Journal of Botany 52 (4), 273-276.

Tinley, K.L. 1985. Coastal dunes of South Africa. South African National Scientific Programmes, Council for Scientific and Industrial Research, Pretoria 109, p. 300.

Tsukuda, S., Sugiyam, M., Harit, Y., Nishimura, K. 2005. Atmospheric bulk deposition of soluble phosphorus in Ashiu Experimental Forest, central Japan:

source apportionment and sample contamination problem. Atmospheric Environment 39, 823–836.

Vanek, R., Draaijers, G.P.J., 1994. Estimates of atmospheric deposition and canopy exchange for three common tree species in the Netherlands. Water, Air, and Soil Pollution 73, 61-82.

Vicars, W.C., Sickman, J.O., Ziemann, P.J., 2010. Atmospheric phosphorus deposition at a montane site: Size distribution, effects of wildfire, and ecological implications. Atmospheric Environment 44, 2813-2821.

Weatherburn, M.W. 1967. Phenol-hypochlorite reaction for determination of ammonia. Analytical chemistry 39 (8), 971–974.

Weathers, K.C., Lovett, G.M., Likens, G.E., Caraco, N.F.M., 2000. Cloudwater inputs of nitrogen to forest ecosystems in southern Chile: forms, fluxes, and sources. Ecosystems 3, 590–595

Weathers, K.C., Lovett, G.M., Likens, G.E., Caraco, N.F.M., 2000. Cloudwater inputs of nitrogen to forest ecosystems in southern Chile: forms, fluxes, and sources. Ecosystems 3, 590–595

Whipkey, C.E., Capo, R.C., Chadwick, O.A., Stewart, B.W., 2000. The importance of sea spray to the cation budget of a coastal Hawaiian soil: a strontium isotope approach. Chemical Geology 168, 37–48

Wilson, D., Stock, W.D., Hedderson, T., 2009. Historical nitrogen content of bryophyte tissue as an indicator on increased nitrogen deposition in the cape metropolitan area-South Africa. Environmental pollution 157, 938–945.

Wind finder - http://www.windfinder.com/windstats/windstatistic_dassen_island_yzerfontein.htm

Witkowski, E.T.F., Mitchell, D.T., 1987. Variation in Soil phosphorus in the fynbos biome, South Africa. Journal of Ecology 75, 1159-1171

Zeman, L.J., 1975. Hydrochemical balance of a British Columbia Mountainous watershed. Catena 2, 81-94.

3 Contribution of marine derived nutrient deposition to nutrient budgets of coastal Strandveld vegetation (South Africa)

3.1 Abstract

The soils associated with coastal Strandveld vegetation in the Cape Floristic Region (CFR, South Africa) are relatively nutrient rich in comparison to the parent aeolian marine-derived sands and support a species-rich relatively dense vegetation. I hypothesized that ecosystem nutrient dynamics, particularly in soil and plant tissues, are strongly influenced by marine-derived nutrient deposition. I collected soil and plant material (green and senesced) from 8 sites along a 17 km transect from the ocean inland within the West Coast National Park and analyzed these for N, P, K, Ca, Mg, Na, Mn and Fe. Nutrient contents in the senesced tissue were used to estimate annual plant nutrient demand. Nutrient concentrations in soils and green tissue were compared with rates of wet deposition and with soil and foliar concentrations in the CFR.. Data from CFR allowed for nutritional comparison between this site and other CFR vegetation types, which grow under similar climatic conditions. Concentrations of P, K, Ca, Mg, Na in the soil were higher in the Strandveld compared to CFR. With the exception of K, concentrations of nutrients were also higher in the green leaf tissue of the Strandveld compared to other regions of the CFR. Soil base cations concentrations were high, possibly reflecting a strong influence of marine derived deposition. Soil nutrients and plant tissue nutrients were higher in the Strandveld than those in the CFR. Nutrients associated with marine sources (Mg, Na and Ca), and which were high in soils in the Strandveld were also elevated in the green leaf tissues of plants in this site. Based on litterfall, atmospheric deposition could potentially supply 36% of N, 64% of P and over 100%

of the annual demand for K and Ca. These results suggest a strong marine influence in the supply of these nutrients to the Strandveld soils and vegetation and identify this vegetation as being a product of sustained nutrient deposition over prolonged periods.

3.2 Introduction

The “Strandveld” coastal vegetation occurs in relatively small pockets within 50 km of the ocean and is embedded within other vegetation components of the Cape Floristic Region (CFR). Within the Strandveld vegetation, there are different forms recognized (Mucina and Rutherford, 2006) that are associated with sandy plains, dunes, limestones, and granite-derived soils (Abanda et al., 2011). Strandveld is floristically distinct from the adjacent vegetation. A narrow band of low stature (< 1 m) Cape Seashore vegetation sometimes occurs coastwards while inland, Fynbos vegetation types are common. In contrast to Fynbos, Strandveld lacks Proteaceae (Mucina and Rutherford, 2006), which is a family with several adaptations for nutrient poor soils, especially soils lacking P (e.g. Shane et al., 2004). Strandveld is a relatively dense shrubland 1 - 2 m in height that comprises sclerophyllous shrubs and low trees (e.g. *Euclea racemosa*, *Pterocelastrus tricuspidatus*, *Searsia* spp.), as well as drought-deciduous shrubs (e.g. *Lycium* spp., *Zygophyllum morgsana*) (Cowling et al., 1999). This turnover of species between Fynbos and Strandveld has been ascribed to the soil characteristics (Mucina and Rutherford, 2006). Soils of Strandveld vegetation, despite having low clay (<1%) and high sand contents (*ca.* 98%) and small amounts of soil organic matter (1.4 – 2.2%), have the highest total P (0.338 – 0.422 mg g^{-1}) and available P (0.068 – 0.072 mg g^{-1} Bray II P) in the CFR (Table 3.1). The Renosterveld vegetation of the CFR, which occupies shale-derived soils, has lower P

(0.159 mg g^{-1}) and available P (0.004 mg g^{-1} Bray II P) despite having much less sand in the soil (28%) (Table 3.1). The relatively nutrient-rich status of the Strandveld is thus at odds with the high sand content in these soils.

Table 3.1: Soil N and P concentrations, % clay, organic matter and sand measured in different studies carried out in various soil types of the Fynbos biome.

Soil type	Total N (mg g^{-1})	Total P (mg g^{-1})	Bray II P (mg g^{-1})	% clay	% organic matter	% sand	Source
Strandveld	1.3		0.07				1
		0.34-0.42	0.068-0.072	<1%	1.8	18-40	2
				<1%		96-98	3
Renosterveld		0.16	0.04		7.9	28	2
Coastal dune	0.084		0.0015				1
Acid sand fynbos	0.5		0.0006				1
Calcareous fynbos	1.3		0.004				1
Lowland fynbos		0.029-0.43	0.0029-0.0083	<1-2%	2.4-10	50-76	2
Mountain fynbos		0.012-0.18	0.001-0.0038	<1-4%	1.4-12	16-34	2

[1] Cramer and Hawkins, 2009, [2] Witkowski and Mitchel, 1987, [3] Abanda et al., 2011

Although the underlying geology of Strandveld varies, much of this vegetation occurs on marine-derived aeolian sands (Abanda et al., 2011). In contrast to the Strandveld sands, the fore-dune nutrient contents of recently deposited sands may be very low (Cramer and Hawkins, 2009). For example, these authors reported 15-, 4.4-, 4-fold higher total N, available P and K concentrations, respectively, in Strandveld soils than in adjacent coastal dune sands. While this may suggest an effect of the underlying granitic bedrock that is rich in P and K or even presence of phosphorite rocks, deposition and accumulation of marine-derived sand over long periods of time makes this less likely. The coastal dune sands also had a higher pH than the Strandveld soils whose pH was in turn higher than other fynbos soils. Electrical conductivities of Strandveld soils and coastal dune sands were, however, similar due to high cation concentrations. These points, and the fact that organic C was 1.2% in Strandveld soils, may indicate that organic C and nutrients accumulate in these sands during pedogenesis. This accumulation of nutrients is possibly similar to the accumulation of N and available P in the Franz Joseph chronosequence soils (Menge et al., 2012). In that system available P is derived from weathering of rock and P-deposition while N is derived from both N_2-fixation and N-deposition (Menge et al., 2012). The low initial nutrient content of aeolian dunes rules out this possibility in Strandveld, and instead suggests potential marine sources for the nutrients that accumulate in the soils.

There is some evidence from prior work that deposition of marine derived aerosols provides ecologically significant contributions of P (0.2 kg ha^{-1} a^{-1}) and N (2 kg ha^{-1} a^{-1}) to lowland coastal Fynbos vegetation within the CFR (Brown et al., 1984; Stock and Lewis, 1986b). Additional evidence for the importance of marine-derived deposition in the area is that water in inland pans close to Strandveld vegetation has molar ratios of Cl to Na and Mg that indicate a predominantly marine source for these ions (Smith and Compton, 2004). The high cation content of Strandveld sands has also been attributed to marine aerosols (Abanda et al., 2011), although wind-blown mineral dust may provide additional Ca, K, P and Fe (Soderberg and Compton, 2007). Thus deposition in the region is likely to be derived predominantly from marine sources, but with some terrigenous contributions. Collectively, these prior studies and observations of soil nutrient characteristics in the Strandveld raise the question as to whether marine aerosols are an important component of the nutrient supply to the Strandveld vegetation.

The nutrient content of ecosystems depends on the balance between inputs and losses from the system. Ecosystem losses may include herbivory, fire-volatilization and displacement of ash, volatilization of nutrients, leaching/runoff of nutrients and tissue senescence (Chapin et al., 2002). In the Strandveld the intensity of herbivory is relatively low (Radloff 2008) and fires are relatively infrequent (Kruger 1983). Nutrient losses from plants are therefore mainly through plant tissue senescence, including both above- and below-ground tissue senescence. Although belowground senescence is likely to be important, this is difficult to assess. The nutrient loss in leaf litter depends both on the volume of litter and the nutrient concentration of the litter. The nutrient content of litter is determined by the capacity of the plant for resorption of different nutrients, which varies strongly between nutrients and between species (Aerts, 1996). Nutrients that are resorbed prior to litterfall are directly available for further growth, whereas nutrients lost in litterfall need to be replaced from the soil. Recycling of nutrient in litterfall requires decomposition over years (Staaf and Berg, 1982) with potential losses from the ecosystem. Thus, in the short-term, nutrient in leaf litter constitutes a loss from the plant (Castle and Neff 2009). In the absence of substantial biomass increase, litterfall can also be used as a measure of the net primary productivity (Gower et al., 1999). In the absence of frequent fires and intense herbivory, the extent to which the annual nutrient demands of individual plants can be satisfied by atmospheric nutrient deposition is thus likely to vary with the amount of nutrient lost in leaf litter, although this must necessarily underestimate the actual nutrient demand of the plant.

In this study, I aimed to compare marine aerosol deposition with soil and leaf chemistry in the active dune cordon environment of the Langebaan dune Strandveld in west coast South Africa (Fig. 2.1). This section of the west coast Strandveld is characterized by a high sedimentation of windblown marine derived calcareous sand. I hypothesized that marine nutrient deposition forms a significant fraction of the nutrient loss through leaf litter. Consequently, over the 1 million years of sand deposition (Abanda et al, 2011), this source of nutrients may have resulted in soil and vegetation characteristics that are associated with the mainly marine origins of this deposition. I also compared the soil and foliar nutrient compositions of Strandveld vegetation in the West Coast National Park to regional CFR values and also to the nutrient composition of wet deposition measured at the site to estimate a possible role of atmospheric deposition. I also used litterfall and the nutrient composition of the litter to indicate nutrient demand in this ecosystem.

3.3 Methods

3.3.1 Study site

The study was carried out in the West Coast national park (33°13'52.26"S, 18°09'50.96"E), approximately 100 km northwest of Cape Town. The study site was along a 17 km active dune cordon running inland from the coast in a northerly direction. The geology of the area consists of basement rocks of the Malmesbury group shale intruded by granite and overlaid by loose aeolian sands that are marine-derived and contain a large proportion of calcareous material (Franceschini and Compton, 2006). The main vegetation type in the area is the Langebaan dune Strandveld, which dominates most of the deep calcareous sands and consists mainly of sclerophyllous shrubs and annual herbs (Mucina and Rutherford, 2006). The area near the ocean has been extensively invaded by a fast growing alien N_2-fixing *Acacia cyclops* which co-occurs with the indigenous *Chrysanthemoides monilifera*. Three *Searsia* spp. (*S. lucida, S. glauca and S. laevigata*) dominate inland vegetation. Other species common within the study site include *Agathosma imbricata, Metalasia muricata* and a native N_2-fixing species, *Morella cordifolia*.

These eight species were selected for green leaf and litterfall sampling. More details on the study site are provided in Chapter 2.

3.3.2 Sampling

I identified 8 different sampling locations within the study site separated from each other by a distance of up to 4.3 km. In each location, I established a sampling plot measuring 50 m^2 in which at least three of the selected study species were present. In each plot, I collected litterfall material every month for 12 months (Jan-Dec 2011), and green leaf and soil samples once in Nov 2011. At least three replicates of each of the 8 study species, distributed variably across the 8 locations, were randomly selected and tagged for repeat sampling. Litter traps made from a nylon mesh (0.2 mm x 0.2 mm) measuring 50 x 50 x 10 cm were placed under each of the selected shrubs at the beginning of the experiment. Mature fully expanded green leaves were collected from each plant. Three replicate soil surface cores (0-10 cm depth) were taken from each sampling location using a soil auger. Much of the soils at this depth were loose sand with no established distinct soil horizons. Samples were stored in plastic bags at 4^{o}C prior to analysis.

3.3.3 Nutrient measurements

Leaves were washed prior to analysis by shaking them with Millipore water in pre-cleaned zipper bags and rinsing them again with Millipore water using a squirt bottle. Leaf and soil samples were oven dried at 60^{o}C for 48 h. The total mass of collected leaf litter was recorded monthly. Leaf litter and green tissue collected in November 2011 were milled to fine powder in a Wiley mill using a 0.5 mm mesh (Arthur H Thomas, Philadelphia, PA, USA) for chemical analysis. Soils were sieved (2 mm x 2 mm), and a sub-sample ground in a mortar for chemical analysis. Vegetation material was chemically digested by adding 0.25 mg of ground sample to 6 ml of 4M HNO_3 and 2 ml of 30% H_2O_2 and then heated by microwave digestion (CEM Mars Xpress, North Carolina, USA). Soil samples were chemically digested using a 3 acid (H_2O_2 and HF, HCl, HNO_3) microwave-assisted digestion (Castle and Neff 2009). All samples were analyzed for elemental composition by Inductively Coupled Plasma Optical Emissions Spectrometry/Mass Spectrometry (ICP-OES/ICP-MS) at the Environmental biochemistry laboratory in the Geological sciences department of the University of Colorado, Boulder Two bedrock standards (Silver Plume Granodiorite and Hawaiian Basalt) were included in each extraction simultaneously with the sample to check for any analytical uncertainty. Analyses of the two yielded an estimated error of <8% for all the elements.

3.3.4 Other data sources

Data on atmospheric nutrient deposition was obtained from a companion study at this field site aimed at establishing the sources, amounts and forms of atmospheric nutrient deposition in the area (Chapter 2). In that study, monthly wet deposition of total N, total P, Na, Mg, Ca, K, Fe and Mn was measured at each of the 8 locations used here. These measurements were summed across the 12 month sampling period to obtain the annual deposition rate. This deposition rate was used to evaluate the potential contribution of marine deposition to plant nutrient demands by comparing it with the annual nutrient demands of the various plant species.

