COASTAL MICROBIALITE SEEPS AS ACCESSIBLE MONITORING LOCATIONS OF LOCAL AQUIFER RESOURCES

Report to the

WATER RESEARCH COMMISSION

by

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Cover page image: a coastal microbialite pool at Seaview, South Africa (photographed by GMR)

EXECUTIVE SUMMARY

Local aquifers and water use

Nelson Mandela Bay Municipality is the largest metropolitan area in the Eastern Cape and is increasing its demand for potable freshwater. Due to climate change and multi-year droughts, alternative supplies to conventional surface water resources for bulk water supply are needed. Groundwater may be a feasible option if it is managed effectively. However, this should be developed in a sustainable manner and the effect of large-scale abstraction on the local environment should be considered. The primary users of groundwater in the area are the agricultural and residential sectors. This is for dairy, citrus, cattle and game farming, as well as forestry and household use. Management of groundwater in the western areas of Nelson Mandela Bay (NMB) is currently not well researched or monitored, unlike similar areas in the Western Cape and the nearby Uitenhage Subterranean Government Water Control Area. Aquifers in the region include the primary aquifer of the Cenozoic Algoa Group deposits and the secondary aquifer of the Palaeozoic metasediments of the Table Mountain Group (TMGA). The quantity and quality of water stored is dependent on local annual rainfall, climate, vegetation, lithology, infiltration, and discharge rates. In general, water derived from the TMGA is of good quality although with high iron content, whereas water from the coastal aquifers have a higher salt content. Currently, the sustainable yield from the primary and secondary aquifers in NMB is not well-constrained but estimated to be around 28 Mm^3 per annum (Murray *et al.,* 2008). Coastal springs in the NMB area are selected for this study due to their accessibility, their proximity to NMB making them potentially viable for extraction, and their associated active microbialite growth which support unique biodiversity and geoheritage. The exemplar microbialite selected sites include those of Seaview, Laurie's Bay, Schoenmakerskop, Sappershoek and Cape Recife. The calcium-rich coastal seeps offer a unique environment that can sustain microbial growth. Modern coastal microbialite systems may be useful as ecosystem health indicators, especially as related to groundwater quality and flow. Pollution and mismanagement pose a potential threat to the sustainable use of groundwater. Contamination is possible through saltwater intrusion due to increased abstraction and/or the introduction of anthropogenic pollutants to the aquifers. Pollutants may be derived from agricultural fertilisers, industries and septic tanks from residential areas.

The management of groundwater resources should, therefore, be improved and the amount and location of boreholes regulated. For example, currently there is no limit to the number of boreholes that can be drilled in the NMB area. However, the current water restrictions issued by the Department of Water and Sanitation does limit the use of groundwater. More knowledge sharing from private parties and local municipalities can improve the sustainable management of groundwater resources and mitigate any negative environmental impacts.

Aquifer discharge through coastal seeps

An objective of this study is to determine the flowrate and amount of groundwater discharge along the coast of Nelson Mandela Bay. Where the freshwater seeps onto rocky intertidal zones, microbialites form due to mineral precipitation and/or sediment trapping-and-binding by microbial communities. These deposits might be used as indicators of past freshwater seeps and may hold anthropological significance. This study was conducted along the southern coastline of NMB, with Maitland's Beach and Cape Recife Nature Reserve being the western and eastern limits, respectively. A total of five main sites were selected based on previous research; these comprise well-developed microbialite biomass, are accessible, and have high flowrates. Along with three supplementary sites per main site, these were used for monitoring of freshwater discharge and microbialite growth rate from July 2022 to June 2023 using capture-cup and tracer measurements of flowrates. A spatial assessment of flowrate was conducted and indicated that the total discharge between Cape Recife and Maitlands is ~45.8 ℓ/s, in the order of 3.96 Mℓ/d. Of the 1,533 freshwater seeps identified, 78% showed microbialite deposits. Topography of the coast indicated that this might influence the flowrate. Calcareous sediment of sandy beaches within the study area supported lower flowrates, while rocky shores with lithified rock had higher discharge. Seasonal differences in the volume discharged were evident, with winter having higher flowrates. Flow paths and discharge rates are affected by inland lithological differences and indicate variability linked to rainfall events that show lag effects depending on aquifer origins. This report is the first spatial analysis of the volume of groundwater discharging through microbialite-fed seeps.

Nutrient inputs to coastal seeps

Modern coastlines receive anthropogenic inputs from various pollutant vectors that are exacerbated by freshwater flow paths which can concentrate and direct these towards the coast. These pathways are well-understood for surface waters such as rivers and estuaries but are less apparent for groundwater hydrological cycles, although not necessarily less impactful on the coastline in terms of inputs. Here we aimed to quantify the nutrient load flowing through microbialite-forming seeps that are fed by groundwater discharge in the supratidal zone of the NMB, South Africa. Results from this study and comparisons to previous work in the area show that inorganic nutrient loads are highest closest to urban developments, likely indicative of nutrient inputs linked to anthropogenic-derived organic waste such as septic tanks. There appears to be some temporal variability in these inputs, reflecting both annual as well as climatic variability, possibly linked to rainfall cycles. Given the quantity of freshwater flowing to the coasts via the microbialite-forming seeps, it is estimated that at least 3.6×10^3 kg/a of dissolved inorganic nitrogen and 0.029×10^3 kg/a of dissolved inorganic phosphorous are entering the coastline via this pathway. The DIN load entering the SSLiME therefore represents a considerable and previously unaccounted nutrient input to the NMB environ that is closer to natural inputs of nutrients at the Alexandria dunefield than it is to local wastewater treatment work nutrient loads. Further research linked to this pathway should aim to better quantify the temporal periodicity as well as to disclose the source of the nutrients using isotopes and organic pollutants as supplementary datasets. The microbialite-forming pools might also be acting as buffers of coastal pollution as there is some indication of nutrient uptake between inflow and outflow water, thereby potentially contributing as an ecosystem service in terms of protection against eutrophication.

Hydrological isotopes and groundwater connectivity

As a drought-stricken region, the Nelson Mandela Bay Metropolitan and Kouga Local Municipalities (NMBM and KLM) are facing dwindling surface water supply. Hence abstraction of groundwater reserves is seen as a potential ameliorating alternative supply, but several aspects of the local hydrological cycle are not well understood, such as the local meteoric water line (LMWL). Furthermore, the potential link between catchment recharge and coastal outflow, including the impacts on groundwater-dependent ecosystems (GDEs), is not well known for this region fed by the Algoa Water Supply System. This study therefore aimed to provide the first LMWL for this region, and by extension the Eastern Cape of South Africa, using monthly rainfall totalisers setup within catchment and coastal sites. Additionally, this was compared to inland springs and boreholes as well as coastal springs during 2022/2023. Samples were analysed for stable isotopes of hydrogen and oxygen. Results suggest that the regional LMWL falls within the range of South African LMWLs. Inland catchment locations had the lowest isotopic ratios, which confirms their higher altitude state. Coastal springs associated with GDEs such as supratidal spring-fed living microbialite ecosystems (SSLiME) revealed mixed isotopic signatures which suggest recharge contributions from both the primary and secondary aquifers in the area. As such, these locations could be used as monitoring points for groundwater within the NMBM and KLM. However, this study represents a preliminary annual baseline and future long-term research is needed to confirm these trends as well as the influence of other groundwater recharge locations (e.g. temporary pans and wetlands) or precipitation events (e.g. cut-off lows or easterly versus westerly storm systems).

Overall aims and report structure

This research report addresses the following aims, as originally outlined in the approved WRC project proposal (C2022/2023-00833):

1. To quantify the amount of groundwater discharging to the coast via SSLiME in NMB.
2. To quantify the extent of nutrient input to SSLiME in NMB.
3. To assess the level of connectivity between SSLiME and inland water sources of NMB.
4. To determine if SSLiME can be used as accessible monitoring location of local aquifer resources.

The report is structured according to these aims such that **Chapter 1** first reviews the available local knowledge of coastal aquifers associated with SSLiME in NMB (originally submitted as Project Deliverable 1, April 2022). Thereafter, each subsequent chapter addresses each subsequent primary aim: **Chapter 2** quantifies the volume of groundwater discharging through SSLiME in NMB (submitted as Project Deliverable 2, October 2022), **Chapter 3** uses this volume estimation and links this with assays of inorganic nutrients to determine the nutrient load entering the coast through this pathway (submitted as Project Deliverable 3, November 2022), and **Chapter 4** uses the stable isotope ratios of water measured from rainfall totalisers over an annual cycle linked to samples at the coast and inland groundwater to map the hydrological connectivity of the region and establish the first LMWL (submitted as Project Deliverable 4, June 2023). Finally, the report is concluded in **Chapter 5** with a synopsis of the new knowledge determined during this project towards utilising the SSLiME as sentinels of inland hydrological processes and anthropogenic impacts.

Key findings and future recommendations

Knowledge on the dynamics and extent of groundwater discharge through coastal seeps is scant in the NMB, with this project's research filling an important knowledge gap especially considering the planned increased utilisation of this water resource in the region. In the order of 4 Mℓ/d of groundwater is flowing through the SSLiME of NMB, and this figure is likely an underestimate of local coastal aquifer discharge considering the undocumented elements of the cycle, for example the submarine groundwater discharge component. Flowrates appear to comprise a persistent baseflow likely from distal aquifers with an ephemeral flow linked to precipitation that displays an approximately monthly or seasonal lag time in flowrate signals coupled to precipitation volume. Given this large amount of groundwater exiting the SSLiME to the coast, and the quantity of nutrients present in the inflowing seepage, that are likely sourced from both environmental and anthropogenic origins, this represents a substantial freshwater input but mostly natural nutrient load. This might be contributing to regional recent coastal primary productivity or eutrophication processes. The stable isotope ratios of water suggest that the recharge source for the SSLiME outflow is predominantly recent and rapid, which confirms the close coupling between flowrates and rainfall. However, the mixed signature also demonstrates that there is some interaction between secondary and coastal primary aquifers. This first instance of a LMWL provides some clues on the periodicity of rainfall processes at the region's interface between winter- and summer-rainfall regions. It also emphasises the need for a longer-term investment in stable isotope monitoring of precipitation events and cycles. Our research shows that the SSLiME can be used as accessible monitoring locations of local coastal aquifers because: (1) they respond rapidly but not immediately to precipitation variability buffered by primary aquifer flow paths or potentially disrupted by abstraction, (2) they display nutrient signatures linked to anthropogenic sources such as septic tank overflow, and (3) they mirror localised hydrological stable isotope tracers to suggest a close coupling between precipitation, groundwater and discharge points. Future efforts should be directed towards regular monitoring of these SSLiME linked to coastal inland aquifers and in this report we provide a suggestion on the nature of this monitoring, including details on what should be collected, how often this should be done, and which key indicators should be noted for potential management interventions. Gaps in this study that could prompt future research efforts include: (1) the identification of other pollutants associated with the SSLiME, particularly given the increasing reliance on coastal aquifers for groundwater abstraction, (2) the setting up of a long-term monitoring station for hydrological stable isotopes in the region given that this only exists in South Africa in Western Cape and Gauteng, thereby missing the interface zone between winter and summer-rainfall regions, (3) the characterisation of the functional role and risk of SSLiME linked to altered inflowing aquifer processes and water quality. Some of these future research priorities and monitoring efforts are already in the planning and proposal stages.

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This is a research output of the Supratidal Spring-Fed Living Microbialite Ecosystems (SSLiME) Project, coordinated by GMR.

Declaration of Publications and Student Projects

The research contained in this report is largely the work of two postgraduate students, Carla Dodd (CD) and Tristin W. O'Connell (TWO), at the Nelson Mandela University, who are both co-authors of this report. Both students are due to submit their thesis and dissertation, respectively, for examination in December 2023/February 2024. As such, many of the results are directly extracted from their postgraduate research outputs. There is therefore some necessary overlap with these, particularly in **Chapter 2** (lead author: TWO), **Chapter 3** (lead author: CD), and **Chapter 4** (lead author: CD). Wherever possible, the text and information in this report has been edited to be different from their thesis and dissertation, respectively, but oftentimes this is not possible nor optimal.

Please see below for specific outputs linked to this WRC Project and their student research. At least three additional peer-reviewed publications are envisaged from their research in the near future.

Postgraduate student theses and dissertations

1. Dodd, C. (submitted for examination in December 2023) "The Algoa Bay region groundwater cycle – linking source to coast". PhD Thesis, Nelson Mandela University, South Africa.

2. O'Connell, T.W. (to submit for examination in March 2024) "Ground- and marine water inputs into supratidal microbialite systems along the Nelson Mandela Bay coastline". MSc Dissertation, Nelson Mandela University, South Africa.

Manuscript submissions

1. Dodd, C, & Rishworth, GM (2023) Coastal urban reliance on groundwater during drought cycles: opportunities, threats and state of knowledge. *Cambridge Prisms: Coastal Futures* 1: e11, 11-13.

2. Dodd, C, Cawthra, HC, Massmann, G, & Rishworth, GM (submitted and returned) Groundwater resources of the Algoa Water Supply System. *Water SA*.

Conference presentations

1. Dodd, C, Rishworth, G, Cawthra, H, & Massmann, G (2022) The Algoa Water Supply System: Drought and Groundwater Use Linked to Coastal Aquifer Discharge. *17th South African Marine Science Symposium*. Durban, South Africa.

2. Dodd, C, Cawthra, HC, Massmann, G, & Rishworth, GM (2023) Flushed away – nutrient load distribution related to supratidal spring-fed living microbialite ecosystems. *GEOHAB*. Reunion Island.

3. Dodd, C, Cawthra, HC, Massmann, G, & Rishworth, GM (2023) Multi-tracers unravel the threats to coastal ecosystems dependent on groundwater during droughts. *INQUA XXI Congress*. Rome, Italy.

4. O'Connell, T, Bornman, T, Dodd, C, Rishworth, G, & Anderson, C (2023) Groundwater discharge and tidal flushing dynamics related to modern microbialite systems on a drought prone rocky coast. *INQUA XXI Congress*. Rome, Italy.

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AG	Algoa Group
AWSS	Algoa Water Supply System
EC	Electric Conductivity
GDE	Groundwater Dependent Ecosystem
GMWL	Global Meteoric Water Line
GNIP	Global Network of Isotopes in Precipitation
GRIP	The Groundwater Resources Information Project
KLM	Kouga Local Municipality
LMWL	Local Meteoric Water Line
NMB	Nelson Mandela Bay
NMBM	Nelson Mandela Bay Municipality
NWRS-1	National Water Resource Strategy Phase 1
SSLiME	Supratidal Spring-fed Living Microbialite Ecosystems
TDS	Total Dissolved Solids
TMG	Table Mountain Group
TMGA	Table Mountain Group Aquifer
USGWCA	Uitenhage Subterranean Government Water Control Area

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1. Literature review and available knowledge of coastal groundwater seeps in the Nelson Mandela Bay environ

Seaview SSLiME
(photographed by GMR)

1.1 Introduction

Water availability has always played a crucial role in human settlement establishment, growth and ultimately survival. This remains evident today as settlements are often near major water resources and many international borders are controlled by major river systems and watersheds (de Wit & Stankiewicz, 2006). Surface water availability in South Africa varies both geographically and seasonally, with the confluence of the eastern summer and western winter rainfall systems occurring along the southern coast (e.g. Mahlalela *et al.,* 2020). The Nelson Mandela Bay Metropolitan Municipality (NMBM) is a Category A municipality located on the southeastern coast of South Africa and includes Gqeberha (previously Port Elizabeth), Kariega (previously Uitenhage) and Despatch (NMBM, 2022). The metro is home to in excess of one million residents and is the largest metropolitan in the Eastern Cape Province (Naidoo *et al.,* 2016; NMBM, 2022).

The City of Gqeberha has a history of water supply issues (Raymer, 2008) and the first colonial structure, Fort Frederick, was constructed to protect the town's water supply and landing place (Ferreira, 1990). After 200 years of city development and population growth, the demand on conventional surface water supplies has increased from ~3.22 Mℓ/d in 1898 to ~300 Mℓ/d in 2021 (Raymer, 2008; NMBM, 2022). Coupled with climate change and the occurrence of multi-year droughts, alternative options for water supply are being investigated to combat the current water crisis experienced in the NMBM (e.g. Pietersen, 2021).

Groundwater is a promising alternative for bulk water supply in the Nelson Mandela Bay (NMB) area. But to manage groundwater use effectively it is necessary to review our current understanding of groundwater resources in NMB, how sustainable the use of these resources is and what other factors may contribute to the overall health of the local environment related to groundwater.

This chapter provides a brief state-of-the-art review of the body of literature (both published and grey literature) dealing with groundwater in the NMB area, with a specific focus on coastal seepage.

1.2 Environmental description

1.2.1 Groundwater terminology and some definitions

Groundwater is the term used when referring to the saturated level of the subsurface water. Subsurface water is divided into saturated and unsaturated zones, with the boundary between these two zones termed the water table. The unsaturated level is the zone above the water table where the water pressure is less than the atmospheric pressure. The saturated level is below the water table and has a water pressure greater than the atmospheric pressure. The saturated level will henceforth be referred to by its common term, the aquifer (Fitts, 2002).

Aquifers are classified based on the type of porosity of the host rock that allows water to be stored and distributed within the lithology. Two types of aquifers occur in the NMBM area, namely primary and secondary aquifers (Lomberg *et al.,* 1996). The primary aquifer refers to an aquifer where water is stored within the primary porosity of the lithology (e.g. interstices within constituent sand grains). Conversely, a secondary aquifer stores water within secondary porosity formed by fractures, joints, and faults. In the NMBM area, the Algoa Group lithologies constitute the primary aquifer, whereas the Table Mountain Group composes the secondary aquifer (Lomberg *et al.,* 1996).

Groundwater resources are naturally accessible to humans through springs and groundwater-fed lakes and rivers, as well as through man-made structures such as boreholes and wells (MacDonald & Davies, 2000). This report and subsequent research will primarily deal with springs, boreholes and wells.

Springs are natural outlets of groundwater where the water table intersects with the ground surface (Kresic, 2010). There are over 500 coastal springs (a.k.a. seeps) along the South African southern coast between Cape Recife and Storms River, several of which flow into microbialite systems (Perissinotto *et al.,* 2014). Microbialites are biogenic sedimentary deposits composed of calcium carbonate and/or trapped sediment built during the metabolism of microorganisms such as cyanobacteria and diatoms (Burne & Moore, 1987). The coastal microbialite systems in South Africa are groundwater dependent and may, therefore, be potentially used as monitoring points for groundwater quality (Rishworth *et al.,* 2020b).

The National Water Act (Act No. 36 of 1998) defines a borehole as: "a well, excavation, or any other artificially constructed or improved underground cavity which can be used for the purpose of intercepting, collecting or storing water in or removing water from an aquifer; observing and collecting data and information on water in an aquifer; or recharging an aquifer" (DWAF, 1998). Boreholes are drilled to reach the subsurface water. Modern technology has made this common practice where springs are not available.

1.2.2 Regional site position and selection criteria

The study sites were selected due to their accessibility, proximity to NMB to be economically viable for extraction, active microbialite growth and previous research. Vegter (1990) divided South Africa into 64 hydrogeological regions. This is based on the region's climate and lithology. The study area of Nelson Mandela Bay falls in the Vegter-region called the "Southern Cape Mountain Ranges" (Figure 1 and Figure 2).

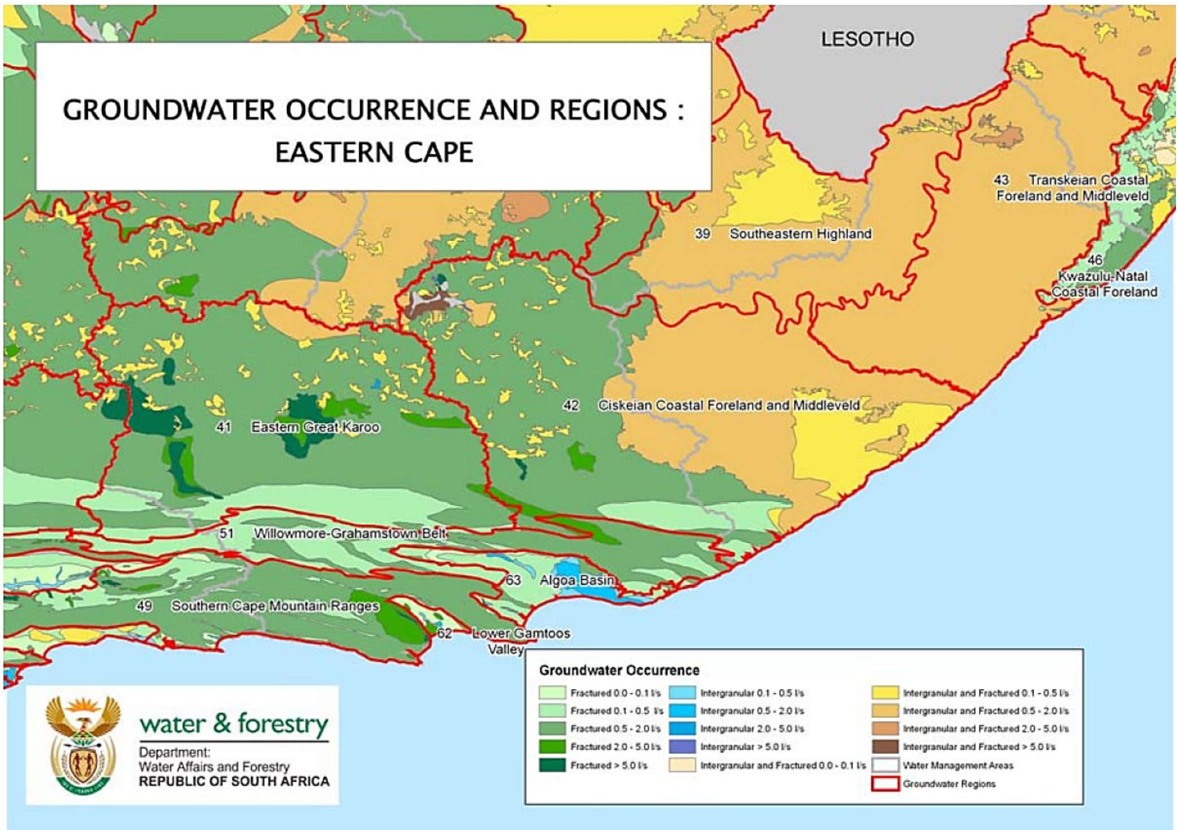


***Figure 1**. Groundwater occurrence in the Eastern Cape Province of South Africa indicating the type and yield of groundwater. Figure reproduced from DWA (2010).*

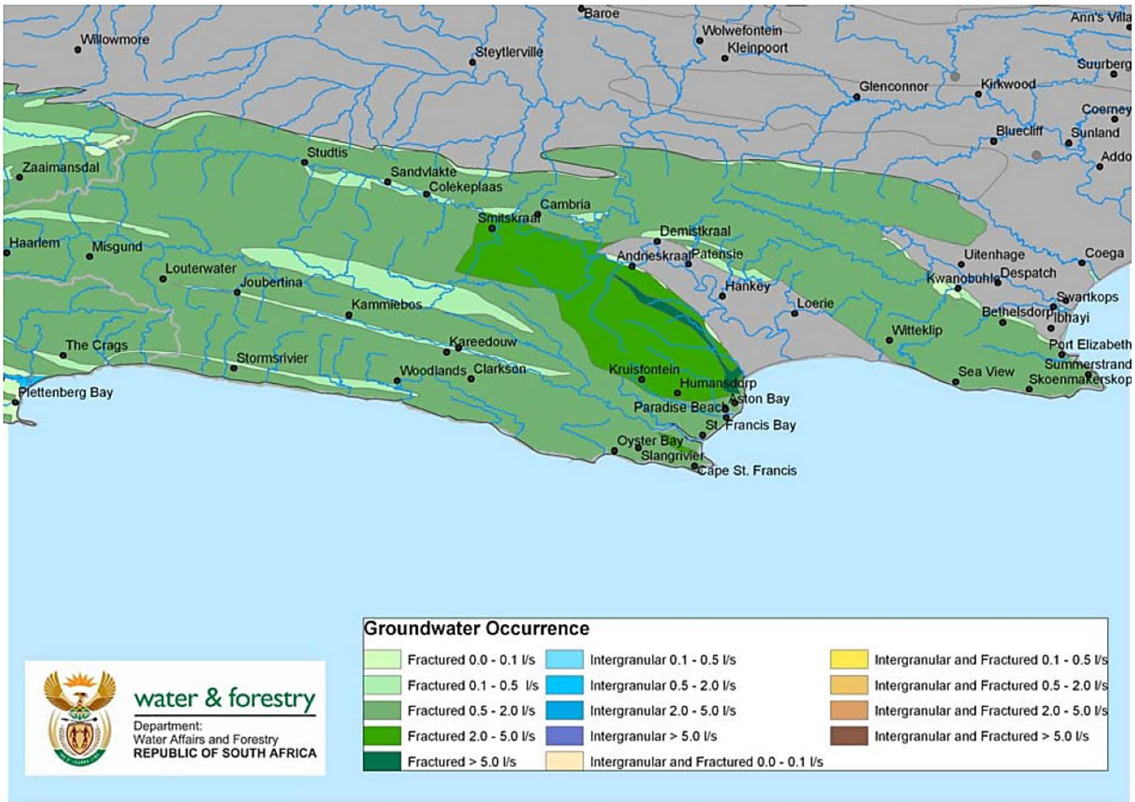


***Figure 2**. Groundwater occurrence in the Vegter-region of the Southern Cape Mountain Ranges indicating the type and yield of groundwater. Figure reproduced from DWA (2010).*

Five well-developed microbialite systems were selected within the Southern Cape Mountain Ranges (Figure 3) for the purposes of this report because they have previously been well-studied, namely (from west to east):

1. Seaview: Lat = -34.017544°; Long = 25.365689°

2. Laurie's Bay: Lat = -34.032372°; Long = 25.402697°

3. Schoenmakerskop: Lat = -34.041045°; Long = 25.538311°

4. Sappershoek: Lat = -34.043196°; Long = 25.551901°

5. Cape Recife: Lat = -34.045090°; Long = 25.568686°

Due to the high pH and alkalinity of the seeps, these sites are some of the best developed microbialite sites in South Africa (Rishworth *et al.,* 2020b).

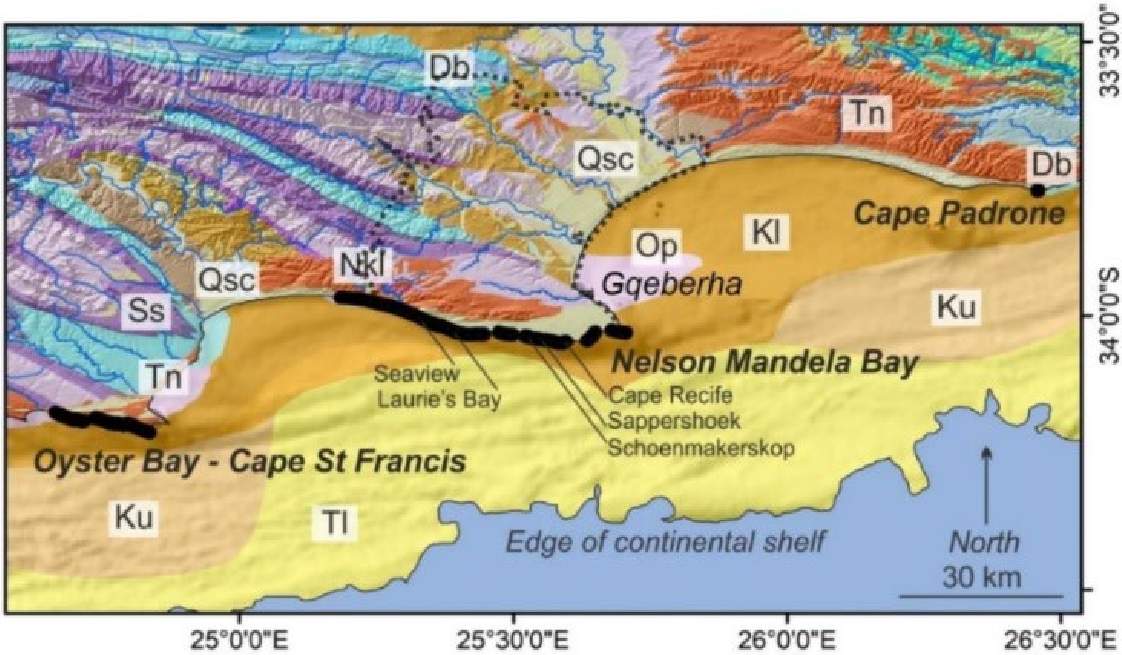


***Figure 3**. Locations of the selected microbialite systems, from Seaview to Cape Recife. The black dots represent known location of seeps in the Nelson Mandela Bay area. Map adapted from Rishworth et al. (2020b).*

1.2.3 Regional use of groundwater and management

Previously, groundwater utilisation was restricted to areas that were suffering from water shortages. It was only since the 1980s that groundwater management and sustainable use have been developed (Jia, 2007). During the 1980s some of the leaking artesian boreholes in the NMB area were closed to increase the yield of the springs in the Uitenhage area (DWA, 2010).

Although the NMBM is the fifth largest municipality in the country, agricultural activities play an important role in its development. The coastal region is home to dairy farming, while inland agriculture includes citrus, cattle, game, and forestry. Sand, stone, and lime mining of the Table Mountain, Algoa and Uitenhage Groups also occur. The primary users of groundwater in the area are the agricultural and residential sectors (DWA, 2010).

The NMB and surrounding areas are currently experiencing a multi-year drought and surface water resources are seriously diminished with local supply dams below 30% of combined capacity for months at a time (NMBM, 2022). Groundwater resources may augment supply for industry, as well as residential and rural communities and is being explored by the municipality as a long-term solution (NMBM, 2022). For example, following the 2008-2011 drought, the NMBM launched a feasibility study regarding the use of groundwater to diversify and augment the conventional surface water resources (David Raymer, personal communication). Consequently, several groundwater schemes and wellfields were developed and commissioned recently (see Table 1). Included in the groundwater development infrastructure is the Coegakop biofiltration unit, which uses biological oxidation and sand filtration to treat the groundwater, especially with regards to high iron and manganese content. It is estimated that groundwater use accounts for 10% of the total NMBM water demand (David Raymer, personal communication). Furthermore, private groundwater development included over 50 boreholes drilled by non-profit organisations and private companies such as the Gift of the Givers and Nelson Mandela Bay Business Chamber (David Raymer, personal communication).

However, it is necessary to understand the use of groundwater and potential pollutants in the selected area, the future projected supply and demand and the economic, social, and ecological importance of the aquifers in the region. Yet research on this in Gqeberha is largely lacking or outdated. On the other hand, the Uitenhage Subterranean Government Water Control Area (USGWCA) was established in 1957 (see Figure 4) and has been well researched and monitored (Heaton *et al.,* 1986; Vogel *et al.,* 1999; Baron, 2000; Maclear, 2001).

The USGWCA utilises groundwater through the Coega Ridge, where the total abstraction in 1998 was 4.8 x 10^6 m^3/a from the northern Coega Ridge, and the southern Uitenhage Trough, where abstraction was approximately 2.05 x 10^6 m^3/a, because some of the boreholes have fallen into disuse (Meyer, 2008). As boreholes are developed and managed in the greater Algoa Bay area, it will be necessary to further monitor the aquifers and ensure the sustainable utilisation of groundwater especially during drought periods. According to Campbell *et al.* (1992) municipalities and other regional services do not have enough knowledge on the extent of the aquifers in the area. Therefore, knowledge sharing and acquirement on the subject can also improve management.

Table 1. *Groundwater schemes and reservoirs that supply the Nelson Mandela Bay Municipality (supplied by David Raymer).*

Source	**Area**	**Yield (Mℓ/d)**	**Date Commissioned**
Coegakop Wellfield	Uitenhage Artesian Basin	10.0	April 2023
Bushy Park Wellfield	Bushy Park	10.2	March 2023
St Georges Park Reservoir	Moregrove Fault	2.1	February 2023
Glendinning	Moregrove Fault	2.3	November 2022
Fort Nottingham Reservoir	Moregrove Fault	1.0	November 2022
Fairview	Moregrove Fault	1.5	November 2022
Uitenhage Springs	Uitenhage Artesian Basin	5.9	

Figure 4. *Map indicating the locality of a) South Africa in an African context; b) the Algoa Water Supply System within the Eastern Cape Province and c) the surface water resources within the AWSS, municipal and Uitenhage Subterranean Government Water Control Area boundaries and places of interest.*

1.3 Groundwater and microbialites

Microbialites are defined as "organosedimentary deposits that have accreted as a result of a benthic microbial community trapping and binding detrital sediment and/or forming the locus of mineral precipitation" (Burne & Moore, 1987). These deposits are the oldest macroscopic evidence for life on earth and have a continuous presence in the geological record spanning from the Archean to the present (Riding, 2011). Microbialites act as a record of environmental changes and have been used to reconstruct palaeoenvironmental conditions (e.g. Webb & Kamber, 2011). However, modern coastal microbialite systems may also be useful as ecosystem health indicators, especially as related to groundwater quality and flow.

In South Africa, extensive microbialite systems form along the supratidal zone of the coast where calcium-rich groundwater is discharged as coastal springs/seeps (Rishworth *et al.,* 2020b). Globally, similar systems are found in Australia and the United Kingdom. Microbialites along the South African coast occur intermittently from Mozambique on the northeastern coast, to the Namaqua National Park on the west coast. These deposits accrete on lithologies ranging from the Precambrian Gamtoos Group to Quaternary mudrock (Rishworth *et al.,* 2020b). However, those occurring on the south coast at NMB are the best developed in terms of thickness and lateral extent (Rishworth *et al.,* 2020b). Since all the supratidal microbialites are dependent on constant groundwater flow from coastal springs, it might be possible to use them as a looking glass into the history of groundwater seepage. For example, remnant inactive systems are indicative of previous groundwater discharge. Further details on the formation, ecological value and potential tourism and research opportunities of supratidal microbialites are described in Rishworth *et al. (*2020b).

1.4 Geology of aquifers in Algoa Bay

The hydrogeology of the Western and Southern Capes is dominated by the Table Mountain Group Aquifer (TMGA), stretching from Vanrhynsdorp in the west to the Algoa Bay in the east (Jia, 2007) (Figure 5). Consolidated rock was formed 800 million years ago and through orogenesis, continental uplift, weathering and erosion, competent rock underwent brittle failure which resulted in fractures (Meyer, 1998). Incompetent rock was less prone to fracturing, thus inhibiting the formation of fracture porosity. According to Meyer (1998), the fractured nature and high annual rainfall in the mountainous regions of the Table Mountain Group results in favourable conditions for aquifer recharge.

Groundwater storage may, however, be limited (Meyer, 1998). Furthermore, it is necessary to determine the sustainable yield of aquifers on a regional level, because the properties of the aquifers in the Table Mountain Group can differ extensively (Jia, 2007). This has been well-studied along the western and southwestern coast (Roets *et al.,* 2008a; Roets *et al.,* 2008b; Colvin *et al.,* 2009; Parsons, 2009; Lin *et al.,* 2014; Miller *et al.,* 2017; Lin & Lin, 2019; Mandiola *et al.,* 2021) but more research is required regarding the local aquifers in NMB.

In terms of groundwater quality, sandstone aquifers like those found in the Table Mountain group generally have better quality and greater yields than those of argillaceous lithologies. A chemical composition of a sodium-chloride-magnesium is typically found in the Table Mountain Group and boreholes that were drilled into more shale-rich deposits delivered less potable water (Meyer, 1998). This means that there is a potential for good quality groundwater to be found in the Algoa Bay region. Table 2 shows the key geological units of the NMB region that have been studied for groundwater exploration and Table 3 shows the geological composition for the Algoa Group. In general, the deeper layers consist mainly of quartzitic sandstone and the upper Cenozoic layer of the Southern Cape Mountain Ranges in the coastal zone consist mostly of dune fields, calcareous sand, soil horizons and shell middens.

The quantity of water stored in an aquifer depends on factors such as local annual rainfall, climate, vegetation, lithology, infiltration, and discharge rates. A sustainable yield of less than 35,515 ℓ/s is possible from the TMGA (Jia, 2007). Regional sustainable yield is not well-constrained (see Murray *et al.,* 2008), but the potential resources in NMB can be determined by calculating the recharge, storage capacity and discharge from the regional aquifers.

In coastal suburbs of NMB, such as Humewood and Summerstrand, recent coastal sands are also present. Yet, little is known about the potential of the primary aquifers in the study area (Lomberg et al., 1996). Compared to stabilised dunes, recent sands are coarser, less compact and have less calcretisation and therefore has higher aquifer potential (Lomberg et al., 1996). The areas with little residential development have a high infiltration potential as rainfall infiltrates the sand and recharges the aquifers. Where dunes have stabilised via alien vegetation, rainwater is less likely to infiltrate and evaporation increases (Lomberg et al., 1996).

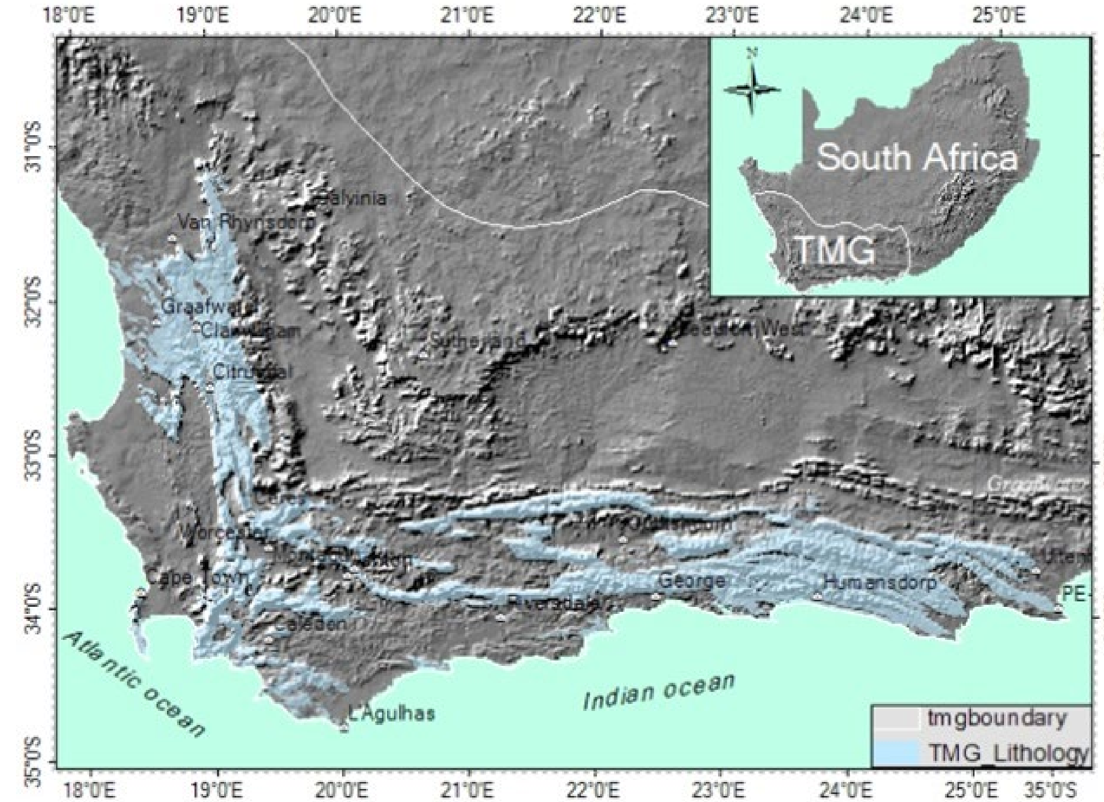


Figure 5. *Extent of the Table Mountain Group Aquifer. The TMGA consists mainly of fractured sandstone, siltstone, shale and mudstone, underlain by Precambrian metaphoric rock and overlain by Neopaleozoic deposits. Figure reproduced from Jia (2007).*

Table 2*. Simplified stratigraphic sequence for the study area as referred to in-text or relating to hydrological literature, that aligns with relevance to groundwater dynamics of the Port Elizabeth (now Gqeberha)/Uitenhage/Addo area. Adapted from Meyer (2008).*

Period / Epoch /Age	Group	Sub-group	Formation	Lithology
Holocene				Alluvium, calcrete and dune fields
Quaternary (1.65-0.1 Ma)	Algoa		Refer to Table 3	
Tertiary (67-1.65 Ma)				
Cretaceous/ Jurassic (210-67 Ma)	Uitenhage		Sundays River	Greenish-grey mudstone, sandstone
			Kirkwood	Reddish, greenish mudstone, sandstone
			Enon	Conglomerate
Devonian (410-360 Ma)	Bokkeveld	Ceres	Gamka	Feldspathic sandstone, fossiliferous
	Table Mountain	Nardouw	Baviaanskloof / Kouga / Tchando	Arenite, quartz sandstone
			Cedarberg / Peninsula	Quartzite, quartz sandstone

Table 3. *Regional geology and ages as found in the Algoa Group of the Southern Cape Mountain Ranges Vegter-region. Sediments associated with Algoa group consist mainly of calcareous sandstone, sandy limestone, conglomerate and coquinite, adapted from Le Roux (1990).*

Group	**Formation**	**Epoch**	**Lithology**
Algoa Group (Cenozoic Period)	Schelm Hoek	Holocene	Unconsolidated wind-blown sand
	Nahoon	Middle – Late Pleistocene	Well consolidated calcareous sandstone, aeolianite, palaeosols
	Salnova	Middle Pleistocene	Pebbly coquina, conglomerate, semi-consolidated calcareous sandstone
	Nanaga	Late Pliocene – Early Pleistocene	Semi-consolidated calcareous sandstone, aeloanite
	Alexandria	Miocene to Pliocene	Calcareous sandstone, pebbly coquina, basal conglomerate with scattered oyster shells

1.5 Groundwater chemistry

Groundwater is considered most pure with the least amount of dissolved solids near its recharge point (Campbell *et al.,* 1992). Rainfall is the main source of recharge to unconfined aquifers and comprises between 8% and 30% of the annual rainfall (Campbell *et al.,* 1992). Upon infiltration, the water is then slightly acidic and high in oxygen and carbon dioxide. It is the movement to the discharge areas that alter the original concentrations via geochemical processes. Movement through organic matter and interactions with mineral constituents increase the dissolved salts, whereas movement through sand and plant roots increase the carbon dioxide concentration (Campbell *et al.,* 1992). The groundwater salinity can be affected by the following factors: evapotranspiration, sea water intrusion, salt leaching, weathering and erosion of rocks, selective retention of salt by plants, and the retention time of the water in the aquifer (Campbell *et al.,* 1992).

1.5.1 Groundwater chemistry in NMB

Coastal aquifers tend to have a higher salinity due to saltwater intrusion and deposition of salt by sea spray (Campbell *et al.,* 1992). In NMB, the groundwater of the inland suburbs is of sodium chloride type, while groundwater from the coastal suburbs has a greater Ca/Mg HCO_3 component (Rosewarne, 2002) (see also Figure 6). Most boreholes in NMB have a high chloride concentration and areas which were irrigated with treated sewage effluent and nitrogenous fertilizers had high nitrate concentrations (Rosewarne, 2002). In the TMG, it is typical to have high iron concentrations, but some boreholes tested in NMB had higher iron concentrations than the normal TMG range. This might be indicative of casing corrosion within the borehole. The boreholes tested did not show significant organic carbon levels or bacteria levels (Rosewarne, 2002).

The TMGA typically contains little dissolved salts as the sandstone is composed of mostly silica and little soluble salts (Rosewarne, 2002). The higher Ca/Mg HCO_3 water found closer to the coastline is due to the lime found in the coastal sands. Boreholes tested from the area are thus likely abstracting from primary aquifers or water from this overlying aquifer is leaking into the underlying secondary aquifer.

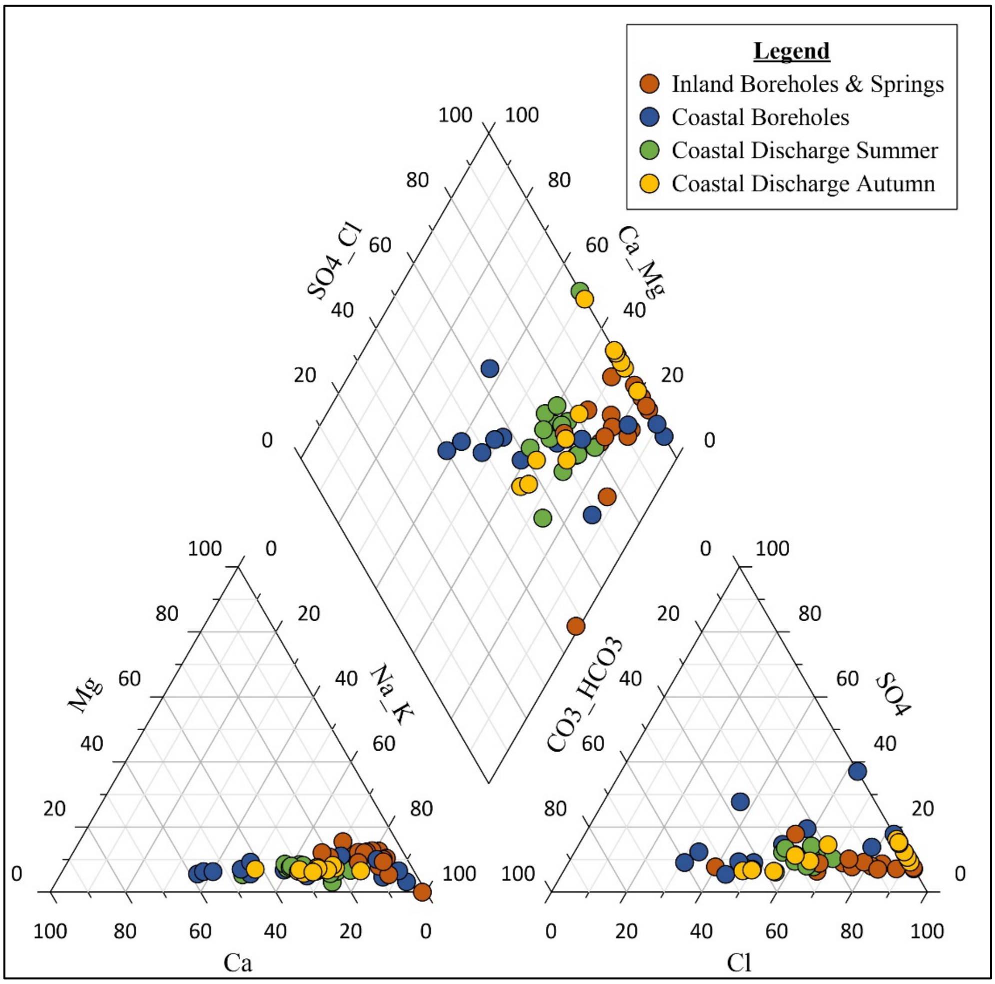


***Figure 6**. Piper diagram of groundwater samples collected within the AWSS area. Samples are separated according to their type/location. "Inland Boreholes & Springs": > 5 km from the coast; "Coastal Boreholes": < 5 km from the coast; Coastal discharge: SSLiME seeps. Data from Dodd (2023).*

Table 4 and Table 5 present the chemical composition of boreholes in the primary aquifers (Algoa Group and recent coastal sands) east of the NMBM that may be useful for comparison to the western portion of the system.

Table 4. *Example of the chemical composition of primary aquifer boreholes to the east of Algoa Bay. A: Farm Seaview southwest of Alexandria; water interception in basal Alexandria conglomerate; yield 2.6 ℓ/s. B: Farm Paarden Valley southwest of Alexandria, water interception in basal Alexandria conglomerate, possibly polluted by underlying formation; yield 0.7 ℓ/s. C: Maximum recommended limit for drinking water. D: Maximum allowable limit for drinking water. Reproduced from Meyer (1998).*

		A	B	C	D
EC	(mS/m)	288.0	212.0	70.0	300.0
TDS	(mg/ℓ)	1 834.0	1 356.0	1 200.0	2 000.0
pH		7.9	8.0	6-9	5.5-9.5
Na	(mg/ℓ)	366.0	280.0	100.0	400.0
K	(mg/ℓ)	3.4	2.9	200.0	400.0
Ca	(mg/ℓ)	187.0	120.0	150.0	200.0
Mg	(mg/ℓ)	66.0	42.0	70.0	100.0
Cl	(mg/ℓ)	856.0	615.0	250.0	600.0
SO_4	(mg/ℓ)	97.0	55.0	200.0	600.0
TAL (as $CaCO_3$)	(mg/ℓ)	202.0	191.0	20-300	650.0
F	(mg/ℓ)	0.2	0.22	1.0	1.5
NO_3 + NO_2 (as N)	(mg/ℓ)	2.45	2.49	6.0	10.0
PO_4 (as P)	(mg/ℓ)	0.012	0.011	-	-
Si	(mg/ℓ)	12.6	10.2	-	-
NH_4 (as N)	(mg/ℓ)	0.05	0.07	6.0	10.0
Fe	(mg/ℓ)	*	*	0.1	1.0

***Table 5**. Example of the chemical composition of boreholes in primary aquifers boreholes to the east of Algoa Bay. A: Boesmansriviermond, southeast of Alexandria. B: Boknes; southeast of Alexandria. C: Maximum recommended limit for drinking water. D: Maximum allowable limit for drinking water. Reproduced from Meyer (1998).*

		A	B	C	D
EC	(mS/m)	233.0	270.0	70.0	300.0
TDS	(mg/ℓ)	1 374.0	1 775.0	1 200.0	2 000.0
pH		7.4	9.6	6-9	5.5-9.5
Na	(mg/ℓ)	260.0	598.0	100.0	400.0
K	(mg/ℓ)	8.0	-	200.0	400.0
Ca	(mg/ℓ)	28.0	50.0	150.0	200.0
Mg	(mg/ℓ)	37.0	30.0	70.0	100.0
Cl	(mg/ℓ)	614.0	745.0	250.0	600.0
SO_4	(mg/ℓ)	29.0	120.0	200.0	600.0
TAL (as $CaCO_3$)	(mg/ℓ)	398.0	427.0	20-300	650.0
F	(mg/ℓ)	*	1.0	1.0	1.5
NO_3 + NO_2 (as N)	(mg/ℓ)	*	*	6.0	10.0
PO_4 (as P)	(mg/ℓ)	*	*	-	-
Si	(mg/ℓ)	*	*	-	-
NH_4 (as N)	(mg/ℓ)	*	*	6.0	10.0

1.6 Groundwater management

Water resources have been defined as "physical, chemical, biological, economic, cultural and many other assets of the nation's wetlands, streams, rivers, lakes and coastal oceans" (Cardwell *et al.,* 2006). It is interesting to note that this definition does not include groundwater. This might indicate a lack of sense of importance when it comes to groundwater as a necessary resource in an increasingly growing and resource-consuming society. Overcapitalisation has caused a rise in the utilisation of natural resources, which may be linked to overuse and ecological tipping points. The resilience of a system can be affected and may cause social and economic strife and a loss in biological diversity (Holling & Meffe, 1996).

1.6.1 Legislation dealing with groundwater

Internationally, both civil and common water laws evolved from the Roman Water Law and ties back to historical Europe (Lomberg *et al.,* 1996). Subsequently, a tendency to greater State control over water resources has evolved. Similarly, South Africa's water law legislation is based on legal systems from the European settlers (Lomberg *et al.,* 1996).

The National Water Policy of South Africa uses three fundamental principles when managing its water resources. These principles are equity, sustainability and efficiency (GCIS, 2016). Table 6 shows the acts in place to manage the water resources in South Africa.

Table 6. *Acts in place to maintain the effective water management in South Africa. Adapted from GCIS (2016).*

State Act	Description or purpose
The National Water Act of 1998	Ensures that South Africa's water resources are protected, used, developed, conserved, managed and controlled in a sustainable and equitable manner, for the benefit of all people
The Water Services Act, 1997 (Act 108 of 1997)	Prescribes the legislative duty of municipalities as water-service authorities to provide water supply and sanitation according to national standards and norms. It also regulates water boards as important water service providers and gives the executive authority
The Water Research Act, 1971 (Act 34 of 1971)	Provides for the promotion of water related research through a Water Research Commission (WRC) and a Water Research Fund.
The National Environmental Management Act (NEMA), 1998 (Act 107 of 1998)	Makes provision for cooperative environmental governance by establishing principles for decision-making on matters affecting the environment, institutions that promote cooperative governance and procedures for coordinating environmental functions exercised by organs of state
Strategic Framework on Water Services (2003) and the Water Services Act of 1997	Sanitation provision

During NWRS-1 (National Water Resource Strategy Phase 1) it was identified that groundwater management should be improved. Following the onset of recent drought conditions, the Department of Water and Sanitation then issued a gazette in March 2015 to limit urban water use in the Eastern Cape by 15% and irrigation use by 20% (Government Gazette No. 38596; No. 240/2015). Subsequently, various curtailments and new water tariffs were issued and in July of 2021 the drought was declared a national disaster (Government Gazette No. 44876; No. 638/2021).

Water that is not received from municipal service providers, a local authority, a water board or a government water scheme is obligated to be registered by its users. This includes surface and groundwater (GCIS, 2016). Regulations for the drilling of a borehole depend on the local authorities and someone wishing to drill a borehole may be required to notify the municipality (Van Deventer, 2021). This is because some areas might not be suitable for borehole drilling, the area may be easily contaminated or the aquifer may not deliver a sustainable aquifer yield. The registration, installation, and maintenance of a borehole is the responsibility of the property owner. Upon registration, the owner receives a registration number, and it must be visible on a sign on the outside of the property indicating the presence of a borehole. Water usage licensing depends on the purpose of the borehole and can vary greatly from domestic to industrial use as well as the quantities used (Van Deventer, 2021).

The first well in Algoa Bay was officially drilled on 28 February 1849 near what is now known as Whites Road (Lomberg *et al.,* 1996). By 2018 this had increased to 466 registered private boreholes in Gqeberha (Van Aardt, 2018). In recent years the drilling of residential boreholes has increased dramatically, with over 1000 boreholes in the suburb of Summerstrand alone although not necessarily registered (Dr Gaathier Mahed pers. comm. 15 July 2021).

There is no limitation on the number of boreholes that can be drilled in Gqeberha and they are currently not being monitored. Eastern Cape Borehole Services owner, Erick Kritzinger, said it is necessary to regulate borehole usage (Van Aardt, 2018). Dr Phumelele Gama from the Nelson Mandela University reiterates that unregulated use of groundwater can lead to environmental damage as it is a significant part of the water cycle (Van Aardt, 2018). Furthermore, groundwater abstraction for municipal use is currently underway and includes abstraction from coastal springs and several wellfields (Rogers, 2021b, a; NMBM, 2022) with already roughly 200 exploratory boreholes drilled (NMBM, 2022).

1.6.2 Dangers of groundwater pollution

One of the best known aquifer springs in Algoa Bay is that of Cape Padrone, which forms part of the Salnova Formation (Rust, 1991; Rossouw, 2012). Here the aquifer is comprised of limestone sloping downward towards sea level. A risk associated with the use of coastal aquifers is that of seawater intrusion. This occurs when saltwater enters the aquifer when the hydraulic gradient is reversed and the water table is below sea level (Rust, 1991). This contaminates the fresh water in the aquifer and must be taken into consideration when assessing if an aquifer is being overused. This is one example where research has proven that overuse of an aquifer can have detrimental effects on its sustainability, although the effects may be mitigated or reversed by artificial recharge (Campbell *et al.,* 1992). Artificial recharge has been practiced in South Africa since the 1970s (Campbell *et al.,* 1992), although not in the NMB area. Most of the secondary aquifers in NMB sit below sea level and this means that over-abstraction from these aquifers can lead to saline intrusion (Van Aardt, 2018). What the long-term effects on the local environment will be must be researched in order to determine how much water from aquifers can be sustainably extracted.

Unconfined aquifers, like those of the Algoa Group and sections of the TMGA, are composed of highly transmissive material and pollutants from the surface and can easily enter the aquifer (Campbell *et al.,* 1992). Aquifers in the Uitenhage area are protected to try and minimise these threats (DWA, 2010). It might be necessary to extend the protection to other local aquifers and to monitor them closely. Furthermore, the unconsolidated primary aquifers in NMB may be at risk of pollution from industries along the Swartkops River and fertilisers from agricultural use, as well as leaching from septic tank systems in residential areas. The Groundwater Resources Information Project (GRIP) was implemented in 2006 to try and gain more information about groundwater (DWA, 2010).

1.7 Conclusions

Groundwater may offer potential relief from the drought in NMB as the need for water continues to grow and surface water supplies are fast diminishing. It is however evident that groundwater studies in the area are largely lacking or outdated, especially with regards to an ecological perspective. Microbialite seeps may be ideal indicators of environmental response and groundwater quality related to abstraction from the local coastal aquifers. Preliminary data regarding the amount of coastal groundwater discharge in the NMB area, pollution sources and groundwater residence time is required to ensure the sustainable use of groundwater. Furthermore, a collaborative approach by private and public parties regarding groundwater use, specifically related to borehole registration and monitoring, is needed to allow the effective management of the local aquifers.

2. Quantifying groundwater discharge through coastal microbialite systems in Nelson Mandela Bay

Discharge flow path of a SSLiME (photographed by GMR)

**This chapter is directly linked to TWO's MSc dissertation (under the supervision of CA, CD and GMR) that is not published and will be examined after March 2024. Therefore, overlap in content and results are inevitable but is minimised wherever possible.*

2.1 Introduction

Coastal biodiversity is dependent on the interactions between freshwater and saltwater. This gives rise to complex ecosystems inhabited by organisms adapted to survive rapid shifts in salinity and aerial exposure. Microbialite systems in Nelson Mandela Bay (NMB) form where fresh groundwater seeps onto rocky intertidal zones along the southern coast of South Africa, forming supratidal spring-fed living microbialite ecosystems (SSLiME) (Rishworth *et al.,* 2020b). Microbialites form due to mineral precipitation and/or sediment trapping-and-binding by microbial communities (Burne & Moore, 1987) and have been present in most shallow coastal environments for much of Earth's history as far back as 3.45 billion years ago (Riding, 2011). However, modern, actively accreting microbialites are rare (Rishworth *et al.,* 2020b).

In the South African coastal context, microbialites are predominantly composed of mineral precipitates, although detrital grains from both the terrestrial and marine environments may be included in their structure (Dodd *et al.,* 2021). Microbialite deposits may be used as indicators of past freshwater seeps and also hold anthropological significance related to the freshwater use and mobility of early human coastal communities (Rishworth *et al.,* 2020a).

The combination of a rising population, economic growth, and climate change has led to increased use and, inevitably, an unsustainable dependence on surface water resources. This unsustainability is highlighted during both historic and current water scarcity where demand exceeds supply (Dodd & Rishworth, 2023). Following post-colonial development, some of South Africa's largest cities and metropolitan areas now occur along the coast. The Nelson Mandela Bay Metropolitan Municipality (NMBM), with a population of over one million people, is the fifth largest metropolitan area in South Africa (Naidoo *et al.,* 2016; NMBM, 2022). As a result, the use of alternative water sources such as groundwater has increased, and will continue to increase with, for example, the ongoing development of municipal wellfields (Table 1).

The protection and preservation of local groundwater resources needs to be informed by research on the nature of aquifers in terms of source, recharge, residence time, spatial extent and contamination. This research is currently lacking but is crucial in understanding the potential risks associated with pollution and unsustainable use. Furthermore, the risk of seawater intrusion due to over abstraction can increase the salinity of the groundwater resources (Winter *et al.,* 1998; Oude Essink *et al.,* 2010), rendering it unusable for human consumption. Finally, changing hydrological regimes in the face of climate change affects both surface and groundwater resources due to, for example, decreased runoff and recharge, respectively (Winter *et al.,* 1998).

There are two major aquifers in the NMB area – the primary Algoa Group (AG) Aquifer and the secondary Table Mountain Group Aquifer (TMGA) (Lomberg *et al.,* 1996). The AG water is stored within the primary porosity (interstices within constituent sand grains), while the TMGA water is stored in the secondary porosity (fractures, joints, and faults) (Lomberg *et al.,* 1996). The Vegter geohydrological region in which the study area falls, forms part of the Southern Cape Mountain Ranges region (Vegter, 1990), which is dominated by fractured groundwater occurrence. The TMGA, within the study area, fall in the fractured 0.50-2.0 ℓ/s category (DWA, 2010). Dodd *et al. (*2018) observed that coastal freshwater seeps emanate on or just above, the unconformity between the underlying, older TMG aquifer and the overlying, younger Algoa Group aquifer. The respective contribution of each aquifer to the coastal discharge remains unclear at present. These freshwater seeps often flow into coastal microbialite systems, with sections of the NMB coastline exhibiting microbialite deposits at up to 90% of the freshwater seeps (10 km section between Seaview and Maitlands) (Perissinotto *et al.,* 2014).

Microbialite growth rate is dependent on numerous factors, many of which are derived from the freshwater seeps, and South African microbialite systems are thought to be the product of intermittent accumulation rather than systematic trapping and binding of sediment (Dodd *et al.,* 2018). Winter *et al. (*1998) suggests that a faster flowrate may mean that sediments do not have enough time to settle and be trapped. But in this case, freshwater seeps contribute little sediment, therefore the effect of sediment load on the flowrate is minimal. Flowrate affects the interaction time the freshwater seep has with the microbialite systems. The higher the flowrate, the less interaction time (and vice versa). This may influence the precipitation of carbonate minerals (such as calcite) since the total dissolved solids (TDS) of freshwater seeps required for carbonate precipitation is flushed quickly from the system, yielding low mineral precipitation. Furthermore, periods of high rainfall, hence higher flowrate, may reduce the interaction time of the water with the substrate resulting in lower alkalinity and thus lower growth. Very high flowrate can result in the erosion of microbialite systems. In contrast, a very low flowrate might mean not enough freshwater is seeping through to facilitate mineral precipitation. Flow can be further influenced by seasonal changes, the local flow systems and tides in adjacent embayments (Millham & Howes, 1994). For example, Schneider *et al. (*2005) reported that the flow rate of a seep into a large mesotrophic lake in New York increased in response to rainfall but was influenced by precipitation patterns up to 10 km away. Schneider *et al. (*2005) also noted that the substrate along the lake's perimeter had no influence on the flow rate of the seeps. Coastal seeps for the NMB's shoreline likely form part of an integrated groundwater flow path. This chapter aimed to determine the volume of groundwater discharged in the supratidal zone of the southern NMB coast and its effects on microbialite pool dynamics and its health.

2.2 Methodology

2.2.1 Study area

The study area is located along the southern coastline of NMB, South Africa (Figure 7). The western and eastern limits are Maitland's Beach and Cape Recife Nature Reserve, respectively. The area extends inland to a maximum of 20 m above the high-water mark along the 40 km stretch of coastline. This entire area was used for the quantification of the freshwater discharge through microbialite-forming seeps of the NMB coast.

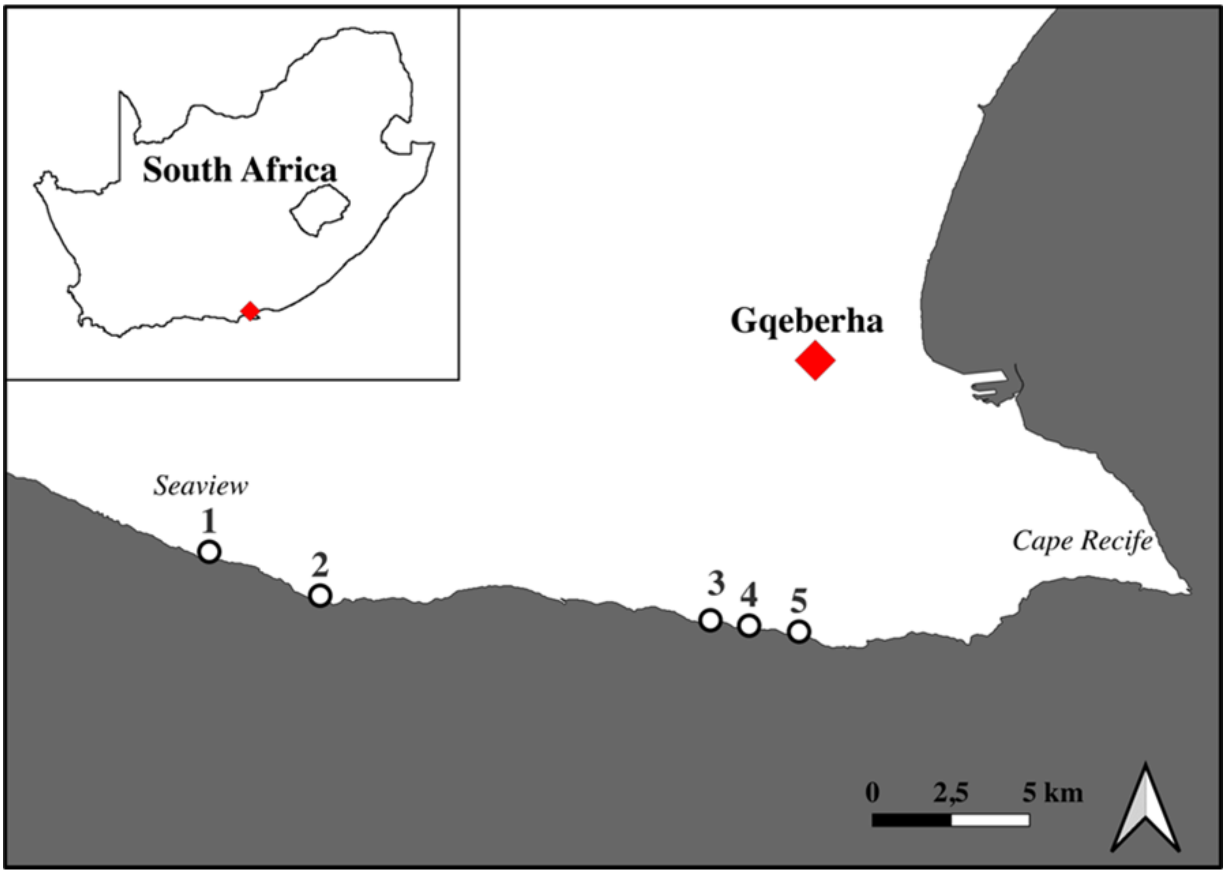


***Figure 7**. Map indicating the relative location of the main study sites (1-5) in relation to South Africa, and Gqeberha. 1: Seaview; 2: Laurie's Bay; 3: Schoenmakerskop; 4: Sappershoek and 5: Cape Recife.*

2.2.2 Study sites

A total of five type-locality (main) sites have been selected, these include 1) Seaview, 2) Laurie's Bay, 3) Schoenmakerskop, 4) Sappershoek, and 5) Cape Recife (Figure 8*)*. These sites have been selected based on the previous literature, their well-developed microbialite biomass, accessibility, and high flowrates (*sensu* Rishworth et al., 2020b). These sites, along with supplementary sites, were used for continued freshwater discharge quantification (monthly) and growth rate (monthly) monitoring from July 2022 to July 2023.

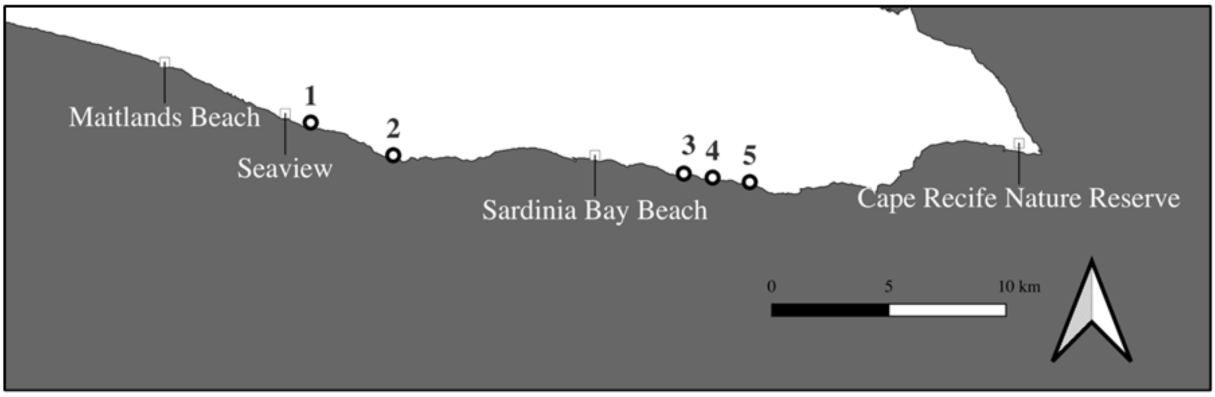


Figure 8. *Map showing the locations of the main study sites (1-5) and the noteworthy locations along the coastline. 1: Seaview; 2: Laurie's Bay; 3: Schoenmakerskop; 4: Sappershoek; 5: Cape Recife.*

2.2.3 Data collection

An initial survey (survey 1) of the entire study area was conducted between the 12th and 15th of April 2022 to establish the GPS locations of groundwater discharge points along the NMB coastline and allocate the 20 monthly flowrate sites. This survey also identified two main types of seeps which require different measurement methods:

(A) Diffuse type: film like flow of water over bedrock, beach rock, vegetation, and sand (e.g. Figure 9a, c, and e) that requires the tracer method.

(B) Stream type: concentrated flow water through various streams and channels (e.g. Figure 9b and d) that requires the capture cup method.

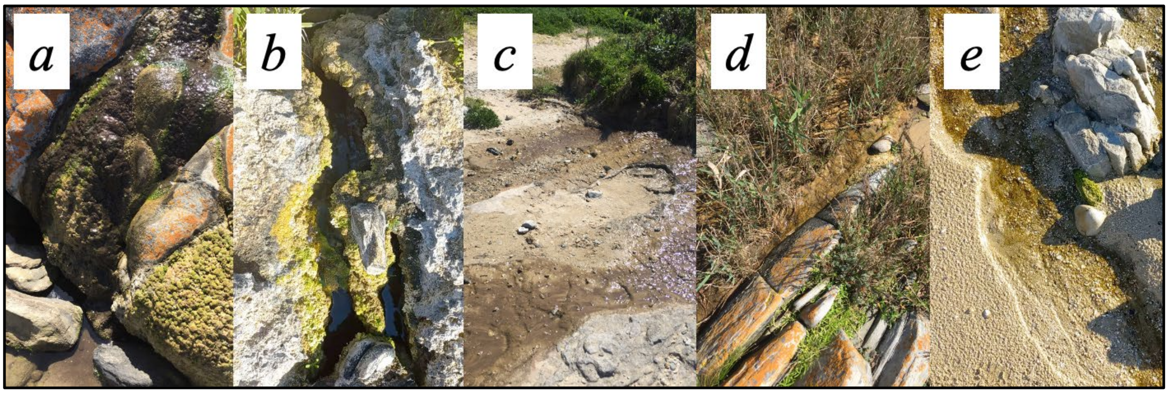


Figure 9. *Images of groundwater seepage over (a) active microbialites, (b)inactive microbialite, (c) beach rock, (d) vegetation and (e) sand.*

Due to the nature and extent of the freshwater discharge locations identified during initial survey, direct measurement of the entire coastline would not be logistically possible in the project time frame. Therefore, an indirect measurement system was also used for discharge spatial analysis of the entire study area (July 2022).

A second survey (survey 2) was conducted between the 24th and 26th of October 2022 for sections of numerous seeps between the study sites to determine the discharge quantity (using the same indirect measurement method) and location for all discharge points along this section of coast.

The monthly discharge flowrate data collection for all 20 study sites was conducted monthly between the July 2022 and June 2023 using only the direct measurement techniques.

2.2.3.1 Direct measurement method

The capture cup method uses a heavy-duty plastic bag to collect water for a specific amount of time. The captured water is measured in a volumetric beaker and the flowrate calculated using the volume of water and capture time (Figure 10). This method is optimal for stream flow locations and a similar method has been previously used at these locations (e.g. Dodd et al., 2018). This method was used for the collection of the monthly discharge through the 20 study sites.

Figure 10. *The Capture Cup method. Water is funnelled into a plastic bag for a set amount of time (T2) and then measured in a volumetric beaker to calculate the flowrate (T3).*

The capture cup method is not suitable for the measurement of diffuse flow, therefore a novel method, the tracer method, was used to determine the discharge categories for diffuse sites

(Figure 11). It consists of three strings deployed parallel to each other, with a set distance of 20 cm between the strings (total distance of 40 cm between outer "sighting" strings). The hanger (outer frame) length can be adjusted according to the size of the pool by replacing it with longer or shorter pipes. The line directions can be adjusted according to the pool shape (curves) using the adjustable arm mounted to the hanger (Figure 11). The outer strings are used as sighting strings for the flow velocity reading.

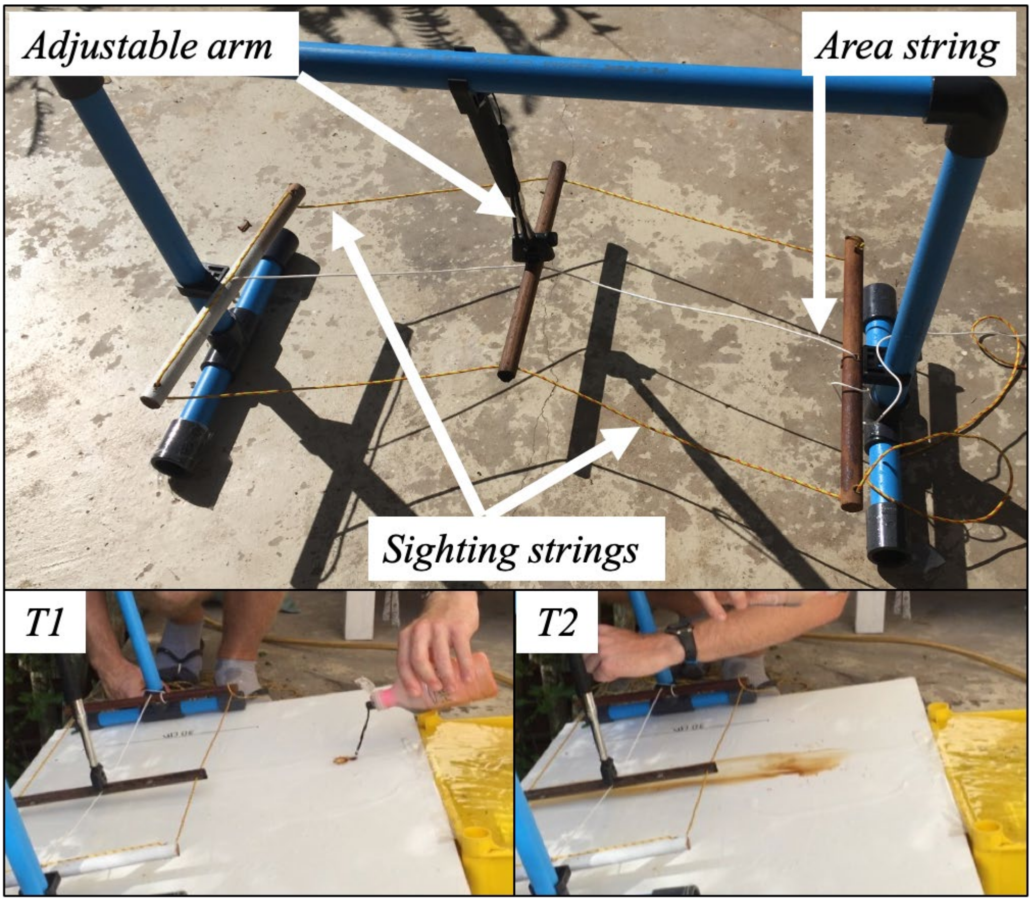


***Figure 11**. Labelled diagram of the tracer flowrate instrument showcasing the adjustable arm (above) and the method for using the instrument (below).*

The instrument is placed perpendicular to the direction of flow at the edge of the pool. A small amount of tracer (food colouring) is added upstream. The time that the tracer takes to travel from one outer string to the other (known distance of 40 cm) is recorded from which the flow velocity can be determined (Figure 11). Triplicate measurements are recorded for each site so that an average velocity can be determined. The middle string is used to determine the area of the water. The string is marked every centimetre providing the length of the flow area. The depth of the water at each centimetre mark is measured. With the depth and length measured, a cross-sectional area of the water passing the instrument is produced. The velocity and area of the flow can then be used to determine the flowrate (Q):

$$Q\ (cm^3/s) = v\ (cm/s) * a\ (cm^2) \qquad \text{Equation 1}$$

2.2.3.2 Indirect measurement method

The system of qualitative measurement developed to estimate flowrate was implemented using subcategories within two major flow types: A – Diffuse flow and B – Stream Flow

The five subcategories based on the flowrate for each flow type are:

1. Low (0.1-5 mℓ/s)
2. Low-Moderate (5-15 mℓ/s)
3. Moderate (15-50 mℓ/s)
4. Moderate-High (50-150 mℓ/s)
5. High (150-500 mℓ/s)

These categories were created for the estimation of flowrate over the entire study area at all seepage locations. Any flow estimated to be above subcategory 5 (flow > 500 mℓ/s) was measured directly. The assignment of the flowrate category was conducted by the same researcher at every flow location to ensure consistency of allocation. This allowed for a qualitative estimate of the groundwater discharge along the NMB coastline.

2.3 Results

2.3.1 Discharge quantification

The flowrate spatial assessment of the entire NMB coastline estimated the total groundwater discharge between Cape Recife and Maitlands is ~45.81 ℓ/s in total or 0.0298 ℓ/s on average per seep (Table 7). The seep density of the entire 40 km study area is one seep every 26 m along the coast and the percentage of seeps bearing microbialite was 78%.

Table 7. *Flowrate spatial analysis results showing the number of seeps and flowrates for each category. A = diffuse flow; B = stream flow.*

Seep type	Category	Category flowrate (ℓ/s)	Count	Total flowrate (ℓ/s)	Average flowrate (ℓ/s)
Diffuse	A1	0.001-0.005	628	1.57	-
	A2	0.005-0.015	202	2.02	-
	A3	0.015-0.05	69	2.24	-
	A4	0.05-0.15	26	2.60	-
	A5	0.15-0.5	14	4.55	-
Stream	B1	0.001-0.005	233	0.58	-
	B2	0.005-0.015	243	2.43	-
	B3	0.015-0.05	61	1.98	-
	B4	0.05-0.15	25	2.50	-
	B5	0.15-0.5	12	3.90	-
Monitoring subset	-	-	*20*	*21.48*	*1.074*
Total	**-**	-	***1533***	***45.81***	***0.0298***

2.3.2 Discharge density

Most of the discharge volume was in the area between the study sites, therefore the discharge heat map seen in Figure 12 was made for this area in survey 2. Areas of high discharge are observed along the rocky shore areas, and areas of low discharge are observed along the sandy shore areas. Note that the discharge is only the observable, terrestrial groundwater discharge during the month of October 2022.