For comparison with data from the Strandveld, soil and foliar nutrient data from 98 sites within the CFR and 14 families (Aizoaceae, Asteraceae, Campanulaceae, Cyperaceae, Ericaceae, Scrophulariaceae, Iridaceae, Orchidaceae, Poaceae, Restionaceae, Rutaceae, Proteaceae and Fabaceae) were obtained from Cramer, Britton and Verboom (unpublished) and averaged. In this survey soils were sampled to 30 cm depth, air dried and sieved (1 mm mesh) and nutrients (total N, total P, Na, Mg, Ca, K, Fe and Mn) measured as described in Cramer et al., (2010). The youngest fully expanded leaves (collected Sep to Nov 2010) were collected, oven dried at 60°C for 48 h and then analyzed using ICP-MS after a nitric acid digestion (Cramer et al., 2010).

3.4 Results

Annual wet depositional fluxes of cations were much higher than deposition rates of other elements, with deposition of Na being highest, followed by Ca, Mg and K (Table 3.2). Rates of N and P deposition were similar to those reported for Lowland Fynbos (Brown et al., 1984; Stock and Lewis, 1986b). Molar ratios to Na for all nutrients in deposition were low (Table 3.3), indicating a dominance of Na in deposition.

Table 3.2: Deposition fluxes (mean ± SE) measured in rain water within the study site and summed between Jan and Dec 2011, soil nutrient concentrations (mg g^{-1}, mean ± SE) measured in the Strandveld site and compared with those measured in various locations within the CFR and in south west Australia. Data from the Strandveld were obtained in Nov 2011 (n = number of sites).

	Deposition flux	Soils	
Nutrient	Strandveld (mg m^{-2} $annum^{-1}$)	Strandveld (mg g^{-1})	CFR (mg g^{-1})
Total N	250 ± 51	0.21 ± 0.04	1.30 ± 0.06
Total P	11 ± 1.7	1.50 ± 0.05	0.47 ± 0.12
K	282 ± 45	0.15 ± 0.00	0.10 ± 0.02
Ca	1576 ± 181	53.0 ± 2.9	1.4 ± 0.2
Mg	630 ± 120	1.10 ± 0.09	0.31 ± 0.03
Na	5624 ± 1182	0.54 ± 0.03	0.07 ± 0.03
Mn	2.3 ± 0.43	0.006 ± 0.001	0.087 ± 0.010
Fe	3.4 ±	0.5 ± 0.1	6.0 ± 0.5
Total N:Total P	22.7	0.14	2.76
n	8	8	97
Source	Chapter 2	This study	Cramer Britton and Verboom (unpublished)

Table 3.3: Molar ratios for total N, (TN) total P (TP), K, Ca, Na, Mg, Mn and Fe to Na in deposition, soil and foliar tissue sampled within the Strandveld study area (mean ± SE). Deposition sampling was from Jan-Dec 2011 while soil and foliar sampling was in Nov 2011.

Molar ratio	Deposition	Soil	Foliar	
			Non-fixing	Fabaceae
TN:Na	0.049±0.0063	0.75±0.14	2.2±0.33	1.6±0.60
TP:Na	0.0051±0.0007	4.1±0.24	0.80±0.10	0.11±0.030
K:Na	0.10±0.0070	0.56±0.055	2.2±0.28	0.42±0.13
Ca:Na	0.76±0.064	178±3.1	17±2.1	8.2±3.7
Mg:Na	0.13±0.0014	2.7±0.12	1.4±0.14	0.54±0.17
Mn:Na	0.0011±0.0001	0.034±0.0046	0.010±0.0018	0.029±0.015
Fe:Na	0.0020±0.0002	3.0±0.45	0.18±0.037	0.073±0.030
n	8	8	6	2

Concentrations of total P, Ca, Mg and Na were higher in Strandveld soils than in the surveyed CFR soils (Table 3.2). In contrast, total N and Fe were low compared to the CFR soils. The exceptionally high Ca:Na ratios (Table 3.3) in the soil confirm the marine origins of these aeolian sands, which contain calcareous shell fragments. A close relationship between molar ratios in deposition and in seawater was also established in Chapter 2. The molar ratios to Na in soils were higher than in deposition.

Non-N_2-fixing foliar concentrations of P, Ca and Na were 2.2-, 2.8- and 1.6-fold higher, respectively, in the Strandveld species compared to the CFR survey (Table 3.4). In contrast foliar K was 3.5-fold lower than in CFR (Table 3.4). Strandveld putatitve N_2-fixers and CFR Fabaceae were relatively similar except that foliar N was 1.6-fold higher in the CFR survey than in the Strandveld, and that K was lower in the Strandveld than the CFR (4.6-fold).

Table 3.4: Foliar concentrations (mg g^{-1}; mean ± SE) for total N, (TN) total P (TP), K, Ca, Na, Mg, Mn and Fe measured in non-N_2-fixing and putative N_2-fixing species in the Strandveld (Nov 2011) and CFR. Replication (n) is shown per species and per family in parentheses. For Strandveld Fabacaeae and Myricaceae were considered to be putatively N_2 fixing, although it is unknown whether the species are actually N_2-fixing.

	Strandveld		CFR	
	Non-fixing	Putative N_2-fixing	Non-fixing	Fabaceae
N	9.2 ± 0.39	16 ± 0.17	11.1 ± 0.6	25.9 ± 2.4
P	1.6 ± 0.14	0.81 ± 0.19	0.73 ± 0.07	0.81 ± 0.14
K	3.5 ± 0.33	2.0 ± 0.37	12.1 ± 1	9.2 ± 1.5
Ca	25 ± 1.4	24 ± 3.6	8.9 ± 0.9	11.1 ± 2.7
Mg	3.5 ± 0.27	3.0 ± 0.34	3.4 ± 0.4	2.1 ± 0.3
Na	6.9 ± 1.3	16 ± 5.6	4.3 ± 0.6	1.3 ± 0.4
Mn	0.10 ± 0.01	0.04 ± 0.02	0.22 ± 0.04	0.15 ± 0.06
Fe	0.18 ± 0.02	0.15 ± 0.03	0.12 ± 0.02	0.09 ± 0.02
N:P	5.8	19.6	15.2	32
n	6 (4)	2 (6)	89 (12)	10 (1)

The leguminous alien invasive *A. cyclops* had > 2-fold greater rates of litter production than the indigenous species (Fig. 1), consistent with the fact that these are bigger plants than the native vegetation (e.g. Morris et al., 2011).

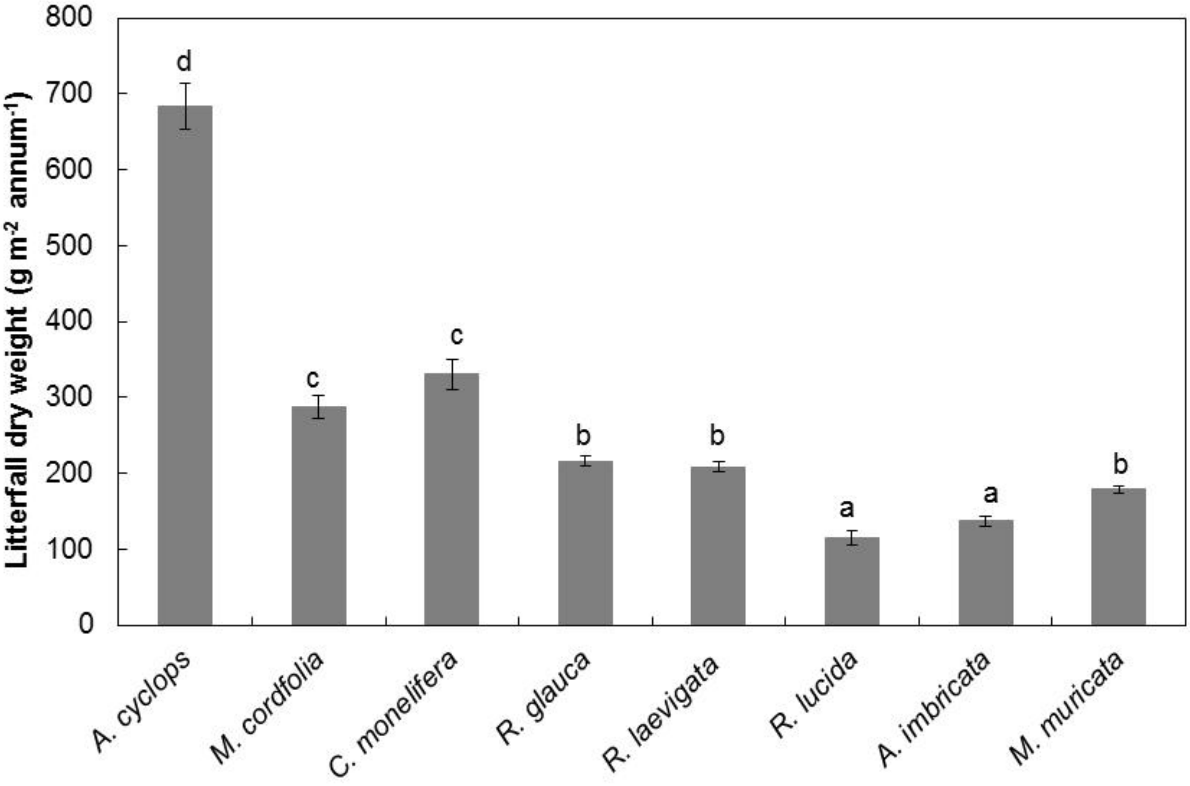

Fig. 3.1: Rates of dry leaf litterfall production for *A. cyclops* (n=3), *M. cordifolia* (*n* =3), *C. monelifera* (*n* =3), *S. glauca* (*n* =9), *S. laevigata* (*n* =15), *S. lucida* (*n*=12), *A. imbricata* (*n* =12) and *M. muricata* (*n* =15). Bars represent SE for litterfall production in each species. Significant differences (p < 0.05) between the species determined by Tukey post-hoc test following a one-way ANOVA and are represented by different letters

The indigenous legume *M. cordifolia* and the non-legume *C. monilifera* had higher rates of litterfall than the other indigenous species. The rates of litterfall were inversely related to the proportion of the annual litter nutrient loss that could be supplied by deposition (Fig. 3.1; Fig. 3.2). As a consequence of this relationship, little of the annual N and P demand of *A. cyclops* could be met by deposition. Deposition could, however, supply a relatively small fraction (< 12%) of N requirements of *M. cordifolia* and *C. monilifera*. In contrast to the case with N, deposition could meet a greater proportion of the P demand of the indigenous species. Deposition of K and Ca exceeded losses of these cations in leaf litter for all species (Fig. 3.2).

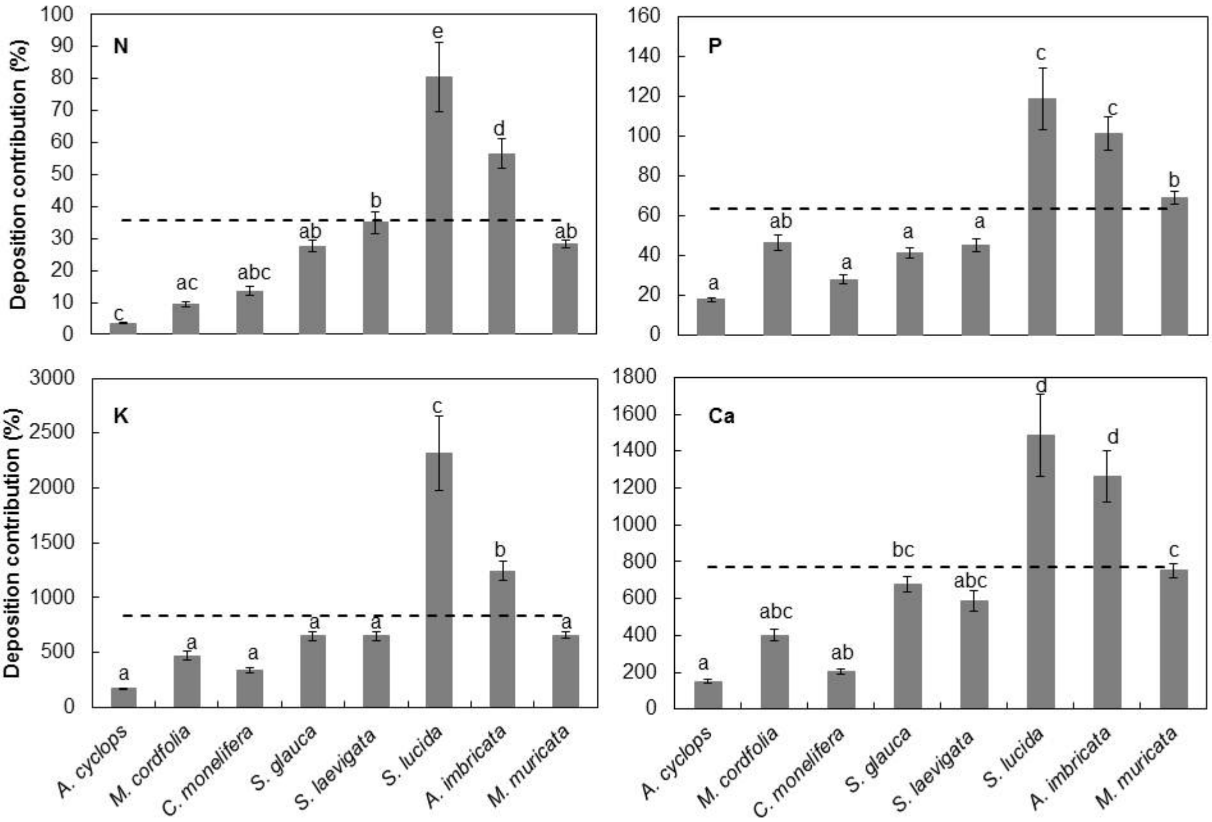

Fig. 3.2: Percentage annual plant nutrient demands that could be met by bulk deposition in rain water for *A. cyclops* (n=3), *M. cordifolia* (n =3), *C. monelifera* (n =3), *S. glauca* (n =9), *S. laevigata* (n =15), *S. lucida* (n=12), *A. imbricata* (n =12) and *M. muricata* (n =15). The dashed line shows the average across the sampled species. Bars are standard errors for percentage nutrient contribution in each species. Significant differences ($p < 0.05$) between the species determined by Tukey post-hoc test following a one-way ANOVA and are represented by different letters

3.5 Discussion

Several lines of evidence support the hypothesis that the Strandveld vegetation receives significant nutritional inputs from predominantly marine deposition. This vegetation is relatively dense with aboveground biomass of up to 18.1 tons ha^{-1} in comparison to Fynbos vegetation (6.5 – 11.6 tons ha^{-1} (Mills et al., 2012). The dune deposits are composed of 96-98% sand made up of a mixture of calcareous shell fragments (40 to 80 wt%) and quartz sand derived from beaches (Franceschini and Compton, 2006). Over time the calcareous grains can be leached by rainfall and result in surface dune soils composed of nearly pure (99.68% SiO_2) quartz sand and organic matter (Compton, 2004; Abanda et al., 2011). These conditions should, in principle, leave the soils with few nutrients to support plant growth. However, despite this, and the initial low nutrient conditions observed in marine sands from which Strandveld soils are formed (Cramer and Hawkins, 2009), I and Abanda et al. (2011) measured soil nutrient concentrations that were high compared to other parts of the CFR (Witkowski and Mitchell, 1987; Cramer and Hawkins, 2009; Abanda et al., 2011). Within the CFR, Strandveld soils have the lowest organic matter content (Witkowski and Mitchell, 1987). My measured soil TN and base cations were higher than those measured by Cramer and Hawkins, (2009) in the acid sand fynbos and calcareous fynbos in the south coast. Soil TP was also higher than that measured in other coastal sites including the lowland fynbos and mountain fynbos by Witkowski and Mitchell, (1987). Like in other CFR ecosystems, most of the P is stored in biomass and litter, and only a small fraction gets leached (Stock and Allsopp, 1992). A substantial fraction of the mineralized P is however unavailable to plants (Stock and Allsopp, 1992). The high soil nutrients in the west coast Strandveld is at odds with the lack of silt and clay in these soils evident from the low Fe relative to other parts of the CFR. One possible explanation for these relatively high nutrient contents may be the less frequent fire incidences and nutrient loss through volatilization (especially N) and runoff. Infrequent incidences of fire could allow nutrient accumulation which is not possible in other fynbos ecosystems where fire is more frequent.