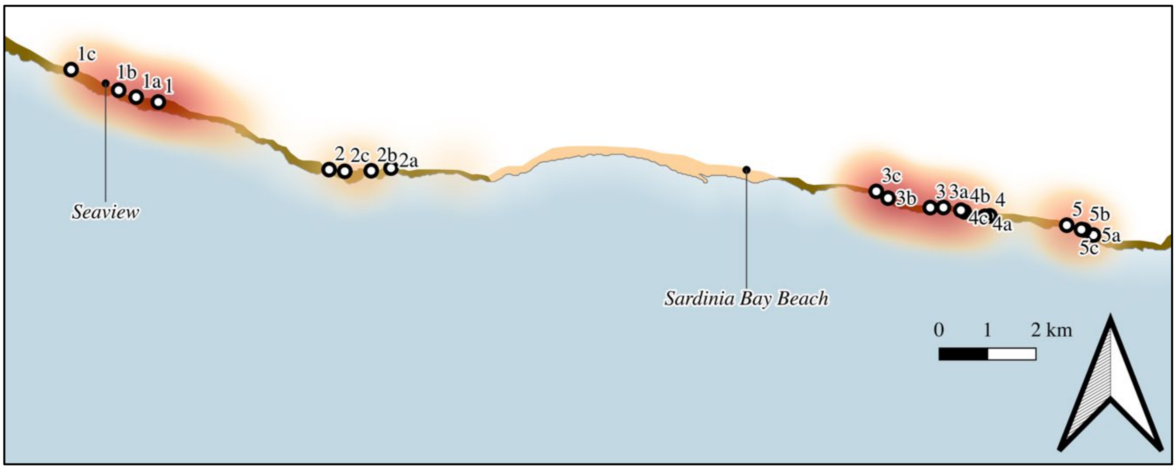


Figure 12*. Discharge heat map for the area between the study sites (white dots) obtained from survey 2. The red shade indicates the discharge quantity, dark = high, and light = low. The shore type is indicated by brown rocky shore and yellow sandy shores.*

2.3.3 Monthly discharge

2.3.3.1 Monthly discharge for individual sites

The monthly discharge for individual sites varied over time and between sites (Figure 13, Figure 14, Figure 15). Notable trends include autumn and winter highs, summer lows, and varying extreme high months. This heterogenous nature of the discharge throughout the coastline may indicate a complex hydrological system.

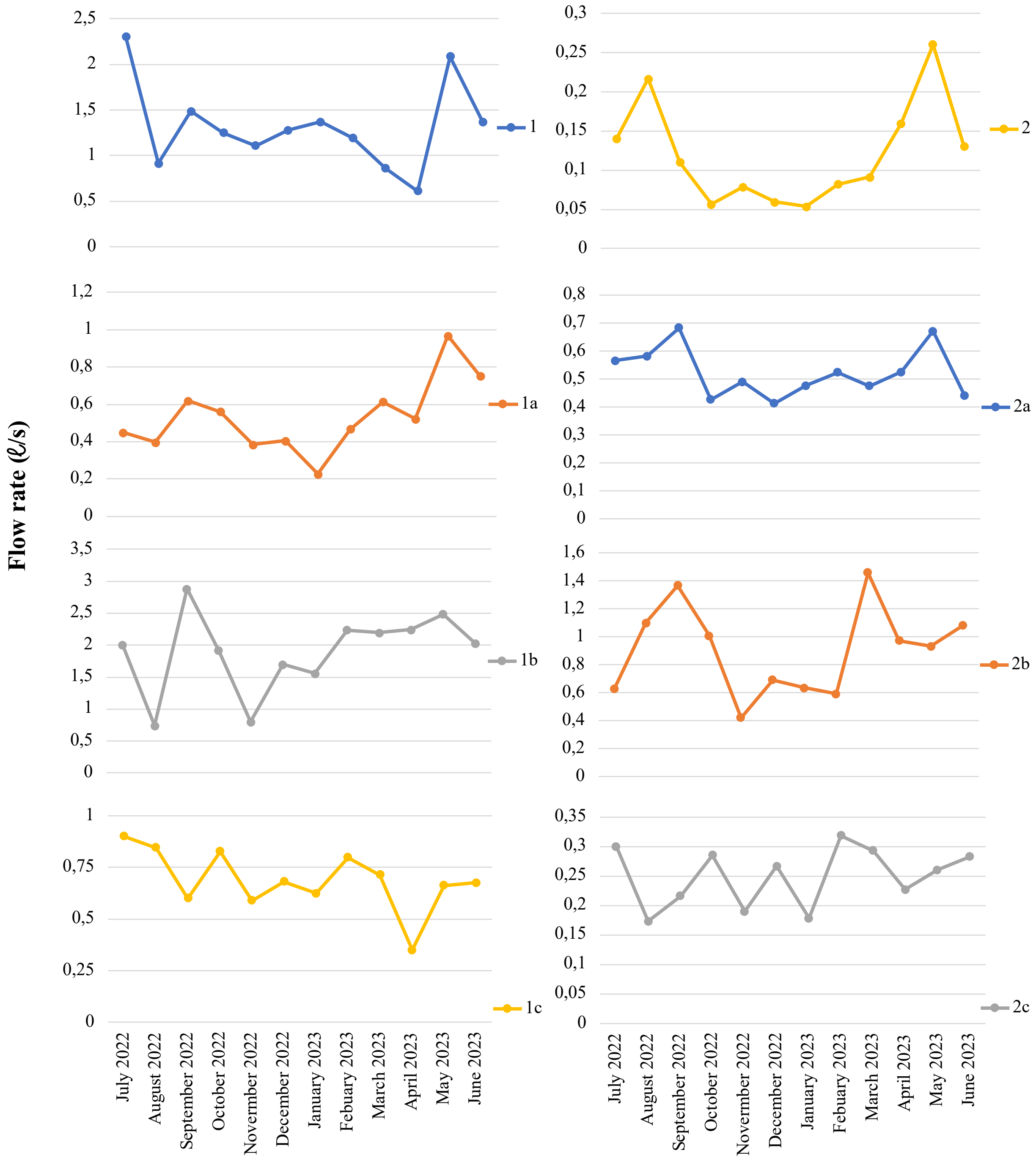


***Figure 13**. Individual monthly discharge for site groups 1 (left) and 2 (right).*

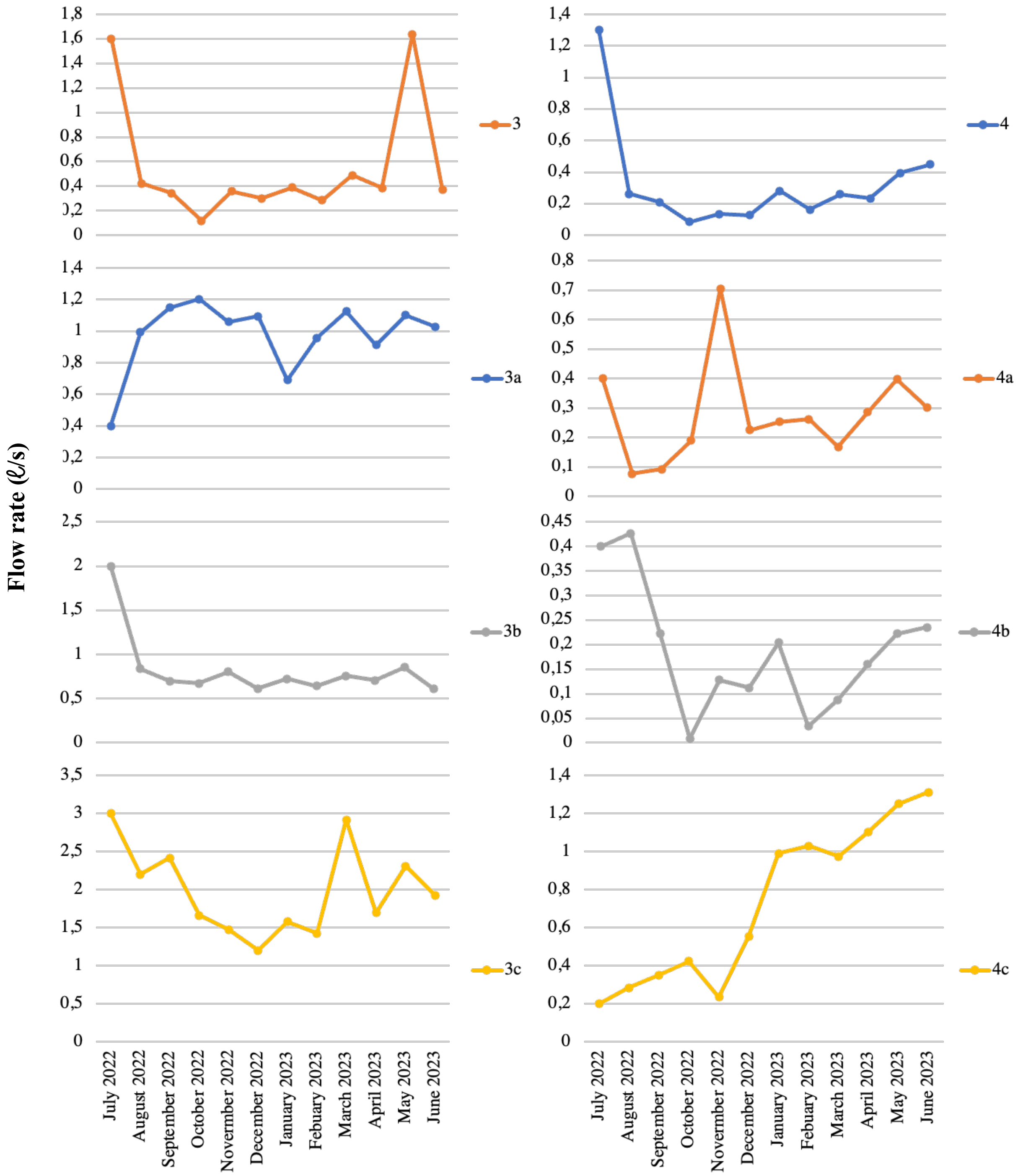


Figure 14. *Individual monthly discharge for site groups 3 (left) and 4 (right).*

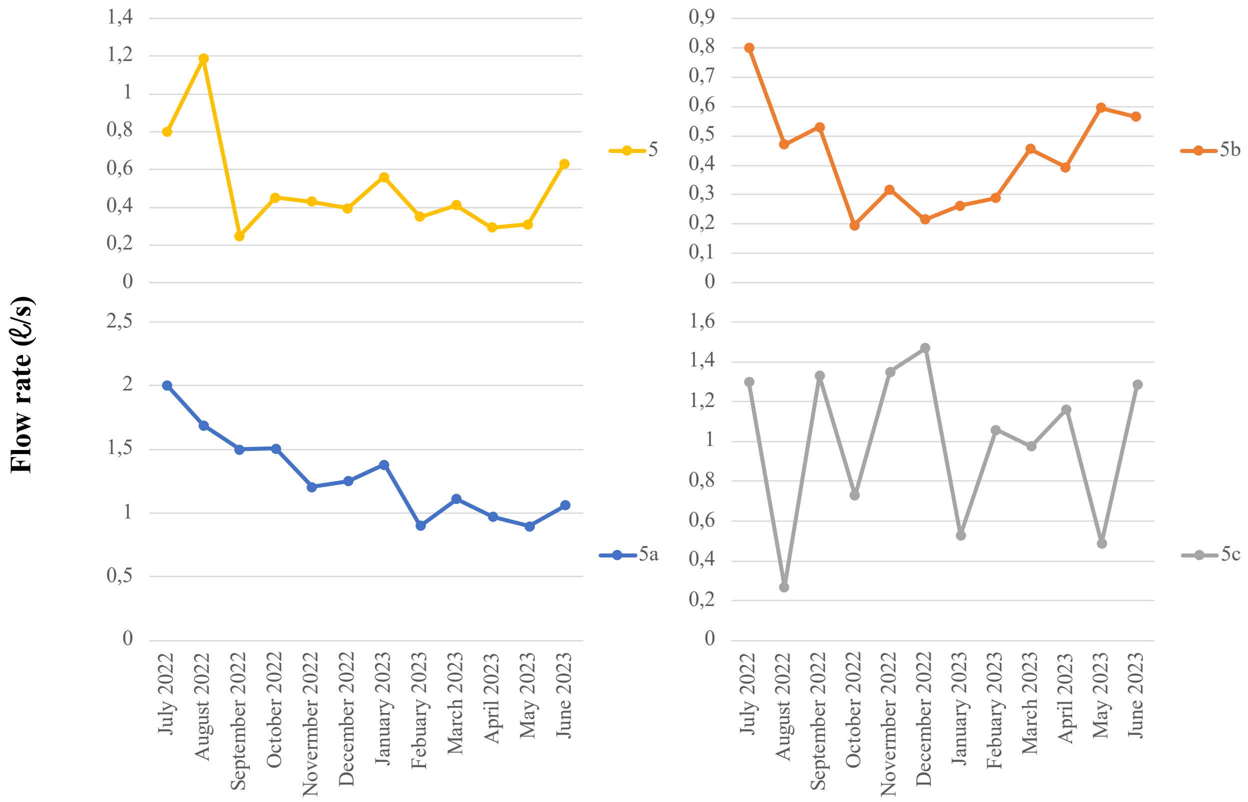


***Figure 15**. Individual monthly discharge for site group 5.*

2.3.3.2 Total monthly discharge for all the study sites

The first monthly discharge data collection for the 20 study sites was conducted simultaneously with the discharge spatial assessment in July 2022. This month was also the highest total discharge (21.48 ℓ/s) recorded throughout the one-year monitoring period. The lowest (12.27 ℓ/s) was recorded during November 2022, which is the austral spring (Figure 16). A clear seasonal trend is observed, with low discharge during the summer months, and high discharge during the winter months. Discharge in spring and autumn is variable with both high and low months.

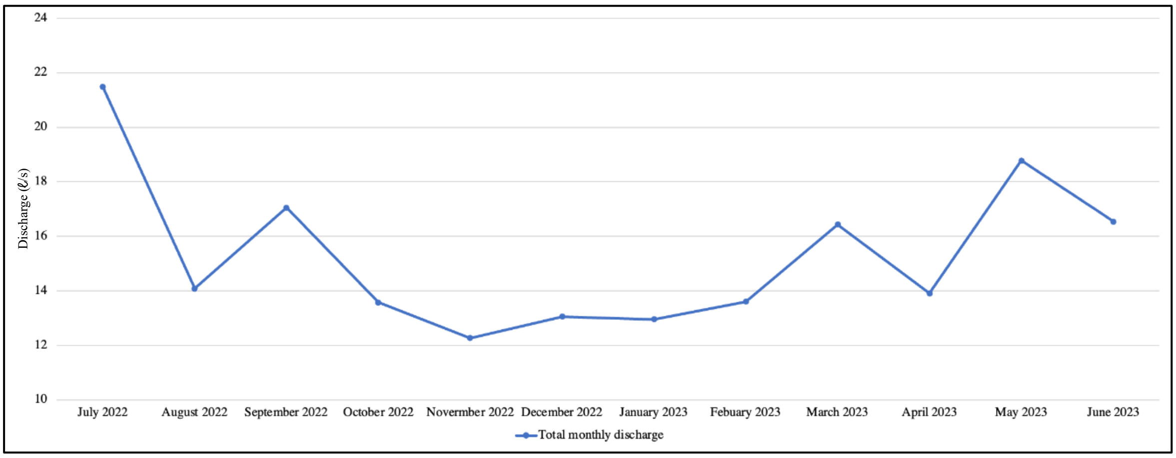


Figure 16. *Total monthly discharge for all sites over the 12-month monitoring period.*

2.4 Discussion

2.4.1 Seep density and flowrate

The flowrate spatial analysis of the entire 40 km coastline identified 1,533 freshwater seeps of which 1,208 showed microbialite deposits (78%). This aligns with the results observed along a 10 km section between Seaview and Maitlands in 2014 where 90% of the freshwater seeps exhibited microbialites (Perissinotto *et al.,* 2014).

On average, one freshwater seep is present every 26 m of the 40 km coastline. This high seep density is magnified when considering that two large areas contained very few freshwater seeps (Figure 12). Approximately 10 km of the study area is classified as sandy beaches with set-back dune cordons (over 100 m from the shore). The converse is seen in the remaining 30 km of study area where the dune cordon is within 50 m of the shoreline (Figure 12).

The contrast in seep density can be seen when comparing areas of low flowrates (such as Sardinia Bay located between Sites 2a and 3c) and high flowrates (Schoenmakerskop) illustrated by Figure 17. These two locations exemplify the differing shore-types. Sardinia Bay is a large sandy beach, whereas Schoenmakerskop is a typical rocky shore (Figure 18). The difference in flowrate in these two shore types is caused by the underlying geomorphology. Groundwater discharge was often observed at the contact between the younger Nanaga formation aeolianite (Algoa Group), and the older Table Mountain Group quartzite (Figure 19). The former unconformably overlying the latter. The porous nature of the Nanaga formation aeolianite allows for infiltration of groundwater whereas the non-porous nature of the TMGA inhibits infiltration of groundwater, creating an aquiclude in places. Groundwater movement occurs along the palaeotopography caused by the aquiclude and forms palaeodrainage systems. This may explain the groundwater discharge observed between these two layers. This mechanism occurs in the subsurface zone of the sandy beach shore-type, resulting in submarine discharge, and in the subaerial zone of the rocky shore shore-type, resulting in surface discharge. Therefore, the sandy beach shore-type is not void of groundwater seepage, rather, it is not present as observable surface discharge.

The topography at Sardinia Bay has low relief with a set-back dune cordon situated extending over 100 m inland from the shore, whereas Schoenmakerskop has high relief, and a near-shore dune cordon. The higher relief over the shorter distance observed at Schoenmakerskop may explain the high occurrence of groundwater discharge at seeps because of the sudden change in relief causing the water table to be closer to the surface. Although, there are sections of Sardinia Bay with similar topography to Schoenmakerskop, yet the low flowrate persists. Therefore, the topography cannot be the only flowrate determining factor.

Figure 17. *Image of Sardinia Bay (a) and Schoenmakerskop (b) as examples of a sandy beach and rocky shore shore-types.*

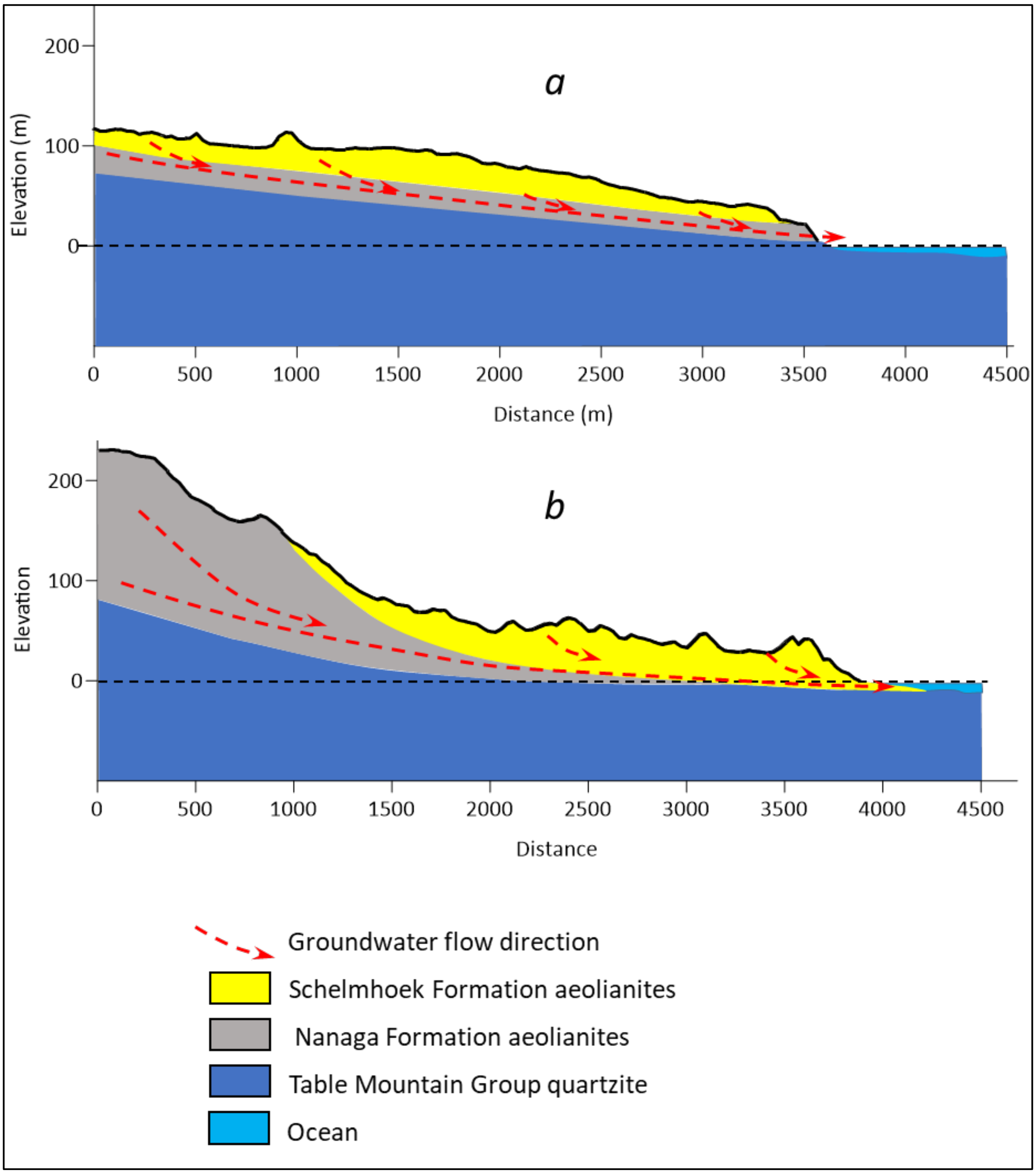


Figure 18. *Cross-sectional diagram of Sardinia Bay (a) and Schoenmakerskop (b) highlighting the respective groundwater discharge mechanisms.*

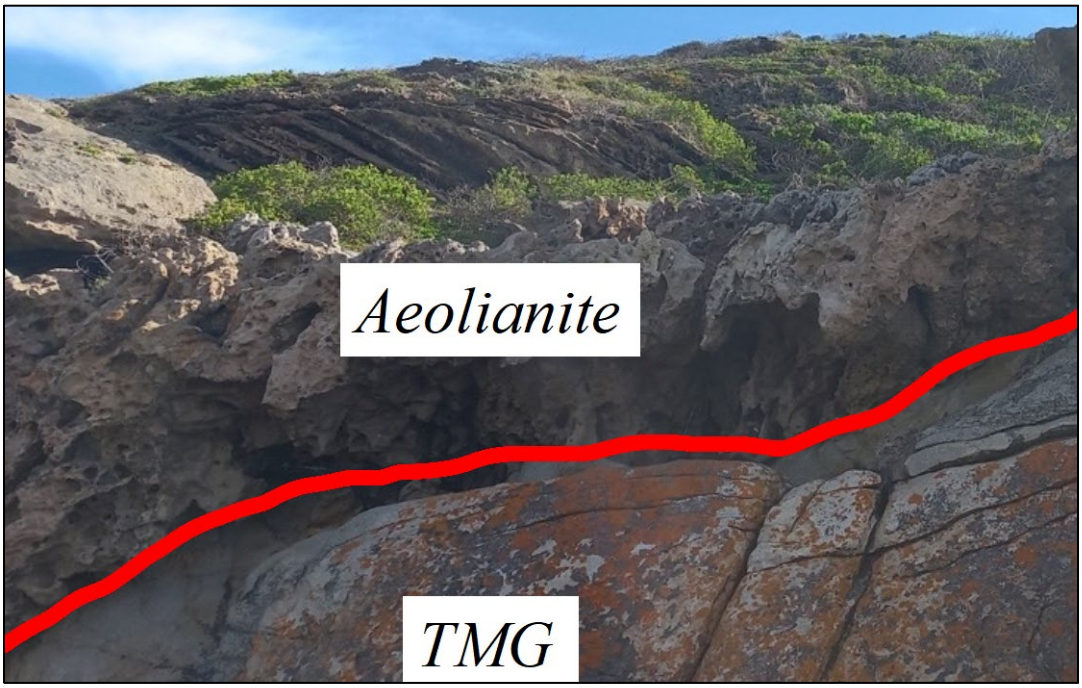
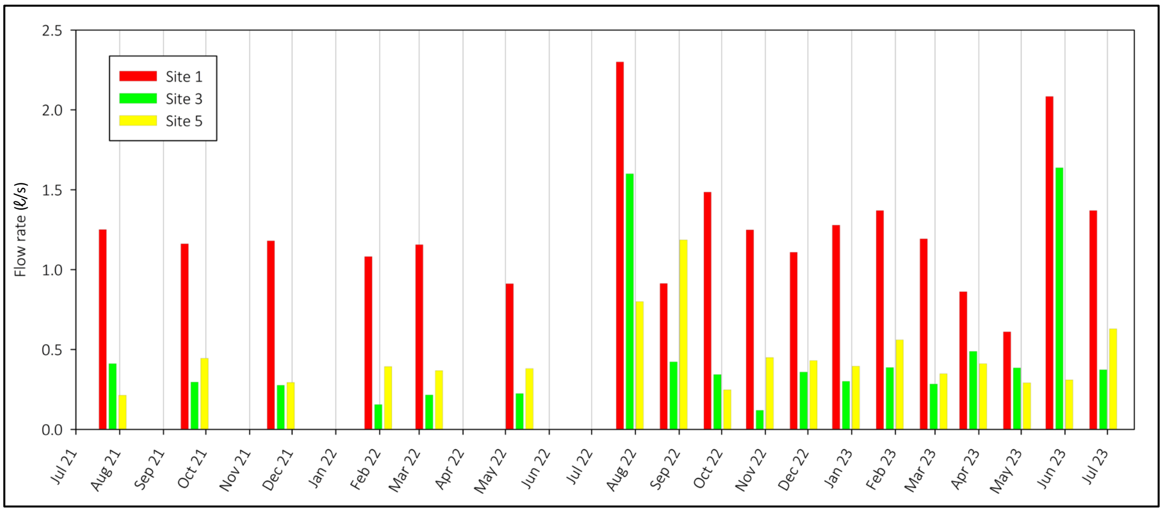


Figure 19. *Illustration of the unconformity between the overlying aeolianite and Table Mountain Group (TMG) layers. Contact is shown by the red line.*

2.4.2 Historical flowrate comparison

Previous flowrate studies (Prinsloo, 2013; Dodd *et al.,* 2018) of these groundwater seeps allow for the comparison to current flowrates. In 2012 the flowrate for the coastal springs in the Laurie's Bay (Site 2) area was between 0.09 to 0.10 ℓ/s. In comparison, the average flowrate in 2022 for the Laurie's Bay main site (Site 2) was 0.16 ℓ/s. In 2017 the Schoenmakerskop main site (Site 3) included flowrate data for winter and spring (Dodd *et al.,* 2018). The flowrates for June (winter) and October (spring) were 0.48 ℓ/s and 0.37 ℓ/s respectively. In 2022 the flowrates for July (winter) and September (spring) were 1.6 ℓ/s and 0.36 ℓ/s respectively. This perceived increase in groundwater flow between 2017 and 2022 is likely linked to short-term changes in drought severity. For example, in 2017 the streamflow flowing into the local surface water dam system was calculated to be only about 20% of the long-term average, however, this increased to about 63% in 2018 (NMBM, 2022). In both 2017 and 2022 the coastal spring flowrates decreased from the winter to spring, with almost identical flowrates for both the spring periods. The winter month of 2022 had a higher flow than that of 2017.

A more recent study of Sites 1, 3 and 5 (Hawkes, 2023) obtained flowrate data between July 2021 and May 2022 at bimonthly intervals (Figure 20). Since March 2022, a higher flowrate for Site 1 was observed. Higher flowrates were observed in July and August 2022 for Sites 3 and 5. Low flowrates (< 0.4 ℓ/s) for Site 1 were observed between July 2021 and January 2022, whilst higher flowrates (> 0.4 ℓ/s) were observed from March 2022 to September 2022. Low flowrates for Sites 3 and 5 were observed from July 2021 to May 2022, and September 2022. The minimum flowrates for each site were within this period. Maximum flowrates for the current assessment were observed in August 2022 and June 2023 for Site 1 and 3, and September for Site 5.



***<u>Figure 20</u>**. Seasonal flowrate data for Sites 1, 3 and 5 between July 2021 and May 2022 (Hawkes, 2023) and monthly flowrate data from July 2022 to July 2023 (from this study).*

2.4.3 The influence of precipitation on discharge

2.4.3.1 Precipitation vs discharge

The precipitation data for the Port Elizabeth Airport weather station was provided by the South African Weather Service. The total monthly precipitation for the collection period varied dramatically, with the highest occurring in May 2023 (191.6 mm) and lowest in November 2022 (4.8 mm) (Figure 21). The relationship between precipitation and discharge trends is also highly variable. Correlation only occurred in the months of September 2022 to January 2023, and April 2023 to June 2023. Note that these trends may correlate, but the relative magnitudes are not always proportional. For example, the large decrease in total precipitation from December 2022 to January 2023 is only a slight decrease in the total monthly discharge. These mismatches in precipitation versus discharge patterns might be indicative of other processes such as inland abstraction, which were not quantified in our data.

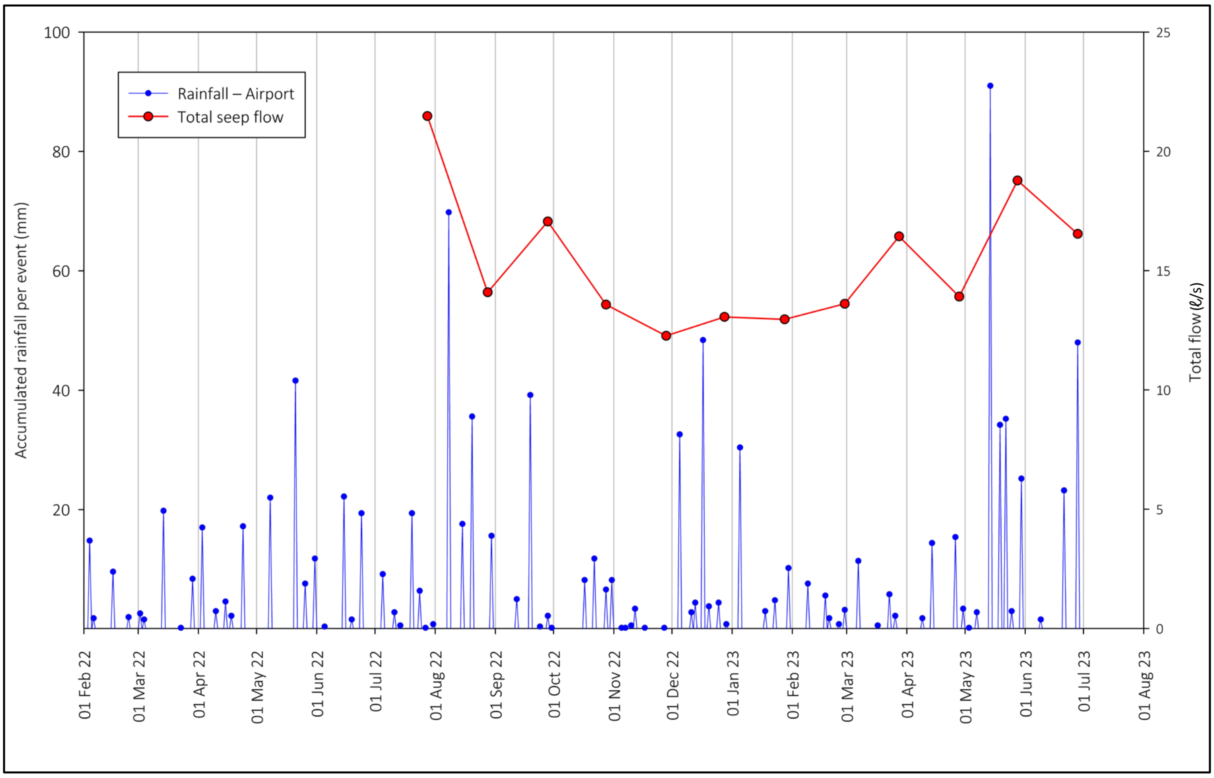


***Figure 21**. Accumulated event-based local precipitation in blue compared to total monthly discharge from monitored SSLiME in red.*

Furthermore, it was evident that the possible response time in seep flowrates between SSLiME sites was largely similar, but there was an indication of inter-site differences (Figure 22). For example, periods of peak flow in winter of both 2022 and 2023 peaked almost a month earlier at site 1 and 3 compared to site 5 (Figure 22). This is likely suggestive of differential flow paths.

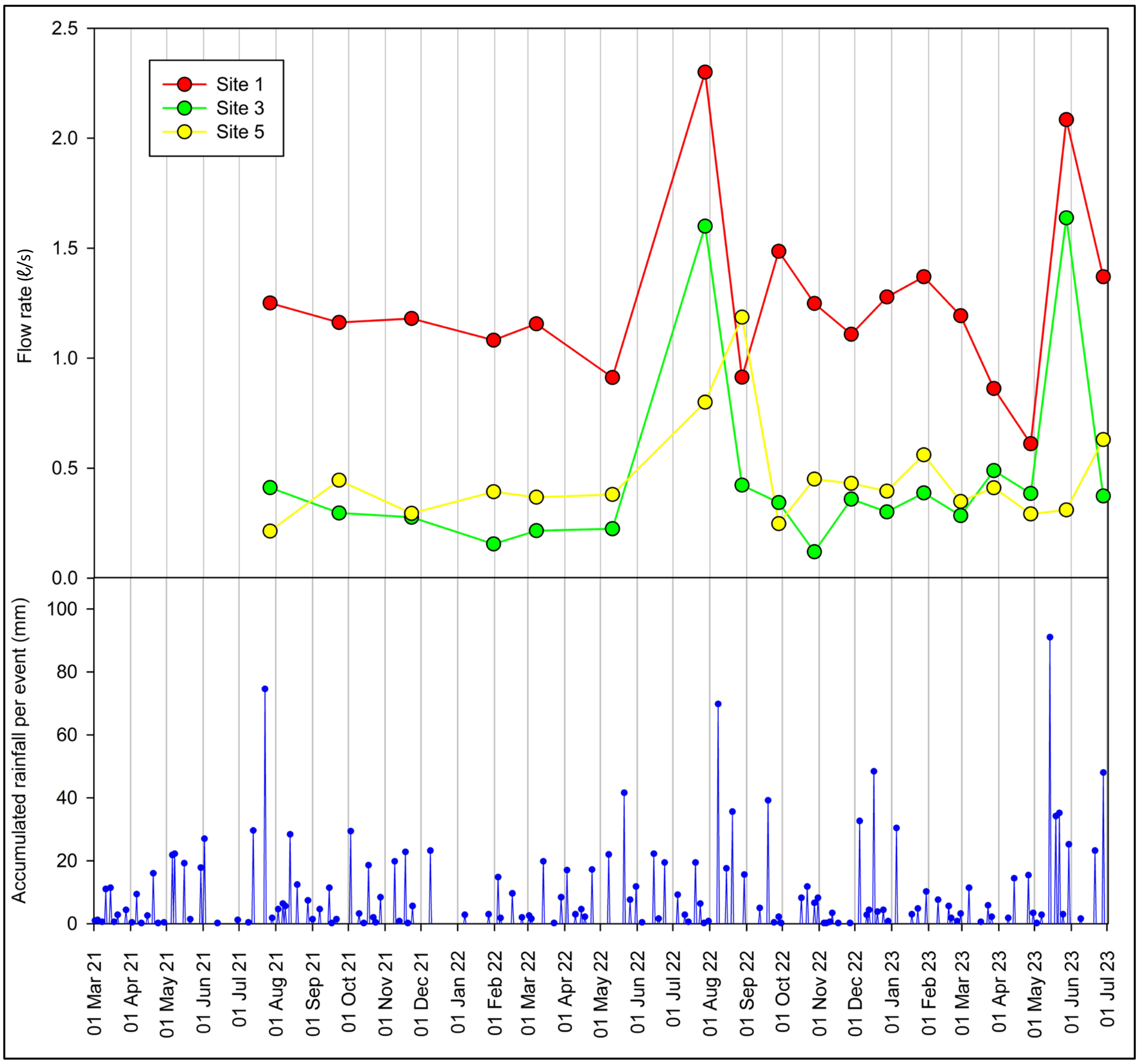


***Figure 22**. Accumulated event-based local precipitation in blue compared to monthly discharge from Seaview (Site 1), Schoenmakerskop (Site 3) and Cape Recife (Site 5) SSLiME in red, green and yellow, respectively.*

2.4.3.2 Lag time estimation

The discrepancies between precipitation and discharge on the same temporal scale may indicate the discharge observed is not only derived from recent precipitation events, and that perhaps a lag time between precipitation and groundwater discharge may be present.

An assessment of the long-term rainfall data from May 2021 to June 2023 was conducted to provide insight into the possibility of a precipitation-discharge lag time (Figure 23). A strong correlation between the precipitation from November 2021 to June 2022 and the discharge form September 2022 to April 2023 was observed (grey dotted line). This would indicate a lag time of 10 months between precipitation and discharge. Notably, the two highest discharge months (July 2022 and May 2022) are not reflected by precipitation in this lag time estimation. A similar lag time is observed at the seasonal scale. The average seasonal total precipitation of Winter 2021 to Winter 2022 correlating with the average seasonal total discharge of Winter 2022 to Winter 2023.

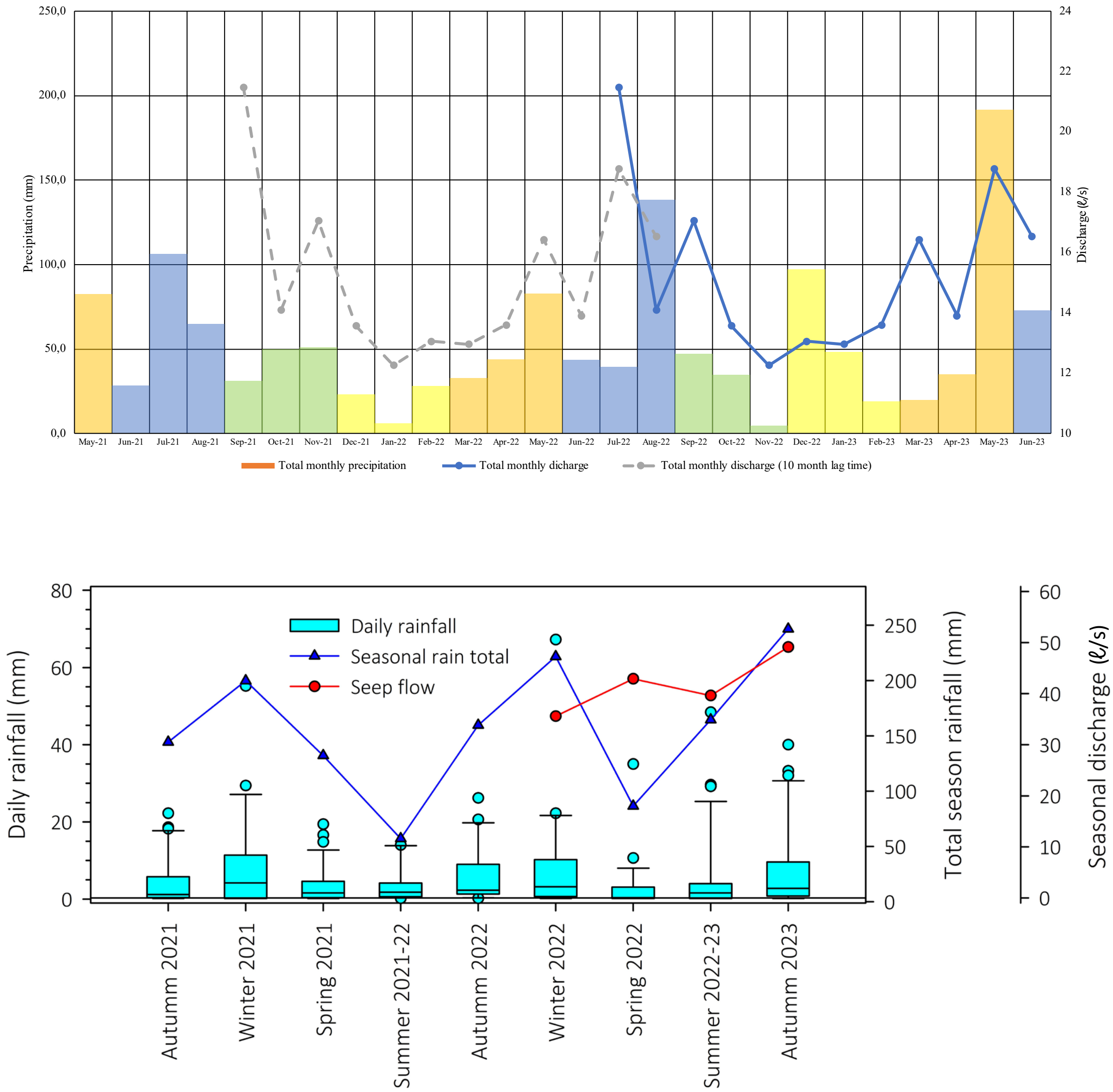


Figure 23. *Top panel: Total monthly precipitation as bar, total monthly discharge as points on a blue line, and a 10-month lagged total monthly discharge as points on a dotted grey line. The austral seasons have been indicated by the bar colours (blue=winter, green=spring, yellow=summer, and orange=autumn). Bottom panel: Seasonal seep flow in relation to cumulative seasonal rainfall as well as daily average rainfall.*

2.5 Conclusion

The aim of this report was to quantify the volume of groundwater discharge along the NMB coast through the SSLiME. Using two methods, a total flowrate of ~45 ℓ/s was measured for the study coastline, equating to a not insignificant total groundwater discharge in the order of 4 Mℓ/d. Considering that the Bushy Park Wellfield production is estimated to be over 10 Mℓ/d (Table 1), this may be a cause of concern for these groundwater seep dependant microbialite systems. Results indicate seasonal differences in the discharge volume, with flowrates peaking in winter, and an increase in the flowrate compared to previous studies conducted at the same sites in the past decade.

There is evidence that groundwater flow paths likely differ to some extent between SSLiME sites, especially at a regional level, which is likely a property of inland aquifer and lithology characteristics. A conceptual schematic of these interactions is shown in Figure 24. Discharge outflow volume appears to reflect a longer term, more consistent baseflow that is hypothesised to emerge from the TMGA, an inter-seasonal lag effect on discharge flowrates buffered by the Nanaga formation inputs, and a more short-term and more responsive to rainfall events discharge that is reflective of the Schelmhoek formation aquifer inputs (Figure 24). A next step would be to characterise this flow variability per SSLiME site in relation to hypothesised catchment lithologies of each flow path to more completely characterise recharge potential and responsiveness.

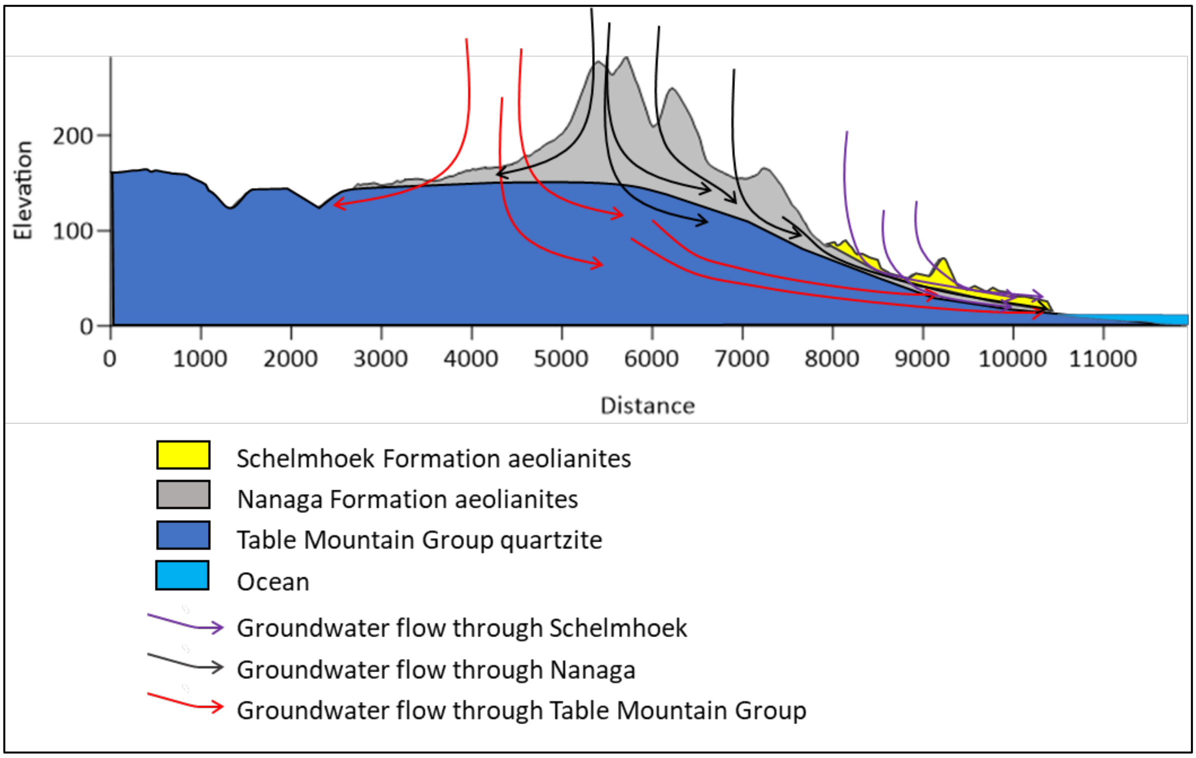
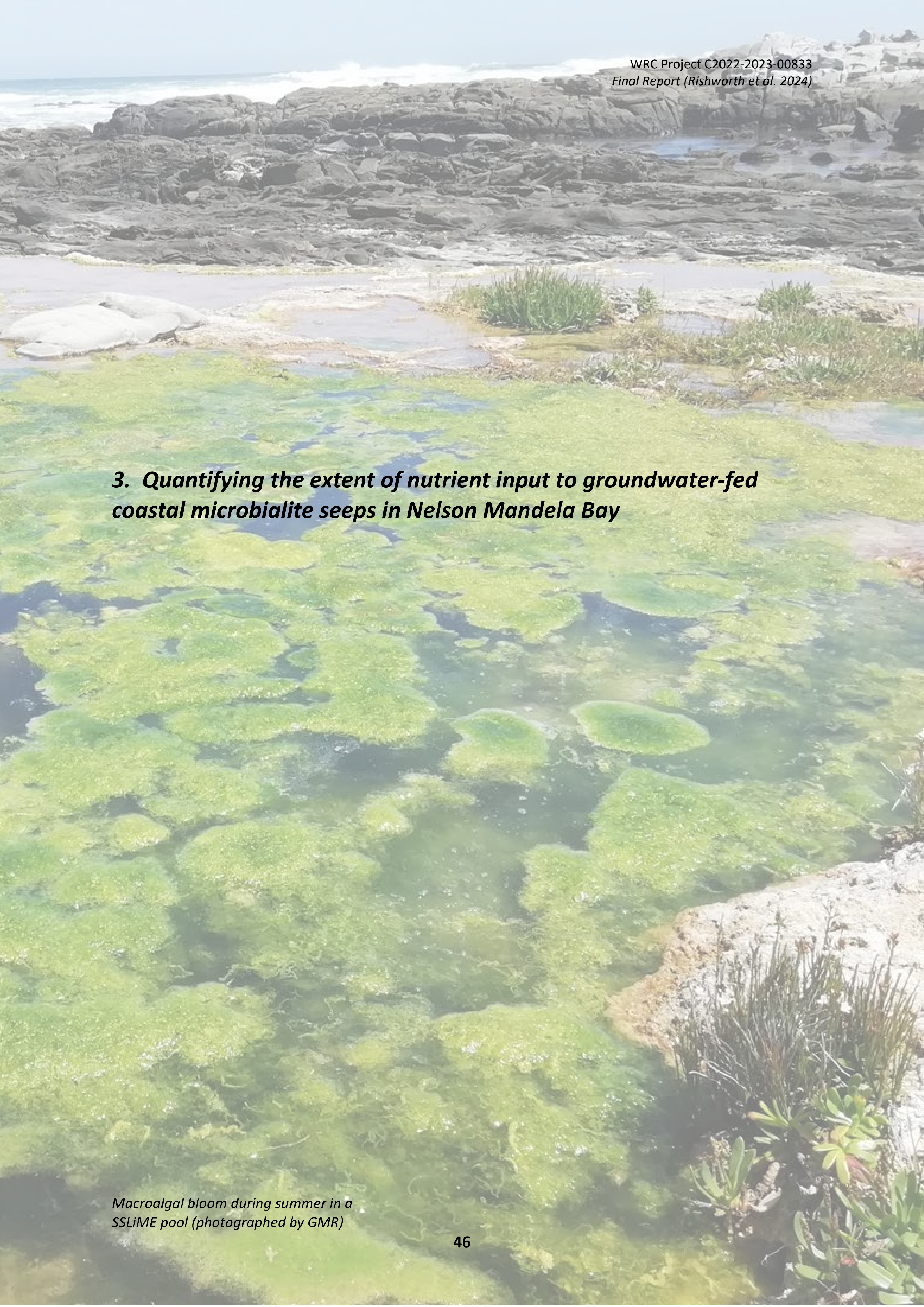


***Figure 24**. Conceptual schematic of supratidal groundwater discharge at a SSLiME site on the NMB coast, accounting for properties of the local lithology of the NMB.*



3. Quantifying the extent of nutrient input to groundwater-fed coastal microbialite seeps in Nelson Mandela Bay

Macroalgal bloom during summer in a SSLiME pool (photographed by GMR)

**This chapter is directly linked to CD's PhD thesis (under the supervision of GMR, HCC and Prof. Massmann) that is not published and will be examined after December 2023. Therefore, overlap in content and results are inevitable but is minimised wherever possible.*

3.1 Introduction

Freshwater from coastal aquifers will follow the down-gradient from the hinterland to the coast and discharge as coastal seeps (and submarine groundwater discharge) where possible (Santos *et al.,* 2021). Coastal freshwater seeps are essential to the functioning of coastal and marine ecosystems (e.g. Campbell & Bate, 1998). For example, Supratidal Spring-fed Living Microbialite Ecosystems (SSLiME) forming along the rocky shores of Nelson Mandela Bay (NMB) rely on groundwater for their formation, often forming microbialite pools and rimstone dams (Rishworth *et al.,* 2020b). These systems capture freshwater from coastal seeps and create an alkaline, carbonate-rich environment that enable cyanobacteria and diatoms to entrap sedimentary matter along with the laminated deposition of calcium carbonate during metabolic processes to form stromatolites (laminated microbialites) (Rishworth *et al.,* 2016b; Rishworth *et al.,* 2017). The supratidal zone where these pools occur are subjected to saltwater intrusion during tidal and storm-induced inundation (Rishworth *et al.,* 2017). Microbialite-forming organisms are able to survive in this dynamic environment, but this inhibits the more salinity-sensitive eukaryotes and invertebrates from competing or ingesting the cyanobacteria (Rishworth *et al.,* 2016a; Rishworth *et al.,* 2016b).

The Nelson Mandela Bay Metropolitan Municipality (NMBM) is currently suffering from a persistent multi-year drought (onset 2015), resulting in the lowest recorded supply reservoir (the Kouga dam) levels (Pietersen, 2021). Together with anthropogenic pressures, such as population growth, urbanisation and pollution, the water supply system of NMBM is severely constrained and should thus be managed effectively to ensure constant supply of potable water to its population of more than one million residents (Naidoo *et al.,* 2016; NMBM, 2022). Fundamental to the management of this should be managing anthropogenic influences such as pollution of the water supplies. In urbanised settings, the nutrient load and heavy metal content of a water body are good indicators of anthropogenic pollution (Malherbe *et al.,* 2018). Assuming that the coastal seeps in the NMB area are connected to the local aquifers, which preliminary evidence suggests (Dodd *et al.,* 2018), pollution might accumulate in this freshwater source and disrupt the ecology of the microbialite pools. It is expected that similarly to other coastal water bodies, an excess nutrient load could disrupt the functioning of the microbialite ecosystems. For example, in estuaries should the nutrient load exceed certain levels, noxious and toxic algal blooms may occur, as well as a loss of aquatic vegetation which can lead to increased turbidity, an oxygen deficiency and ultimately habitat and biodiversity loss (Rabalais, 2002). This has likely occurred recently in Nelson Mandela Bay linked to high nutrients inputs from for example the Swartkops Estuary (Lemley *et al.,* 2019).

However, it is not only pollution that influences the nutrient load of waterbodies, which may also be influenced by geological, ecological (vegetation) and climatic features. For instance, according to Wurtsbaugh *et al. (*2019) the underlying geology and the age of watersheds also influence the release of nitrogen and phosphorous. Phosphorous leaching decreases with geological age and nitrogen export can increase if it is fixed by microbes terrestrially. Thus, older rock formations will have higher phosphorous-levels and younger soils will have higher nitrogen-levels.

Coastal vegetated habitats also have the potential to act as sinks or filters of anthropogenic organic pollutants, buffering the potential negative effects of eutrophication in coastal waterbodies. This approach has both been intentionally applied as a mitigation tool along South Africa's coastline (e.g. artificial wetland at Swartkops Estuary: Lemley *et al.,* 2022) but other smaller ecosystems might potentially buffer the loading of coastal nutrients through uptake processes (e.g. coastal microbialite pools: Rishworth *et al.,* 2020b).

The aim of this chapter is to elucidate the state of knowledge of the nutrient load of coastal seeps in the NMB area. Specifically, those flowing into well-developed microbialite systems. Ultimately, this would be informative regarding the anthropogenic influence on the coastal aquifers in this region.

3.2 Methodology

3.2.1 Study area

The study area is located along the southern coastline of NMB, South Africa (Figure 25). The western and eastern limits are Maitland's Beach and Cape Recife Nature Reserve, respectively. The area extends inland to a maximum of 20 m above the high-water mark along the 40 km stretch of coastline. This entire area was used for the quantification of the freshwater discharge through microbialite-forming seeps of the NMB coast (Chapter 2).

The coastline of the area of investigation is composed of mixed rocky shores and sandy beaches or a combination thereof. Rock platforms consist of the Pre-Cape Gamtoos Group or the TMG group of the Cape Supergroup. The coastline is also interspersed with aeolianite cliffs and slabs (Garner, 2013) and/or stabilised (vegetated) dunes. Microbialite pools are limited to the supratidal area of rocky shores, where bedrock acts as a point of attachment and wave energy is dissipated by the seaward rock platform.

The study area is considered warm temperate, with an average annual daily temperature of 17.7°C, a maximum of 22.6°C and minimum of 12.9°C. According to Schael and Gama (2019), the mean annual rainfall in the study area is 600-1,000 mm. The NMBM precipitation is bimodal with the highest precipitation being recorded in late spring and early autumn.

The geology of the study area supports two major aquifers – the primary Algoa Group (AG) Aquifer and the secondary Table Mountain Group Aquifer (TMGA) (Lomberg *et al.,* 1996). This influences the heavy metal and nutrient content of the freshwater within the aquifers. The quartz-rich Table Mountain Group (TMG) contains little dissolved salts. Water from aquifers closer to the coast contain higher Ca/Mg HCO_3 levels, due to the lime found in the coastal sands and areas that are irrigated with treated sewage and nitrogenous fertilizers that contain a higher nitrate concentration (Rosewarne, 2002).

3.2.2 Study sites

A total of five type-locality (main) sites have been selected, these include 1) Seaview, 2) Laurie's Bay, 3) Schoenmakerskop, 4) Sappershoek, and 5) Cape Recife (Figure 25; *sensu* Chapter 2). These sites have been selected based on the previous literature, their well-developed microbialite biomass, accessibility, and high flow rates (sensu Rishworth *et al.,* 2020b). These sites, along with three supplementary sites per main site (i.e. 20 sites), were used for continued freshwater nutrient and heavy metal load and flowrate monitoring. The sites were sampled seasonally for pollution indicators (nutrients). Four seasonal sampling campaigns for pollution indicators were done concurrently with flowrate monitoring. These sampling campaigns were conducted during the austral winter (22-23 August 2022), spring (3-5 October 2022), summer (25-26 January 2023) and autumn (20-24 March 2023). Triplicate samples were collected for each inlet and outlet (Figure 26). In August, the 20 "standard" flowrate monitoring sites were sampled, while in October an additional 26 sites were selected. These additional sites were selected based on strong flow or noteworthy features (e.g. directly connected to residential plots). The October campaign (*sensu* Survey 2 in Chapter 2) was considered a pseudo once-off assessment of the groundwater nutrients of the NMBM coastal zone since a once-off assessment of nutrients for all 1,533 seeps was not logistically feasible. This was done in October rather than August to coincide with the bimodal spring rainfall signature.

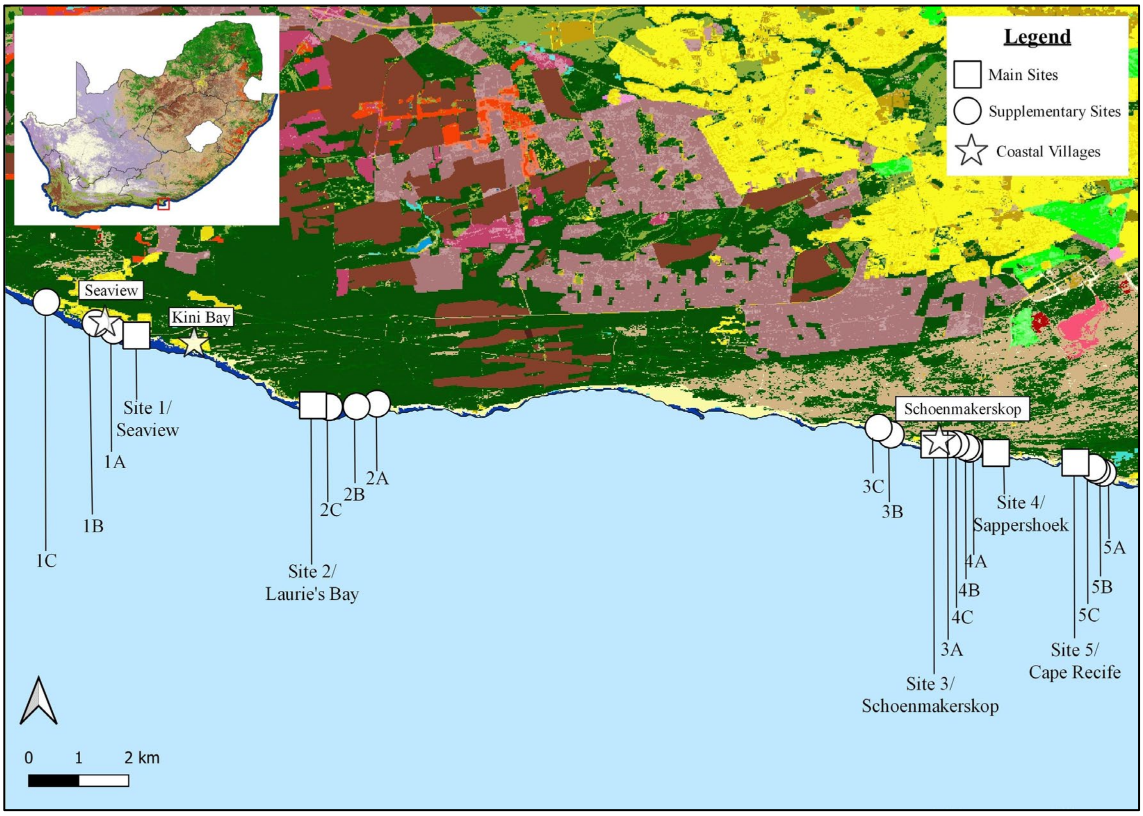


Figure 25. *Map indicating the five main type sites (square), fifteen supplementary sites (circles) sampled and the study area landcover (modified after DEA 2019). Inset shows South Africa and study area location. Most notable at the sampling sites were residential (bright yellow), "natural vegetation" (dark green) and "secondary dunes" (sand colour).*

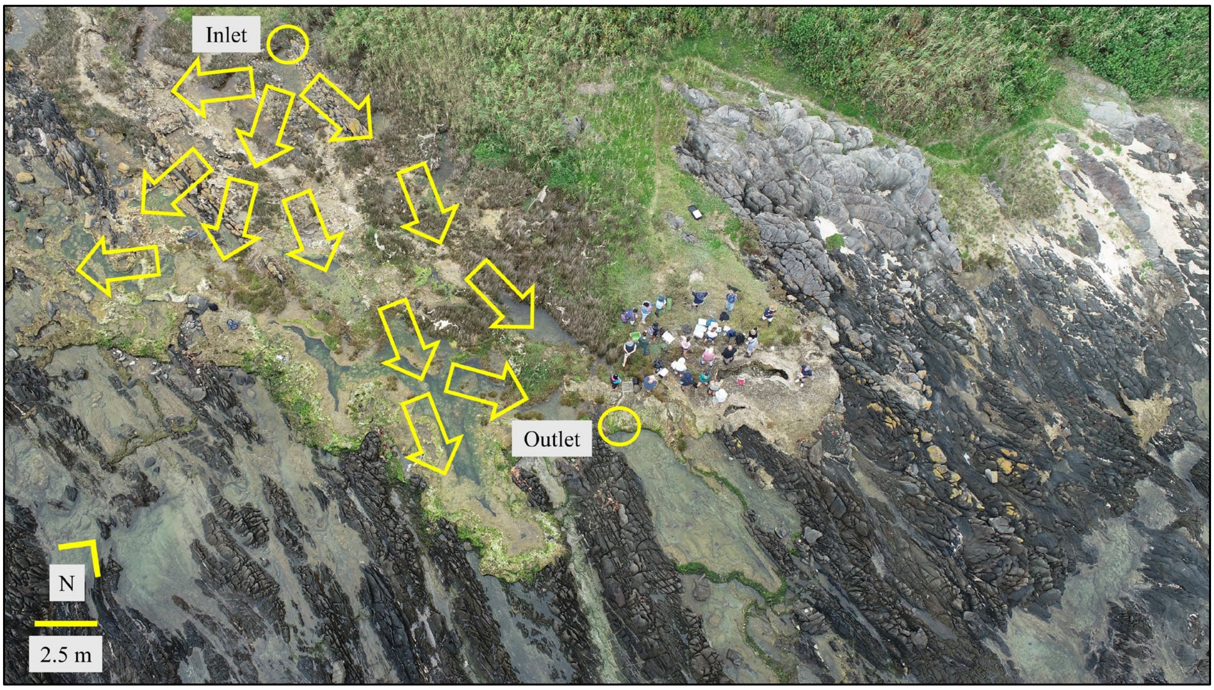


Figure 26. *Example of a SSLiME (site 1) indicating the sample locations of an inlet and outlet (yellow circles) and groundwater flow paths (yellow arrows).*

3.2.3 Sample collection

Using a sterile syringe, water from the inflow source groundwater and outflow was collected and then filtered using a single-use 0.22 µm GVS syringe filter with cellulose acetate membrane. The filtered aliquot was collected in a sterile 15 mℓ Cellstar centrifuge tube, leaving approximately 1 mℓ head space to compensate for expansion during freezing. Samples at the inflow and outflow of the 20 "standard" sites were done in triplicate. Only inflow water was collected for the additional 26 sites since many were not microbialite-bearing. This amounted to 20 inlet and 20 outlet samples collected in August, January and March. In October 45 inlet samples were collected and 19 outlet samples (two samples lost due to breakages). Samples were kept in a cooler with ice packs and frozen in a -80°C freezer upon return to the lab and until analysis.

3.2.4 Analysis

The samples were analysed for major nutrients (nitrate, nitrite, ammonia, silicate and phosphorous) at the South African Environmental Observation Network's Elwandle Node Coastal Biogeochemistry platform. Analysis was conducted using a Seal XY-2 AutoSampler (Figure 27). The nitrate was analysed as nitrogen following reduction to nitrite using a copper-cadmium column. The nitrite reacts with sulphanilamide to produce a diazo compound under acidic conditions, which, in turn produces a purple azo dye (measured at 550 nm on the AutoSampler) upon reacting with N-1-nathylene diamine dihydrochloride. The silicate was measured as silicon dioxide following the reduction of silicomolybdate to molybdate dye (measured at 820 nm on the AutoSampler) in an ascorbic acid solution. Interferences from phosphates are minimised using oxalic acid. Finally, phosphorous is measured at 880 nm wavelength by reacting orthophosphate, molybdate and antimony which is reduced using ascorbic acid. Caveats in the ammonium dataset for the summer and autumn samples occurred due to infrastructural issues but are considered negligible due to low concentrations observed in general, often below detection limits.

***Figure 27**. Operation of the AutoSampler for nutrient analysis.*

3.3 Results

3.3.1 Spatio-temporal nutrient patterns

The nutrient content of samples collected at Seaview (Site 1), Schoenmakerskop (Site 3) and Cape Recife (Site 5) in August and October 2022 are compared to previous sampling campaigns linked to microbialite seeps in the Nelson Mandela Bay and adjacent areas that took place in October 2019 (Rishworth et al., unpublished data) and bimonthly from July 2021 until May 2022 (Hawkes 2023).

3.3.1.1 Dissolved Inorganic Phosphorous (DIP)

In terms of the main sampling locations, the DIP concentration of inflowing seep water ("inlet") was lowest for the Cape Recife samples in all cases with comparably higher concentrations for Seaview and Schoenmakerskop. Conversely, no consistent trend in DIP content was evident between sites for the freshwater flowing out of the microbialite pools ("outflow") before reaching the high tide margin (Figure 28). The DIP content followed an increasing trend from 2019 until present. The DIP content for all inlets sampled in August 2022 ranged from 0.25-1.33 µmol/ℓ and 0.61-1.62 µmol/ℓ in October 2022, with an average of 0.69 µmol/ℓ and 0.88 µmol/ℓ, respectively. On the other hand, the concentration of outflow DIP ranged from 0.20-0.91 µmol/ℓ, average 0.57 µmol/ℓ in August. Finally, in October outflow DIP ranged from 0.55-1.44 µmol/ℓ with an average of 0.71 µmol/ℓ.

The inlets of the Nelson Mandela Bay sites generally had higher DIP concentration than those of adjacent microbialite bearing areas (i.e. Cape Padrone to the east and Cape St Francis to the west) (Figure 28 and Figure 29). While the DIP content of the outlets was variable between sites and the different sampling years. Notably, the Cape St Francis site had the highest concentration in 2019 and Seaview the highest concentration in 2021 and 2022. In general, the inlet samples had a higher DIP content than the outflow samples, with Cape St Francis being a notable exception.

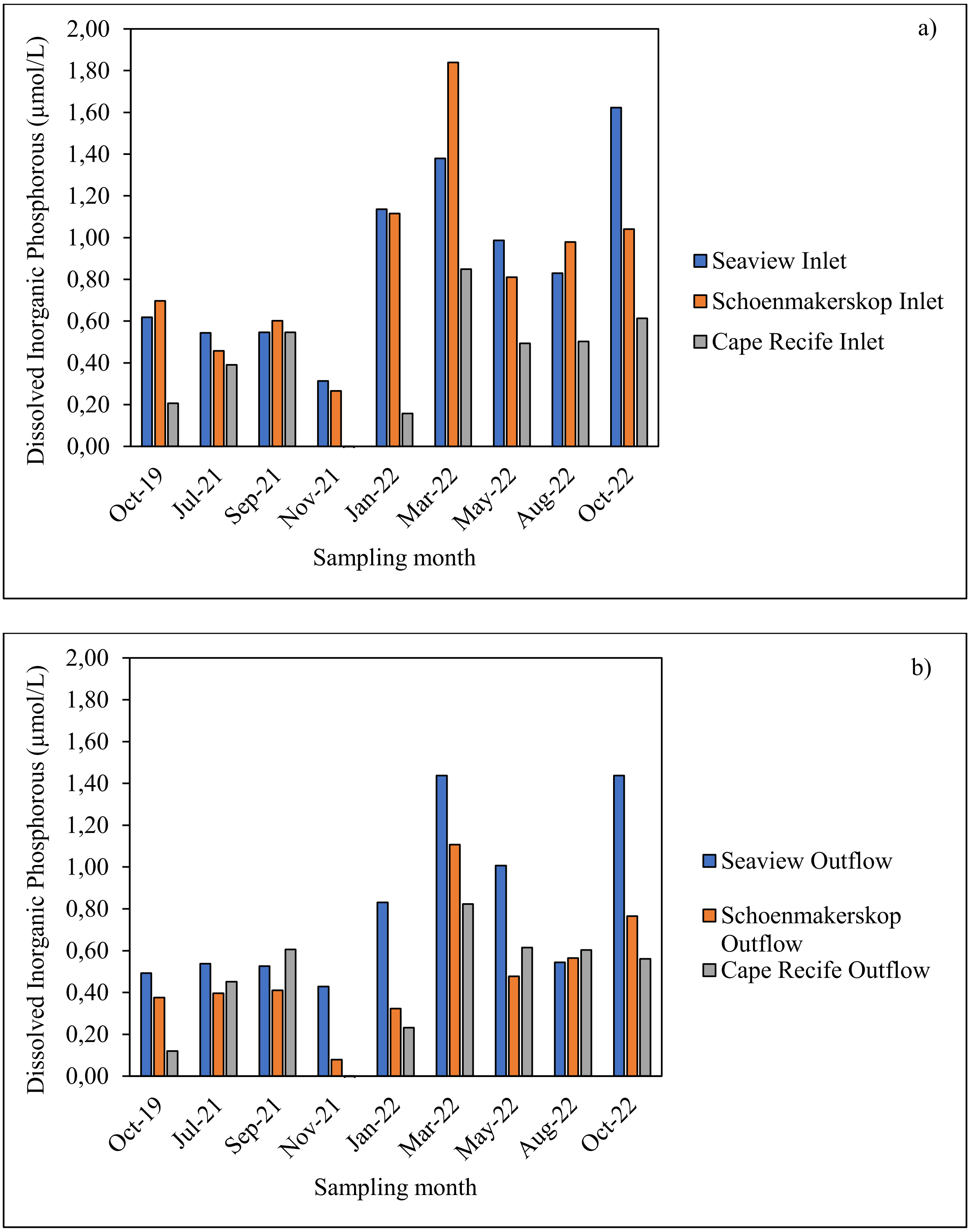


***Figure 28**. Dissolved Inorganic Phosphorous (DIP; µmol/ℓ) content of the a) inlets and b) outflow at three main microbialite sites along the Nelson Mandela Bay coast.*

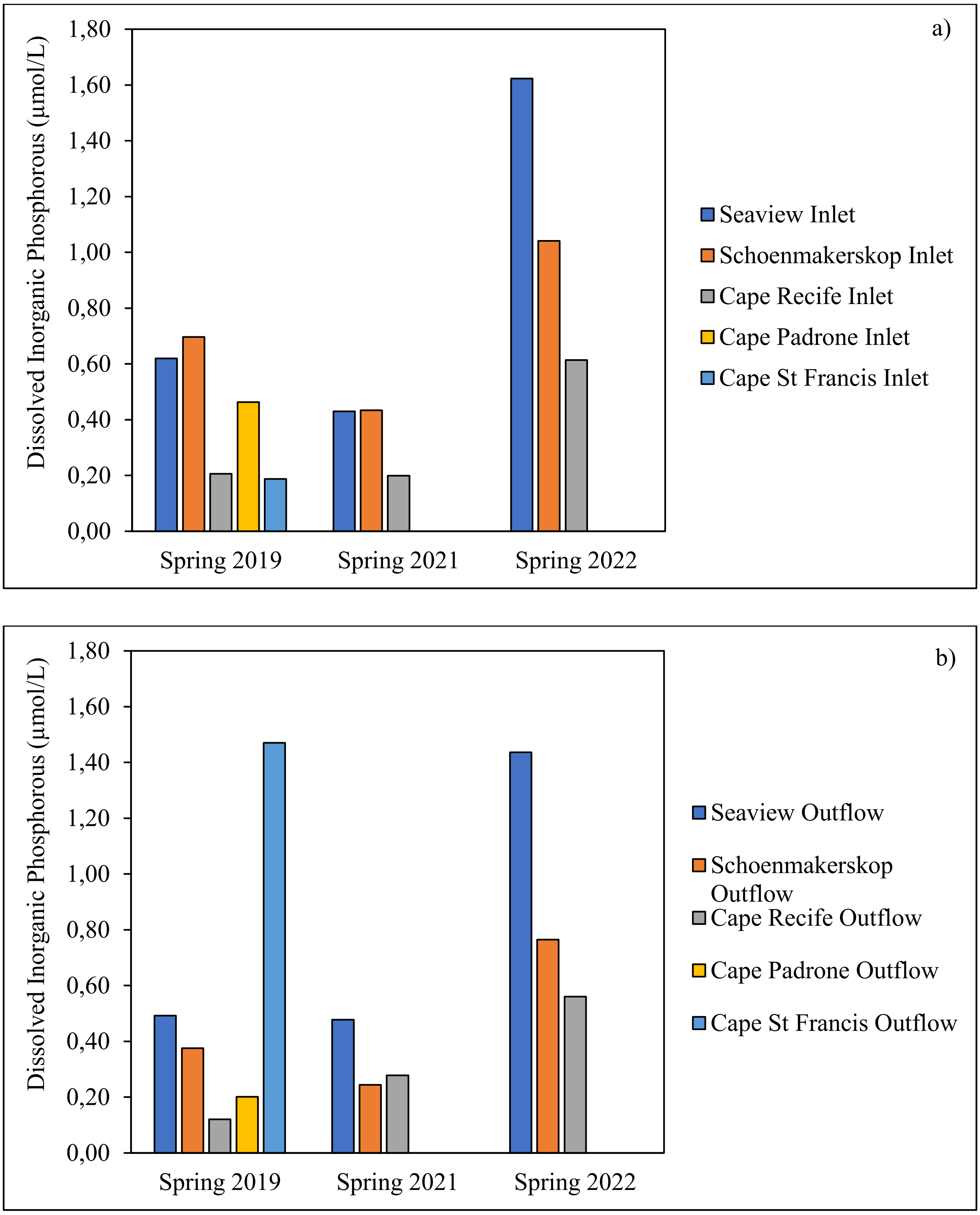


Figure 29*. Dissolved Inorganic Phosphorous (DIP; µmol/ℓ) of the a) inlets and b) outflow at selected microbialite sites in the Algoa and St Francis Bays during the Spring 2019, 2021 and 2022.*

3.3.1.2 Dissolved Silicate

The dissolved silicate content of both the inlets and outflow remained relatively consistent with previous measurements (Figure 30). For all samples the silicate content was highest at the Seaview site, with the Schoenmakerskop and Cape Recife samples being similar and consistently lower than that measured at Seaview. The average content of inlet samples collected in 2022 was 180.28 µmol/ℓ and 282.52 µmol/ℓ for August and October, respectively. Similarly, the average silicate content of outflow samples was 180.25 µmol/ℓ and 254.58 µmol/ℓ for August and October, respectively. Therefore, there was little difference between the inlet and outflow samples, with the biggest difference noted at Cape Recife (Figure 31). The silicate content was similar for the Nelson Mandela Bay area and adjacent capes, although this was highest at Seaview, followed by Cape Padrone.