In prior work at this site, I found evidence for large fluxes of Na, base cations, N and P from marine systems to the coastal Strandveld ecosystem (Chapter 2). Of this N deposition *ca.* 90% is organic and *ca.* 50% of the P is soluble reactive P, both suggesting a predominantly marine origin for these elements. The characteristics of deposition, together with the proximity to the ocean and the strong southerly (maritime) winds that characterize the area for most of the year all suggest the ocean plays a major role in nutrient deposition at this site. Although most parts of the CFR coastline may also be influenced by the strong southerly winds, other factors may explain the existing differences between them and the Strandveld vegetation. These may include bedrock geology, climatic variations (e.g. precipitation and wind) and topography. Climate and topography are important for deposition of marine sands that form Strandveld soils. As a consequence of the marine origin of the sands, it is not surprising that these soils are enriched in Ca, as evidenced by the ratio of Ca:Na in soils (*ca.* 98) relative to that in deposition (*ca.* 0.5). Presence of marine-derived sands and high levels of Ca in the soil may therefore constitute a major difference between the Strandveld and other CFR coastal ecosystems. There is, however, evidence that the soils of the Strandveld are enriched by marine nutrient deposition. The soil concentrations of Na and base cations were considerably higher than would typically be expected in similar dune sites in non-marine settings (e.g. Titus et al., 2002; Virginia and Jarrell, 1983) and higher than in other CFR soils. Total P to Na ratios in soils (*ca.* 3) were higher than those in precipitation (0.002). Although the granitic bedrock is rich in N and P, and its weathering may be a possible source of the high P, high amounts of sand deposited on the bedrock over long time periods makes its influence as a nutrient source less likely. It is possible that P is advected from nearby Neogene P deposits inland from the study site that could contribute P to soils via dust deposition. The prevailing wind direction for much of the year is, however, not favorable for this type of transport and deposition (Chapter 2). Alternatively, P enrichment in these soils may result from P deposition being bound to Ca to form Ca-P in the soils (e.g. Birch, 1977) and thus may be protected from leaching from the sands. Another possible source of this enrichment may be retention of P in the soil in the form of organic complexes. It is also likely that litter fall would result in the accumulation of nutrients in the sampled surface soil (Jobbágy and Jackson, 2000). Overall, marine deposition appears likely to be an important factor in enriching these soils in Na, Mg, K, and P with soil sources responsible for the high Ca concentrations at the site. The low soil N and C concentrations at the sites are likely due to limited capacity for these soils to stabilize organic matter on silt or clay surfaces or in aggregate structures (e.g. Schimel et al., 1994).

Concentrations of P, Na, Mg, and Ca were all higher in Strandveld vegetation than in the surveyed CFR, indicating that the potentially marine-derived nutrients in soils support higher foliar nutrient concentrations than in other areas of the CFR. In contrast, K was substantially lower than would be expected based on deposition and soil nutrient patterns and much lower than observed in other sites of the CFR. Sodium is known to competitively inhibit K uptake at the root plasmalemma (Maathuis and Amtmann, 1999), sometimes leading to a deficiency of K in the plant leaves. The high Na concentration in the Strandveld soils may thus inhibit K uptake.

The foliar N:P ratios of non-N_2-fixing Strandveld species were very low (5.8), predominantly as a consequence high foliar P concentrations, but also lower foliar N concentrations. This accords with the low total N:total P concentration in the Strandveld soils compared to the CFR soils. Confirming this, the N:P ratios of the putative N_2-fixing species were also lower than those of the CFR Fabaceae. Besides, there were only 2 N_2-fixing species at this site which were confined to 2 separate sites. Influence of N_2-fixation may therefore have been low. *Acacia cyclops* that was one of the N_2-fixing species has also been shown to be only partly dependent on fixation for its N within the Strandveld (Stock et al., 1995). It is possible that limitation on K uptake by high Na concentrations results in K-limitations, constraining growth with the consequent accumulation of some nutrients in excess of plant demand.

The combination of elevated nutrients in soils and similar elevation of elements in foliar tissue suggest that the accumulation of marine derived nutrients in soils and/or direct foliar interception of marine deposition could be important to plant nutrient budgets. We compared the estimated demand across all species with deposition of N, P, K and Ca and found that on average 36% of annual N-demand, 64% of P-demand and an excess of K and Ca demands could be supplied from annual precipitation. Not surprisingly, the fastest growing plants (especially the invasive legumes) that produced the most leaf litter had the highest annual demand (i.e. litter nutrient content), and therefore the lowest proportions of nutrient demand that could potentially be supported by deposition.

Comparing across the different essential elements examined in this study, I conclude that marine deposition could support significant proportions of annual demands for N, P, K and Ca for all the indigenous species based on their individual above-ground nutrient demands. The alien *A. cyclops* may exploit its greater biomass and rooting depth (Morris et al., 2011) to supplement its nutrient demands. This analysis of nutrient demands neglects below-ground loses through the roots, herbivory and fire, all of which are likely to incur nutrient losses. Also neglected from this analysis is the potential input of nutrients in dry deposition and the possibility that the vegetation traps significant quantities of fog or marine aerosols, as suggested by Abanda et al. (2011).

3.6 References

Abanda, P.A, Compton, J.S., Hannigan, R.E., 2011. Soil nutrient content, above-ground biomass and litter in a semi-arid shrubland, South Africa. Geoderma 164, 128-137

Aerts, R., 1996. Nutrient resorption from senescing leaves of perennials: are there general patterns? Ecology 84, 597-608.

Birch, G.F., 1977. Phosphorites of the Saldanha Bay region. Transactions of the Royal Society of South Africa 42, 223-240.

Brown, G., Mitchell, D.T., Stock, W.D., 1984. Atmospheric deposition of phosphorus in a coastal Fynbos ecosystem in the south western cape South Africa. Ecology 72 (2), 547-551

Castle, S.C., Neff, J.C., 2009. Plant response to nutrient availability across variable bedrock geologies. Ecosystems 12, 101-113.

Chapin III, F.S., Matson, P. A., Mooney, H., 2002. Principles of terrestrial ecosystem ecology. Springer-Verlag, New York, New York, USA.

Compton, J., 2004. The rocks and mountains of Cape Town. Double Storey Books. Cape Town.

Cowling, R.M., Esler., K.J, Rundel., P.W., 1999. Namaqualand, South Africa – an overview of a unique winter-rainfall desert ecosystem. Plant Ecology 142, 3-21.

Cramer, M.D., Hoffmann, V., Verboom, A., 2008. Nutrient availability moderates transpiration in Ehrharta calycina. New Phytologist 179, 1048-1057.

Cramer, M.D., Hawkins, H.J., 2009. A physiological mechanism for the formation of root casts. Palaeogeography, Palaeoclimatology, Palaeoecology 274, 125–133.

Cramer, M.D., van Cauter, A., Bond, W.J., 2010. Growth of N_2-fixing African savanna Acacia species is constrained by below-ground competition with grass. Journal of Ecology 98,156-167.

Franceschini, G., Compton, J.S., 2006. Holocene evolution of the sixteen mile beach, Western Cape, South Africa. Journal of Coastal Research 22 (5), 1158-1166.

Gower, S.T., Kucharik, C.J., Norman, J.M., 1999. Direct and indirect estimation of leaf area index, fpar and net primary production of terrestrial ecosystems. Remote Sensing of Environment 70, 29–51.

Jobbágy, E., Jackson, R., 2000. The vertical distribution of soil organic carbon and its relation to climate and vegetation. Ecological Applications 10, 423-436.

Kruger, F.J. 1983., Plant community diversity and dynamics in relation to fire. In: Kruger F.J. (Eds.), Mediterranean-type ecosystems. The role of nutrients, Springer, New York, pp. 446-472

Maathuis, F.J.M., Amtmann, A., 1999. K^+ Nutrition and Na^+ Toxicity: The Basis of Cellular K^+/Na^+ Ratios. Annals of Botany 84, 123-133

Menge, D.N.L., Hedin, L.O., Pacala, S.W., 2012. Nitrogen and Phosphorus Limitation over Long-Term Ecosystem Development in Terrestrial Ecosystems. PLoS One 7(8): e42045. doi:10.1371/journal.pone.0042045

Mills, A.J., Burch, S.C., Stephenson, J.D., Bailey, R.V., 2012. Carbon stocks in fynbos, pastures and vineyards on the Agulhas Plain, South Africa: a preliminary assessment. South African Journal of Plant and Soil, DOI:10.1080/02571862.2012.730636

Morris, T.L., Esler, K.J., Barger, N.N., Jacobs, S.M., Cramer, M.D., 2011. Ecophysiological traits associated with the competitive ability of invasive Australian acacias. Diversity and Distributions 17, 898-910

Mucina, L., Rutherford, M.C., 2006. The Vegetation of South Africa, Lesotho and Swaziland. SANBI, Pretoria pp. 804.

Radloff, F.G.T., 2008. The ecology of large herbivores native to the coastal lowlands of the fynbos biome in the Western Cape, South Africa. PhD thesis. University of Stellenbosch, Stellenbosch.

Schimel, D.S., Braswell, B.H., Holland, E.A., McKeown, R., Ojima, D.S., Painter, T.H., Parton, W.J., Townsend, A.R., 1994. Climatic, edaphic and biotic controls over storage and turnover of carbon in soils. Global Biogeochemical Cycles 80 (3), 279-293

Shane M.W., Cramer M.D., Funayama-Noguchi S., Cawthray G.R., Millar A.H., Day D.A., Lambers H., 2004. Developmental physiology of cluster-root carboxylate synthesis and exudation in harsh Hakea. Expression of phosphoenolpyruvate carboxylase and the alternative oxidase. Plant Physiology 135, 549-560.

Smith, M., Compton, J.S., 2004. Origin and evolution of major salts in the Darling pans, Western Cape, South Africa. Applied Geochemistry 19, 645-664

Soderberg, K., Compton, JS., 2007. Dust as a nutrient source for fynbos ecosystems, South Africa. Ecosystems 10, 550–561.

Staaf, H., Berg, B., 1982. Accumulation and release of plant nutrients in decomposing Scots pine needle litter. Long-term de- composition in a Scots pine forest II. Canadian Journal of Botany 60, 1561-1568.

Stock, W.D., Lewis, O.A.M., 1986. Atmospheric input of nitrogen to a coastal Fynbos ecosystem of the south-western Cape Province, South Africa. South African Journal of Botany 52 (4), 273-276.

Stock, W.D., Allsopp, N., 1992. Functional perspective of ecosystems. In: Cowling, R.M. (Eds.), The Ecology of Fynbos: Nutrients, fire and diversity, Oxford University press, Cape Town, pp.241-257.

Stock, W.D., Wienand, K.T., Baker, A.C., 1995. Impacts of invading N2-fixing Acacia species on patterns of nutrient cycling in two Cape ecosystems: evidence from soil incubation studies and ISN natural abundance values. Oecologia 101:375-382

Tinley, K.L., 1985. Coastal dunes of South Africa. South African National Scientific Programmes, Council for Scientific and Industrial Research. Pretoria 109: p 300.

Titus, J.H., Nowak, R.S., Smith, S.D., 2002. Soil resource heterogeneity in the Mojave Desert. Journal of Arid Environment 52, 269-292.

Virginia, R.A., Jarrell, W.M., 1983. Soil Properties in a Mesquite-Dominated Sonoran Desert Ecosystem. Soil Science Society of America Journal 47 (1), 138-144.

Witkowski, E.T.F., Mitchell, D.T., 1987. Variation in Soil phosphorus in the Fynbos biome, South Africa. Ecology 75, 1159-1171

4 The contribution of horizontal precipitation to nutrient deposition on the west coast of South Africa

4.1 Abstract

The Strandveld ecosystem of west coast South Africa supports floristically diverse vegetation extending from the Atlantic Ocean to several kilometers inland. The region occupied by this ecosystem is highly seasonal with wet winters and dry summers with little precipitation. During summer, however, the region experiences frequent fogs near the coast where the cold waters of Benguela upwelling interact with warm air advected over the surface by southerly winds. Fog frequently extends several kilometers inland and could be an important source of moisture during dry summers and nutrients to vegetation growing on relatively nutrient poor dune sands. To evaluate the possible role of fog and other forms of horizontal precipitation in nutrient supply and water acquisition in this ecosystem, we measured horizontal precipitation for 12 consecutive months and compared concentrations of N, P, K, Ca, Mg, Na, Mn and Fe with those in rain water collected in the area over the same period. During the summer months, horizontal precipitation was the dominant form of precipitation in this region. Horizontal precipitation also had higher concentrations of most nutrients compared to rain water. Contents of Na, Mg, Ca and K decreased significantly with increasing distance from the ocean suggesting a marine origin for these nutrients. All nutrient contents also varied significantly throughout the year except TN and TP with base cations and Soluble Reactive Phosphorus (SRP) being highest in summer and spring. We also examined the capacity of plants in the area to intercept and take up nutrients in fog precipitation and found plants with small leaves intercepted more moisture and nutrients than bigger leaves. Plants could

benefit from the deposited nutrients either directly through the leaves or through the soils. The capacity of these plants to absorb different forms of N (glycine, NO_3^- and NH_4^+) and Li (a tracer for K) from their leaf surface confirmed their ability to benefit from deposited nutrients through direct foliar uptake. It is likely therefore that horizontal precipitation, mainly marine derived fog, is an important nutrient and moisture source for the vegetation of the west coast Strandveld ecosystem and the small leaves of plants in the area may be an adaptation for interception and uptake of nutrients from this precipitation.

4.2 Introduction

The coastal Strandveld vegetation in the Cape Floristic Region (CFR) of South Africa is a relatively dense shrubland containing sclerophyllous and drought deciduous shrubs and low trees (Cowling et al. 1999). This Strandveld vegetation commonly occurs on sand dunes that extend several kilometers inland from the Atlantic Ocean. Unlike some of the other low-nutrient status vegetation zones of the CFR, the Strandveld is characterized by comparatively high soil and plant P, base cations, and organic matter, despite having soils that are 96-98% sand that should be low in nutrient content (Abanda et al. 2012; Witkowski et al. 1987). This region is also characterized by a high degree of seasonality in precipitation with dry summers and wet winters.

Wet deposition is an important source of nutrients to ecosystems around the world, and especially in coastal areas (Derry and Chadwick, 2007). In many instances precipitation is transported and deposited horizontally as clouds, mist, drizzle and fog (e.g. Azevedo and Morgan 1974; Cavelier et al. 1996; Dawson 1998; Weathers et al. 2000; Rollenbeck et al. 2011). Sea spray aerosols form the largest component of the marine boundary layer particulate concentrations (O'Dowd and Leeuw 2007) and these aerosols can be elevated in a variety of nutrients including the base cations, N, and P. Marine aerosols are produced due to agitation of the surface waters by wind (Fitzgerald 1991). Interaction between these aerosols and fog within the marine boundary layer may cause the aerosols to be dissolved in the fog moisture resulting in enrichment of the precipitation with marine salts and organic matter (O'Dowd and Leeuw 2007). This nutrient-rich fog precipitation may be may be carried by wind onshore and deposited in terrestrial ecosystems further inland where it could form an important nutrient source (Azevendo and Morgan 1974). Sea spray may also be blown directly off the sea surface onto the shore where it could be an important nutrient source for the immediate terrestrial ecosystem (Franzen 1990).