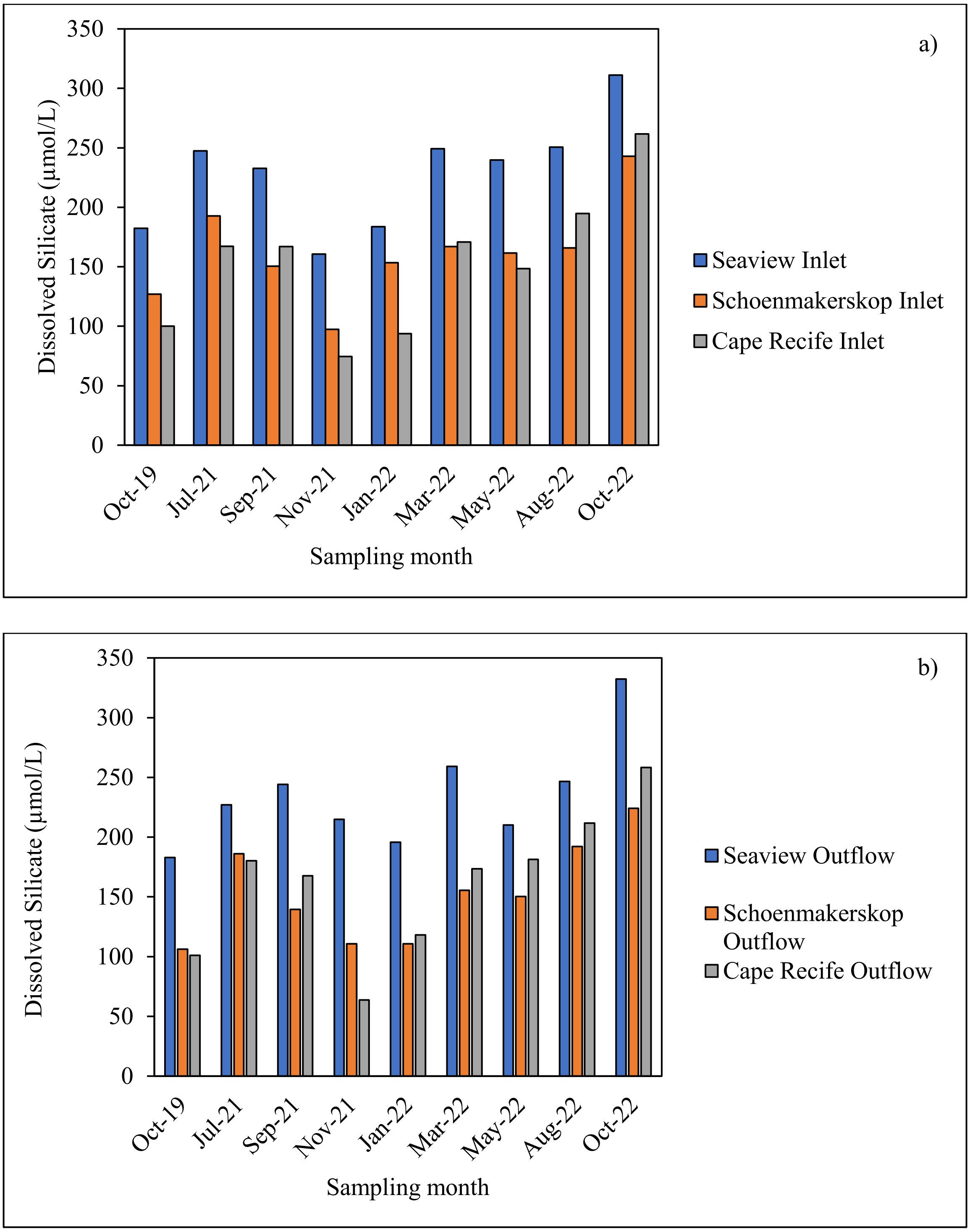
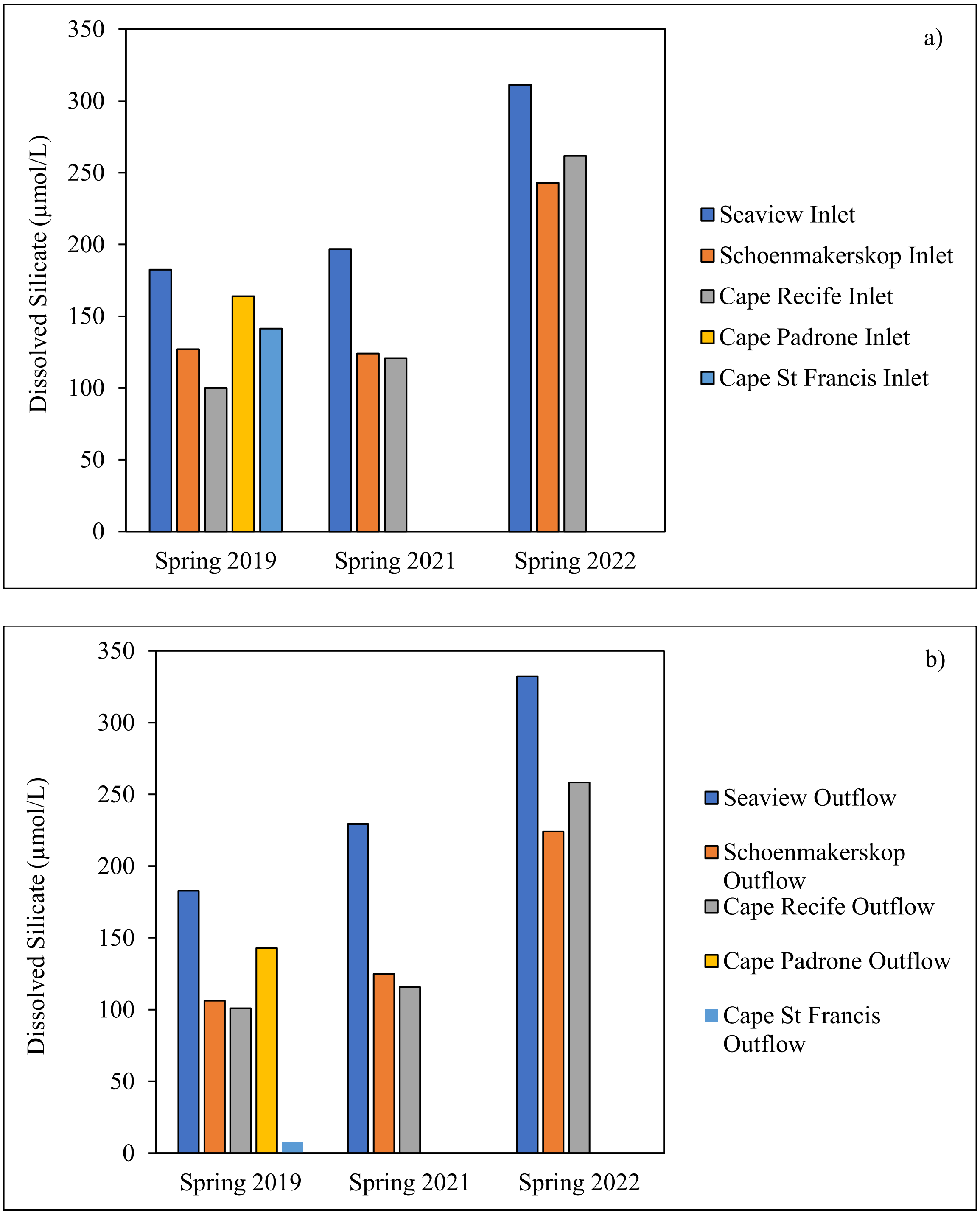


Figure 30. *Dissolved silicate (µmol/ℓ) content of the a) inlets and b) outflow at three main microbialite sites along the Nelson Mandela Bay coast.*



***<u>Figure 31</u>**. Dissolved silicate (µmol/ℓ) of the a) inlets and b) outflow at selected microbialite sites in the Algoa and St Francis Bays during the Spring 2019, 2021 and 2022.*

3.3.1.3 Dissolved Inorganic Nitrogen (DIN)

The DIN content indicated little seasonal variation between bimonthly sampling collections for July 2021-May 2022 (Figure 32). However, there is a clear progressive increase in the DIN content of both inlet and outflow samples, with the Seaview samples having the highest concentrations. The lowest values were recorded in 2019 and the DIN content for both inlet and outflow samples of Seaview and Schoenmakerskop peaked in August of 2022. All inlet samples and most of the outflow samples collected at Seaview had a higher DIN content than those collected at Schoenmakerskop and Cape Recife. The largest contributor to the DIN content was nitrate, followed by ammonia, with nitrite being the smallest contributor. For example, comparing the inlet samples, the average nitrate content was 343.74 µmol/ℓ in August 2022 and 200.85 µmol/ℓ in October 2022. On the other hand, the average nitrite content was 0.20 µmol/ℓ for August and 0.12 µmol/ℓ for October. Lastly, the average ammonia content was 0.40 µmol/ℓ and 0.45 µmol/ℓ for August and October, respectively. The average total DIN was 344.34 µmol/ℓ and 201.42 µmol/ℓ for the inlet and outflow in August, respectively. In October the concentrations for inlet and outflow were 298.65 µmol/ℓ and 186.82 µmol/ℓ, respectively.

When compared to Cape Padrone and Cape St Francis, the Nelson Mandela Bay had higher DIN concentrations, although only marginally (Figure 33). Large positive differences were observed between the inlet and outflow samples of Schoenmakerskop during the springs of 2021 and 2022. Finally, little difference was observed at Seaview in 2019, while in 2021 and 2022 the outflow samples had higher DIN concentrations than the inflow samples (Figure 33).

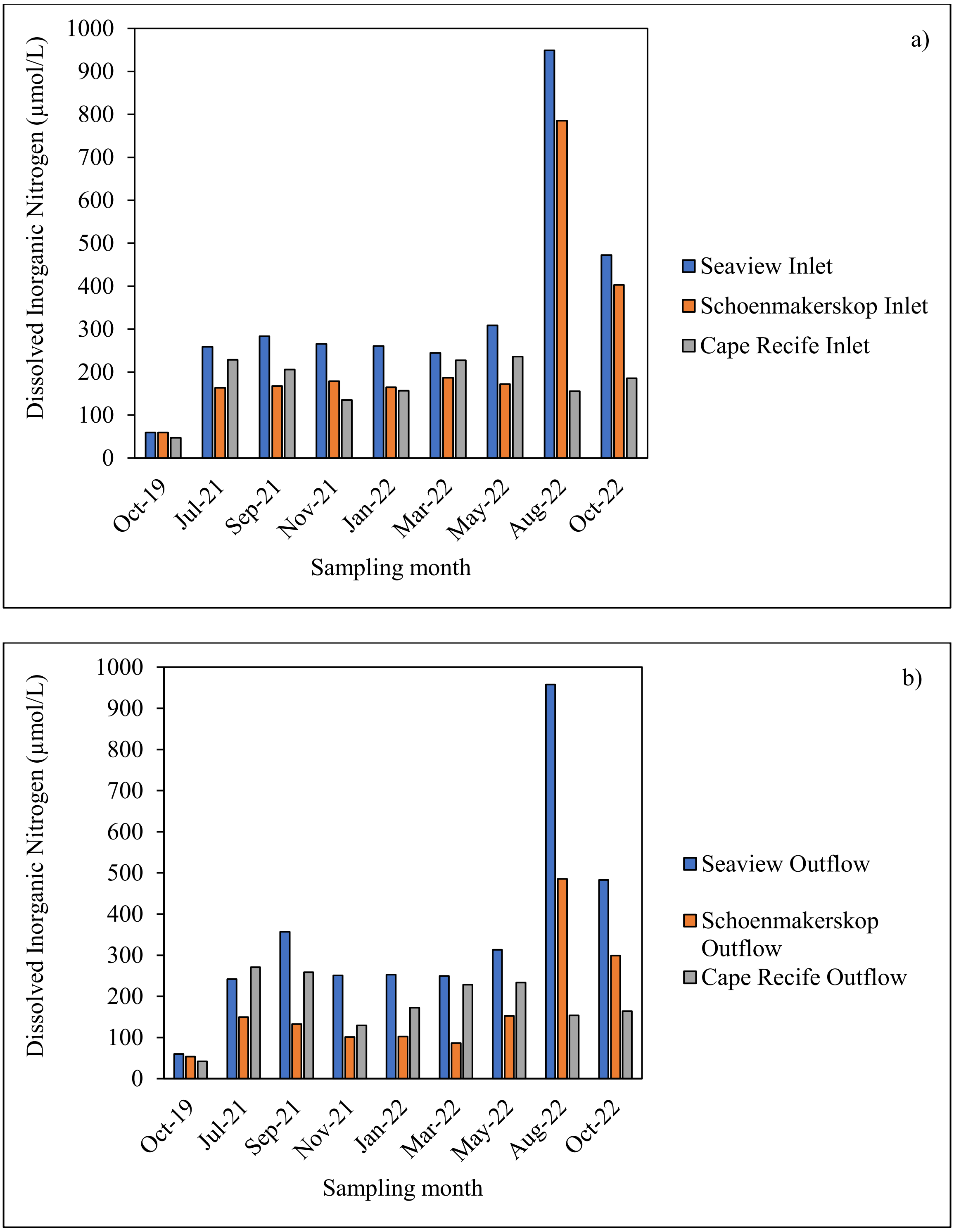


Figure 32. *Dissolved Inorganic Nitrogen (DIN; µmol/ℓ) content of the a) inlets and b) outflow at three main microbialite sites along the Nelson Mandela Bay coast.*

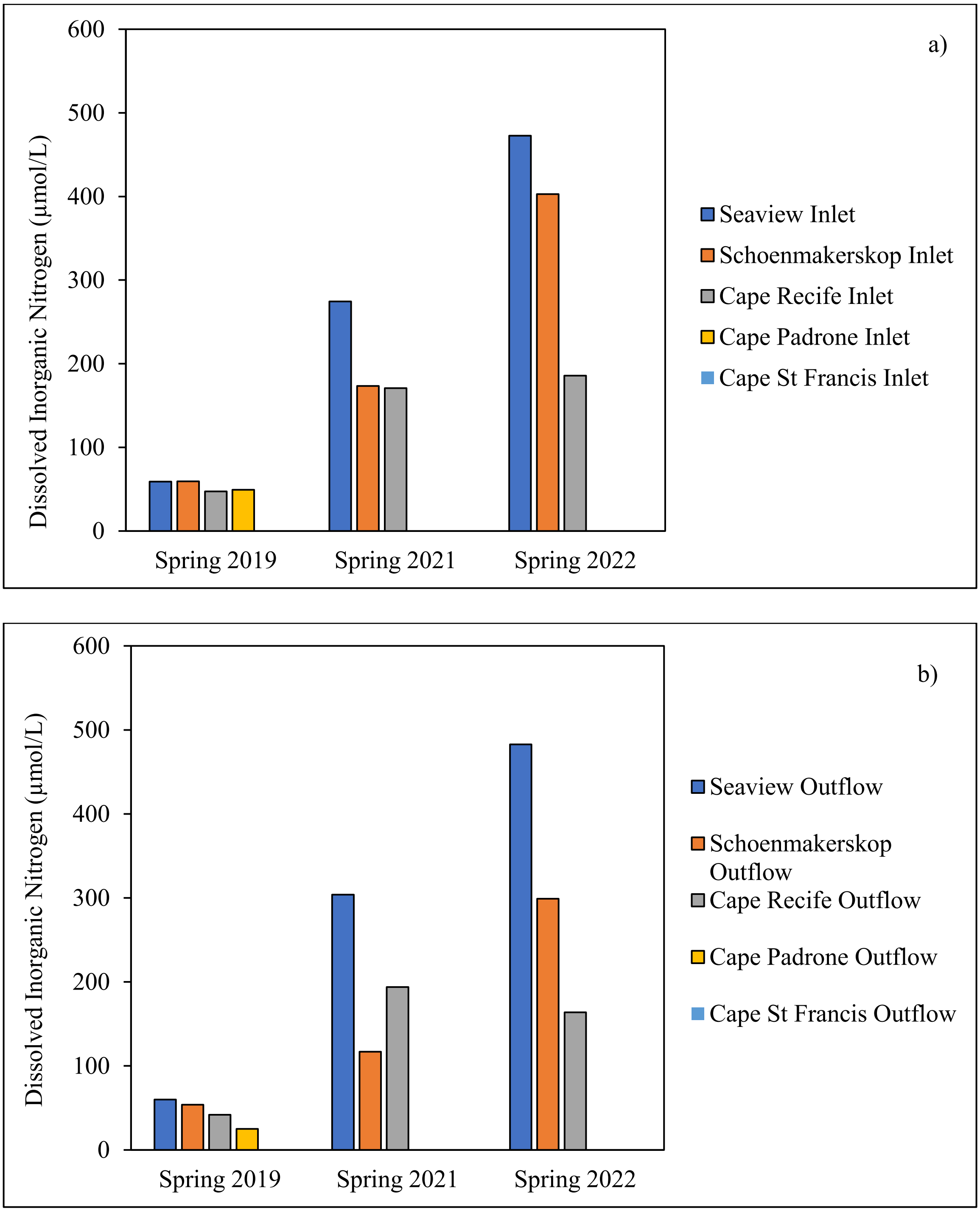


***Figure 33**. Dissolved Inorganic Nitrogen (DIN; µmol/ℓ) of the a) inlets and b) outflow at selected microbialite sites in the Algoa and St Francis Bays during the Spring 2019, 2021 and 2022.*

3.3.1.4 Nutrient heat maps

The heatmaps indicated that spatially the "hotspot" for high DIP load was between the Schoenmakerskop and Sappershoek section of the NMB coast (Figure 34). Whereas, the Seaview surrounds had the highest DIN, followed by the Schoenmakerskop to Sappershoek area (Figure 35).

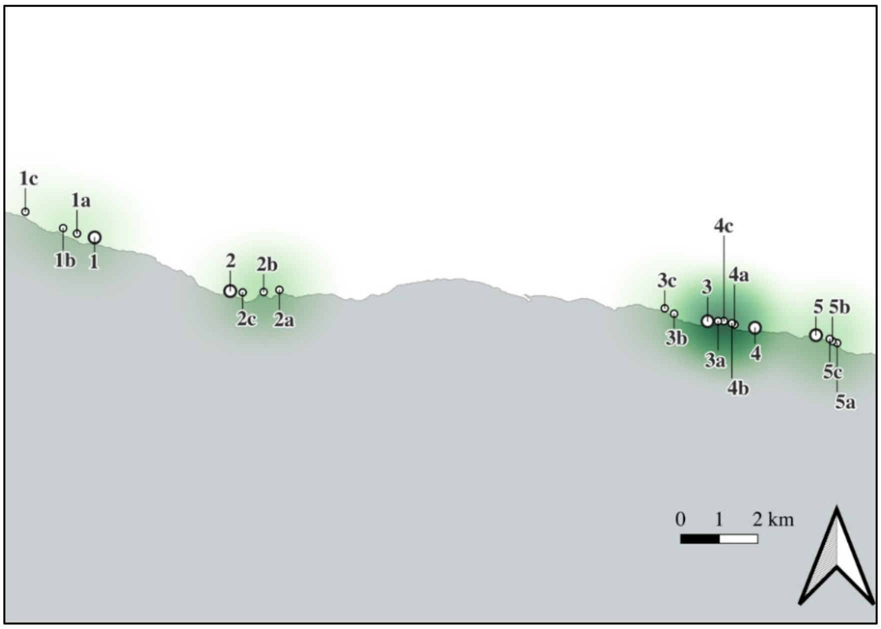


Figure 34. *Heat map indicating the spatial variability of the DIP concentrations of monitored inlet samples.*

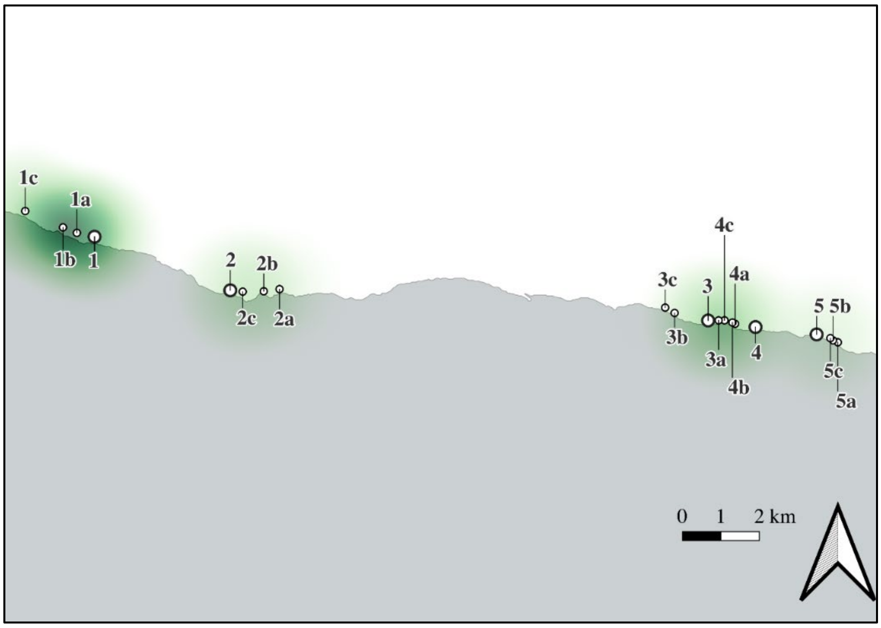


Figure 35. *Heat map indicating the spatial variability of the DIN concentrations of monitored inlet samples.*

3.3.2 Intra-site nutrient patterns: uptake

3.3.2.1 Nutrient content of inlets and outlets

Excepting selected samples from four sites (2A, 2B, 2C, 3B) the dominant (> 50%) nitrogen-species for all samples was nitrate. In fact, nitrate constituted > 85% of the dissolved inorganic nitrogen in the majority (93%) of samples. The mean dissolved inorganic nitrogen (DIN) concentrations of inlet samples ranged from a minimum of 0.18 µmol/ℓ to a maximum of 981.08 µmol/ℓ (Figure 36). On the other hand, the mean DIN of outlet samples ranged from 0.17 µmol/ℓ to 973.39 µmol/ℓ (Figure 36). Maximum DIN concentrations were observed during the winter for both inlet (mean: 373.36 µmol/ℓ) and outlet (mean: 291.24 µmol/ℓ) samples, followed by spring samples (mean inlet: 201.37 µmol/ℓ; mean outlet: 186.82 µmol/ℓ). In terms of spatial variability, the samples with the highest concentrations were those in the vicinity of the Seaview coastal village (sites 1-1C). High concentrations were also observed in samples taken from sites proximal to the Schoenmakerskop village (e.g. site 3, 4B and 4C). With the exception of site 2A which is associated with a man-made weir, generally the samples with the lowest concentrations were located on the less developed sections of the coast (e.g. Laurie's Bay vicinity – 2, 2B, 2C) and/or located in nature reserves (e.g. 3B and 3C).

The mean dissolved inorganic phosphorous (DIP) concentrations of inlet and outlet samples ranged from 0.12 to 1.86 µmol/ℓ and 0.11 to 1.84 µmol/ℓ, respectively (Figure 36). Peak concentrations of DIP were observed during the spring for both inlet and outlet samples (mean inlet: 0.88 µmol/ℓ; mean outlet: 0.71 µmol/ℓ) followed by winter samples (mean inlet: 0.71 µmol/ℓ; mean outlet: 0.60 µmol/ℓ). No clear spatial trend was visible in terms of the DIP concentrations.

The mean dissolved silicate (DSi) content of samples ranged from 112.96 to 343.57 µmol/ℓ for inlet and 45.15 to 336.81 µmol/ℓ for outlet samples (Figure 36). The maximum mean concentration was observed in spring for both inlet (mean: 282.52 µmol/ℓ) and outlet (mean: 254.56 µmol/ℓ) samples. Although the concentrations varied slightly spatially and temporally, in general, the highest concentrations were associated with samples from the Seaview region (sites 1-1C).

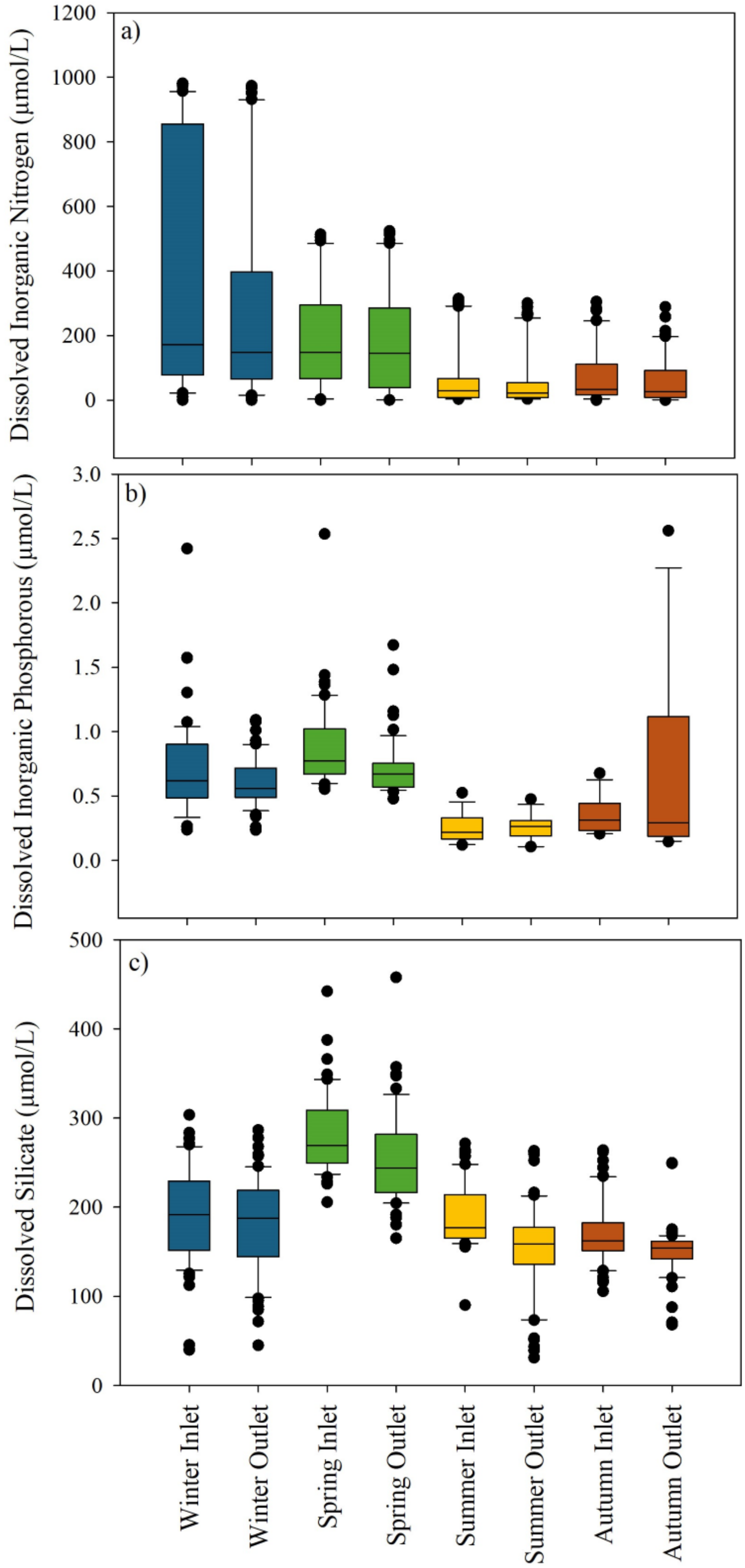


***Figure 36**. Box plots of a) dissolved inorganic nitrogen, b) dissolved inorganic phosphorous, c) dissolved silicate of all groundwater samples collected during the austral winter, spring, summer and autumn in 2022/2023.*

3.3.2.2 Nutrient ratios

All samples were enriched in DSi or DIN relative to the Redfield ratio. In other words, the limiting nutrient for all samples was phosphorous (Figure 37). Excluding four samples, all samples had DIN:DIP ratios above 16:1, even if the samples were rich in DSi. No clear trends in terms of nutrient limitation were observable between seasons or between inlet and outlet samples. The only distinction was that the samples enriched in nitrogen were predominantly from winter and spring samples.

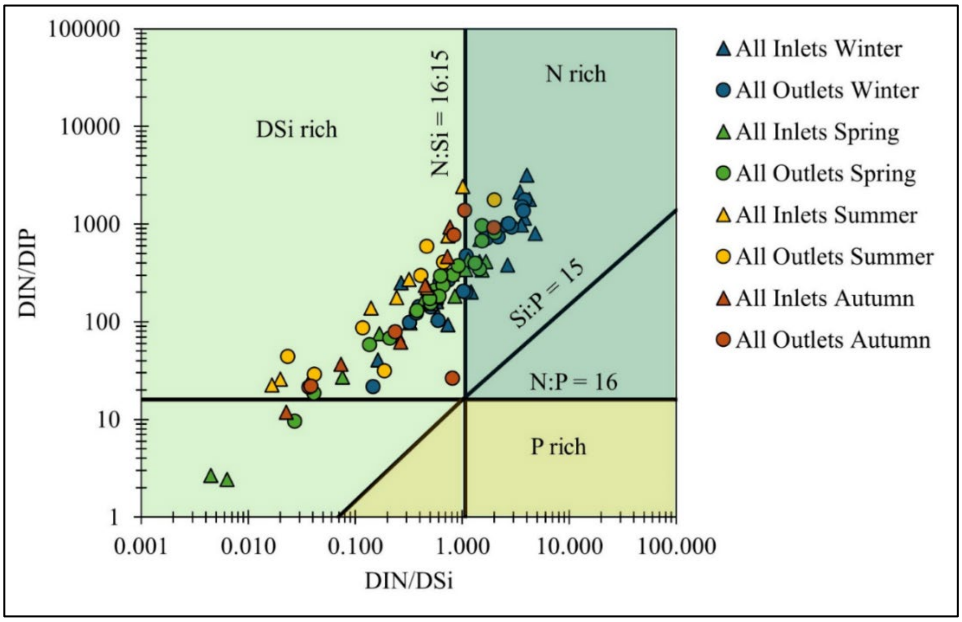


***Figure 37**. Nutrient limitation graph indicating DIN:DIP as a function of DIN:DSi.*
DIN = dissolved inorganic nitrogen; DIP = dissolved inorganic phosphorous; DSi = dissolved silicate.

3.3.2.3 Nutrient load and uptake potential

In terms of nutrient uptake, no clear trend was seen either spatially or temporally, although individual sites did consistently have higher concentrations in the inlet than outlet samples (e.g. DIN: 1C, 2A, 3, 4B, 4A, 5, 5A; DIP: 2B, 3; DSi: 1C; 2C; 3C; 3B; 4A) and were therefore more effective at attenuating nutrients (Figure 38, Figure 39 and Figure 40). Furthermore, the DIP flux (i.e. concentration multiplied by flow rate and extrapolated to per annum) for both the summer and autumn seasons were higher for outlet samples than inlet samples (Table 8). The SSLiME systems seemed to be more effective at attenuating DIN than DIP, except during the spring when the outlet flux was higher than the inlet flux (Table 8).

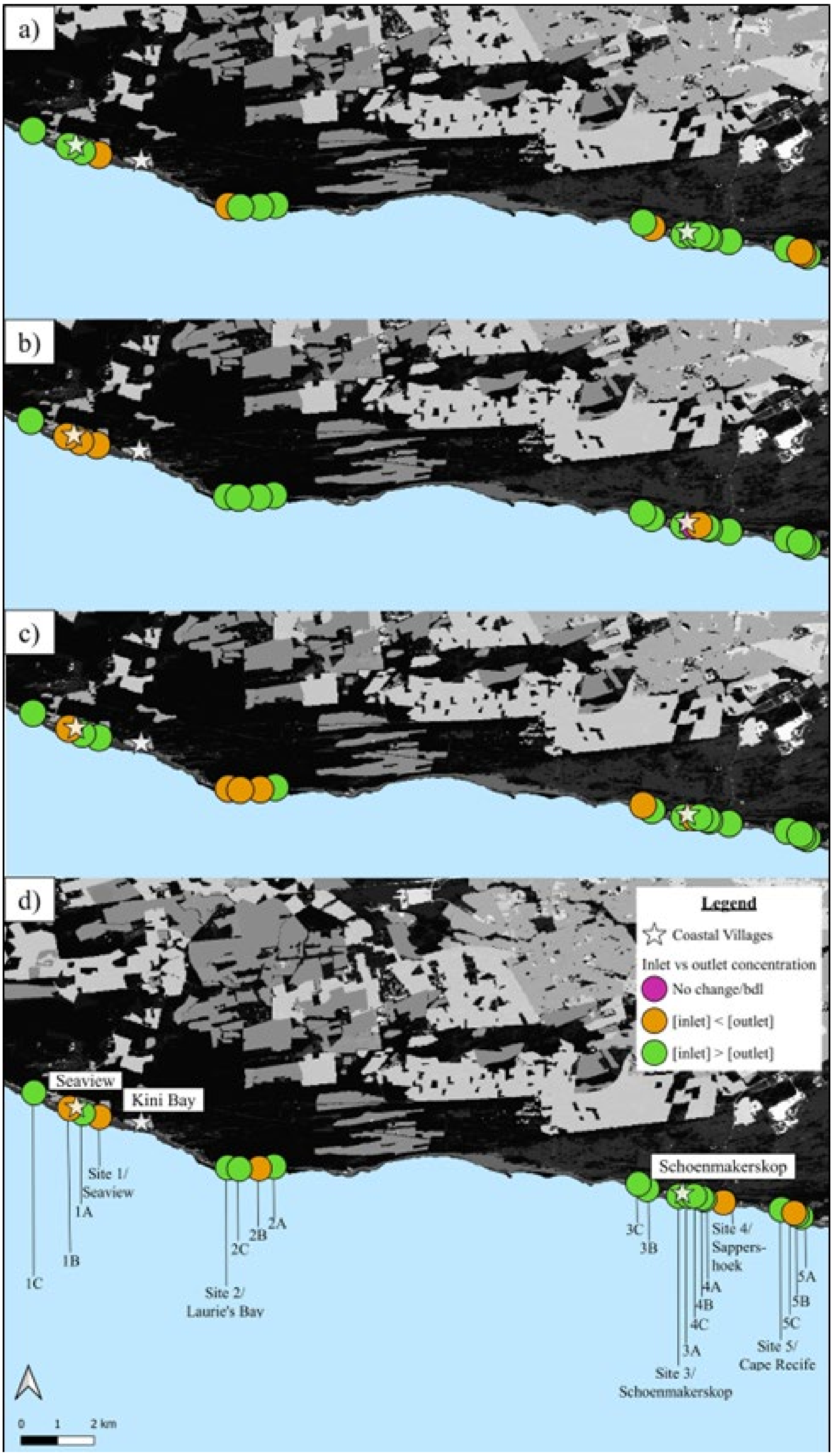


***Figure 38**. Difference between the inlet and outlet dissolved inorganic nitrogen concentrations for samples collected during the austral a) winter 2022; b) spring 2022; c) summer 2023; d) autumn 2023.*

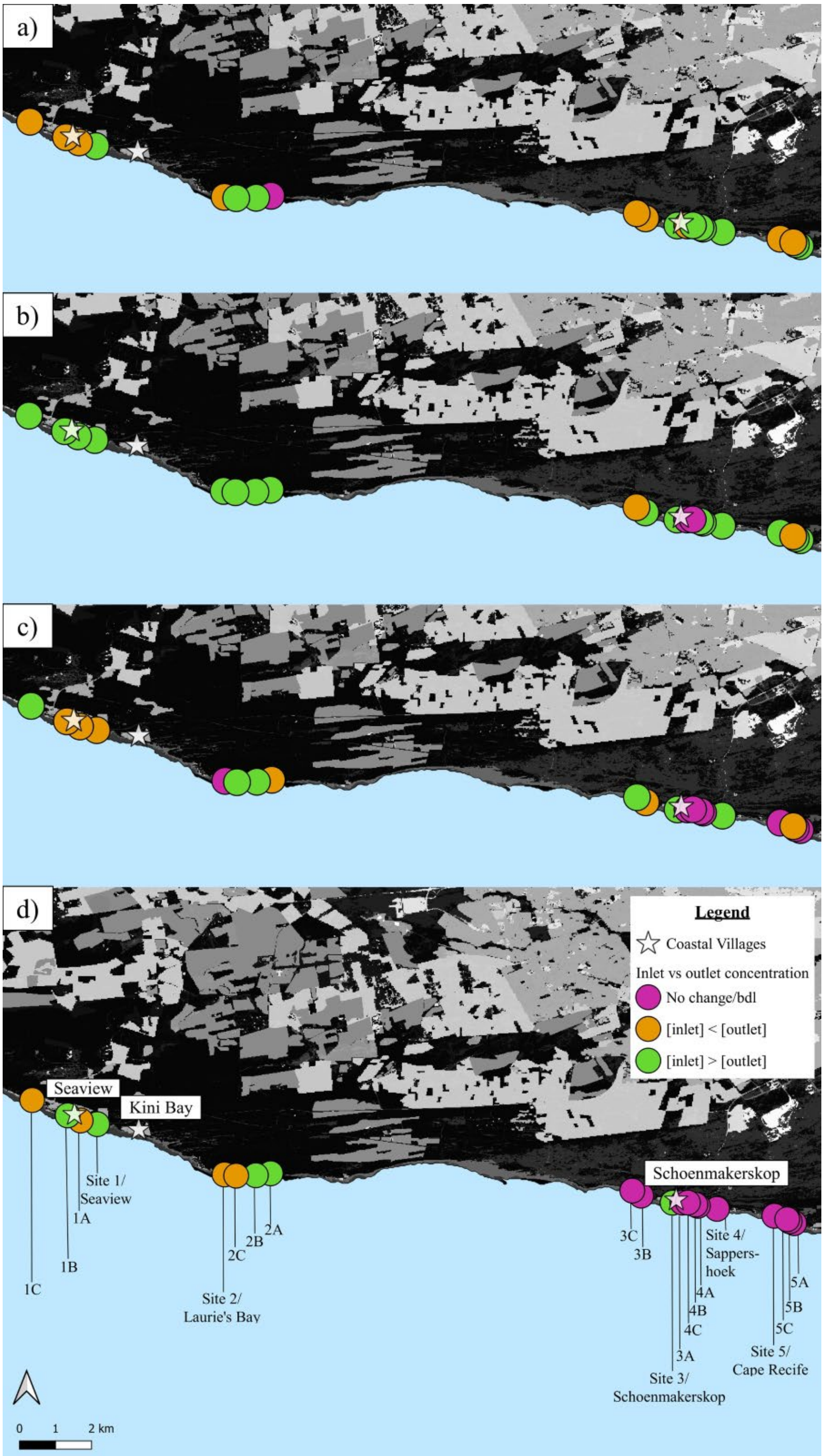


__Figure 39__. Difference between the inlet and outlet dissolved inorganic phosphorous concentrations for samples collected during the austral a) winter 2022; b) spring 2022; c) summer 2023; d) autumn 2023.

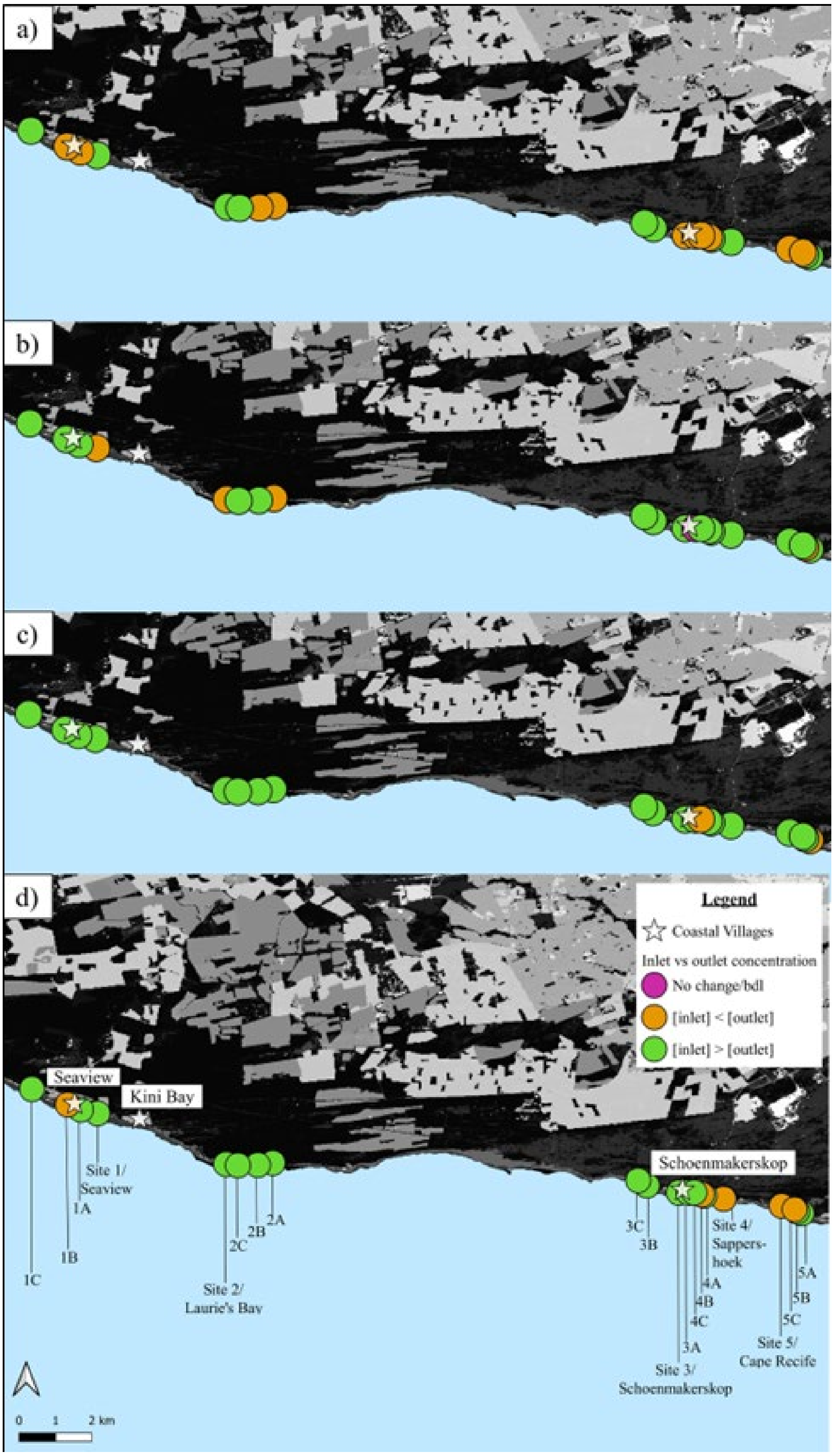


Figure 40. *Difference between the inlet and outlet dissolved silicate concentrations for samples collected during the austral a) winter 2022; b) spring 2022; c) summer 2023; d) autumn 2023.*

Table 8. *Mean nutrient concentration, measured flowrate, and nutrient flux for each season.*

	DIP Conc. (µmol/ℓ)	DIN Conc. (µmol/ℓ)	Flow Rate (ℓ/s)	P Flux (kg/a)	N Flux (kg/a)
			Winter (August 2022)		
Inlet	*0.71*	*363.60*	*0.70*	*0.49*	*112.43*
Outlet	*0.60*	*291.24*	*0.70*	*0.41*	*90.05*
			Spring (October 2022)		
Inlet	*0.88*	*201.37*	*0.68*	*0.58*	*60.48*
Outlet	*0.71*	*186.82*	*0.68*	*0.47*	*56.11*
			Summer (January 2023)		
Inlet	*0.23*	*72.18*	*0.65*	*0.15*	*20.72*
Outlet	*0.24*	*55.83*	*0.65*	*0.15*	*16.03*
			Autumn (March 2023)		
Inlet	*0.34*	*75.72*	*0.82*	*0.27*	*27.43*
Outlet	*0.60*	*59.90*	*0.82*	*0.48*	*21.70*
			Overall		
Inlet	*0.65*	*177.92*	*0.71*	*0.45*	*55.80*
Outlet	*0.59*	*147.96*	*0.71*	*0.41*	*46.40*

3.4 Discussion

The spatial variability in both the DIN and DIP content of inlets (i.e. lowest at Cape Recife and higher at Schoenmakerskop and Seaview) is consistent with what was observed for previous studies and is likely due to the differences in human occupation – with development being higher at Schoenmakerskop and Seaview compared to Cape Recife (Rishworth *et al.,* 2017; Dodd, 2019).

The silicate content for the coastal seeps is likely lithologically controlled with little seasonal variation or site variation with similar lithologies (Cape Recife and Schoenmakerskop) occurring. The higher silicate content of Seaview may be related to the weathering of the bedrock lithologies rather than supply from foreland dunes and corresponds to the higher detrital sediment content within microbialites for this site compared to the other Nelson Mandela Bay sites (Dodd, 2019). For example, quartz-bearing (and therefore silicate containing) phyllites is a dominant lithology at the Seaview site (Dodd *et al.,* 2018) and is more readily weathered than the quartzites occurring at Cape Recife and Schoenmakerskop.

The combined total nutrient load supplied by rivers and wastewater treatment works (WWTWs) to the Algoa Bay was calculated to be 8.7×10^5 kg/a and 1.4×10^5 kg/a for DIN and DIP, respectively (Lemley *et al.,* 2019). These estimates include the cumulative load for all WWTWs supplying the Algoa Bay environ, as well as other riverine nutrient loads and the groundwater discharge of the Alexandria dunefield. For comparability to this study in terms of the stretch of coast immediately west of Algoa Bay containing microbialites, the groundwater discharge on the 40 km tract of Alexandria dunefield has a total N discharge estimated to be 0.6×10^5 kg/a (upscaled from the published estimate of 1.5 kg/a per metre of beach: Campbell & Bate, 1998). In comparison, this study estimates that 3.6×10^3 kg/a DIN and 0.029×10^3 kg DIP enters the 40 km stretch of coastal zone between Cape Recife and Maitlands Beach through the SSLiME. This input therefore represents a considerable and previously unaccounted nutrient input to the NMB environ that is closer to (but still less than) natural inputs of nutrients at the Alexandria dunefield than it is to local WWTW nutrient loads.

Furthermore, very high DIN:DIP ratios are often associated with sewage-impacted groundwater since phosphorous is attenuated faster than nitrogen (Santos *et al.,* 2021), which is supported by samples near coastal villages (especially Seaview) consistently having higher ratios compared to sites not immediately adjacent to human settlements. The bulk of the water released to the ocean (all but one outlet sample) had DIN:DIP above the Redfield ratio and could offset natural coastal waters that are N-limited (Rishworth *et al.,* 2017) and lead to phosphorous limitation (Zhang *et al.,* 2020). This could promote primary productivity, alter community structure and cause an increase in macrophyte (e.g. *Ulva* spp.) cover in coastal ecosystems (Santos *et al.,* 2021). Coastal groundwater discharge with high DIN:DIP or DIN:DSi ratios may cause phytoplankton blooms (Oehler *et al.,* 2021; Santos *et al.,* 2021). For example, harmful algal blooms may be associated with DIN:DSi > 1 (Santos *et al.,* 2021), which was the case for several of the winter and spring samples. That being said, the majority of samples had DIN:DSi ratios < 1 which is generally associated with diatom blooms rather than blooms of harmful dinoflagellate species (Santos *et al.,* 2021).

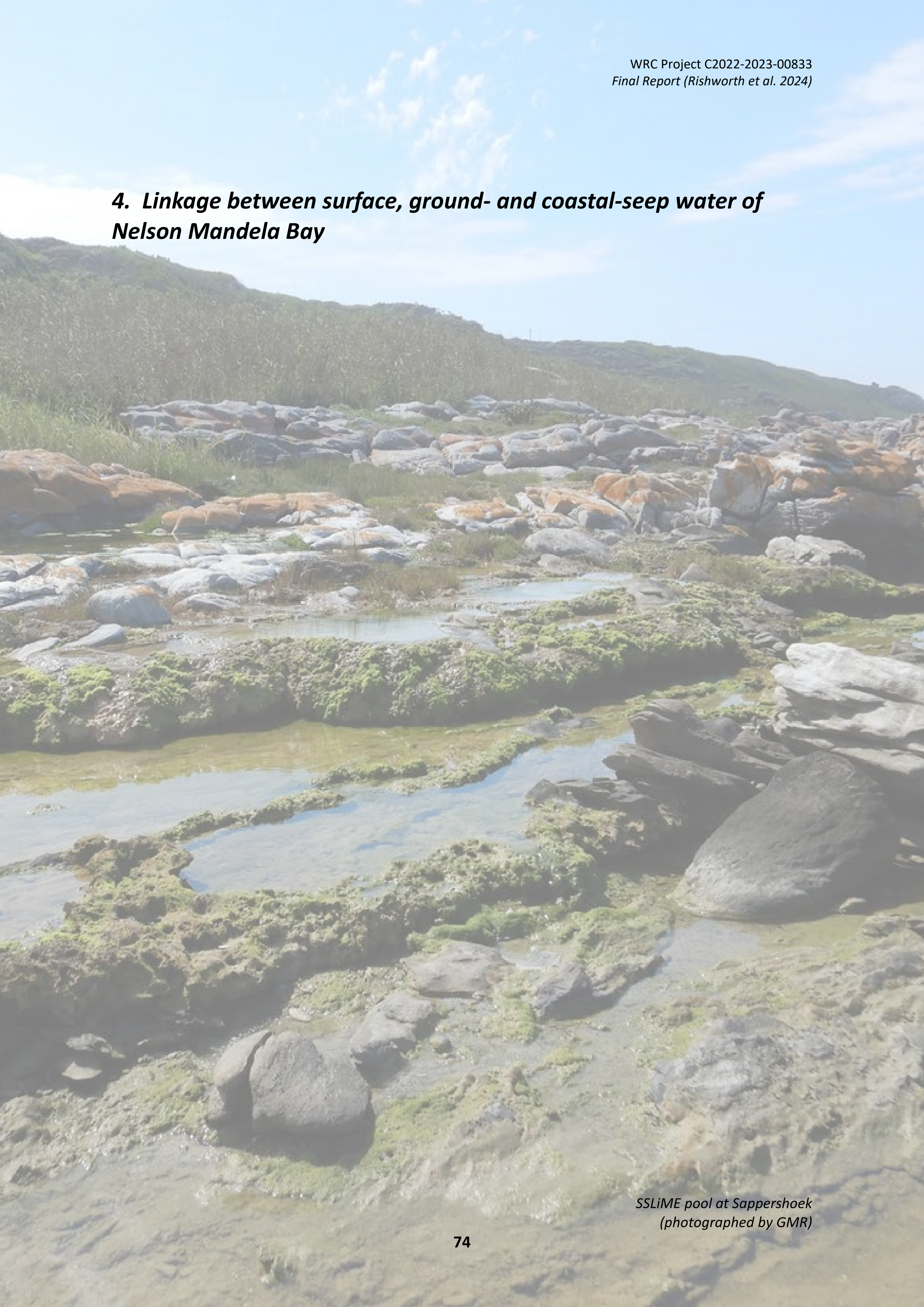
It has previously been suggested that the microbialite-forming pools might be performing a nutrient buffering ecosystem service to the local coastline (Rishworth *et al.,* 2020b) although data demonstrating this has not been shown as of yet. This preliminary study shows that 3.0×10^3 kg/a DIN and 0.026×10^3 kg/a DIP discharges via the monitored coastal seeps at the outlets. This means that approximately 606.24 kg/a DIN is taken up within the microbialite pool system and 2.68 kg/a of DIP. This was estimated from the monitored seeps that represent 44.98% of the total flow (3.96 Mℓ/d; Chapter 2). Whether the differences between the nutrient content of the inflow and outflow samples represent uptake as a result of nitrogen fixation within the microbialite matrix or due to some other process is still unclear. Earlier reports of decreasing DIN concentrations down the elevation gradient of SSLiME was attributed to the utilisation of nutrients by primary producers, such as microphytobenthic algae, phytoplankton, macroalgae and macrophytes (Rishworth *et al.,* 2017) and groundwater mixing with saline, nitrate-poor water from below the SSLiME pool halocline (Dodd *et al.,* 2018). Incubation experiments indicated that roughly 80% of the initial macronutrient concentrations could be depleted by nutrient uptake by the microbial mats (du Plooy *et al.,* 2020). However, the nutrient output from numerous SSLiME sites was not previously quantified. Although macronutrient concentrations decreased consistently at certain sites from the inlet to the outlet, no conclusive trends were distinguishable at several of the sites. Nevertheless, the overall DIN flux was substantially diminished during the winter and the DIP flux during the spring, indicating that to some degree seasonal nutrient attenuation in SSLiME does occur.

3.5 Conclusion

Modern microbialite-forming seeps along the NMB coastline clearly receive a large inorganic nutrient load of DIN and DIP, especially in terms of concentration. This potentially has knock-on effects and represents a risk to coastal eutrophication, potentially exacerbating the local prevalence of coastal threats such as harmful algal blooms which have recently been documented for NMB. Nonetheless the total nutrient load entering the NMB SSLiME is orders of magnitude less that that entering the coast from local WWTWs. The clear link between nutrient discharge hotspots and coastal residential urbanisation means that management intervention could be effectively targeted to mitigate these inputs, such as septic tanks that are closed without leeching into the groundwater table. Future research linked to this project will aim to both better elucidate the temporal nature of the nutrient cycle within the microbialite pools, but also to more conclusively link the sources of these nutrients using other supplementary tools such as stable isotopes of nitrogen or persistent organic pollutants (POPs) in the seep water as well as inland groundwater. This research will be ongoing until at least early 2024.

There is also evidence that the microbialite-forming pools themselves, as well as the co-occurring macrophytes and macroalgae, might be demonstrating some level of nutrient uptake in these systems whereby the nutrient load in inflowing water is higher than that of the outflowing water entering the coast. These results are not conclusive and will become more apparent with ongoing monitoring. Nutrient pollution also potentially presents a threat to the microbialites themselves, as has been proposed in Western Australia (Forbes *et al.,* 2010). It is therefore crucial that in tandem with this groundwater research that the biological community is also assessed to understand whether there is a risk of other organisms outcompeting or disrupting the microbialite formations under higher nutrient inputs. This biological research is underway as part of a separate SSLiME project led by GMR.

4. Linkage between surface, ground- and coastal-seep water of Nelson Mandela Bay



SSLiME pool at Sappershoek (photographed by GMR)

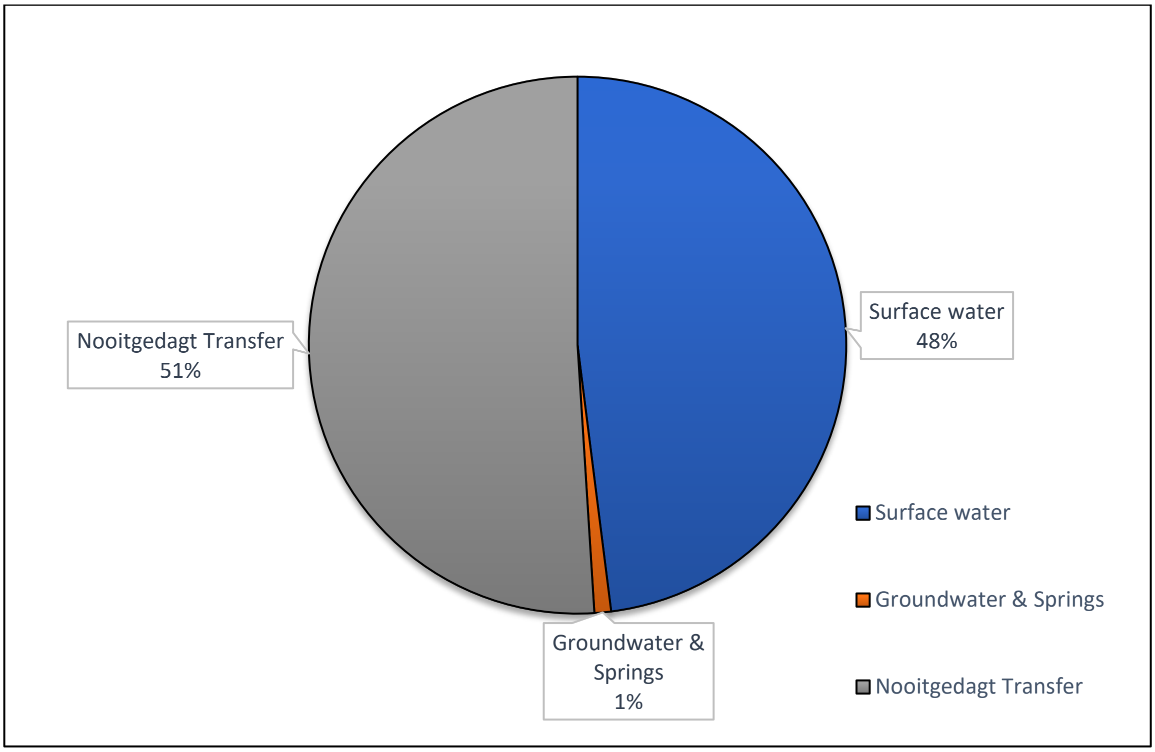
**This chapter is directly linked to CD's PhD thesis (under the supervision of GMR, HCC and Prof. Massmann) that is not published and will be examined after December 2023. Therefore, overlap in content and results are inevitable but is minimised wherever possible.*

4.1 Introduction

Since the Nelson Mandel Bay (NMB) area is prone to persistent drought conditions, it is crucial to understand the dynamics and connections between all water resources for future sustainable water use. Certain coastal regions of South Africa have in the past been or are currently being hampered by several years of drought conditions (Mahlalela *et al.,* 2020; Botai *et al.,* 2021; Dodd & Rishworth 2023). This is exemplified in the Nelson Mandela Bay Metropolitan Municipality (NMBM) and Kouga Local Municipality (KLM) of the Eastern Cape Province, which both receive water from the severely constrained Algoa Water Supply System (AWSS) (Dodd & Rishworth, 2023). For example, the largest supply dam within the AWSS, the Impofu Dam, was decommissioned in early 2023 following record-low dam levels with no further water abstraction possible (Bezuidenhout, 2023) (see Figure 41). The effects of the drought conditions are further amplified by a growing human population and an increase in socio-economic pressures (Taylor *et al.,* 2023). With the freshwater resources being under such severe pressure in the Nelson Mandela Bay (NMB), it is important to understand how the available resources can be effectively managed and protected.

Figure 41. *Low water levels of Impofu Dam shortly before it was decommissioned (October 2021, photographed by CD).*

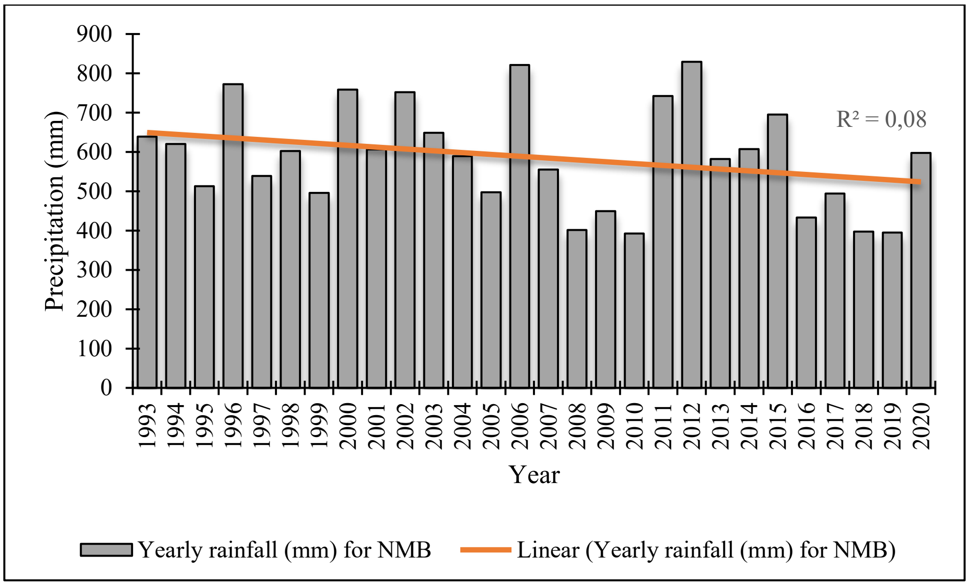
Groundwater utilisation is often considered a viable option to mitigate drought effects. However, groundwater resources in the NMB area are perhaps under-utilised currently (Figure 42) but the knowledge regarding the state of NMBM's groundwater resources is limited, especially as informed by long-term monitoring. Towards ensuring the sustainable use of groundwater during droughts, it is necessary to understand the recharge, residence time, and extent of freshwater in aquifers. A lack of understanding or paucity of data can lead to mismanagement of groundwater resources and the improper enforcing of regulations (Abiye *et al.,* 2021; Taylor *et al.,* 2023). In turn, over-utilisation of the groundwater resources could threaten globally important groundwater-dependent ecosystems such as the supratidal spring-fed living microbialite ecosystems (SSLiME) that occur along the coast of NMB (Rishworth *et al.,* 2020b; Dodd & Rishworth, 2023).



<u>Figure 42</u>*. Water use proportion of the three main water resource types in NMBM (modified from Taylor et al., 2023)*

Precipitation is the primary source of recharge for surface- and groundwater (Abiye *et al.,* 2021). The natural variation of climate, geology and topography in South Africa often makes it difficult to calculate recharge, which is further complicated by changes in rainfall patterns brought about by climate change. Across South Africa, rainfall differs spatially and temporally.

In the east and northeast precipitation occurs mostly in the summer, and in the southwestern and western regions, it occurs mostly in the winter (Rouault *et al.,* 2013; Pohl *et al.,* 2014; Braun *et al.,* 2017). According to Braun *et al.* (2017) this seasonal precipitation is driven by tropical, subtropical, and temperate atmospheric pressure systems. The IPCC Sixth Assessment Report (IPCC, 2021) stated that rainfall has decreased on a national scale. In the western and eastern provinces, especially, this is leading to an increase in aridity associated with agricultural and ecological droughts (Taylor *et al.,* 2023). Specifically, precipitation in the southwestern and southeastern regions has decreased substantially over the last several years (Mahlalela *et al.,* 2020; Botai *et al.,* 2021; Dodd & Rishworth, 2023). For example, the annual rainfall in the AWSS over the past three decades shows a decreasing trend (Figure 43).



***<u>Figure 43</u>**. Annual rainfall in NMB from 1993-2020 (precipitation data supplied by the South African Weather Service).*

The variable climate of the NMB is attributed to its location within the transitional zone of summer and winter rainfall. As such, many weather systems from tropical and mid-latitude origin are ultimately missing this region. In addition, the varying topography also influences the meteorology, contributing to the rainfall variability (Mahlalela *et al.,* 2020). The complex rainfall patterns make it increasingly difficult to predict future scenarios regarding water resource availability in NMB. However, if the rainfall in the region continues to decrease, drought conditions can be expected to worsen. It remains unclear what the impact of increased drought effects would be on the groundwater resources.

The aim of this study is to determine the recharge origin of coastal groundwater discharge associated with SSLiME in the NMB area of South Africa using stable environmental isotopes of water. The stable environmental isotope ratios of hydrogen ($^2H/D$, ^1H) and oxygen (^{18}O, ^{16}O) in water are widely used in hydrology as these constituents are useful tracers in delineating the temporal and spatial variability of hydrological processes (Yin *et al.,* 2011; Stowe *et al.,* 2018; Bedaso & Wu, 2021). The premise is that precipitation replenishes groundwater and that shallow aquifers tend to have the same isotopic signature as the local rainfall, whereas the isotopic ratios of deeper aquifers may be influenced by recharge from different sources or rock interactions (Abiye *et al.,* 2021). This is based on the principle of isotopic fractionation (equilibrium and kinetic fractionation). For example, equilibrium fractionation may occur during condensation in clouds. On the other hand, kinetic fractionation may occur during evaporation from soil or open water. Fractionation varies predictably with temperature, amount, continental effects, altitude, and latitude (e.g. Jasechko, 2019 and references therein). A global network of approximately 900 stations was created in more than 100 countries where monthly samples are collected to determine the isotopic values of rainfall. This network is called the Global Network of Isotopes in Precipitation (GNIP) and was established 60 years ago by the International Atomic Energy Agency and the World Meteorological Organisation (e.g. Scholl *et al.,* 2009; Gröning *et al.,* 2012).

Around the same time, a Global Meteoric Water Line (GMWL) was developed and is characterised by the equation:

$\delta^2H = 8*\delta^{18}O + 10$ (Craig, 1961),

and the equation of best fit was later revised to:

$\delta^2H = 8.13*\delta^{18}O + 10.8$ (Rozanski *et al.,* 1993)

However, since fractionation patterns may vary regionally, the establishment of a Local Meteoric Water Line (LMWL) is necessary to understand the isotopic signature of precipitation (and therefore recharge) in a specific area (Putman *et al.,* 2019).

Although several LMWLs have been developed for South Africa, the closest known LMWL to NMB is situated in Mossel Bay more than 300 km away (Braun *et al.,* 2017). Mahlalela *et al.*

*(*2020) emphasises that the lack of knowledge on the rainfall patterns in the Eastern Cape is contributing to the mismanagement of water resources. The development of an isoscape, or isotopic landscape, may mitigate this issue and aid in the sustainable management of water resources and the protection of dependant ecological systems. This study provides the first known isotopic dataset for rainfall and groundwater resources within the NMB area towards developing an isoscape, with a specific focus on monthly cumulative precipitation, as well as boreholes, cold-water springs, and coastal seeps. This will ultimately assist in understanding the connectivity between rainfall and groundwater resources in NMB and may provide insight for sustainable water resource management in the area and the longevity of groundwater-dependent ecosystems such as SSLiME (Figure 44).

Figure 44. *An example of a SSLiME within the study area where freshwater enters from a coastal seep (arrow). Microbial assemblages and several species of fauna and flora form an integral part of a healthy, functioning microbialite system.*

4.2 Methodology

4.2.1 Study area and environmental setting

The study area is located along the eastern portion of the southern cape coast in the Eastern Cape Province of South Africa. The sampling area is limited to the AWSS from which the NMBM receives its water supply. The AWSS is located within the Mzimvubu-Tsitsikamma Water Management Area, with several large rivers draining the region along geological weaknesses. The sampling locations were limited to the western and central regions of the AWSS, since this is most likely to contribute to the recharge of coastal springs.

The study area lies within the transitional rainfall zone of the Eastern Cape Province, which receives year-round rainfall. The annual rainfall of the region varies from 350-550 mm (Zengeni *et al.,* 2016; Botai *et al.,* 2021) and potential evaporation exceeds the mean annual precipitation.

Cape Supergroup lithologies (Table Mountain, Bokkeveld and Witteberg Groups), predominantly form the mountain ranges and topographic highs of the region. The Uitenhage Group's Cretaceous sediments fills the valleys while the coast is typified by the Cenozoic Algoa Group. Outcrops of the Pre-Cape Gamtoos Group are also visible in the area (Figure 45).

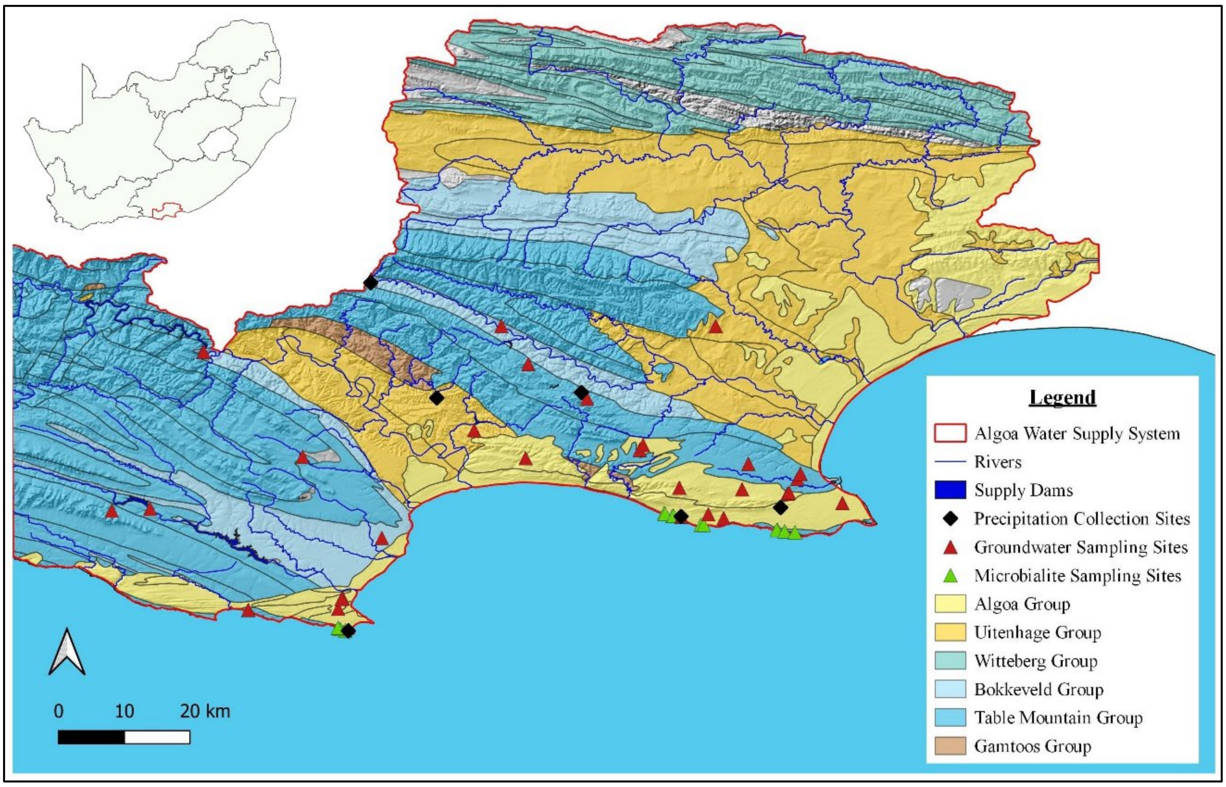


***Figure 45**. Sampling locations within the Algoa Water Supply System area (red boundary) for monthly precipitation collections (black diamonds) and groundwater from non-microbialite sites (red triangles) and microbialite sites (green triangles). Inset shows AWSS location within South Africa.*

4.2.2 Precipitation collection

A total of six precipitation collection stations were established (three catchment, three coastal). The criteria for the site selection were that they should be easily accessible for sample retrieval, safe from vandalism and they should provide a good spread throughout the study area (see Figure 45). Sites were selected to occur in the catchments of major rivers in the area, as aquifers are likely also recharged in these locations. The Kromme catchment in the far-west was not sampled for rainfall, but it is expected that the isotopic ratios of rainfall should be similar to the central Elands River catchment due to similarities in topography, climate and geology.

Samples were taken monthly and represented the total precipitation at a station within a sampling month (i.e. cumulative integrated sampling sensu IAEA, 2014). Event-based sampling was not performed since this is expensive, requires a lot of manpower and is not logistically feasible for large study areas. Nonetheless, cumulative sampling provides sufficient temporal resolution for groundwater and catchment hydrology (IAEA, 2014) and, therefore, is appropriate for the objectives of this study. Cumulative data also ensures comparability with other studies with monthly averaged data (IAEA, 2014). However, the cumulative integrated approach is subject to limitations which include: precipitation events with distinctive isotopic signatures are missed and sample evaporation might occur (IAEA, 2014) but the latter was minimised as elaborated below.

The monthly cumulative samples were collected using dip-in precipitation totalisers (sensu IAEA, 2014) based on the commercial sampler design used at GNIP stations (Gröning *et al.,* 2012; available from PALMEX, Zagreb, Croatia). See schematic and components in Figure 46, Figure 47 and Figure 48. Totalisers such as this limit the difficulties experienced with other conventional sampler designs used in isotopic studies such as the paraffin oil layer (e.g. contamination issues) or daily rain gauges (e.g. logistical issues) and are considered suitable for isotopic studies located in temperate to semi-arid climates (Hughes & Crawford, 2013; Michelsen *et al.,* 2018) such as the AWSS. Reported problems with the dip-in totalisers include the enrichment in deuterium and ^{18}O of samples of small (<5 mm) precipitation events (Hughes & Crawford, 2013; Michelsen *et al.,* 2018). To account for this, a smaller sample bottle (500 mℓ) than the commercial design (3 ℓ) was used to reduce the effect that bottle volume has on evaporation of the collected sample (Michelsen *et al.,* 2018). Furthermore, every rainfall collection station was equipped with a duplicate totaliser which was protected from rain (Figure 49). The rain-protected totalisers were filled with a known amount (100 mℓ, i.e. 20% of the sample bottle volume) of a "standard" water with a known isotopic composition. The standard water was sampled at the end of a sampling month and replaced with a new aliquot (Figure 50). This allowed for post-sampling assessment of evaporative effects (Michelsen *et al.,* 2018).

The totalisers were assembled using a funnel (138 mm internal Ø; 150 mm external Ø) which was glued to a PVC stop end (110 mm). A plastic mesh (4 mm internal Ø) was glued to the inside of the funnel to restrict debris from entering the sample bottle. A clear plastic collection pipe (15 cm; 6 mm internal Ø) was inserted into the tip of the funnel and extended to the bottom of the sample bottle. The sample bottle consisted of a HDPE bottle (500 mℓ) with cap inlay. The funnel tip, as well as a pressure equilibration tube (3 mm internal Ø), was inserted through drilled holes of the cap and cap inlay, attached and sealed using hot glue and silicon sealant. This unit comprised the totaliser (Figure 46) and was inserted into a section (26 cm) of PVC underground pipe (110 mm) which was fitted to another stop end (110 mm). The containing unit was coated with silver paint to deflect solar radiation. The sampling unit could be accessed from both the top and bottom of the containing unit during sampling and/or routine checks. The rainfall samplers were equipped with bird deterrents which consisted of wire mesh (2 cm mesh size) that was wrapped around the top of the funnel using thin binding wire that could be easily attached/removed during sampling. The entire totaliser was attached to a pole/wall (~1.2 m height) using aluminium brackets (110 mm) and cable ties for extra support. The sampling unit of the rain-protected collectors was covered using a plastic "roof" that was attached to the pole to prevent precipitation entering the sample bottle.

***Figure 46**. Dip-in precipitation totaliser sample unit (right) that was placed inside the PVC pipe containing unit (left).*

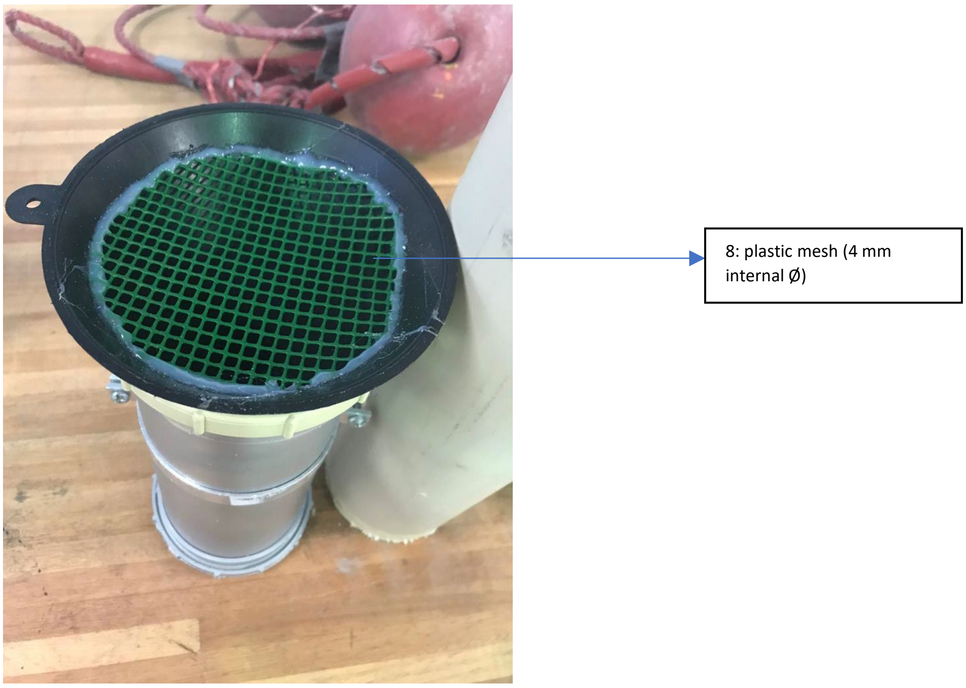


***Figure 47**. Assembled dip-in precipitation totaliser top view.*

Figure 48. *Assembled dip-in precipitation totalisers side view.*

Both the precipitation and control totalisers were set up on 29/30 March 2022 and the first sample collected on 28 April 2022 and continued on a monthly basis thereafter until 30 March 2023. Samples were collected during the last week of every calendar month or after a minimum of 4 weeks elapsed since the previous sampling. Samples were collected in sterile 50 ml polypropylene centrifuge tubes with HDPE screw caps. No headspace was left in the sample bottle and the caps were securely sealed with parafilm. Samples were stored at room temperature until analysis.

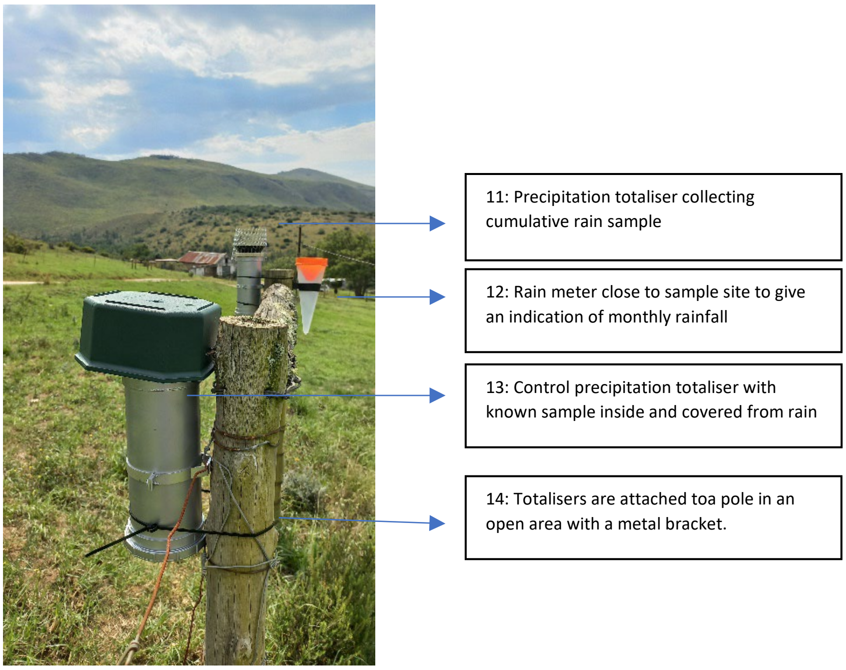


Figure 49. *Precipitation totaliser setup at a catchment sample site.*

Figure 50. *The sample is easily accessible from the top or bottom via the stop ends.*

4.2.3 Groundwater collection

Groundwater samples from boreholes and springs were collected throughout the study area (Figure 45). Eighteen cold-water springs (< 25°C) were sampled (inland n = 4 and coastal n = 14). All except one (CSF-S4) of the coastal springs were selected due to their association with SSLiME (Rishworth *et al.,* 2020b). CSF-S4 was a strong flowing seep directly adjacent to an urban garden and therefore targeted for potential importance in terms of nutrient and micropollutant indicators as part of another project. Inland spring locations were selected based on their accessibility and geographic location. In addition to the cold-water springs, twenty-seven boreholes spread throughout the study area were sampled. Boreholes were also selected based on their accessibility, geographic and geological locations, as well as frequency of use or artesian character. Due to data privacy of property owners, the exact sampling locations of all sites are not given.

Boreholes were pumped or artesian boreholes (if sealed) allowed to flow for a minimum of 20 minutes before sample collection. A large once-off late spring/early summer sampling campaign was conducted between the 24th of October and the 20th of December 2022. Coastal springs were re-sampled in March 2023 (autumn) for a seasonal comparison. Groundwater samples for isotopic analyses were collected in 50 mℓ sterile polypropylene tubes, filled with no headspace and caps sealed with Parafilm®. Samples were stored at room temperature until analysis.

4.2.4 Sample analyses

All precipitation and groundwater samples were analysed for stable water isotopes at the Biogeochemistry Research Infrastructure Platform (BIOGRIP) Node for Water and Soil Biogeochemistry at the Stellenbosch University.

The stable water isotope analysis was conducted using a Los Gatos Triple Liquid Water Isotope Analyser (LGR T-LWIA-45-EP, Canada). Sample aliquots (1.9 mℓ) were filtered through syringe filters (0.22 µm cellulose acetate) into glass vials (2 mℓ) with PTFE septum caps. A sample array consisted of two calibration standards and a control standard, which was followed by ten unknowns (samples), which was followed by another set of standards. The calibration standards used are LGR1 and BIHS3, the latter being an in-house standard calibrated against known isotopic LGR standards. The in-house standards BIHS1 and BIHS2 are used as control standards and are similarly calibrated against known LGR standards (see Table S 7, Figure S 1 and Figure S **2** for the calibration curves and isotopic values of all standards for the period of February 2022-August 2023).

Each sample run consisted of a maximum of four sample arrays. Each standard/sample was measured with nine injections, of which only the last five measurements were averaged for absolute isotope ratios. Using linear regression, the δ-values were calculated from the absolute isotope ratios by using the known δ-values of the calibration standards (with respect to Vienna Standard Mean Oceanic Water – VSMOW) before each array of 10 unknowns. The δ-values reported are the mean values of two sample runs (i.e. two repeat measurements of sample arrays each containing ten individual samples).

4.2.5 Data analyses

The d-excess for samples were calculated using the following equation (Dansgaard, 1964; Jasechko, 2019):

$d\text{-}excess = \delta D - 8 * \delta^{18}O$ *Equation 2*

Annual amount-weighted δ-averages ($\delta_{p\ (annual)}$) were calculated using the following equation:

$$\delta_{P(annual)} = \frac{\sum_{i=1}^{12} \delta_{P(i)} * P_i}{\sum_{i=1}^{12} P_i} \qquad \textit{Equation 3}$$

where $\delta_{P\ (annual)}$ is the annual amount-weighted average, $\delta_{P(i)}$ is the isotopic composition (δD or δ^{18}O) of the rainfall for month i and Pi is the amount of precipitation measured during month i (Jasechko, 2019).