These forms of precipitation may coat plant leaves in nutrient-containing moisture. This "horizontal precipitation" (HP) could be an important determinant of ecological and plant physiological properties in ecosystems such as the coastal Strandveld. For example, Martorell and Ezcurra, (2007) observed a significant evolutionary tendency towards development of small narrow leaves on species growing closer to areas where fog is frequent. They also observed that large numbers of small leaves increased fog interception by plant canopies, and suggested that small narrow leaves may be an adaptation for fog harvesting. Since fog and other aerosols may have high concentrations of some nutrients, it is possible that this interception contributes to ecosystem nutrients (Wrzesinsky et al. 2004). These observations suggest that HP may play an important role in ecosystems such as the coastal Strandveld and the two suggested mechanisms by which this may occur are through water interception and nutrient acquisition. By providing moisture and nutrients to the plants both via the leaves and soil, fog affects the water balance and nutrient cycling within these coastal ecosystems and possibly influence species composition, soil and plant characteristics (Vogelmann, 1973; Azevedo and Morgan 1974; Dawson,1998; Lundquist and Bourcy, 2000; van Dijk and Keenan 2007; Rollenbeck, et al., 2006). In these ecosystems, fog constitutes both a moisture (Bruijnzeel and Proctor 1995) and nutrient (Unsworth and Crossley 1987) input that varies in amount depending on its frequency, wind speed and vegetation characteristics (Vogelmann, 1973).

In Mediterranean coastal ecosystems, including the west coast of South Africa, fog is the primary form of precipitation during summer (Azevedo and Morgan 1974; Dawson 1998; Olivier 2002). Moisture provided by fog to these ecosystems during dry seasons could ameliorate water stress of vegetation by reducing canopy transpiration (Huntley et al. 1997). Nutrients contained in this moisture may enhance plants growth and could influence biochemistry of the ecosystem (Dawson, 1998). This precipitation is intercepted by plant canopies where it coalesces into droplets that fall to the ground as “fog drip” (Vogelmann, 1973; Azevedo and Morgan 1974), thus providing moisture and nutrients to the plants through the soil. Moisture in fog may also be directly absorbed by plants through leaves (Yates and Huntley, 1995). There is also evidence that plants can take up nutrients from their leaf surfaces. For example, Peuke et al. (1998a) found that plants could assimilate N in the same amounts in shoots and roots, with NH_4^+ being taken up more readily than NO_3^- by the leaves. Besides being a source of nutrients, HP may also rewet past dry deposition on plant surfaces enabling foliar uptake of nutrients within it. HP may also wash off the nutrients from the canopy thus making them available to the plants through the soil (Madgwick and Ovington, 1959)

Within the Strandveld there is considerable variation in leaf size and arrangement. Some species have small narrow leaves arranged densely on thin twigs to form thick canopies that might be highly effective at scavenging nutrients and water from horizontal precipitation. To examine the role that fog plays in the nutrient and hydrologic cycles of the coastal Strandveld of South Africa, I carried out a study of nutrient and moisture deposition to a range of woody species that are an important component of the Strandveld vegetation over one year. In this study, I evaluated whether HP has the potential to be an important moisture and nutrient source to these ecosystems.

4.3 Methods

4.3.1 Study site

The study was carried out in the West Coast National Park (33^{o}13'52.26"S, 18^{o}09'50.96"E) on a 17 km migrating dune cordon running inland from the coast in a northerly direction. The park is approximately 100 km northwest of Cape Town along the Atlantic Ocean coastline. The area has a Mediterranean climate with mild wet winters and hot dry summers, and experiences strong southerly winds for most of the year. During the summer months, however, rainfall is light and infrequent ranging between 8-10 mm from Nov-Feb compared to 30-40 mm from May-Aug. Winds are strong with 20-40 km h^{-1} winds attained in 25% of the year and gale force winds exceeding 52 km h^{-1} in less than 4% of the year (Franceschini and Compton, 2006). The area is exposed to moderate to high wave energy, with 90% of waves having heights of 1-3 m (Franceschini and Compton, 2006). The soils are mainly Aeolian dune sands deposited over long periods by winds blowing from the coast. The main vegetation type is the Langebaan dune Strandveld consisting mainly of evergreen sclerophyllous shrubs, grasses and annual herbs (Mucina and Rutherford, 2006). A full description of this site is provided in Chapter 2.

4.3.2 Horizontal precipitation sampling

I selected 8 different sampling locations at varying distances from the ocean, (0.1, 3.6, 6.1, 8.0, 10.7, 12.5, 14.6 and 16.8 km) along the dune plume. The horizontal precipitation collector (Figure 4.1) consisted of a screen (343 mm x 644 mm) made of 128 nylon lines creating a collecting surface of 2077 cm^2 draining into a collecting channel (27 cm^2). The channel at the bottom of the screen was open and could intercept some precipitation resulting in the collector not differentiating between horizontal and vertical precipitation. The surface area of the collector that was effective for collecting horizontal precipitation was estimated as the sum of the surface areas of all the 128 strings and the channel below them. A row of stainless steel spikes was fitted on top of the screen to prevent birds perching and possible contamination. Samples were discarded if there was any evidence of contamination (e.g. bird droppings or insects) on the collectors. Only one sample was found to have been physically contaminated during the whole sampling period. The collecting channel was connected to a 2 L Schott bottle by a 6 mm ID tube (1 m long) that was looped to form a moisture trap and thus reduce sample evaporation.

The sampling bottles were thoroughly cleaned and multiple-rinsed with Millipore water (Elix 20 water system, Merk Millipore, Darmstadt, Germany). A biocide, (200 mg

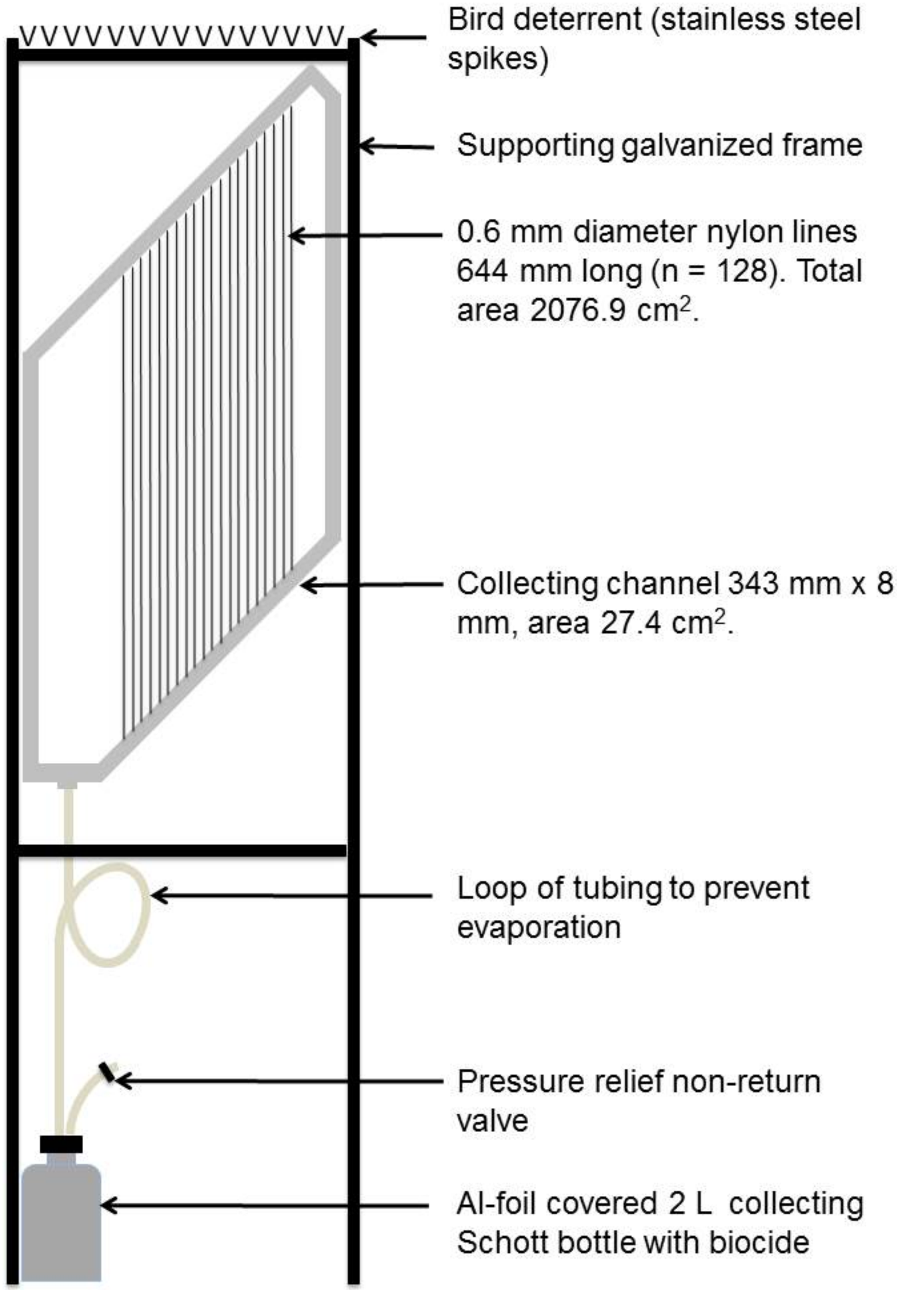

Fig. 4.1: A diagram of the apparatus used to trap horizontal precipitation (HP) in the field. See text for more details.

of 2-isopropyl-5-methylphenol) was added to each of the bottles, including those used to store Millipore water that was used as blank samples, to minimize microbial degradation of the sample (Cape et al. 2010). They were changed monthly for 12 consecutive months (Jan 2011 to Dec 2011). Prior to sample removal, the screen was washed with 50 ml ultra-pure Millipore water that was included in the sample. Washing was done by applying water on the nylon lines of the screen using a squirt bottle and letting it flow to the collecting channel. This was done to wash down any dry deposition that may have been trapped on the collector. Sample volumes and concentrations were corrected for the volume of the water rinse. All samples were stored at 4°C for a maximum of 2 d prior to transfer to 50 ml centrifuge tubes and storage at -20°C.

4.3.3 Nutrient washing from leaves

Terminal twigs (5-10 cm length) were cut from the 6 dominant woody species at the study site (*C. monilifera*, *S. glauca, S. lucida*, *M. cordifolia*, *M. muricata* and *A. imbricata*) in Nov. 2011, bagged in plastic and stored in a cooler box. In the lab, 50 ml of Millipore water was used to wash the leaves within the bag and stored at -20°C prior to analysis.

4.3.4 Leaf and canopy water holding capacity

I obtained 3 replicates of each of the 6 field plant species from the Kirstenbosch nursery in Cape Town and kept in them in a greenhouse for 5 days prior to this experiment. The plants had been grown in mixture of sand and compost (ratio of 1:1) in 2 L plastic bags. A mature green leaf from each plant was weighed and its area determined using a LI-3000 Area Meter (LICOR Lincoln, NE USA). Leaf dimension was determined as the diameter of the largest circle that can be accommodated within the leaf perimeter (Yates et al. 2010). The leaf was dipped in water and reweighed to determine its water holding capacity. Leaf water holding capacity was expressed as the difference between the fresh weight and wet weight (kg m^{-2}).

The canopy water holding capacity was determined by gradually wetting a pre-weighed intact branch obtained from each plant to saturation in a simulated horizontal precipitation experiment inside a wind tunnel (150 cm length x 30 cm diameter). The branches were suspended *ca.* 70 cm from the fan generating a wind speed of *ca.* 10 m s^{-1}. A mist stream generated using a pressurized sprayer was introduced between the fan and the suspended branches *ca.* 20 cm from the fan. Branches were saturated with water and reweighed, and the difference between the fresh weight and wet weight expressed per canopy area (kg m^{-2}). The leaves were removed and the total leaf area measured using LI-3000 Area Meter (LICOR Lincoln, NE USA).

4.3.5 Nutrient enrichment

Solutions of 1.87 mg of each of the ^{15}N-labeled $NaNO_3$, NH_4Cl and glycine (98% atom, Sigma-Aldrich, St. Louis Missouri, USA) were separately dissolved in 100ml of water to form 0.22, 0.35 and 0.25 mM solutions of the labels respectively. These were applied on replicates of separate attached young to medium age fully expanded leaves of each plant. Three replicate leaves on each plant were marked as controls. The label was applied by covering the leaf with a blotting paper soaked in a solution of the label. Leaves were harvested and rinsed 3 times in a 1 mM $CaCl_2$ solution to remove excess label on the surface of the treated leaves. They were then oven dried at 60°C for 48 h and milled to fine powder (Mixer Mill MM400, Retsch GmbH, Haan, Germany). Sample (2.8-3.0 mg) of the ground sample weighed in 5 × 9 mm tin capsules (Santis Analytical AG, Teufen, Switzerland) was prepared for analysis of N isotope ratios by combustion methods (Minagawa et al. 1984) using a Thermo Flash EA 1112 series elemental analyzer. The stable N isotopes (δ^{15}) were measured using a Delta Plus XP isotope ratio mass spectrometer (Thermo Electron Corporation, Milan, Italy). The ^{15}N enrichment was expressed as the difference between the δ^{15} values measured in the treated leaves and those measured in the control leaves. Isotope analysis was done at the isotope laboratory in the department of Archeology of the University of Cape Town. Lithium chloride was applied in a similar procedure used for the ^{15}N label on 3 replicate leaves of each plant. Both the control and treated leaves were harvested after 6 h and rinsed in 1 mM $CaCl_2$ solution to remove excess LiCl on the surface. They were then oven dried, ground and the tissue analyzed for Li concentration at Bemlaboratory laboratory, Cape Town. Lithium enrichment was expressed as the concentration difference between treated and control leaves (mg g^{-1}).

4.3.6 Colorimetric procedures

All precipitation and leaf wash samples were analyzed for NO_3^-, NH_4^+ and PO_4^{3-} using colorimetric procedures. Analysis for NH_4^+ was done following the method by (Weatherburn 1967) while NO_3^- analysis followed the method of (Doanea and Horwath 2003). Dissolved organic nitrogen (DON) was calculated as the difference between TN and the sum of NH_4^+ and NO_3^-. The malachite green oxalate method (Motomizu et al., 1983) was used to determine the concentration of PO_4^+, but other phosphates can be hydrolyzed to orthophosphate during this analysis (Motomizu et al., 1983). The measured P is thus reported as soluble reactive P (SRP). A 1500 Multiskan spectrum plate reader (Thermo electron corporation, Vantaa, Finland) was used to determine sample absorbencies. The detection limit for each analysis was determined by dividing the standard error of the standard sample absorbencies by the slope of the standard curve (Doyle et al. 2004). None of the samples had concentrations falling below the detection limit. The detection limits for NH_4^+, NO_3^- and SRP were determined to be 0.0458 mg L^{-1}, 0.0251 mg L^{-1} and 0.0095 mg L^{-1} respectively. Most NH_4^+ values were found to be below the detection limit. Five duplicate runs of a randomly selected sample produced analytical variances of 7.8%, 5.0% and 4.3% for NH_4^+, NO_3^- and SRP analysis, respectively.

4.3.7 ICP analysis

Precipitation samples were analyzed for total N, total P, Na, Mg, Ca and K using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) The ICP-AES detection limits for the various elements (mg L^{-1}) were 0.05 for dissolved N, 0.077 for dissolved P, 0.095 for Na, 0.005 for Mg, 0.052 for Ca, and 0.141 for K. None of the samples had concentrations falling below the detection limit. . A standard sample was analyzed alongside the water samples for up to six duplicate runs and gave analytical variances of 0.5% for dissolved total P, 3.37% for Mg, 1.43% for Ca, 3.19% for Na and 1.74% for K.

4.3.8 Data analysis

Monthly nutrient contents (mg day^{-1}) in horizontal precipitation for each site were calculated as the product of the total measured monthly precipitation volume (corrected for the wash water volume added) and concentration of the nutrient in the sample. The surface area of the collectors was constant across the transect and since the amount of deposition is dependent on the collector design, it was not expressed on the basis of area as it was not deposition per land surface area.

Annual nutrient concentrations (mg L^{-1}) were calculated as the average of the monthly concentrations for each element. Data on rain precipitation concentration was obtained from a simultaneous study at the 8 locations of the study site aimed at determining the sources, amounts and forms of rainfall deposition in the area (Chapter 2). The monthly data was grouped into four climatically distinct seasons of three months each: Autumn (Mar, Apr and May), winter (Jun, Jul and Aug), spring (Sep, Oct and Nov) and summer (Dec, Jan and Feb). The effect of seasonality and distance from the ocean on nutrient content and concentration was evaluated by comparing across the four seasons and the various distances from the ocean. Data from the first site (*ca.* 0.1 km from the ocean) were excluded from the analysis due to high base cation concentration values that were much higher than those of the other sites. The extremely high deposition measured at this completely dominated the statistics. It is likely to have received a consistent input of sea spray from breaking waves and although not part of the statistical analysis, the nutrient deposition concentrations at this location are presented. Although I have included this site in Chapter 2, the influence of this site is greater in HP data than in the rainfall data. I therefore handled that site separately to get a better idea of how most of the transect differs between HP and rain. To evaluate the effects of distance and seasonality on nutrient content and concentration, analysis of co-variance (ANCOVA) was used with season as a categorical variable and distance as a continuous variable. Analysis of variance (ANOVA) was used to test the seasonal variability of elemental concentration ratios to Na. All statistical analyses were with STATISTICA ver. 8 (StatSoft, Inc., Tulsa, OK, USA).

4.4 Results

4.4.1 Nutrient deposition

The design of the horizontal precipitation (HP) collectors (Fig. 4.1) was intended to mimic the potential trapping of wind-blown aerosols, fog and horizontal rainfall by vegetation. Both rainfall volume and HP volume peaked in the rainy winter months of May-July (Table 4.1). During this period, the HP collectors intercepted about 2.7 times more water than the precipitation collectors. Similarly both HP and rainfall collectors intercepted lower volumes in October through December. However, in January through April the HP collectors captured *ca.* 4 to 7 times as much moisture as the rainfall collectors (Table 4.1). The ratio of HP to rainfall during the very low rainfall months of August and September was also elevated (4.4 and 3.2, respectively).

Table 4.1: Monthly volume in horizontal precipitation (HP) and rainfall collectors (ml) and ratios of HP:Rain across the study transect. Values show the mean ± SE (n = 7 sites). The monthly average wind speed is from the Geelbek weather station at the West Coast National Park

Month	HP (ml)	Rain (ml)	HP/Rain Ratio	Wind speed (m s^{-1})
Jan	597±108	135±27	4.7±0.99	2.7
Feb	677±144	82±5.2	6.1±1.6	1.6
Mar	648±104	97±19	6.7±1.4	1.8
Apr	382±73	71±14	4.1±1.5	2.1
May	1233±111	384±60	2.7±0.57	2.8
Jun	1911±135	697±113	2.7±0.66	3.4
Jul	1426±109	463±17	2.6±0.84	2.4
Aug	763±88	95±9.2	4.4±0.43	3
Sep	358±43	84±9.6	3.2±0.24	2.2
Oct	546±39	300±28	1.9±0.24	2.2
Nov	253±53	102±16	2.7±0.49	3.2
Dec	201±40	81±5.2	2.7±0.60	4.2

Over the course of an annual sampling cycle, the HP collectors had substantially higher concentrations of NO_3^-, total N, DON, total P, K, and Fe compared to the rainfall collectors (Table 4.2). The concentrations of NO_3^- , DON and total N were considerably higher in HP than in rainfall. The annual differences in concentration appear to be influenced by a high degree of seasonality in the concentrations of nutrients in HP (Table 4.3). All the nutrients measured in this study except SRP, Fe, and Al, had considerably higher concentrations in spring and summer compared to winter.

Table 4.2: Annual concentrations (mean ± SE; mg L^{-1}) of various nutrients in rain and horizontal precipitation (HP) measured at 7 sites in the study area (between 3.5 and 16.8 km from the ocean) and also for HP at the site closest to the ocean (0.1 km). *p* values indicate significant differences ($p < 0.05$) between rain and HP concentrations determined using Student's t-tests. All samples were collected for 12 consecutive months (Jan-Dec 2011).

Element	Rain Precipitation	HP	t-value	*p*	HP at 0.1 km
NO3-	0.52±0.094	3.37±0.49	4.985	**<0.001**	1.3
SRP	0.19±0.063	0.14±0.031	-0.591	0.480	0.48
Total N	1.9±0.36	26±1.9	10.485	**0.001**	39
DON	1.4±0.31	22±1.5	10.041	**<0.001**	23
Total P	0.11±0.016	0.39±0.034	6.105	**<0.001**	2
Mg	52±39	67±8.5	0.494	0.622	645
Ca	112±85	39±4.3	-0.858	0.393	206
Na	478±356	542±72	0.320	0.750	6125
K	6.1±1.3	21±2.5	4.973	**<0.001**	201
Si	2.5±1.9	0.53±0.083	-1.009	0.315	5.2
Mn	0.14±0.10	0.048±0.0051	-0.913	0.363	0.039
Fe	0.026±0.0046	0.043±0.0081	2.112	**0.037**	0.25
Al	0.083±0.025	0.073±0.012	-0.228	0.820	0.032

Table 4.3: Seasonal horizontal precipitation (HP) volume (L) and elemental concentrations (mg L^{-1}) of nutrients measured in HP collected in the study area (mean ± SE; n = 7). Different letters indicate significant seasonal differences ($p < 0.05$, bold text) determined using ANCOVA (categorical variable = season; continuous variable = distance from ocean) followed by post-hoc Tukey tests. There was no distance or distance x season effect on any of the nutrients. All the data was collected for 12 consecutive months (Jan-Dec 2011).

	Autumn	Winter	Spring	Summer	F	*p*
HP (L)	0.73±0.10b	1.4±0.13c	0.39±0.037a	0.44±0.079ab	24.99	**<0.001**
NO_3^-	1.1±0.057a	2.4±0.77ab	4.3±0.60ab	5.5±1.6b	4.37	**0.007**
SRP	0.056±0.012a	0.028±0.0067a	0.12±0.024a	1.1±0.79a	1.85	0.146
Total N	26±2.7a	11±1.4a	32±2.9a	35±4.6b	5.07	**0.003**
DON	24±2.1ab	9.5±1.0a	22±2.0a	32±3.6b	6.73	**0.001**
Total P	0.36±0.049b	0.15±0.17a	0.42±0.049b	0.65±0.090c	12.54	**<0.001**
Mg	39±4.0ab	20±2.7a	88±12bc	120±29c	9.15	**<0.001**
Ca	29±3.2ab	13±1.5a	43±5.3b	75±14c	13.22	**<0.001**
Na	289±31a	157±24a	764±95b	951±251b	9.41	**<0.001**
K	11±1.3a	6.5±0.94a	27±3.3b	39±8.0b	12.52	**<0.001**
Si	0.28±0.041a	0.15±0.018a	0.63±0.13ab	1.1±0.28b	7.092	**<0.001**
Mn	0.051±0.0075b	0.016±0.0025a	0.041±0.0051ab	0.092±0.016c	13.67	**<0.001**
Fe	0.077±0.017b	0.0084±7.2E-05a	0.050±0.018ab	0.035±0.018ab	3.41	**0.023**
Al	0.15±0.031b	0.019±0.0030a	0.075±0.025ab	0.046±0.020a	6.03	**0.001**

Distance from the coast also played a role in the control of HP concentrations in some, but not all, nutrients. The site immediately adjacent to the ocean (*ca.* 0.1 km inland) provides a reference point for deposition that is heavily influenced by sea spray caused by intense wave action on the beachfront (Table 4.2). This site had very elevated concentrations of total N, total P, base cations, Na, and Si. Notably, the site was only moderately elevated in SRP compared to the inland sites and lower in NO_3^-, Fe, Al, and Mn. Along the remaining transect of sites inland from the ocean, Mg, K, Na, and Ca all declined inland from the coast (Fig. 4.2) whereas all the other elements did not exhibit trends with distance from the ocean (data not shown).

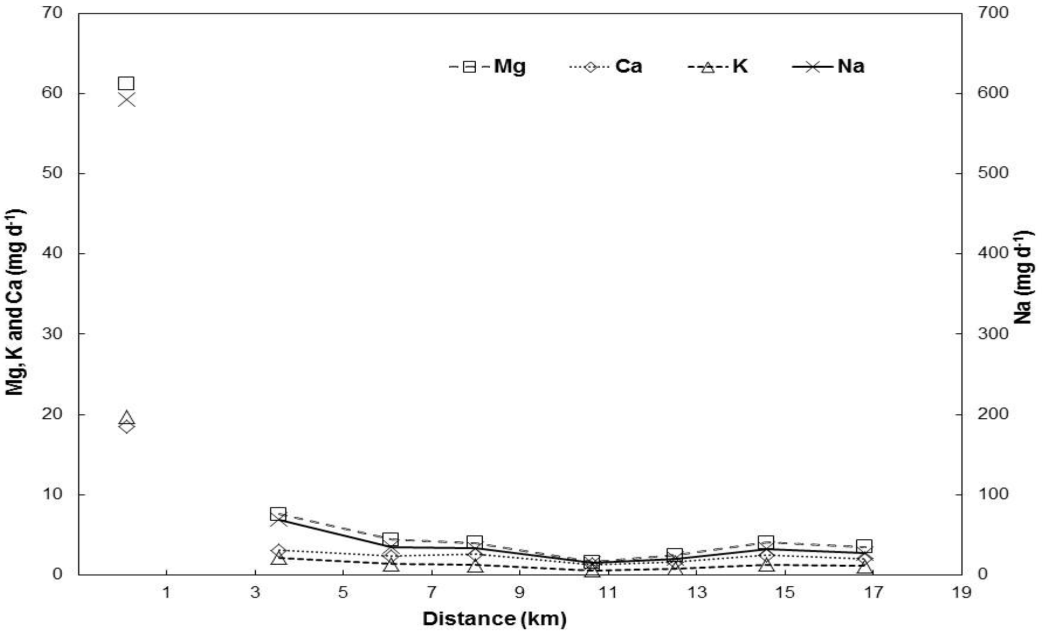

Fig. 4.2: Deposition contents (mg day^{-1}) of base cations measured in horizontal precipitation (HP) at various distances from the ocean (n = 7 sites). Data was collected between Jan-Dec 2011.

All nutrient concentration ratios to Na, except SRP:Na, varied significantly throughout the year (Table 4.4). The ratios were generally low except for those of Ca and Mg, indicating predominance of Na in the horizontal deposition. Total N:Na and DON:Na were highest in autumn and winter and lowest in spring. In contrast, NO_3^-:Na was highest in winter and spring. Ratios of TP, Mg and Ca to Na were lowest in spring while K was elevated relative to Na only in summer.

Table 4.4: Seasonal variations of elemental concentration ratios to Na (used as an index of marine origin) for horizontal precipitation (HP) samples collected from in study area between Jan-Dec 2011 (mean ± SE). Different letters indicate significant differences ($p < 0.05$) determined using one way ANOVA followed by post-hoc Tukey test for homogeneity, ($n = 7$).

	Autumn	Winter	Spring	Summer	F	*p*
NO_3^-/Na	0.0048a	0.011b	0.0071ab	0.0037a	4.12	**<0.001**
Total N/Na	0.097b	0.097b	0.047a	0.084ab	3.42	**0.022**
DON/Na	0.09a	0.094a	0.037b	0.077ab	5.30	**0.003**
SRP/Na	0.0001a	0.0002a	0.0000a	0.0003a	2.36	0.79
Total P/Na	0.0015b	0.0011ab	0.0006a	0.0009ab	4.97	**0.004**
Mg/Na	0.14b	0.12a	0.11a	0.12ab	6.08	**0.001**
Ca/Na	0.10b	0.086ab	0.059a	0.097b	6.61	**0.001**
K/Na	0.039a	0.039a	0.036a	0.046b	8.87	**<0.001**

The nutrient content of HP varied seasonally for most nutrients (Table 4.5). The nutrient content of HP is the product of water volume and concentration and therefore serves as a non-spatially explicit measure of nutrient flux to the study site. Despite a trend toward higher summer time nutrient concentrations for many nutrients, the high water volume collected in winter led to increased nutrient flux in the rainy winter season than would have been predicted by concentration alone. Despite the large differences in water volume between seasons (Table 4.3), however, fluxes of many nutrients were at or near their peaks in the spring and summer seasons (Table 4.4). This pattern stands in stark contrast to the flux of nutrients in rainfall, which is more heavily weighted toward the wet winter season (Chapter 2).

Table 4.5: Seasonal nutrient contents (mean ±SE; mg day^{-1}) measured in horizontal precipitation (HP) at 7 sites in the study area (between 3.54 and 16.82 km away from the ocean). Different letters indicate significant seasonal differences ($p < 0.05$, bold text) determined using ANCOVA (categorical variable = season; continuous variable = distance from ocean) followed by post-hoc Tukey tests. Values in bold indicate significant differences at $p \leq 0.05$ confidence interval. Contents for Na, Ca, Mg and K also varied significantly with distance from ocean (p = 0.002, 0.042, 0.008 and 0.02, respectively). All the data was collected for 12 consecutive months (Jan-Dec 2011).

Element	Autumn	Winter	Spring	Summer	F	*p*
NO_3^-	0.095±0.012a	0.23±0.061a	0.23±0.041a	0.12±0.028a	3.26	**0.027**
SRP	0.0036±0.0006a	0.0042±0.0010a	0.0052±0.0009a	0.0092±0.0015b	5.71	**0.002**
Total N	1.8±0.17a	1.7±0.20a	1.6±0.11a	1.9±0.37a	1.23	0.304
DON	1.5±0.17a	1.2±0.24a	1.3±0.079a	1.7±0.35a	2.40	0.077
Total P	0.024±0.0021a	0.021±0.0020a	0.023±0.0033a	0.027±0.0048a	1.03	0.385
Mg	3.0±0.35ab	2.8±0.32a	4.5±0.47b	3.8±0.71ab	2.76	**0.049**
Ca	2.0±0.15ab	1.7±0.15a	2.1±0.17ab	2.6±0.34b	3.78	**0.014**
Na	22±2.8a	23±2.6a	39±4.0b	32±5.9ab	4.23	**0.008**
K	0.85±0.09a	0.89±0.10a	1.4±0.13b	1.4±0.20b	4.91	**0.004**
Si	0.020±0.0023a	0.021±0.0004a	0.030±0.0026ab	0.037±0.0032b	2.78	**0.048**
Mn	0.0035±0.0023bc	0.0021±0.0003ab	0.0021±0.0001a	0.0035±0.0005c	5.61	**0.002**
Fe	0.0085±0.0054b	0.0013±0.0002a	0.0025±0.0009a	0.0012±0.0012a	6.52	**0.001**

4.4.2 Foliar nutrient interception and uptake

Plant leaf size and canopy structure played an important role in both water capture and nutrient acquisition at this site. The water holding capacity of both leaves and canopies were strongly influenced by leaf dimension, with larger leaves retaining less moisture, expressed per leaf area (Fig. 4.3). Individual leaves had a higher water holding capacity than the canopy, especially for the smaller leaves, indicating that the dense packing of smaller leaves may have partially limited water retention. The fact that the water holding capacities of individual leaves and canopies followed similar logarithmic trajectories indicates that the water holding capacity of the canopy was strongly related to leaf dimension. The smallest leaves also had the largest amount of soluble nutrients on leaf surfaces (Fig. 4.4). In both these cases, the plants studied here had similar negative logarithmic relations between water capture and leaf dimension and nutrient content and leaf dimension, indicating that nutrient retention on the leaf surface may be related to the capacity of the leaf to intercept aerosols.