The LMWL was determined using ordinary least-square regression analysis.

4.3 Results

4.3.1 Precipitation

The stable water isotopes of precipitation collected in the study area between April 2022 and March 2023 ranged from -26.5 ‰ to 15.2 ‰ for δD (mean: -6.9 ‰) and -6.11 ‰ to -0.20 ‰ for δ^{18}O (mean: -3.60 ‰) (Table S 1 to Table S 6). The calculated d-excess of samples ranged from 13.3 ‰ to 34.2 ‰ (mean: 21.9 ‰). These values are within the range observed for other South African studies (Figure 51). Annual amount-weighted averages calculated from monthly isotopic values and precipitation totals at each station ranged from -11.3 ‰ to -7.4 ‰ for δD (mean: -9.5 ‰) and -4.11 ‰ to -3.66 ‰ for δ^{18}O (mean: -3.92 ‰). On the other hand, the d-excess calculated from the amount-weighted values ranged from 20.7 ‰ to 22.7 ‰ (mean: 21.8 ‰).

Mean values of δD, δ^{18}O and d-excess in relation to mean monthly precipitation are shown in Figure 52. No consistent trends are apparent in terms of seasonal variation at first glance. Furthermore, the d-excess as a function of monthly precipitation at individual stations indicate large d-excess variations (Figure 53) without any obvious trends in terms of rainfall or seasonality. However, slight peaks in d-excess are visible during austral winter months (JJA) at individual stations, and this is also reflected by the higher amount weighted d-excess overall mean of 23.1 ‰ for winter months compared to 20.2 ‰ for summer. D-excess peaks are also observed during November (e.g. Melkhoutboom, Loerie, Cape St Francis and Gqeberha stations), which coincides with low precipitation totals.

In addition, seasonal averages were calculated for winter (April-September) and summer months (October-March) (sensu Harris et al., 2010). From these calculations it is evident that the isotopic signature of rainfall in the study area is more depleted in the winter (weighted mean δD: -11.1 ‰; weighted mean $\delta^{18}O$: -4.27 ‰) compared to the summer (weighted mean δD: -7.1 ‰; weighted mean $\delta^{18}O$: -3.41 ‰) (Figure 54). Compared to the weighted means, unweighted means were more positive for both winter (mean δD: -10.5 ‰; mean $\delta^{18}O$: -4.56 ‰; mean precipitation: 386 mm) and summer (mean δD: -3.9 ‰; mean $\delta^{18}O$: -3.10 ‰; mean precipitation: 273 mm). There is also a strong relationship between the isotopic values of precipitation and the elevation of sampling stations (e.g. for $\delta^{18}O$: R2 = 0.72; Figure 55), with low-lying coastal sites being more enriched in deuterium and ^{18}O compared to the higher-elevation catchment locations.

The combined LMWL for all the precipitation samples (Figure 56) is provided as well as the amount-weighted averages. The slope of the LMWLs corresponded well with other LMWLs reported for South Africa, however, the intercept was generally higher (Table 9). Finally, the plot of $\delta^{18}O$ versus d-excess indicates a distinct rainfall seasonality group when compared to the summer and winter rainfall zones of (Geppert et al., 2022) (Figure 57).

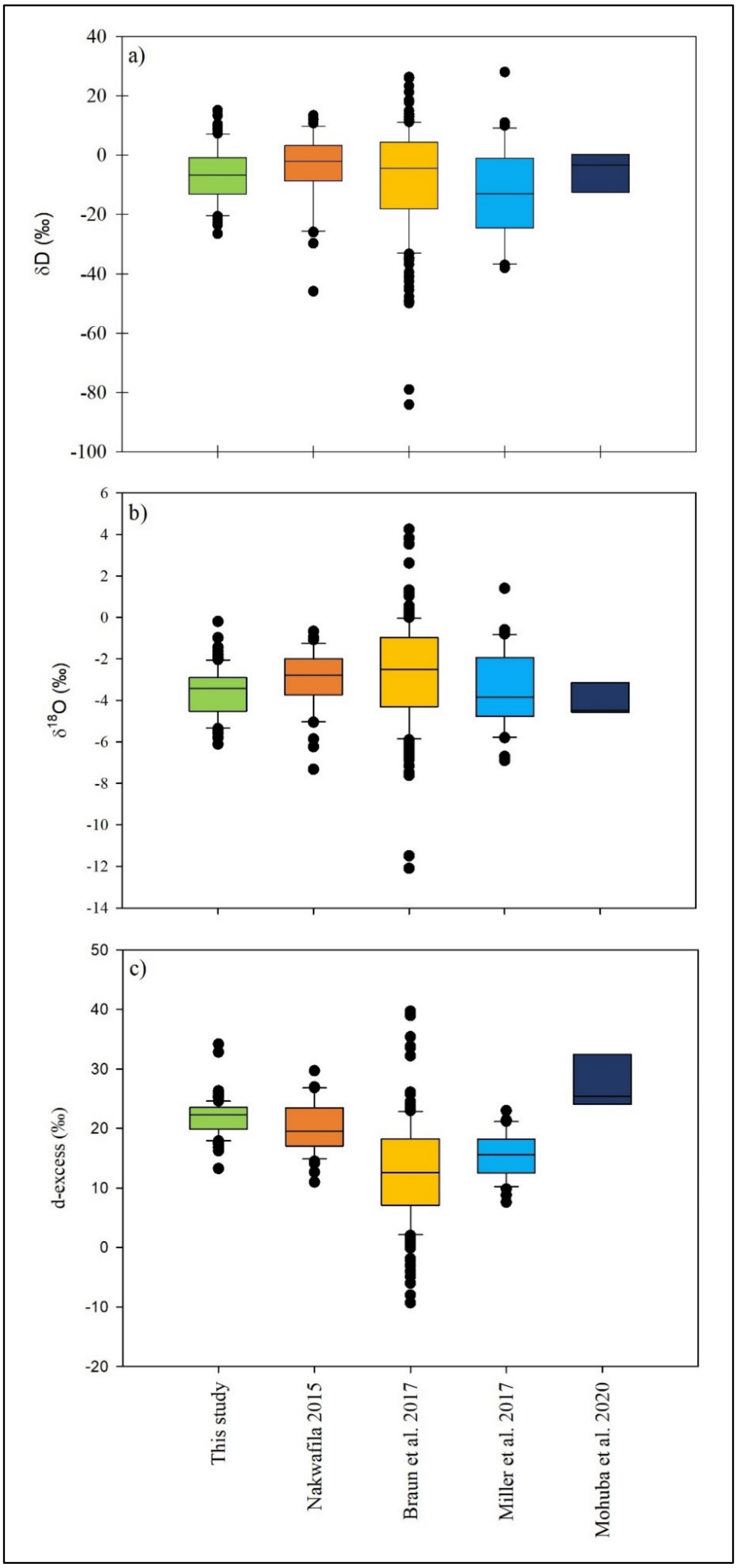


***Figure 51**. Box-and-whisker plots for the isotopic values of rainfall samples in selected southern African studies.*

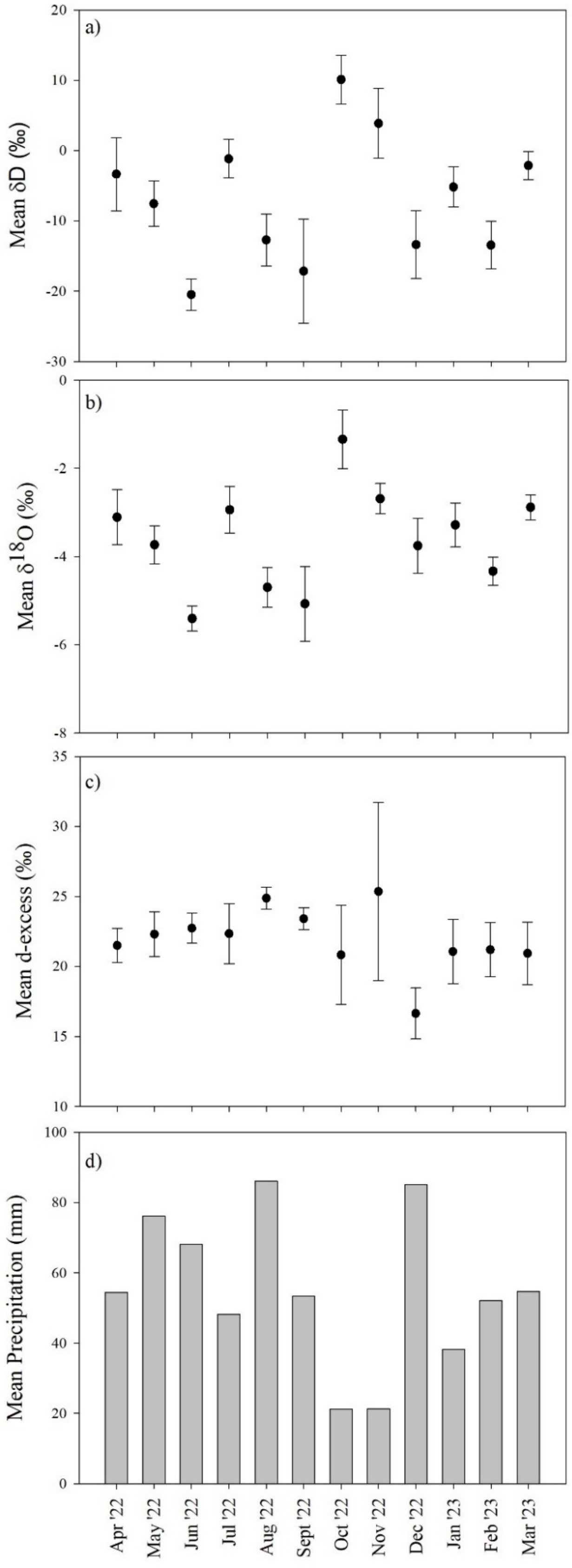


Figure 52. *Monthly variation of mean a) δD (‰); b) $\delta^{18}O$ (‰); c) d – excess and d) precipitation (mm).*

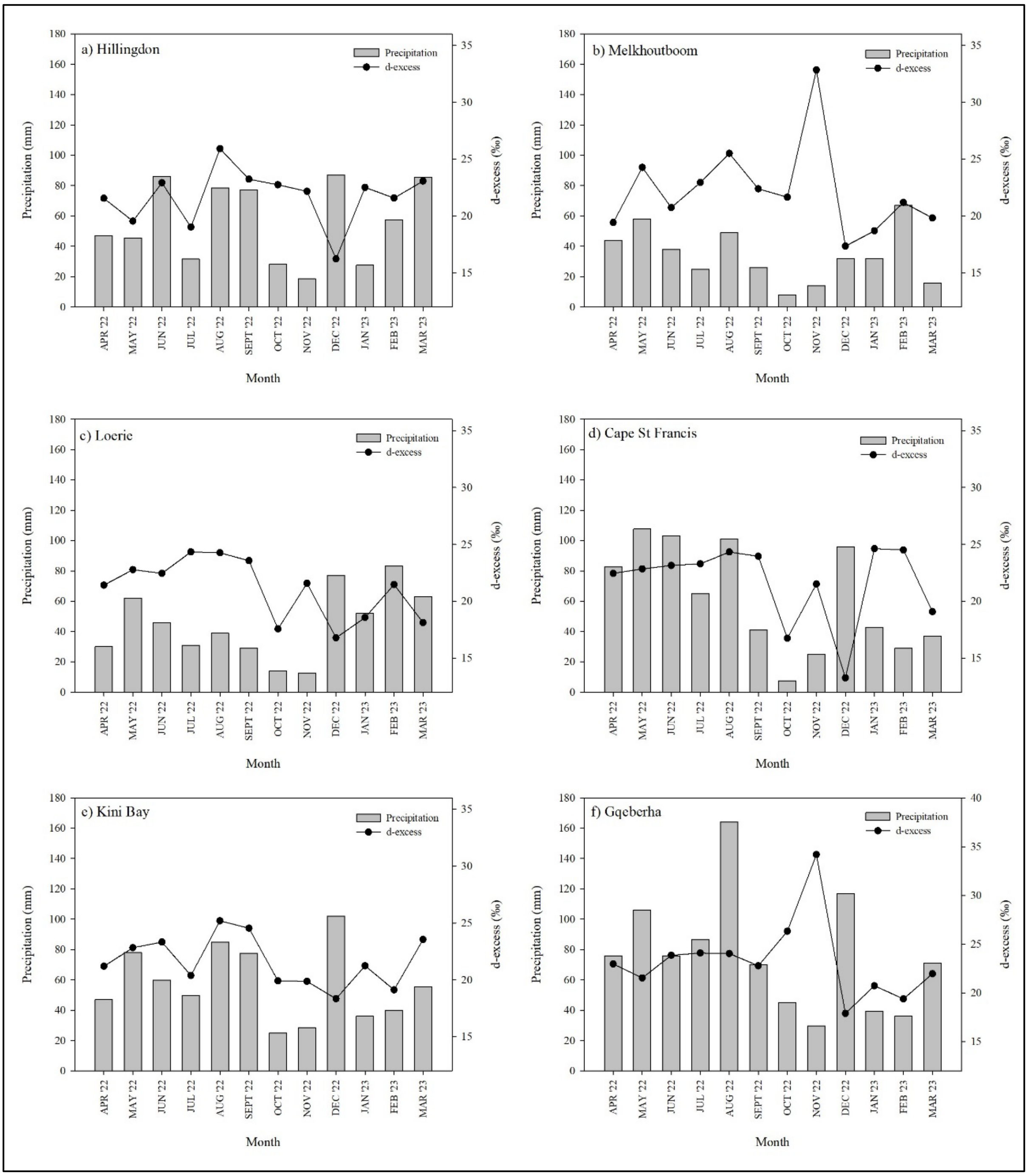


Figure 53. *Precipitation and d-excess variation between April 2022 and March 2023 for the six rainfall collection stations: a) Hillingdon; b) Melkhoutboom; c) Loerie; d) Cape St Francis; e) Kini Bay and f) Gqeberha. (a)-(c) are catchment sites and (d)-(f) are coastal sites.*

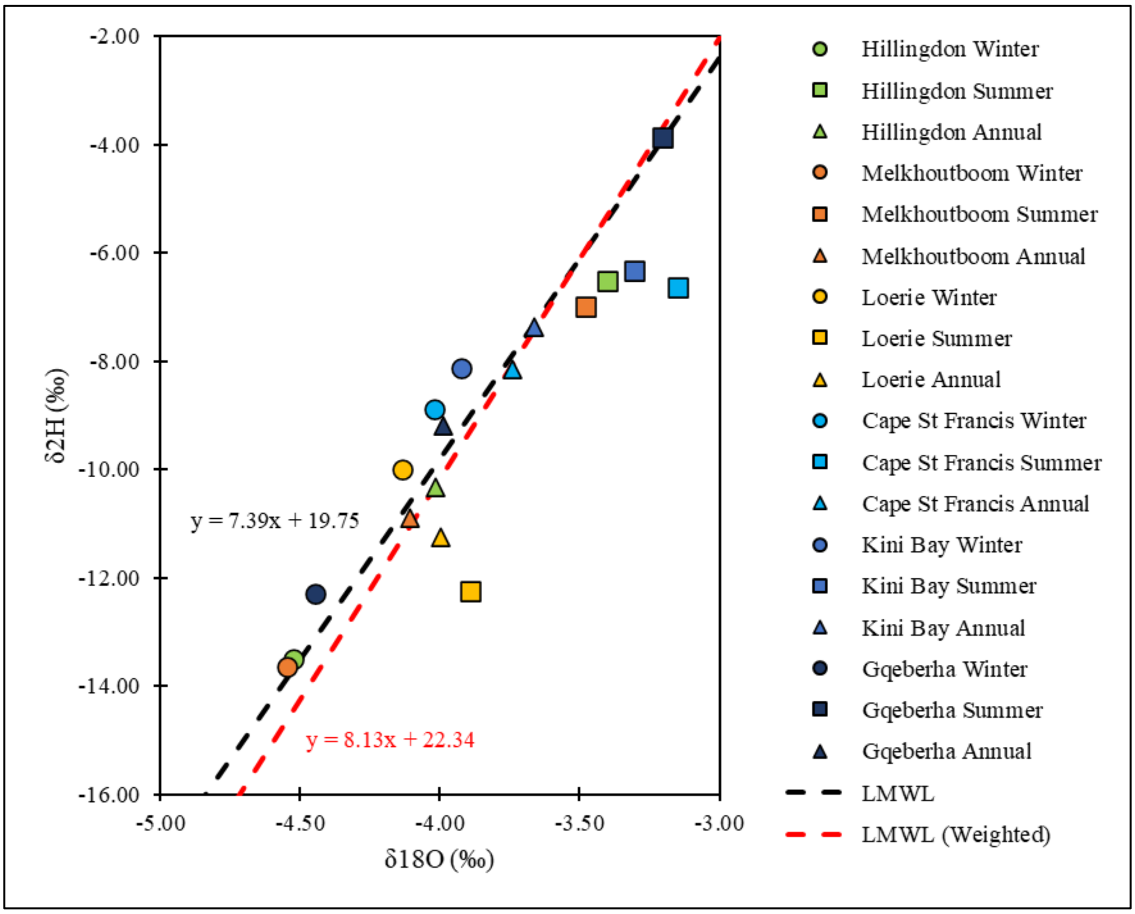


__Figure 54__. Amount-weighted stable water isotope values of precipitation samples collected at the six precipitation stations between April 2022 and March 2023. Circles indicate amount-weighted means for winter months (April, May, June, July, August, September), squares indicate amount-weighted means for summer months (October, November, December, January, February, March), and triangles indicate the annual amount-weighted precipitation at each station (sensu Harris et al., 2010).

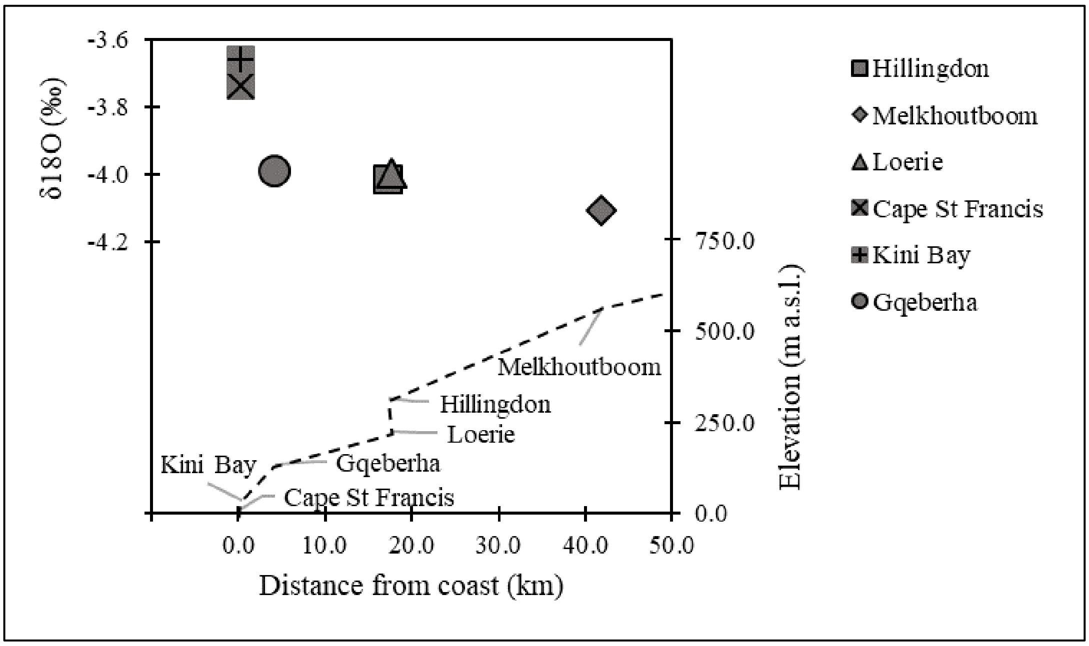


***Figure 55**. The annual amount-weighted means of $\delta^{18}O$ (‰) for precipitation samples as a function of station elevation and distance from coast.*

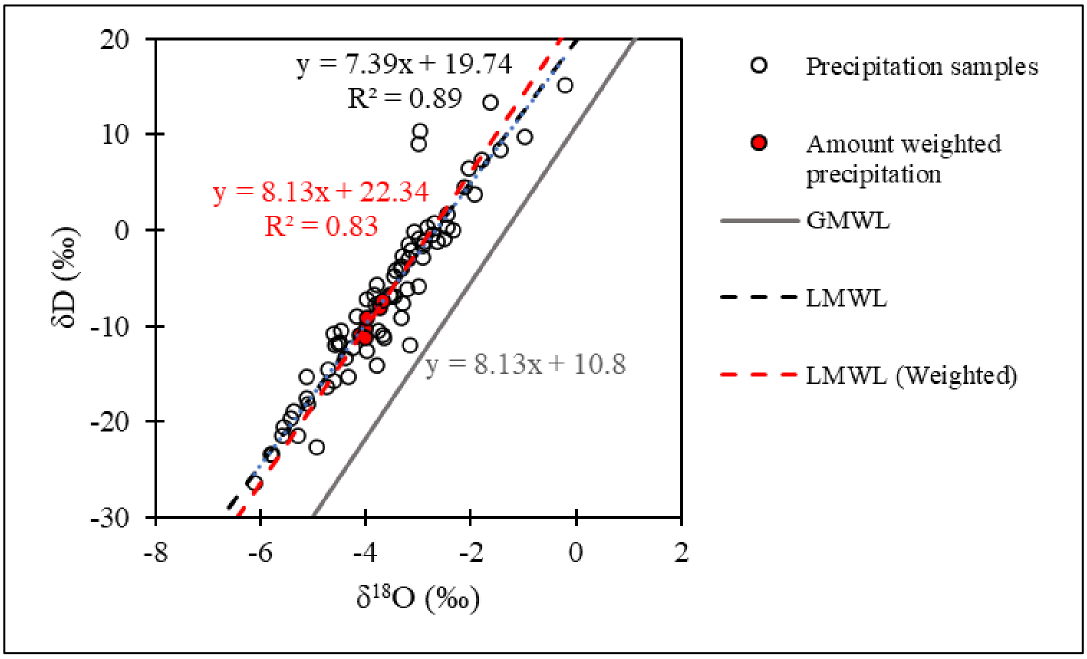


***Figure 56**. Monthly stable water isotope values (open circles) and annual amount-weighted averages (red circles) of rainfall samples from the AWSS region (open circles) collected between April 2022 and March 2023. Local meteoric water lines from monthly (black dashed line) and amount-weighted (red dashed lines) are compared to the global meteoric water line (Rozanski et al., 1993).*

Table 9. *Examples of the slopes and intercepts of local meteoric water lines (LMWL) for different areas in South Africa (adapted from Wanke et al., 2018). EC = Eastern Cape; WC = Western Cape; NC = Northern Cape; LP = Limpopo Province; KZN = Kwa-Zulu Natal; GP = Gauteng Province.*

Rainfall Season	Region	Province	LMWL Slope	LMWL Intercept	Reference
Transitional	AWSS (monthly, unweighted) - (see Figure 45)	EC	7.39	19.74	This study
Transitional	AWSS (monthly, weighted) - (see Figure 45)	EC	8.13	22.34	This study
Transitional	Mossel Bay (daily)	WC	7.35	11.21	(Braun *et al.,* 2017)
Transitional	Mossel Bay (monthly)	WC	7.70	12.10	(Braun *et al.,* 2017)
Winter	Western Cape	WC	6.10	8.60	(Diamond & Harris, 1997)
Winter	Central Namaqualand	NC	7.00	8.00	(Adams *et al.,* 2004)
Winter	Cape Town (monthly)	WC	6.41	8.66	(Harris *et al.,* 2010)
Winter	Cape Town (event)	WC	6.64	11.89	(Harris *et al.,* 2010)
Winter	Cape Town (storm)	WC	7.89	19.35	(Harris *et al.,* 2010)
Winter	Table Mountain National Park	WC	5.70	6.90	(West *et al.,* 2012)
Winter	Buffels River	NC	7.70	19.30	(Nakwafila, 2015)
Winter	Paarl	WC	8.25	15.7	(Miller *et al.,* 2017)
Winter	Cape Town GNIP	WC	5.28	5.23	(Wanke *et al.,* 2018)
Summer	Kruger National Park	LP	8.66	2.23	(Petersen, 2012)
Summer	Kuruman River	NC	6.10	2.60	(Schachtschneider & February, 2013)
Summer	Mohlapitsi Catchment	LP	6.63	5.44	(Mekiso & Ochieng)
Summer	Lake Sibayi Catchment	KZN	5.60	6.67	(Weitz & Demlie, 2014)
Summer	Pretoria GNIP	GP	6.55	7.92	(Wanke *et al.,* 2018)
Summer	Thohoyandou	LP	7.56	10.64	(Durowoju *et al.,* 2019)

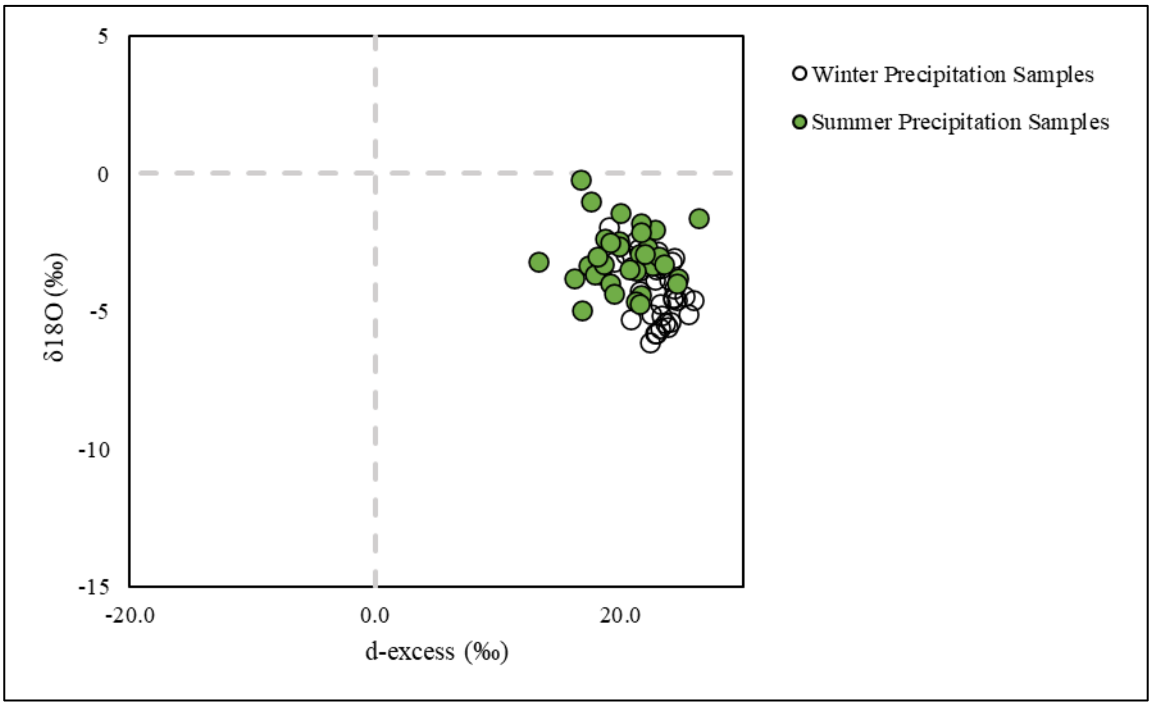


***Figure 57**. Scatterplot of $\delta^{18}O$ (‰) versus d-excess (‰) sensu Geppert et al. (2022).*

4.3.2 Groundwater

The δD of the groundwater samples ranged from -23.4 ‰ to -0.3 ‰ (mean: -14.2 ‰) and the $\delta^{18}O$ ranged from -6.36 ‰ to -2.40 ‰ (mean: -5.04 ‰). The minimum calculated d-excess for the groundwater samples was 16.2 ‰ and the maximum value was 32.1 ‰ (mean: 26.1 ‰). While the δD range corresponded well to that of other South African studies, the $\delta^{18}O$ was slightly lower and the d-excess higher than comparable national studies (Figure 58).

The stable water isotopic values of the groundwater samples fell within the range of the precipitation samples for the study area with a slight depletion in $\delta^{18}O$ from the local meteoric water line (Figure 59 and Figure 60). Groundwater sites were separated according to their type location, namely: 1) Inland Boreholes & Springs – located > 5 km from the coast; 2) Coastal Boreholes – located within 5 km from the coast; 3) Coastal Discharge (summer & autumn campaigns) – groundwater discharge along the coast, all associated with SSLiME except CSF-S4 (Figure 61). In addition, sites were also separated according to their elevation above mean sea level (0-100 m; 101-200 m; 201-300 m; 301-400 m and >400 m) (Figure 62). Similarly to the precipitation samples collected, groundwater samples from coastal and low-lying sites were generally enriched in deuterium and ^{18}O compared to samples further from the coast or high elevations. Furthermore, the coastal discharge samples collected during the autumn campaign were more depleted in deuterium and ^{18}O than the coastal discharge samples collected during the summer campaign (Figure 61 to Figure 63).

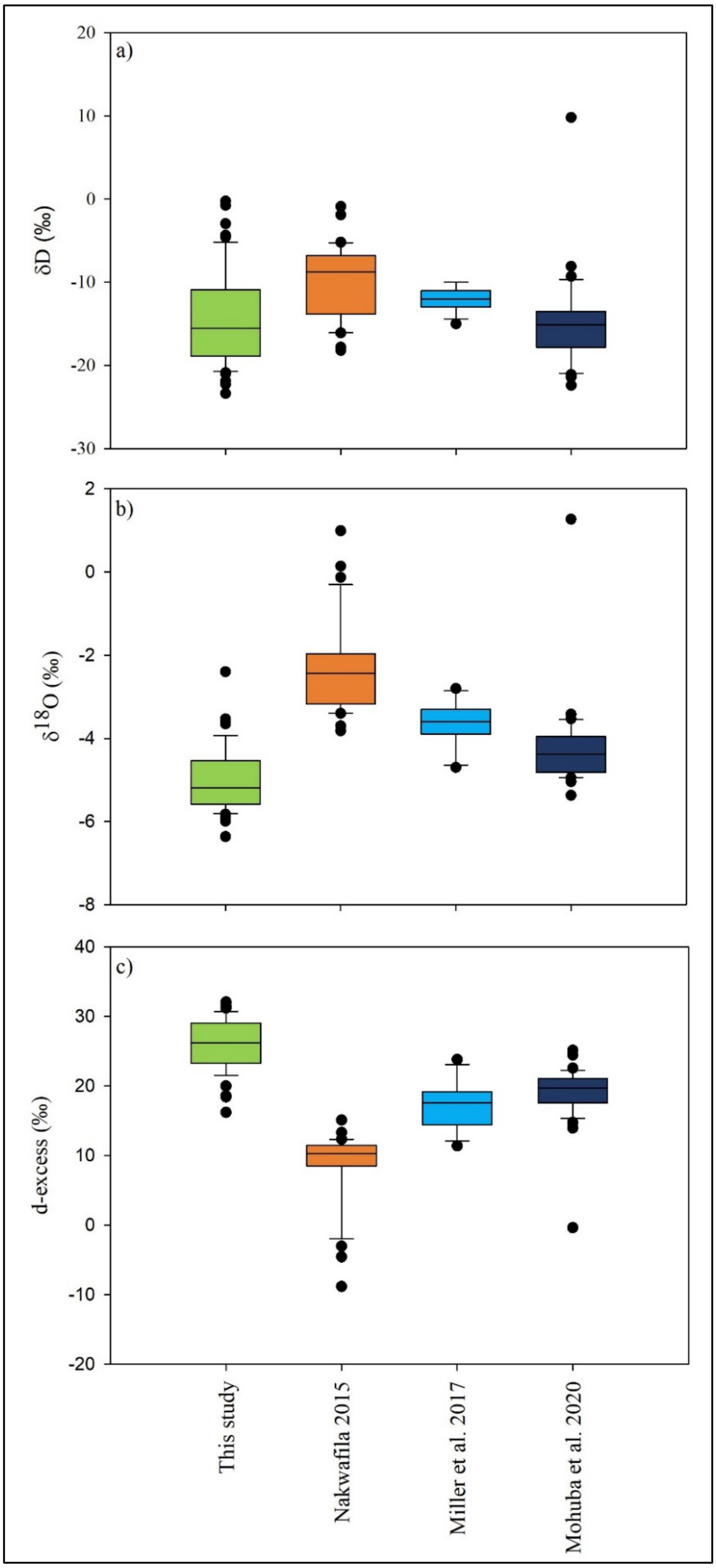


Figure 58. *Box-and-whisker plots of the isotopic values of groundwater samples from selected southern African studies.*

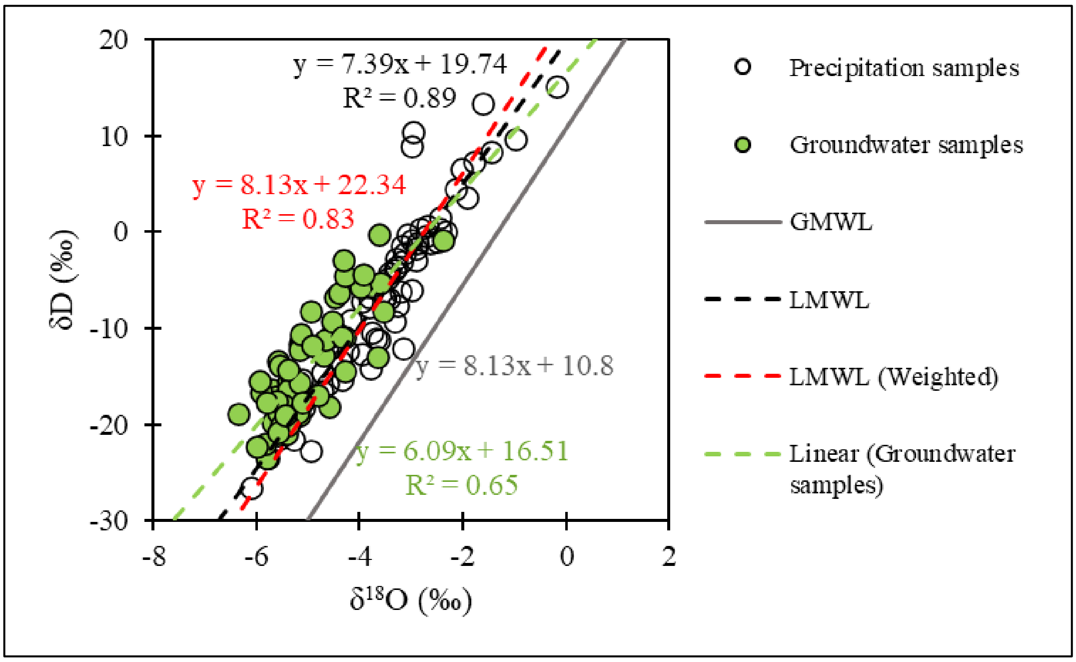


Figure 59. *Stable water isotope values of all precipitation (open circles) and groundwater (solid green circles) collected during the sampling campaigns.*

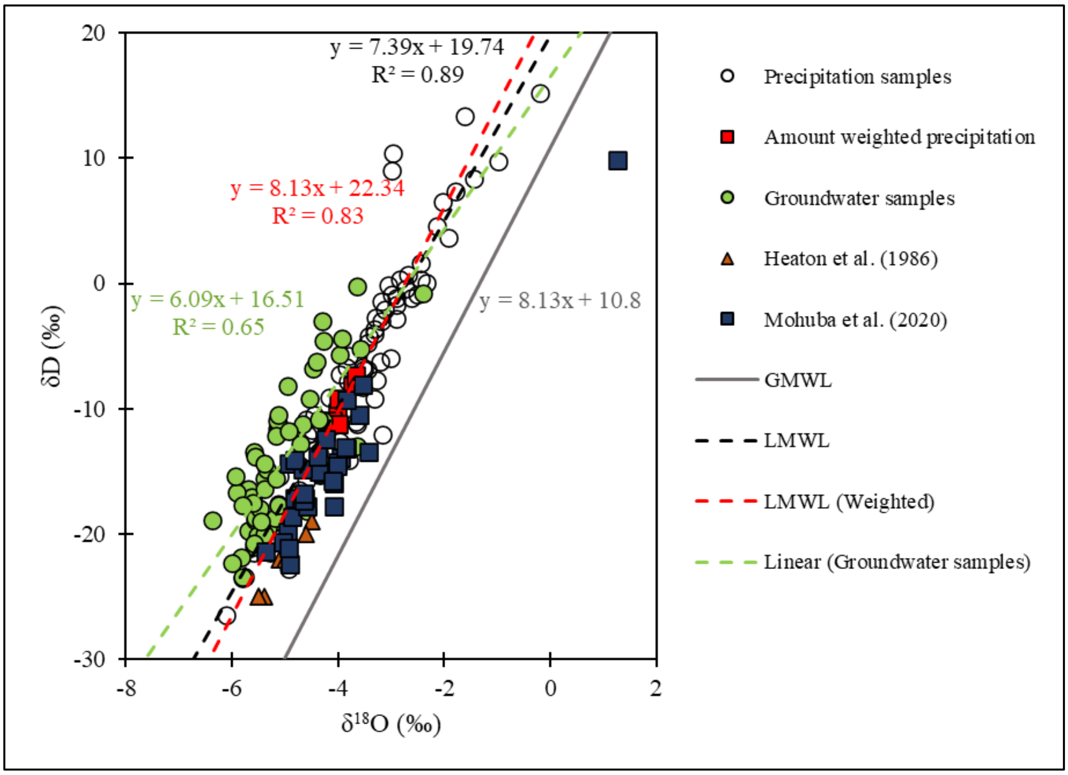


Figure 60. *Stable water isotope values of groundwater samples from this study and previous published data for the area (solid symbols) (Heaton et al., 1986; Mohuba et al., 2020) compared to precipitation samples (open circles) collected during April 2022 and March 2023.*

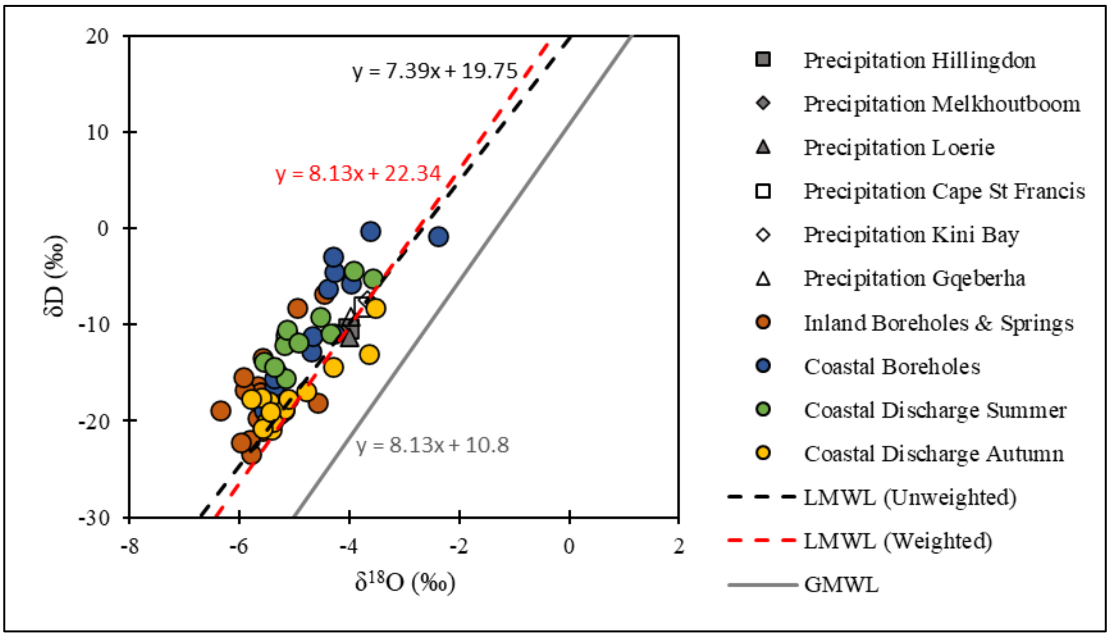


Figure 61. *Stable water isotope values of groundwater samples separated by location: >5 km from the coast = inland boreholes & springs; <5 km from the coast = coastal boreholes; groundwater discharge within the supratidal zone = coastal discharge.*