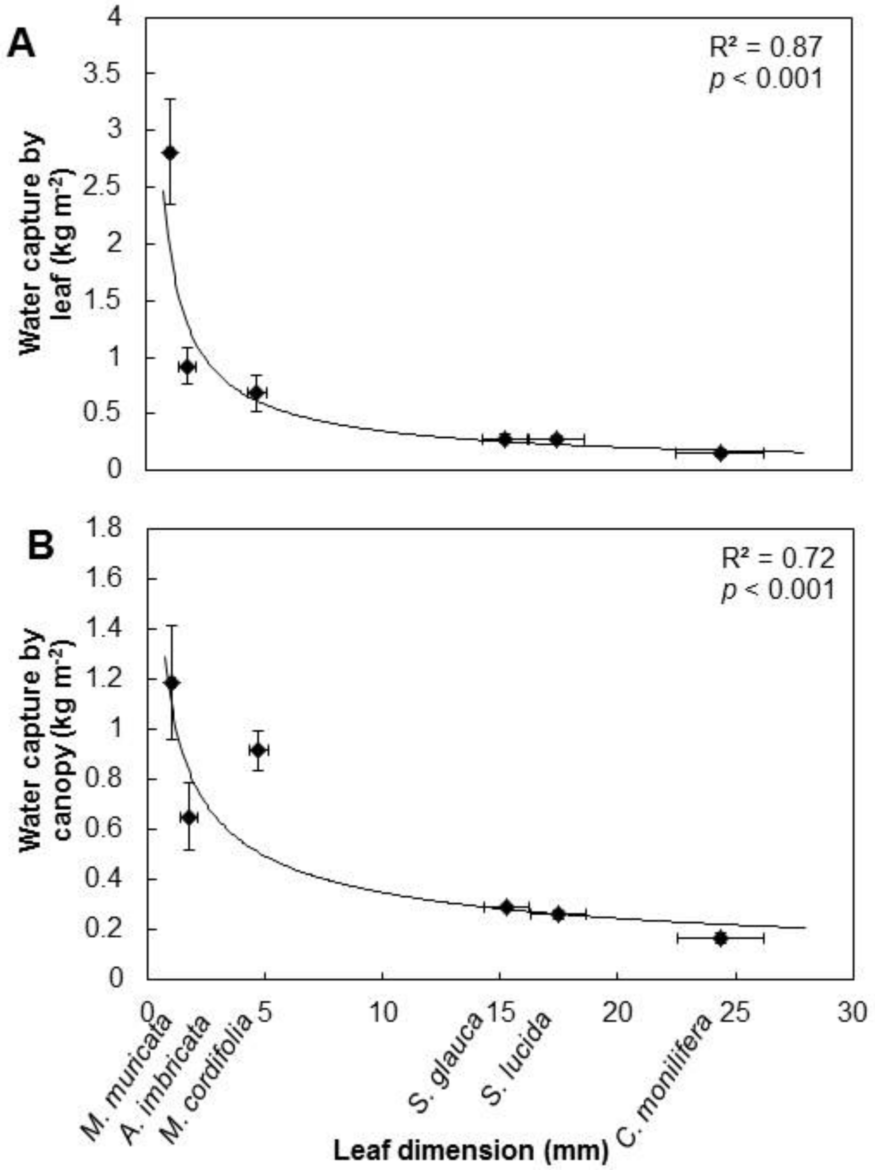

Fig. 4.3: The variation in the amount of water (kg m^{-2}) held on individual leaves and canopies of the various species with leaf dimension (LD, mm). Leaf dimension was determined as the diameter of the largest circle that could be fitted on the plant leaf. Points represent mean ± SE (n = 6). Individual leaves were wetted by dipping them in water while canopy branches were wetted in a simulated horizontal precipitation experiment in a wind tunnel at a 10 m s^{-1} wind speed until saturation. The relationship between water held on individual leaves and by canopies canopy with LD were fitted by the equations 1.99 LD^{-75} and 1.12 LD^{-50} respectively.

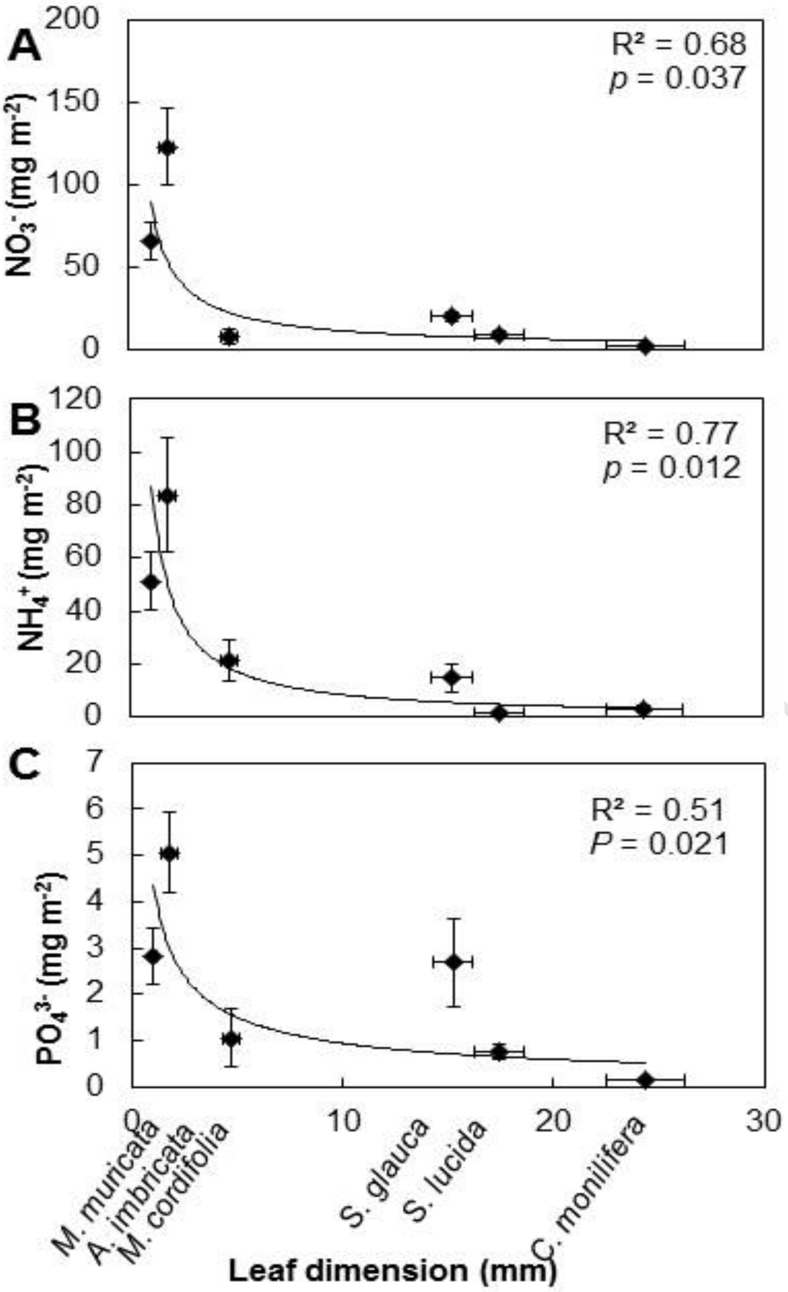

Fig. 4.4: Concentration (mg m^{-2}) of nutrients on leaves of various leaf dimensions (LD, mm). Leaf dimension was determined as the diameter of the largest circle that could be fitted on the plant leaf. Points represent mean ± SE (*n* = 6). The nutrients were measured in Millipore water used to rinse leaves of the various plant species collected from the field in Nov 2011.The relationship between NO_3^-, NH_4^+ and PO_4^{3-} at LD were fitted by the equations 91.57 $LD^{-0.91}$; 90.05 $LD^{-1.02}$ and 4.46 $LD^{-0.07}$, respectively.

All the plants examined at this site had the capacity to directly absorb foliar glycine, NO_3^-, NH_4^+, and Li (Fig. 4.5). The three plants with the smallest leaf dimension exhibited the highest uptake of Li and tended toward higher uptake of glycine. Patterns of NO_3^- and NH_4^+ uptake were variable between species.

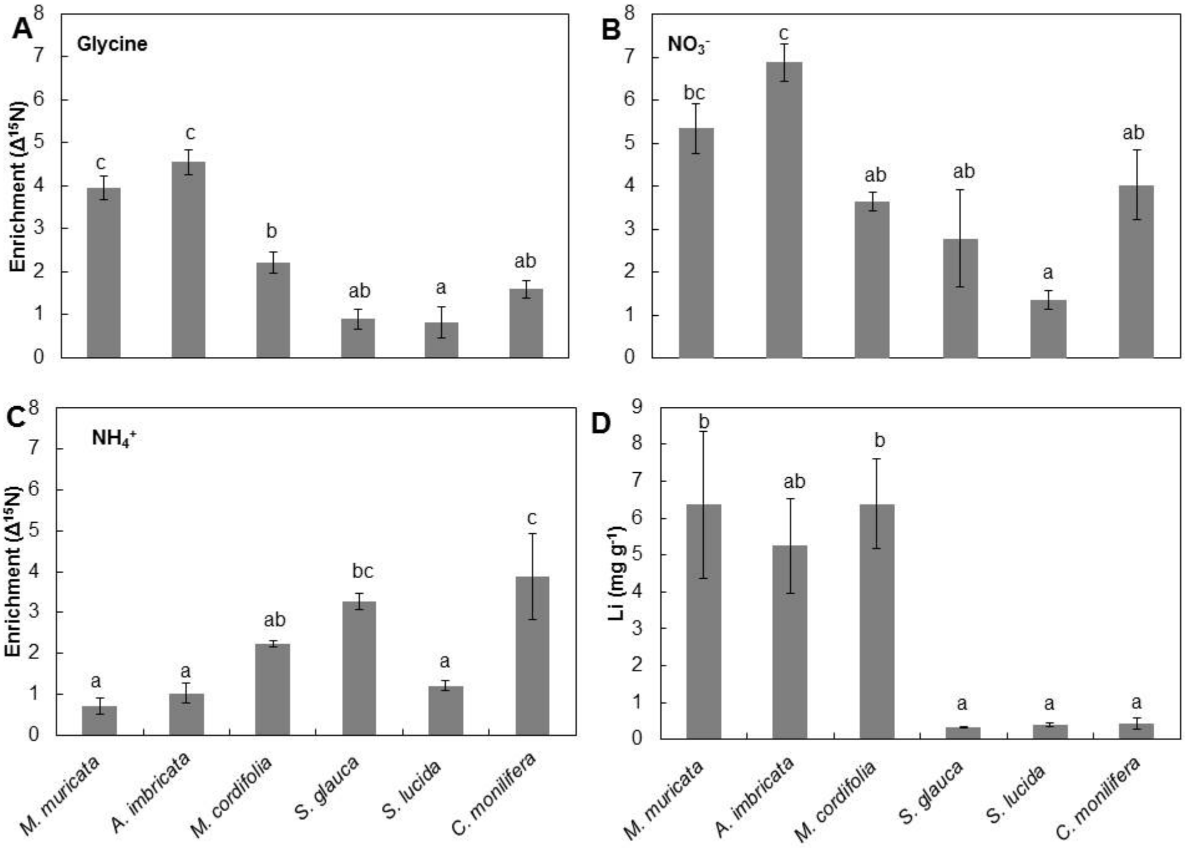

Fig. 4.5: Leaf N-isotope ($\delta^{15}N$) and enrichment foliar concentrations of Li (mg g^{-1}) after supply of ^{15}N-glycine $^{15}NO_3^-$, $^{15}NH_4^+$ and LiCl. Bars (arranged left to right in order of increasing leaf dimension) represent means (± SE) for nutrient enrichment in each species (*n* = 6). The different letters above the error bars represent significant differences between species determined by Tukey post-hoc test following a one-way ANOVA.

4.5 Discussion

The west coast Strandveld ecosystem of South Africa receives 60% of its rainfall during the three months of May, June, and July and so this period of time should be responsible for most of the hydraulic recharge and nutrient delivery for the ecosystem. During the remaining months, however, a variety of additional mechanisms appear to bring both moisture and nutrients into the ecosystems that border the Atlantic Ocean on the West Coast of South Africa. Horizontal precipitation can take a number of different forms including clouds, mist, drizzle and fog (e.g. Azevedo and Morgan 1974; Cavelier et al. 1996; Dawson 1998; Weathers et al. 2002; Rollenbeck et al. 2011). Fog is a crucial component of moisture delivery to Cape Columbine north of this study area and is responsible for 90% of precipitation volume there (Olivier, 2002). Fog is most common in the summer months due to advection of sea fog inland (Heydoorn and Tinley 1980; Bailey and Chapman 1991). Sea fog in this area is formed due to the cooling effect of the cold ocean waters of the Benguela upwelling combined with an onshore breeze that can transport fog several kilometers inland. Fog and other forms of HP can deliver moisture to both conventional rainfall collection instruments and to those designed to capture HP. Although we cannot estimate an absolute fraction of precipitation that is related to HP in this study, it is clear that the relative contribution of moisture shifts dramatically from winter to summer with 2-3 times as much HP falling during the summer months as in the winter months. This phenomenon is most notable during the months of January through March, which have low rainfall, but the highest ratio of HP to rain.

The west coast of South Africa is notable for rough seas and extensive wave action. Marine aerosols are a dominant component of the total atmospheric aerosol load near the coasts of South Africa (Piketh et al 2002) and during the summer months, a low haze frequently extends several kilometers inland from the ocean. During this period, there are greatly elevated concentrations of a number of nutrients in HP. The elevated nutrient content during the summer months is unlikely to be the result of anthropogenic nutrient deposition given the limited industrial sources of aerosols and nitrogen oxides in the region (Chapter 2). A more likely contribution to nutrient deposition during this period is the dry deposition of marine aerosols onto the lines of the HP collectors and/or the enrichment of these nutrients in fog and other forms of HP. The variation of nutrient concentrations in HP across seasons and with distance from the ocean provides some insight into these potential pathways of deposition. In the case of Na and the base cations, the decline in deposition rates inland from the ocean and the very high concentrations (particularly of Na) immediately adjacent to the ocean provides a strong indication that the presence of these elements in HP is related to coastal aerosol production. Besides, there are strong correlations between the concentrations of Na and base cations in HP (r^2=0.916, $p < 0.001$ for Mg; r^2=0.945, $p < 0.001$ for Ca and r^2=0.986, $p < 0.001$ for K) (data not shown). Using Na as a sea water reference, and sea water ratios given by Keene et al. 1986, the average annual proportion of Mg, K and Ca in HP that can be attributed to sea water are 91%, 97% and 56% respectively. Fog collected in this area has been found to have Cl to Na and Mg ratios similar to those of sea water (Olivier, 2002), suggesting a strong influence of marine aerosols on fog precipitation. For nutrients such as Al and Fe, the lack of seasonality and effect of distance from the ocean suggests another source, most likely in the deposition of mineral aerosols transported from inland settings. At sites inland from this study, mineral aerosol deposition is an important component of nutrient fluxes from the atmosphere to the land (Soderberg and Compton 2007) and mineral aerosols make up a large fraction of total atmospheric aerosol loads at inland South African sites (Piketh et al., 2002).

The concentrations of NO_3^- and total N in HP are considerably higher than those in rainfall, yet neither of these nutrients decline in concentration away from the ocean. There are a variety of sources of dissolved organic N in marine aerosols, including free amino acids, although concentrations are typically much lower than those observed in this study (Kawamura and Sakaguchi 1999). On average, DON constituted 82% of TN in HP on an annual basis. This proportion is similar to the 84% measured in rain water at this site (Chapter 2), and is within the range of 15-97% measured in cloud water at a remote coastal site in Chile (Weathers et al, 2000). The enrichment of DON in HP relative to rainfall by a factor of 16 is comparable with the 13-fold enrichment of DON in cloud water relative to rain water measured in a variety of remote locations worldwide (Weathers et al, 2000). Elevated total N is also a consistent feature across all the collection sites in this study with no evidence for outliers that would skew the resulting concentrations. Total N concentrations are also most elevated in the dry summer months when HP is high and vertical precipitation is low. Although we cannot provide a conclusive explanation for these variations, there are a number of possibilities including the deposition of very organic rich aerosols derived from phytoplankton during sea-spray aerosol formation. Such aerosols can have organic matter content ranging from 3-77 percent (Facchini et al., 2008) and might provide one plausible explanation for the very high total N values observed here.

Despite unanswered questions regarding the source of elevated nutrient content in HP, it is clear that HP is an important potential source of nutrient deposition to the coastal Strandveld ecosystems studied here. The flux of nutrients in rainfall is dominated by the high precipitation periods of the year (Chapter 2) whereas the combination of elevated HP (relative to rain) in the dry months and elevated concentrations of many nutrients during this period mean that HP provides a relatively constant flux of nutrients to ecosystems through the year. The nature of HP is such that nutrients are deposited directly to leaf surfaces and therefore bypass potential nutrient loss pathways in soils (e.g. leaching). Prior work at these sites suggests that there is considerable elevation of nutrient content in the soils around vegetation clumps (Abanda, et al., 2011) and vegetation trapping of nutrient contained in aerosols and/or horizontal precipitation may be one mechanism that can help explain these observations. The nutrients in HP may also play an additional important role in these ecosystems by providing both moisture and nutrients to plants.

The smallest leaved Strandveld species captured the most moisture on a per area basis with large differences between species. Of the species intercepting the largest amounts of moisture are *A. imbricata,* a low-growing perennial with an abundance of fine narrow leaves and *M. muricata* which has hairy leaves. These modifications may contribute to retention of moisture by these species. Similar observations of the relationship between leaf size and fog interception have led to the suggestion that leaf size may be an adaptation for fog capture (Martorell and Ezcurra 2007). Plants can take up intercepted water either directly through the leaf surfaces (Yates and Huntley 1995; Dawson 1998) or indirectly from the soil as fog drip and stem flow (Azevedo and Morgan 1974; Dawson 1998). Thus HP may be an important source of moisture to the Strandveld vegetation, particularly during the otherwise relatively dry summer months.

The amount of nutrient that leaves can acquire from wet deposition depends on several factors including the form of the nutrient and its ionic properties (Peuke et al., 1998b), the amount deposited (Peuke et al., 1998a), the moisture duration on the leaf and the capacity of the leaf to take up the nutrient (Azevedo and Morgan 1974). As with water retention, the smaller-leaved Strandveld species had higher nutrient concentrations per unit surface area compared to the other species, indicating that nutrient deposition on leaf surfaces at least partially scales with water retention by the leaves. Considering the significant potential contribution of HP to nutrient deposition, it is likely that the vegetation participates in both the direct interception of the nutrients and deposition in the canopy, as well as increasing deposition to the soil, as previously suggested for the region by Abanda, et al. (2011).

The potential exists for some forms of nutrients to be directly absorbed by leaves. The capacity for direct foliar uptake of nutrients has been observed in a number of plant species and depends on stomatal diffusivity and cuticular transportation (Boyce et al., 1996), although ion exchange on the leaf surface may also be important (Sparks, 2009). The variations in uptake of glycine, NO_3^- and NH_4^+ between species may be due to differences in leaf surface properties and/or capacity to transport the N into the leaf tissue, as observed previously with deciduous and coniferous species (Garten et al., 1998). The uptake of glycine, as a potential organic N source is particularly important considering the high proportion of organic N in HP. Foliar uptake of the organic N (e.g. peroxyacetyl nitrate) by crop species is related to stomatal conductance (Okano et al. 1990). Li uptake by some of the Strandveld species, as a tracer for K uptake, is consistent with foliar uptake of base cations (Tyree et al., 1990). Thus the potential exists for plants to intercept HP and take up this nutrient source through leaves during the dry season when nutrient mobility in the soil is low.

4.6 References

Abanda, P.A, Compton, J.S., Hannigan, R.E., 2011. Soil nutrient content, above-ground biomass and litter in a semi-arid shrubland, South Africa. Geoderma 164, 128-137

van Dijk, A.I.J.M., Keenan, R. J., 2007. Planted forests and water in perspective. Forest Ecology and Management 251: 1-9

Azevedo, J., Morgan, D.L., 1974. Fog precipitation in coastal California forests. Ecology 55, 1135-1141

Bailey, G.W., Chapman, P., 1991. Short-term variability during an anchor station study in the southern Benguela upwelling system: Chemical and physical oceanography. Progress in Oceanography 28:9-37.

Boyce, R.L., Friedland, A.J., Chamberlain, C.P., Poulson, S.R., 1996. Direct canopy nitrogen uptake from ^{15}N-labeled wet deposition by mature red spruce. Canadian Journal of Forest Research 26 (9), 1539-1547.

Bruijnzeel, L.A., Proctor, J., 1995. Hydrology and biogeochemistry of tropical mountain cloud forests: what do we really know? In: Hamilton, L.S., Juvik, J.O., Scatena, F.N. (Eds.) Tropical montane cloud forests. Springer, Berlin Heidelberg New York, pp. 38-78.

Cape, J.N., Sheppard, L.J., Crossley, van Dijk, A.,N., Tang, Y.S., 2010. Experimental field estimation of organic nitrogen formation in tree canopies. Environmental Pollution 158, 2926-2933

Cavelier, J., Solis, D., Jaramillo, M.A., 1996. Fog interception in montane forests across the central cordillera of Panamá. Journal of Tropical Ecology 12:357-369

Cowling, R.M., Esler., K.J, Rundel., P.W., 1999. Namaqualand, South Africa – an overview of a unique winter-rainfall desert ecosystem. Plant Ecology 142, 3-21.

Dawson, T.E., 1998. Fog in the California redwood forest: ecosystem inputs and use by plants. Oecologia 117, 476-485.

Derry, L.A., Chadwick, O.A., 2007. Contributions from earth's atmosphere to soil. Elements 3, 333–338.

Doanea, T.A., Horwáth, W.R., 2003. Spectrophotometric determination of nitrate with a single reagent. Analytical Letters 36 (12), 2713-2722.

Doyle, A., Weintraub, M.N., Schimel, J.P., 2004. Persulfate digestion and simultaneous colorimetric analysis of carbon and nitrogen in Soil Extracts. Soil science society of America Journal 68 (2), 669-676.

Facchini, M.C., Rinaldi, M., Decesari,S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E.D., de Leeuw, G., Martino, M., Woeltjen, J., O'Dowd, C.D., 2008. Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates.Geophysical Research Letters 35(17), DOI: 10.1029/2008GL034210.

Fitzgerald, J.W., 1991. Marine Aerosols. Atmospheric Environment. 25A (3/4), 533-545.

Franceschini, G., Compton, J.S., 2006. Holocene evolution of the sixteen mile beach, Western Cape, South Africa. Journal of Coastal Research 22 (5), 1158–1166.

Franzen, L.G., 1990. Transport, Deposition and Distribution of Marine Aerosols over Southern Sweden during Dry Westerly Storms. Ambio. 19 (4), 180-188.

Garten, C.T., Schwab, A.B., Shirshac, T.L., 1998. Foliar retention of N-15 tracers implications for net canopy exchange in lowand high-elevation forest ecosystems. Forest Ecology and Management 103, 211-216.

Heydoorn, A.E., Tinley, K.L., 1980. Estuaries of the Cape. Part 1: Synopsis of the Cape Coast. CSIR Research Report 380.

Huntley, L.B., Doley, D., Yates, D.J., Boonsaner, A., 1997. Water balance of an Australian subtropical rainforest at altitude: the ecological and physiological significance of intercepted cloud and fog. Australian Journal of Botany 45, 311-329.

Kawamura, K., Sakaguchi, F., 1999. Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics. Journal of Geophysical Research: Atmospheres 104 (D3), 3501-3509.

Keene, W.C., Pszenny, A.A.P., Galloway, J. Hawley, M.E., 1986. Sea-salt corrections and interpretations of constituent ratios in marine precipitation. Journal of Geophysical Research, 91, 6647-6658.

Lundquist, J.D., Bourcy, T.B., 2000. California and Oregon humidity and coastal fog. Scripps Institution of Oceanography, La Jolla, California, 6A. 17

Madgwick, H.A.I., Ovington, J.D., 1959. The chemical composition of precipitation in adjacent forest and open plots. Forestry 32, 14-22.

Martorell, C., Ezcurra, E., 2007. The narrow-leaf syndrome: a functional and evolutionary approach to the form of fog-harvesting rosette plants. Oecologia 151, 561–573.

Minagawa, M., Winter, D.A., Kaplan, I.R., 1984. Comparison of Kjeldahl and combustion methods for measurement of nitrogen isotope ratios in organic matter. Analytical Chemistry 56 (11), 1859–1861

Motomizu, S., Wakimoto, T., Toi, K., 1983. Spectrophotometric Determination of Phosphate in River Waters with Molybdate and Malachite Green. Analyst. 108, 361-367

Mucina, L., Rutherford, M.C., 2006. The Vegetation of South Africa, Lesotho and Swaziland. SANBI, Pretoria pp. 804.

O'Dowd, C.D., Leeuw, G.D., 2007. Marine aerosol production: a review of the current knowledge. Philosophical Transactions of the Royal Society of America 365: 1753–1774.

Okano, K., Machida, T., Totsuka, T., 1990. Foliar uptake of peroxyacetyl nitrate (PAN) by herbaceous species varying in susceptibility to this pollutant. New Phytologist 114, 139–145

Olivier J, 2002 Fog-water harvesting along the west coast of South Africa: a feasibility study. Water SA 28, 349–360.

Peuke, A.D., Jeschke, W.D., Hartung, W., 1998a. Foliar application of nitrate or ammonium as sole nitrogen supply in *Ricinus communis*: I. Carbon and nitrogen uptake and inflows. New Phytologist 138, 675-687

Peuke, A.D., Jeschke, W.D., Hartung, W., 1998b. Foliar application of nitrate or ammonium as sole nitrogen supply in *Ricinus communis* II. The flows of cations, chloride and abscisic acid. New Phytologist 140, 625-636.

Piketh, S.J., Swap, R.J., Maenhaut, W., Annegarn, H. J. Formenti, P., 2002. Chemical evidence of long-range atmospheric transport over southern Africa. Journal of Geophysical research 107 (D24), doi:10.1029/2002JD002056.

Rollenbeck, R., Bendix, J., Fabian, P., 2011. Spatial and temporal dynamics of atmospheric water inputs in tropical mountain forests of South Ecuador 25, 344-352.

Rollenbeck, R., Fabian, P., Bendix, J., 2006. Precipitation dynamics and chemical properties in tropical mountain forests of Ecuador. Advances in Geosciences 6, 73-76

Soderberg, K., Compton, J.S., 2007. Dust as a nutrient source for fynbos ecosystems, South Africa. Ecosystems 10, 550-561.

Sparks, J.P., 2009. Ecological ramifications of the direct foliar uptake of nitrogen. Oecologia 159, 1-13

Tyree, M.T., Scherbatskoy, T.D., Tabor, C.A., 1990. Leaf cuticles behave as asymmetric membranes. Evidence from the measurement of diffusion potentials. Plant Physiology 92, 103-109

Unsworth, M.H., Crossley, A., 1987. Capture of wind driven cloud by vegetation. In Coughtrey, P.J., Martin, M.H., Unsworth, M.H. (Eds.), Pollutant transport and fate in ecosystems. Blackwell, Oxford, UK, pp 125-137.

Vogelmann, H. W., 1973. Fog Precipitation in the Cloud Forests of Eastern Mexico. BioScience 23 (2), 96-100.

Weatherburn, M.W., 1967. Phenol-hypochlorite reaction for determination of ammonia. Analalytical Chemistry 39 (8), 971-974.

Weathers, K.C., Lovett, G.M., Likens, G.E., Caraco, N.F.M., 2000. Cloudwater inputs of nitrogen to forest ecosystems in southern Chile: forms, fluxes, and sources. Ecosystems 3, 590-595.

Wilson, A.J., Tiley, C., 1998. Foliar uptake of wet-deposited nitrogen by norway spruce: an experiment using 15N. Atmospheric Environment 32 (3), 513-518

Witkowski, E.T.F., Mitchell, D.T., 1987. Variation in Soil phosphorus in the fynbos biome, South Africa. Journal of Ecology 75, 1159-1171

Wrzesinsky, T., Scheer, C., Klemm, O., 2004. Fog Deposition and its Role in Biogeochemical Cycles of Nutrients and Pollutants. In: Matzner, E. Biogeochemistry of Forested Catchments in a Changing Environment. Ecological Studies 172, pp. 191-202

Yates, D.J., Huntley, L.B., 1995. Foliar uptake of water by wet leaves of Sloanea woollsii, an Australian subtropical rainforest tree. Australian Journal of Botany 43, 157-167.

Yates, M.J., Verboom, A., Rebelo, A.G., Cramer, M.D., 2010. Ecophysiological significance of leaf size variation in Proteaceae from the Cape Floristic Region. Functional Ecology 24: 485–492.

5 Synthesis

5.1 Characteristics of the Strandveld ecosystem

The west coast Strandveld vegetation forms part of the Fynbos biome which is associated with soils that are generally low in nutrients, but especially in N and P (Kruger, 1983). In contrast, the soils of Strandveld vegetation have relatively higher nutrient contents (Witkowski and Mitchel, 1987). Indeed, soil and foliar concentrations of most nutrients apart from N were higher in the Strandveld than in the CFR. (Chapter 3). Unlike most of the other components of the Fynbos biome, fire in this vegetation type is relatively infrequent (Kruger, 1983). Cowling et al., (1997) suggested that the Strandveld vegetation may have developed from replacement of the species rich, fire dependent fynbos vegetation by the thicket shrubs characteristic of the Strandveld due to absence of fire. Thus nutrient loss through fire within the Strandveld may be expected to be minimal. Herbivory is also low in this area, partly due to a high presence of succulent plant species that are generally believed to be unpalatable (Radloff, 2008). Despite lower nutrient losses than from Fynbos systems, the relatively high nutrient contents in the Strandveld soils and vegetation (Chapter 3), is surprising because these soils are commonly formed from marine derived aeolian sands (Cowling et al, 2009) that are known to be low in most nutrients (Cramer and Hawkins, 2009). In the study area for this thesis on the west coast of South Africa (Fig. 2.1), Strandveld vegetation is found on aeolian sands deposited inland on the Yzerfointein-Geelbeek sand plume.

These Strandveld soils also support relatively dense vegetation with a higher aboveground biomass (*ca.*18.1 tons ha^{-1}) than the Fynbos (6.5 – 11.6 tons ha^{-1}) (Mills et al., 2012). This means that the Strandveld has a different species composition with different growth forms compared to the rest of the Fynbos. For example, two main plant families common within the Fynbos biome, Proteaceae and the Ericaceae, are absent in the Strandveld vegetation (Mucina and Rutherford, 2006). The most dominant species in the Strandveld are the evergreen fleshy-fruited sclerophyllous plants with long life spans and ability to resprout after disturbance (Cowling et al., 2005). These thicket formations are ancient, and are thought to have been initially formed from forest elements (Cowling et al., 2005). Evolution of such thickets in the South Africa cape region has been associated with subtropical grasslands and Afromontane forests (Cowling, 1983). The combination of vegetation composition, relatively high productivity, and relatively low inherent nutrient content in bedrock all together raise the question as to the source of nutrients in the Strandveld. One possible source is deposition of atmospheric aerosols.

5.2 Potential sources of atmospheric deposition within the Strandveld

Industrial sources of nutrients to the Strandveld should be relatively limited. This is because a large part of the west coast Strandveld, including the site of this study, is within a protected area (West Coast National Park) and therefore expected to be minimally influenced by anthropogenic activities. However, agricultural farms north and east of the study area, like the orange farming area near Citrusdal and urban settlements such as Langebaan and Saldahna are potential sources of anthropogenic pollution. This pollution could impact the area particularly during winter when winds are predominantly northerly and easterly (Fig. 2.2) and in autumn during the first rain events. At present, these potential industrial sources appear to have a minimal effect on nutrient deposition in this region which experiences very low rates of nutrient deposition compared to other more industrialized portions of the world (Chapter 2; Chapter 4).

In contrast to the limited potential for industrial activity to contribute nutrients to this region, the ocean appears to be a major source of nutrients in both rainfall and horizontal precipitation (Chapter 2 and 4). The study site is in an area adjacent to a highly productive section of the Atlantic Ocean (Andrews and Hutchings, 1979) that also experiences frequent incidences of sea fog (Olivier, 2002) driven by the effect of seasonal Benguela upwelling. This makes marine aerosols likely to dominate atmospheric deposition in the area.

5.3 Nutrient deposition in the Strandveld

The high Na and base cation fluxes in rain precipitation compared to those measured in similar places around the globe (Table 2.8) are one of the strongest indicators of marine contributions to nutrient deposition in the area. High concentrations of Na, Mg and Ca in rain (Table 2.1) alongside Na and all base cations in horizontal precipitation during summer (Table 4.3) suggests that marine aerosols had a significant influence in both precipitation forms. Base cations are known to have high concentrations in sea water (Chadwick et al. 1999) and Na is generally used as a sea water index (Schlesinger 1982) in many deposition studies. Base cation contents in horizontal precipitation were also higher close to the ocean compared to inland sites (Fig. 4.4). Furthermore, concentrations of Na, Ca and Mg were all approximately 10 times higher and K was six times higher at the site closest to the ocean than the average concentrations for all the inland sites (Table 4.1). Although these could be partly attributed to interception of sea sprays blown directly to the horizontal precipitation collectors, the gradual decrease in nutrient amounts from the ocean to inland sites (Fig. 4.2) suggests a higher marine influence at near coastal sites. High marine influence in coastal areas is also evident from the high base cation fluxes in rain water compared to those measured at a site further inland near Citrusdal (ca. 100 km inland from this study) (Soderberg and Compton, 2007). Further evidence for marine contributions comes from other studies in the region. For example, the high Na and base cations concentrations measured in soils and plant material from this area by Abanda et al, (2011) suggest an influence of marine aerosol deposition on vegetation growth. Water samples from pans within Strandveld also have Cl to Na and Mg ratios similar to those of sea water (Smith and Compton, 2004). This evidence supports the findings of high base cations and Na amounts measured in rain and horizontal precipitation, soil and plant material (Chapter 2; Chapter 3; Chapter 4)

In other areas around the world, ecosystems adjacent to highly productive coastal areas are known to be influenced by deposition of marine aerosols, including the coastal areas of California (Dawson, 1998) and Chile (Weathers et al., 2002). In these locations, it is not just the base cations and Na that are elevated due to marine sources but also N and P. This appears to be the case at West Coast National park as well as the contents and concentrations of N and P in both rain and horizontal precipitation suggest a variety of possible sources, including marine, for both nutrients. The high proportions of organic forms of N and P in total N (TN) and total P (TP) in rainfall, and TN in horizontal precipitation points to a marine influence in both precipitation forms (Chapter 2; Chapter 4). The high concentration of soluble reactive P (SRP) and organic N in horizontal precipitation and rainfall are good evidence for marine contributions as both of these types of nutrients tend to more enriched near oceans than in areas dominated by industrial emissions (Chapter 4).

Although the ocean appears to be an important source of nutrients to this study area, there are other sources, including dust, that may also play important roles. During extended portions of the year, rainfall is light and the Strandveld of West Coast National park is shrouded in a haze of suspended particulates. Such coastal haze is common near oceans and is formed from high relative humidity and the suspension of particulates during intense wave activity along the coasts (O'Dowd and Leeuw 2007). Over time, these particulates appear to be deposited to surfaces inland from the coast. The evidence for this in this thesis comes from the very high nutrient concentrations measured in rain (Chapter 2) and horizontal precipitations (Chapter 4) during summers when rainfall is infrequent. During these periods, aerosols likely accumulate on surfaces and are then washed into collection bottles during sampling or during small rain events. In the rainy winter seasons, concentrations of most nutrients are lower indicating that dry deposition plays a proportionately lesser role, however, in these periods, the concentration ratios of some elements to Na including Fe, Al, and Si are elevated (Chapter 2). These elements are associated with terrestrial rocks and soils, rather than marine deposition, and suggest that dust from the drier areas north of the study area are carried offshore by strong northerly and easterly winds during winter. Dust is known to contribute nutrients to deposition in other sites inland from the study area (Soderberg and Compton, 2007) and the results of this study indicate the Strandveld vegetation zone may benefit from the deposition of both marine and terrestrial-derived nutrients at different times of the year.

5.4 Importance of nutrient deposition for vegetation in the Strandveld

During the dry season, dry deposition trapped by plant foliage between precipitation events may be washed off by either rain or horizontal precipitation increasing nutrient availability in the soil (Ochoa-Hueso et al. 2011). This study, however, provided evidence for the accumulation of nutrients on plant surfaces and possible uptake of nutrients through leaves (Chapter 4).

The amount of precipitation and nutrients intercepted by plant canopies varies with canopy structure. For example, small, narrow leaves have large surface areas and form denser canopies than big leaves (Westoby and Wright, 2003) and are therefore expected to intercept more water and nutrients from precipitation. Indeed, Strandveld species with small leaves intercepted larger amounts of water and nutrients (NO_3^-, NH_4^+ and PO_4^{3-}) than big leaves (Fig. 4.1). Nutrients held within the foliage can be taken up by plants through the leaves, but are also available through the roots when washed off the canopy. There was evidence that's Strandveld species could take up different forms of N (Glycine, NO_3^- and NH_4^+) and Li from leaf surfaces (Fig. 4.2). Thus Strandveld vegetation is likely to acquire deposited nutrients from both the soil and directly through foliar uptake, accounting for enriched soils (Table 3.1) and leaves (Table 3.3) compared to the rest of the averages for the CFR.

5.5 Ecological consequences of deposition to the Strandveld

The characteristics of Strandveld plant architecture may also be an important aspect in the long-term nutrient supply to this ecosystem. Strandveld vegetation occurs in clumped patterns with clumps differing in size and composed of different species, although in most clumps one species would tend to dominate (Eccles et al., 1999). These thickets may intercept dry deposition, horizontal and rain precipitation that can provide large nutrient amounts particularly during the dry season (Chapter 4).

The relatively eutrophic status of the Strandveld (Kruger 1983) probably developed over long periods with continued deposition of calcareous sands of marine origin and nutrients. The sand plume in the Langebaan dune Strandveld is the product of prolonged accretion of sands, probably over the last 1 million years (Abanda et al, 2011). These calcareous sands may be partly responsible for the relative richness of the Strandveld soils. The high pedogenic Ca could help facilitate P retention through formation of secondary Ca-phosphates (e.g. Birch, 1977) thus protecting P from leaching and causing it to accumulate in the soil (Hinsinger, 2001). One possible source of this P may be atmospheric deposition, particularly of marine aerosols (Chapter 2). Besides deposition, other factors that may contribute to nutrient richness in the west coast Strandveld may include the weathering of its shale and granite bedrocks. However, these bedrocks have been covered by the nutrient poor marine sands over a long period, and thus are unlikely to influence surface soil nutrient richness. It is, however, possible that low nutrient losses from the CFR through infrequent fires and relatively limited herbivory also contribute to the relative nutrient richness in the Strandveld (Kruger, 1983; Radloff, 2008).

5.6 Role of atmospheric deposition for development of Strandveld ecosystems

The possible contribution of deposition of marine derived nutrients (Chapter 3; Chapter 4) to the development of Strandveld ecosystems is in part determined by the proximity of these areas to nutrient sources from the ocean. Much of the coastal CFR is likely exposed to significant deposition of marine aerosols, although, Strandveld vegetation type is not that common. The absence of Strandveld type vegetation in other coastal locations may be attributed to a number of factors. One of them may be presence of Ca-rich sands in the Strandveld, which retain P through formation of less leachable Ca-P (Hinsinger, 2001). Additionally, annual wind patterns throughout the CFR are variable and the dominant wind direction on parts of the coastline may not be favorable for inland transport and deposition of sand and marine aerosols. Movement of sand and aerosols from the coast inland is also related to climate (rainfall, wind strength), which influences vegetation and dune stability. Climate varies along the coastline and changes over time. These variations, alongside presence of geographical formations like cliffs and mountains on some sections of the coastline which may act as wind barriers, are expected to affect sand deposition and hence establishment of Strandveld.

Distance from the sea is also an important variable in Strandveld vegetation development and is usually correlated with change is soil type. This is probably related to sand deposition from the coast. Within the west coast where dune cordons are common (e.g. Cape flats, Atlantis and the Yzerfontein-Geelbek), sandy beaches appear to be shielded from ocean swell and strong wave action by geological landforms in the direction of prevailing ocean currents. Shielding of beaches allows accumulation of fine sand which can be blown inland by wind. Franceschini and Compton, 2006 suggested that Cape Peninsula and Dassen Island, and Robben Island act as wave shadows to the coastal beaches that supply the sand responsible for the formation of the Cape flats dune cordon and the Langebaan dune cordon respectively. The Cape flats dune Strandveld and the Langebaan dune Strandveld associated with these cordons are more extensive than other Strandveld ecosystems as they tend to extend the whole length of the dune cordons. In general, although nutrient enrichment, partly due to marine aerosol deposition, and the calcareous nature and depth of marine derived aeolian sands may be important factors in development of Strandveld-type vegetation, a combination of other factors including geology, presence of wave barriers, coastal topography, variations in sea level and climate may ultimately be responsible for establishment of these vegetation units along the CFR coastline.

5.7 References

Abanda, P.A, Compton, J.S, Hannigan, R.E., 2011. Soil nutrient content, above-ground biomass and litter in a semi-arid shrubland, South Africa. Geoderma 164, 128-137

Andrews, W.R.H., Hutchings, L., 1979. Upwelling in the southern benguela current. Progress in Oceanography 9, 1-81.

Birch, G.F., 1977. Phosphorites of the Saldanha Bay region. Transactions of the Royal Society of South Africa 42, 223-240.

Campbell, B.M., 1986. Plant spinescence and herbivory in a nutrient poor ecosystem. Oikos 47, 168-172

Chadwick, O.A., Derry, L.A., Vitousek, P.M., Huebert, B.J., Hedin, L.O., 1999. Changing sources of nutrients during four million years of ecosystem development. Nature 397, 491-497.

Cowling, R.M., 1983. Phytochorology and Vegetation History in the South-Eastern Cape, South Africa. Journal of Biogeography 10 (5), 393-419.

Cowling,R.M., Kirkwood, D., Midgley, J.J., Pierce, S.M., 1997. Invasion and persistence of bird-dispersed, subtropical thicket and forest species in fire-prone coastal fynbos. Journal of Vegetation Science 8 (4), 475-488

Cowling, R.M., Proche, S., Vlok, J.H.J., 2005. On the origin of southern African subtropical thicket vegetation. South African Journal of Botany 71(1), 1-23

Cowling, R.M., Knight , A.T., Privett, S.D.J., Sharma G., 2009. Invest in opportunity, not inventory of hotspots. Conservation Biology 24 (2), 633-635.

Cramer, M.D., Hawkins, H.J., 2009. A physiological mechanism for the formation of root casts. Palaeogeography, Palaeoclimatology, Palaeoecology 274, 125–133.

Dawson, T.E., 1998. Fog in the California redwood forest: ecosystem inputs and use by plants. Oecologia 117, 476-485.

Eccles, N.S., Esler, K.J., Cowling, R.M., 1999. Community structure and dynamics Spatial pattern analysis in Namaqualand desert plant communities: evidence for general positive interactions. Plant Ecology 142, 71-85

Franceschini, G., Compton, J.S., 2006. Holocene evolution of the sixteen mile beach, Western Cape, South Africa. Journal of Coastal Research 22 (5), 1158–1166.

Hinsinger, P., 2001. Bio-availability of inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. Plant and Soil 237, 173-195

Jarman, P.L., 1974. The social organization of antelope in relation to their ecology. Behaviour 48, 215-265.

Jury, M.R., 1987. Aircraft observations of meteorological conditions along Africa's west coast between 30^o-35^o south. Journal of climate and applied meteorology. 26, 1540-1552.

Kruger, F.J. 1983., Plant community diversity and dynamics in relation to fire. In: Kruger F.J. (Eds.), Mediterranean-type ecosystems. The role of nutrients, Springer, New York, pp. 446-472.

Mills, A.J., Burch, S.C., Stephenson, J.D., Bailey, R.V., 2012. Carbon stocks in fynbos, pastures and vineyards on the Agulhas Plain, South Africa: a preliminary assessment. South African Journal of Plant and Soil DOI:10.1080/02571862.2012.730636.

Mucina, L., Rutherford, M.C., 2006. The Vegetation of South Africa, Lesotho andSwaziland. SANBI, Pretoria pp. 804.

O’Dowd, C.D., Leeuw, G.D., 2007. Marine aerosol production: a review of the current knowledge. Philosophical Transactions of the Royal Society of America 365: 1753-1774.

Ochoa-Hueso, R., Allen, E.B., Branquinho, C., Cruz, C., Dias, T., Fenn, M.E., Manrique, E., Pérez-Corona, M.E., Sheppard, L.J., Stock, W.D., 2011. Nitrogen deposition effects on mediterranean-type ecosystems, an ecological assessment. Environmental pollution 159, (10) 2265-2279.

Olivier, J., 2002. Fog-water harvesting along the West Coast of South Africa: A feasibility study. Water South Africa 28 (4), 349-360.

Radloff, F.G.T., 2008. The ecology of large herbivores native to the coastal lowlands of the fynbos biome in the Western Cape, South Africa. PhD thesis. University of Stellenbosch, Stellenbosch.

Schlesinger, W.H., Gray, J.T., Gilliam, F.S., 1982. Atmospheric deposition processes and their importance as sources of nutrients in a chaparral ecosystem of southern California. Water Resources Research. 18 (3), 623-629.

Smith, M., Compton, J.S., 2004. Origin and evolution of major salts in the Darling pans, Western Cape, South Africa. Applied Geochemistry 19, 645-664.

Soderberg, K., Compton, J.S., 2007. Dust as a nutrient source for fynbos ecosystems, South Africa. Ecosystems 10, 550–561.

Stock, W.D., Lewis, O.A.M., 1986. Atmospheric input of nitrogen to a coastal fynbos ecosystem of the south-western Cape Province, South Africa. South African Journal of Botany 52 (4), 273-276.

Weathers, K.C., Lovett, G.M., Likens, G.E., Caraco, N.F.M., 2000. Cloudwater inputs of nitrogen to forest ecosystems in southern Chile: forms, fluxes, and sources. Ecosystems 3, 590–595

Westoby, M., Wright, I.J., 2003. The leaf size – twig size spectrum and its relationship to other important spectra of variation among species. Oecologia 135, 621–628.

Witkowski, E.T.F., Mitchell, D.T., 1987. Variation in Soil phosphorus in the fynbos biome, South Africa. Journal of Ecology 75, 1159-1171.