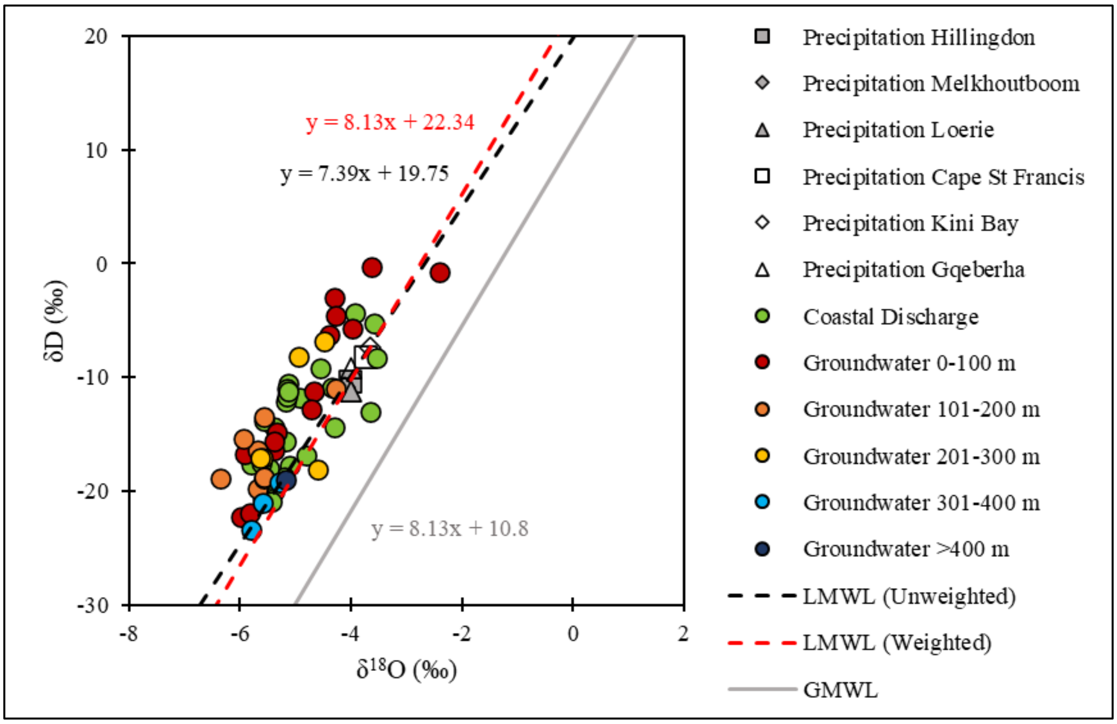


Figure 62. *Stable water isotope values of precipitation and groundwater samples collected during the sampling campaigns. Annual amount-weighted means for precipitation samples are indicated by squares, diamonds and triangles for catchment (solid) and coastal (open) precipitation stations. Groundwater samples are separated based on the elevation at which they were collected.*

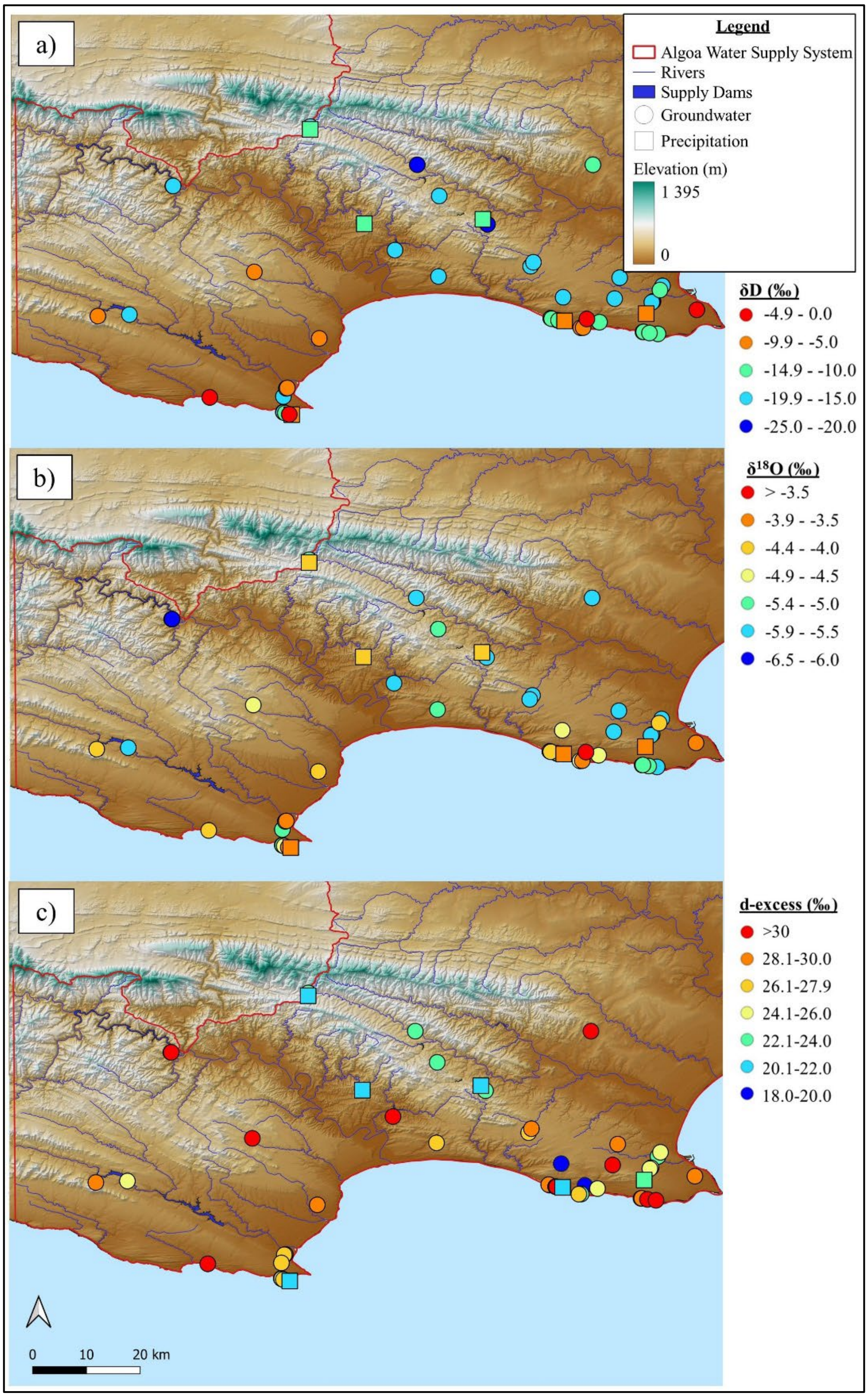


***Figure 63**. Observed variation of a) δ^2H (‰), b) $\delta^{18}O$ (‰) and c) d-excess (‰) with topography of annual amount-weighted precipitation (squares) and groundwater (circles) sampled in this study. Data for the baseline topographic map was retrieved from the Africa Geoportal of the Regional Centre for Mapping of Resource for Development.*

4.4 Discussion

The local meteoric water lines developed during this study are the first of its kind for the AWSS or NMB areas and, in fact, for the Eastern Cape Province to our knowledge. The slopes of both the unweighted and annual amount-weighted water lines fall within the range reported for other Southern African water lines (Table 9). The unweighted slope is in good accordance with the nearest local meteoric water line (Braun *et al.,* 2017), while the weighted slope matched the GMWL slope more closely (Rozanski *et al.,* 1993). However, the LMWLs of this study was most comparable with a study from the Buffels River in the Northern Cape (Nakwafila, 2015) and a study from storm samples in the Western Cape (Harris *et al.,* 2010). The mean d-excess of the precipitation samples was high relative to the global mean (10 ‰) and predicted values (Pfahl & Sodemann, 2014; de Wet *et al.,* 2020) for the area. However, high d-excess in precipitation is not uncommon for arid areas with low humidity such as, for example, the eastern Mediterranean, northern Africa, and Western Australia (Bowen & Revenaugh, 2003; Clark & Fritz, 2013).

The dissimilarities with the LMWL from the only other transitional rainfall area data may be due explained by the local climate. For example, the Braun *et al. (*2017) study area is located in the arid (BSk – arid, steppe, cold) Köppen-Geiger climate classification, whereas the study area for this study fell within both the arid (BSk; Hillingdon & Melkhoutboom precipitation stations) and the temperate (Cfb – temperate without dry season, warm summer; Loerie, Cape St Francis, Kini Bay and Gqeberha precipitation stations) classes (Peel *et al.,* 2007; Putman *et al.,* 2019). Precipitation from the arid Köppen-Geiger class is predicted to have a LMWL slope of 5-7 and intercept of 10-15 ‰, while the temperate class is predicted to have a LMWL slope of 8-9 and intercept of 5-20 ‰ (Putman et al., 2019). As such, the expected LMWL parameters for a combination of the arid and temperate classes (as is the case for this study) would be between 5 and 9 for the slope and 10 and 20 ‰ for the intercept. This corresponds well with the parameters produced by this study (slope weighted: 8.13 and intercept weighted: 22.3 ‰), while the parameters reported by Braun *et al. (*2017) (slope: 7.70 and intercept: 12.1 ‰) are consistent with that anticipated for an arid class only. Another potential contributing factor to the high d-excess/LMWL intercept values is the progressive rainout of precipitation along a transport path, such as, e.g., rainout of cold fronts from the southern Atlantic Ocean. Similar trends were observed, for example, in southern Australia for west-to-east storm tracks (Liu *et al.,* 2010). Furthermore, although this study provides a useful first-order dataset of precipitation in the AWSS area, long-term monitoring of precipitation in the region would be required to provide a more robust dataset for analysis.

Furthermore, although temperature data at the specific precipitation collection stations were not available, a seasonal effect (winter vs summer) was visible. The weighted means of δD and $\delta^{18}O$ for the winter period (April-September) were -11.1 ‰ and -4.27 ‰, respectively (unweighted means: -10.4 ‰ and -4.16 ‰) with a mean winter precipitation of 386 mm. Conversely, during the summer period (October-March) this increased to -7.1 ‰ for δD and -3.41 ‰ for $\delta^{18}O$ (unweighted means: -3.4 ‰ and -3.05 ‰) with a mean precipitation of 273 mm. Similar trends were observed in the Western Cape for the winter (or wet season) compared to the summer (or dry season) (Harris *et al.,* 2010; Mokua *et al.,* 2020). In addition, excepting the Gqeberha station, the summer weighted means fell below the LMWL, likely indicating the effect of increased evaporative processes during this period.

The principal source of atmospheric moisture is low-latitude oceanic regions, and the initial composition of the moisture is controlled by isotopic fractionation during evaporation and boundary layer diffusion between the ocean and atmosphere (Bowen & Revenaugh, 2003). Precipitation derived from the source region is usually enriched in deuterium and ^{18}O compared to regions further afield. This is related to cooling and rainout effects, which are in turn controlled by meteorological processes such as transport along longitude or from oceanic to continental regions, orographic lifting, and convective processes (Bowen & Revenaugh, 2003).

The d-excess of precipitation samples (and the related parameter of LMWL intercept) has been generally attributed to evaporation processes in the moisture source origin (Rozanski *et al.,* 1993) influenced primarily by relative humidity and surface sea temperature and has been widely used to determine the moisture origin of precipitation (Natali *et al.,* 2022). However, the d-excess of precipitation may also change as a result of sub-cloud evaporation, continental moisture recycling and the “pseudo-altitude effect” (Natali *et al.,* 2022). The identification of moisture source regions is especially important in the face of climate change since regions with only one or two moisture sources may be more vulnerable to changes in the hydrological cycle than those with multiple source regions (Geppert *et al.,* 2022).

The climate and, therefore, the isotopic values of precipitation in southern Africa is variable and complicated by the influence from both tropical and midlatitude circulation systems (Braun *et al.,* 2017; Geppert *et al.,* 2022). For example, the winter rainfall zone of southern Africa derives most of its moisture from the Southern Atlantic Ocean. However, the summer rainfall zone receives most of its moisture from continental Africa, as well as the Indian Ocean while the predominant moisture source region for the year-round rainfall zone remains unknown (Geppert *et al.,* 2022).

The stable water isotope ratios of all groundwater samples collected follow the trend of the local meteoric water lines determined for the AWSS region. This confirms that aquifers are recharged locally/regionally from precipitation. Furthermore, groundwater samples from catchments and inland locations had the lowest isotopic ratios, which is consistent with water recharged from high elevations or the continental interior (Jasechko, 2019). Conversely, samples taken during the same spring/summer (October-December 2022) campaign from coastal regions (e.g. seaside villages or SSLiME systems) were more enriched in deuterium and ^{18}O compared to the catchment areas, which is consistent with what is expected for samples from coastal aquifers (Jasechko, 2019). On the other hand, the groundwater samples collected from the SSLiME inlets during the autumn (March 2023) show the seasonality effect of recharge during colder months (Jasechko, 2019) as these signatures were more depleted than those collected during the spring/summer. Similarly to the isotopic signatures of the precipitation samples, the groundwater samples were depleted in ^{18}O relative to samples from the winter rainfall and western transitional rainfall areas of South Africa. Consequently, the groundwater of the region is characterised by high d-excess. This indicates a distinct isotopic signature for the eastern section of the Southern coast and is in accordance with previous records for the area (e.g. Heaton et al., 1986). For example, the intercept of the line of best fit through the groundwater samples collected during this study (16.5) is similar to that reported for the Uitenhage Artesian Basin (17). Positive d-excess values for all of the groundwater samples likely indicate that the aquifers are recharged by modern water with low degrees of evaporation (Nakwafila, 2015).

4.5 Conclusion

This study provides the first stable water isotopic dataset for the Eastern Cape Province and specifically the Nelson Mandela Bay area. The local meteoric water lines and isotopic data presented here are likely the product of the mixing of rainfall derived from different moisture sources, consistent with the transitional nature of local rainfall patterns between summer and winter east to west regional trends. Nevertheless, the slopes of the LMWLs are within the range of other reported Southern African studies.

The development of a LMWL is especially significant with regards to the implications for groundwater recharge. For example, the groundwater samples collected during this study indicate local/regional recharge with little evaporation taking place before recharge (and therefore likely little delay). This is especially significant as this may confirm that SSLiME systems could be effectively used as groundwater monitoring points for inland/catchment processes affecting aquifers. The variation of the isotopic ratios within a specific sample classification (e.g. coastal groundwater discharge) reflects the complex hydrogeology and climate of the study area. Overlap of the isotopic signatures of coastal groundwater discharge with both coastal boreholes and groundwaters inland or at higher elevations indicates some hydrological connectivity between the catchment and coastal aquifers or a common recharge area. In other words, coastal groundwater discharge likely receives recharge from both the primary and secondary aquifers (see also *Chapter 2*). In addition, similar environmental factors such as seasonal effects, rainfall amount and moisture source origin may influence the isotopic signature of groundwater in the region and long-term monitoring of both rainfall and groundwater discharge into SSLiME systems would be useful to further validate this finding. Furthermore, future studies should include the influence of all potential groundwater recharge locations, such as temporary pans and wetlands (which potentially have a higher evaporative kinetic fractionation effect), as well as the influence of event-based isoscape effects should be incorporated into a holistic assessment of local groundwater hydrology.

5. Microbialites as monitoring locations for local aquifer resources

Underwater in a SSLiME pool
(photographed by GMR)

5.1 Synthesis of core findings

At the completion of this Water Research Commission Project, a valuable contribution to our understanding of the functioning of SSLiME pools is apparent, particularly from a hydrological perspective. These findings are informative for management and future monitoring efforts of these unique coastal habitats. It is envisaged that at least three peer-reviewed scientific articles will emanate directly from this research, comprising at the core Chapter 2, 3 and 4. We will also seek to disseminate this knowledge during planned public interactions during 2024, led by CD and TWO as the two core postgraduate students on this project.

The following key findings and interpretations can now be made about the SSLiME and the AWSS hydrological cycle to which they associate with:

1) A substantial quantity of groundwater is discharging directly through the SSLiME, in the order of 3.96 Mℓ/d.

2) Flowrate of groundwater discharge through the SSLiME pools is coupled to precipitation levels, but not perfectly so, which is suggestive of lag effects, a potential distal baseflow from inland recharge origins, short-term responses to large precipitation events, and potential effects of abstraction of this groundwater at the coast. Continued future monitoring of these dynamics will tease apart the drivers of any spatiotemporal variability.

3) Similarly to when these SSLiME were first discovered and described (Perissinotto *et al.,* 2014), a high proportion of all coastal groundwater discharge points of the NMB still support SSLiME formation (78% in during this study period, in excess of over 1,000 distinct SSLiME sites). This is a significant network of coastal habitats that has both an important biodiversity heritage (Rishworth *et al.,* 2019) but also offers potential extensive opportunities for monitoring the source and processes linked to the groundwater flow paths directed to these sites.

4) As previous research has suggested (Rishworth *et al.,* 2017), which is expanded upon in this report by a broader network of SSLiME sites, those areas which are closely associated with anthropogenic activities display recognisable signatures of nutrient

pollution. When coupled with the first comprehensive assessment of the region's discharge rates, we were here able to show that the quantity of inorganic nutrients discharging through the NMB SSLiME sites is more similar to nutrient-rich natural coastlines (e.g. the Alexandria dunefield) than the much higher nutrient load processed and discharged to the coast through local wastewater treatment works. Nonetheless, the groundwater fed SSLiME discharge is not an insubstantial coastal nutrient load.

5) Although the nutrient levels entering the SSLiME are high, particularly for DIN, there is some evidence of uptake of these nutrients and thereby a buffering capacity by the SSLiME pools against coastal nutrient loading. This observation supports the hypothesis suggested by Rishworth *et al. (*2020b) that the SSLiME provide an ecosystem service as a nutrient sink.

6) Several lines of evidence suggest that groundwater throughout the study area was recharged relatively recently and reflects the current climate and environmental factors and/or the isotopic signature of precipitation has remained relatively consistent since the period of recharge. Recent recharge of the coastal groundwater discharge sites is supported by the seasonal influences observed for summer versus autumn samples. Due to the similarities between groundwater and precipitation samples, recharge is likely rapid, with little evaporation, as is the case for springs located in the Table Mountain Group elsewhere (Miller *et al.,* 2017). Although there are differences in the isotopic ratios of coastal groundwater discharge and inland groundwater, there is also an overlap in signatures, which may indicate that at least some of the coastal groundwater discharge sites are hydrologically linked to the Table Mountain Group Aquifer or that recharge occurs in the same area (see also Mohuba *et al.,* 2020).

7) This study is the first to generate, using amount-weighted means of precipitation, a LMWL for the Easter Cape, to our knowledge. While admittedly this is only an estimate from a single annual cycle, with a much longer decadal scale dataset needed to fully justify any conclusions, it is already a positive step towards further understanding local hydrological processes of the AWSS. For example, interpretations can already be made

that the amount-weighted means of precipitation, and in particular those of the catchment sites, resemble more closely the mean groundwater isotopic composition of both coastal groundwater discharge and inland locations. Therefore, amount-weighted precipitation means may be a good proxy for the isotopic composition of groundwater recharge and vice versa (Harris *et al.,* 2010; West *et al.,* 2014).

Combined, these interpretations provide the basis for identifying new research opportunities but also suggestions for future intentional monitoring efforts that could be useful for managing this groundwater resource linked to the SSLiME.

5.2 Future opportunities and knowledge gaps

The following are specific research gaps that should be prioritised in the future:

1. The SSLiME rely upon a regular exchange of seawater storm and tidal intrusion with inflowing freshwater from springs to maintain optimum microbialite growth conditions (Rishworth *et al.,* 2020b). On cycles of just under a week, most pools can revert back to a freshwater state following marine input (Rishworth *et al.,* 2017). This process therefore creates an opportunity to measure salinity conditions as a proxy for flowrate, or in other words, the time taken after marine intrusion for the SSLiME pool to recharge to a freshwater state. This can be achieved using relatively inexpensive conductivity-temperature loggers (sensu Rishworth *et al.,* 2017) which can be deployed at the base of monitored pools to measure hourly salinity conditions to supplement manual, but less regular, measurements of flowrate. To some extent TWO has begun this research as part of his MSc dissertation, but this has not formally been assessed and nor was it a component of this WRC Project. More details are given for the way forward of this in section 5.3 below.
2. A key component to the monitoring efforts of the SSLiME with respect to hydrological processes are that those sites chosen to represent proximal aquifer conditions are reflective of all other sites within that region. In this report we accounted for this potential variability by increasing our sample size of sites. However, for any long-term monitoring procedure, there is an effort cost that must be balanced against how

informative the data are. Therefore, a future assessment should be made regarding the SSLiME sites within a region to determine if sample size can be reduced to a single or fewer representative site(s) for that region. Data from our report does suggest this to be the case, but nonetheless a systematic assessment of spatial autocorrelation is warranted before the monitoring approach suggested in section 5.3 is adopted.

3. Any coastline where groundwater emanates will not exclusively discharge above the highwater mark, as is the case for that entering the SSLiME. Therefore, to accurately quantify the total groundwater budget for a region such as the NMB coastline between Maitland's and Cape Recife, all components of the groundwater system should be accounted for. This would be important, for example, to know whether the 3.96 Mℓ/d flowing through the SSLiME is a large or minor component of the budget. There is an active history of groundwater research in the region, particularly stemming from reactive approaches during recent drought cycles seeking to supplement water reserves with groundwater in NMB (see literature cited in Dodd & Rishworth 2023), but this knowledge is not readily available to, for example, comment upon the quantity of submarine and nearshore groundwater discharge along this stretch of coast. Effectively enumerating all of these components is not straightforward, but is nonetheless a crucial task if the groundwater resources are to be adequately managed given the propensity for borehole drilling in the region.

4. Inorganic nutrients such as nitrogen and phosphorus are of course not the only potential signatures of pollution that affect groundwater, as monitored and addressed in this report. Therefore, for any accurate assessment of true levels of anthropogenic impacts on groundwater, all major and micro pollutants should be assayed. This includes for example, heavy metals, organic micropollutants (e.g. pesticides, pharmaceuticals, industrial derivatives) and biological contaminants such as *E. coli*. The SSLiME are well-positioned to be used as test sites for assaying these pollutants, and some strides have been made in this regard with heavy metals through the Coastal Biogeochemistry Platform of SAEON, and through the PhD of CD which is assessing organic micropollutants in the SSLiME and inland groundwater. This is a developing research field gathering knowledge of pollutant levels, which is a first step but then

naturally should also include at a later point an assessment of the interactive "cocktail" effects of these pollutants, as well as their potential impacts on biota. This complexity is also not simple to assess.

5. It is crucial that a multi-year isotopic dataset for precipitation is developed to account for long-term hydrological variation. This should include event-based sampling, since small precipitation event signatures or isotopic changes during a large event are obscured in cumulative samples. It should also be noted that samples in this report were collected during a severe multi-year drought period and may deviate from "normal" precipitation signatures. Furthermore, to constrain the predominant moisture source(s), it may be useful to correlate isotopic signatures to rain events and prevalent wind directions. We are proposing that a long-term station be setup within the AWSS, potentially on the Nelson Mandela University campus, to initiate such research, to the benefit of all hydrologists and meteorologists in the region (see further details in section 5.3 below).

6. While this research report was principally focussed on the effectiveness of the SSLiME pools in reflecting local hydrological processes and groundwater contamination, it must be noted that there is also academic interest in understanding how the inflowing dynamics of the spring discharge is affecting microbialite growth conditions and ultimately stromatolite layering processes. Full elucidation of this geobiological dynamic is a knowledge gap within the microbialite literature, framed in addition to other formative and destructive processes such as bioturbation, for example (Rishworth *et al.,* 2016a; Rishworth *et al.,* 2020b). Furthermore, it is not known how altered flow rates or polluted inflowing spring water might affect the persistence of these unique habitats, but available data deduces that these effects are likely to be negative. Should the SSLiME be lost or depleted, the buffering capacity of these sites, not to mention the other ecosystem services that they provide, would similarly be affected and thereby would also impact the adjacent coastline.

7. Although not the focus of this research report, conventional water quality parameters such as TDS and major anions and cations should be included in a monitoring programme. The major hydrochemistry is a useful tool in the interpretation of, for

example, lithological origin of groundwater and could contribute to the understanding of groundwater recharge.

5.3 Suggested monitoring protocol

A substantial reason for developing the framework of this project with which this report is emanated from was that the SSLiME along the NMB coast are easily accessible, compared to for example traditional groundwater wells, and the SSLiME are also numerous and regularly spaced. This accessibility and representativeness therefore facilitates sampling logistics. Hence, given that we show in this report the usefulness of the SSLiME in reflecting several key coastal aquifer and hydrological processes, we propose that continued monitoring of these systems be facilitated (as outlined in Table 10).

The motivation for the details of this monitoring approach is built around quarterly sampling of the five key regions identified as SSLiME hotspots along the NMB coast, using sampling approaches that are relatively quick (single day), not tide or weather dependent, and have minimal sampling costs involved. Laboratory analyses are straightforward to facilitate given established partner laboratory processes, some of which are financially subsidised through National Research Platform imperatives (e.g. SAEON).

The most logistically complicated and potentially expensive component is number 6 of Table **10**, the establishment of a long-term precipitation station aligned with international (GNIP) standards. This requires long-term budget commitment, infrastructure and operational support, and effective data repository and monitoring mandates. Fortunately, plans are in place for all these potential hindrances as part of future research proposals, and also through engagement with existing environmental monitoring platforms.

Not listed below, but given the transdisciplinary nature of the SSLiME, it would also be advisable if biological and other routine ancillary monitoring metrics were established to complement and maximise the potential of such data as collected in Table 10. Presently these efforts form part of ongoing but separate and loosely coordinated research undertakings within the SSLiME Project coordinated by GMR. Furthermore, although the suggested programme focuses on SSLiME systems, a similar protocol could be implemented at inland boreholes and springs to improve the systems understanding of groundwater within the greater NMB area and ultimately provide a catchment-to-coast assessment of groundwater quality and quantity. This expanded monitoring network would be especially useful to constrain an aquifer protection zone aimed at protecting the recharge area of the SSLiME and quantifying the contribution from the different aquifers to coastal groundwater seepage. Potential future research trajectories also include vulnerability assessments to establish the thresholds of groundwater flow/nutrients required for SSLiME functioning.

***Table 10**. Recommended minimum long-term monitoring protocol for the SSLiME of Nelson Mandela Bay as indicators of local aquifer conditions.*

Variable	*Regularity*	*Spatial scope*	*Fieldwork*	*Laboratory analysis*	*Data analysis*	*Key indicators*
Flow rate						
1. Discharge rate	Quarterly	Minimum: 5 sites, but ideally all 20 locations, as in Chapter 2	Capture cup method, see Chapter 2	None	Graphical and coupled to local precipitation totals	Year upon year monitoring of % change in flow; Correlation patterns, including lag, with precipitation
2. SSLiME pool recharge	Hourly	Five main sites: Seaview, Kini Bay, Schoenmakerskop, Sappershoek, Cape Recife	In situ conductivity-temperature loggers at the deepest point of pool, following Rishworth *et al.* (2017)	None	Modelling of state shifts between freshwater and marine pool conditions following storm surges (need swell data)	Time taken for pool to recharge to baseline freshwater state following marine intrusion
3. SSLiME counts	Annual	All ~1,500 along the NMB coast (Cape Recife to Maitlands)	Geo-referenced photos of all seepage / discharge points and associated SSLiME	None	Geo-referenced time-stamped images; Count of proportion of SSLiME seeps	Year upon year monitoring of % change in number of seeps and proportion thereof with SSLiME
Nutrients						
4. DIN, DIP, DSi	Quarterly	Five core sites, inlet and outlet, as in Chapter 3	50 mℓ water filtered through 0.2 µm in triplicate, see Chapter 3	AutoAnalyser using the SAEON Coastal Biogeochemistry Platform	Graphical	Year upon year monitoring of % change
Hydrology						
5. SSLiME δ^2H and $\delta^{18}O$	Quarterly	Inlet water at five core sites	50 mℓ water collected from inlet & 50 mℓ standard (e.g. Evian water) (no headspace), see Chapter 4	BIOGRIP facility	Stable isotope biplot, with respect to the GMWL and LMWL	Year upon year deviation from LMWL

***Table 10*. continued.**

Variable	*Regularity*	*Spatial scope*	*Fieldwork*	*Laboratory analysis*	*Data analysis*	*Key indicators*
6. Local precipitation δ^2H and $\delta^{18}O$	Event-based, Monthly	Single site, Gqeberha – Nelson Mandela University Campus	Collection of rainwater as for (5), see Chapter 4	BIOGRIP facility, budget will determine if analysis is event-based or totalised monthly	To be used for the generation of a long-term LMWL	Ancillary data for (5) and other users
7. Major hydrochemistry & physicochemistry	Quarterly	Inlet water at five core sites	Cations: 250 ml water collected from inlet, filtered (0.45 µm CA) & acidified to pH <2 (HNO_3). Anions: 250 ml water collected from inlet, filtered (0.45 µm CA). Physicochemistry: Bucket of water collected from inlet – measure TDS, pH, temperature, EC, etc. using YSI multiprobe.	In-house alkalinity measurement using HACH titration kit within 48 hours of sampling. Element Environmental (cations & anions)	Water quality plots, e.g. Piper/Stiff.	Year upon year variation of physicochemistry and monitoring of change in water types.

6. Literature cited

Abiye, TA, Demlie, MB, & Mengistu, H (2021) An overview of aquifer physiognomies and the $\delta^{18}O$ and $\delta^{2}H$ distribution in the south african groundwaters. *Hydrology* 8: 68.

Adams, S, Titus, R, & Xu, Y (2004) Groundwater Recharge Assessment of the Basement Aquifers of Central Namaqualand. Water Research Commission WRC Report No. 1093/1/04

Baron, J (2000) Groundwater management using a GIS case study: Uitenhage Subterranean Government Water Control Area. University of Cape Town. PhD thesis

Bedaso, Z, & Wu, S-Y (2021) Linking precipitation and groundwater isotopes in Ethiopia – Implications from local meteoric water lines and isoscapes. *Journal of Hydrology* 596: 126074.

Bezuidenhout, C (2023) Impofu Dam decommissioned as levels plummet. *Port Elizabeth Express*.

Botai, CM, Botai, JO, de Wit, JP, Ncongwane, KP, Murambadoro, M, Barasa, PM, & Adeola, AM (2021) Hydrological drought assessment based on the Standardized Streamflow index: A case study of the three cape provinces of South Africa. *Water* 13: 3498.

Bowen, GJ, & Revenaugh, J (2003) Interpolating the isotopic composition of modern meteoric precipitation. *Water resources research* 39.

Braun, K, Bar-Matthews, M, Ayalon, A, Zilberman, T, & Matthews, A (2017) Rainfall isotopic variability at the intersection between winter and summer rainfall regimes in coastal South Africa (Mossel Bay, Western Cape Province). *South African Journal of Geology* 120: 323-340.

Burne, RV, & Moore, LS (1987) Microbialites: organosedimentary deposits of benthic microbial communities. *PALAIOS* 2: 241-254.

Campbell, E, Parker-Nance, T, & Bate, G (1992) A compilation of information on the magnitude, nature and importance of coastal aquifers in Southern Africa. Water Research Commission WRC Report No. 370/1/92.

Campbell, EE, & Bate, GC (1998) Tide-induced pulsing of nutrient discharge from an unconfined aquifer into an *Anaulus australis*-dominated surf-zone. *Water SA* 24: 365-370.

Cardwell, HE, Cole, RA, Cartwright, LA, & Martin, LA (2006) Integrated water resources management: definitions and conceptual musings. *Journal of Contemporary Water Research & Education* 135: 8-18.

Clark, ID, & Fritz, P (2013) *Environmental isotopes in hydrogeology*: CRC press.

Colvin, C, Riemann, K, Brown, C, Le Maitre, D, Mlisa, A, Blake, D, Aston, T, Maherry, A, Engelbrecht, J, & Pemberton, C (2009) Ecological and environmental impacts of large-scale groundwater development in the Table Mountain Group (TMG) aquifer system. *Report to Water Research Commission of South Africa No 1327*.

Craig, H (1961) Isotopic variations in meteoric waters. *Science* 133: 1702-1703.

Dansgaard, W (1964) Stable isotopes in precipitation. *Tellus* 16: 436-468.

de Wet, RF, West, AG, & Harris, C (2020) Seasonal variation in tap water δ^2H and δ^{18}O isotopes reveals two tap water worlds. *Scientific Reports* 10: 13544.

de Wit, M, & Stankiewicz, J (2006) Changes in surface water supply across Africa with predicted climate change. *Science* 311: 1917-1921.

DEA (2019) DEA E1434 Land-Cover. Version 004, 25-09-2019. P. South African National Land-Cover 2018 Report & Accuracy Assessment. Pretoria, South Africa, pp. 1-39.

Diamond, R, & Harris, C (1997) Oxygen and hydrogen isotope composition of Western Cape meteoric water. *South African Journal of Science* 93: 371-374.

Dodd, C, Anderson, CR, Perissinotto, R, du Plooy, SJ, & Rishworth, GM (2018) Hydrochemistry of peritidal stromatolite pools and associated freshwater inlets along the Eastern Cape Coast, South Africa. *Sedimentary Geology* 373: 163-179.

Dodd, C (2019) A geochemical comparison of southern African stromatolites and stromatolite pools. Port Elizabeth, South Africa: Nelson Mandela University. MSc dissertation

Dodd, C, Anderson, CR, Rishworth, GM, Perssinotto, R, & Van Niekerk, X (2021) Metazoan activity facilitates passive sediment trapping in modern supratidal microbialites: revealed using µ-CT-scanning and microscopy. *Geobiology* 19: 585-600.

Dodd, C (2023) The Algoa Bay Region Groundwater Cycle – Linking Source to Coast. Nelson Mandela University. unpublished PhD thesis

Dodd, C, & Rishworth, GM (2023) Coastal urban reliance on groundwater during drought cycles: opportunities, threats and state of knowledge. *Cambridge Prisms: Coastal Futures* 1: e11, 11-13.

du Plooy, SJ, Rishworth, GM, Perissinotto, R, & Dodd, C (2020) Nutrient uptake and primary production in lithifying peritidal tufa stromatolites. *Journal of Experimental Marine Biology and Ecology* 525: 151314.

Durowoju, OS, Odiyo, JO, & Ekosse, G-IE (2019) Determination of isotopic composition of rainwater to generate local meteoric water line in Thohoyandou, Limpopo Province, South Africa. *Water SA* 45: 183-189.

DWA (2010) Eastern Cape Groundwater Plan. Department of Water Affairs, South Africa.

DWAF (1998) National Water Act (No. 36). Department of Water Affairs and Forestry, South Africa.

Ferreira, OJO (1990) Thomas Ignatius Ferreira (c. 1743-1814), Oosgrenspionier en Britse bevelvoerder van Fort Frederick. *Historia* 35: 20-38.

Fitts, CR (2002) *Groundwater Science*: Academic Press.

Forbes, M, Vogwill, R, & Onton, K (2010) A characterisation of the coastal tufa deposits of south-west Western Australia. *Sedimentary Geology* 232: 52-65.

Garner, CJ (2013) Characterisation and biotic classification of Eastern Cape mixed substrate shores. Nelson Mandela Metropolitan University. PhD thesis

GCIS (2016) Water and Sanitation. *South Africa Yearbook 2015/2016 (23rd ed)*. Lentsoane, ETN (ed): Department of Government Communication and Information System, SA, pp. 441-456.

Geppert, M, Hartmann, K, Kirchner, I, Pfahl, S, Struck, U, & Riedel, F (2022) Precipitation over southern Africa: moisture sources and isotopic composition. *Journal of Geophysical Research: Atmospheres* 127: e2022JD037005.

Gröning, M, Lutz, HO, Roller-Lutz, Z, Kralik, M, Gourcy, L, & Pöltenstein, L (2012) A simple rain collector preventing water re-evaporation dedicated for $\delta^{18}O$ and $\delta^{2}H$ analysis of cumulative precipitation samples. *Journal of Hydrology* 448-449: 195-200.

Harris, C, Burgers, C, Miller, J, & Rawoot, F (2010) O- and H-isotope record of Cape Town rainfall from 1996 to 2008, and its application to recharge studies of table mountain groundwater, South Africa. *South African Journal of Geology* 113: 33-56.

Hawkes, S (2023) Food quality as a predictor of macroinvertebrate dietary consumption in modern supratidal microbialite ecosystems of Nelson Mandela Bay, Gqeberha. Nelson Mandela University. MSc dissertation

Heaton, THE, Talma, AS, & Vogel, JC (1986) Dissolved gas paleotemperatures and ^{18}O variations derived from groundwater near Uitenhage, South Africa. *Quaternary Research* 25: 79-88.

Holling, CS, & Meffe, GK (1996) Command and control and the pathology of natural resource management. *Conservation Biology* 10: 328-337.

Hughes, CE, & Crawford, J (2013) Spatial and temporal variation in precipitation isotopes in the Sydney Basin, Australia. *Journal of Hydrology* 489: 42-55.

IAEA (2014) IAEA/GNIP precipitation sampling guide (V2.02 September 2014).

IPCC (2021) *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*: Cambridge University Press.

Jasechko, S (2019) Global Isotope Hydrogeology—Review. *Reviews of Geophysics* 57: 835-965.

Jia, H (2007) Groundwater resource evaluation in Table Mountain Group Aquifer systems. University of the Western Cape. PhD thesis

Kresic, N (2010) Chapter 2 – Types and classifications of springs. *Groundwater Hydrology of Springs*. Kresic, N, & Stevanovic, Z (eds). Boston: Butterworth-Heinemann, pp. 31-85.

Le Roux, F (1990) Algoa Group (Cenozoic). *Catalogue of South African Lithostratigraphic Units*. Johnson, M (ed): SA Committee for Stratigraphy.

Lemley, DA, Adams, JB, Bornman, TG, Campbell, EE, & Deyzel, SHP (2019) Land-derived inorganic nutrient loading to coastal waters and potential implications for nearshore plankton dynamics. *Continental Shelf Research* 174: 1-11.

Lemley, DA, Lakane, CP, Taljaard, S, & Adams, JB (2022) Inorganic nutrient removal efficiency of a constructed wetland before discharging into an urban eutrophic estuary. *Marine Pollution Bulletin* 179: 113727.

Lin, L, Lin, H, & Xu, Y (2014) Characterisation of fracture network and groundwater preferential flow path in the Table Mountain Group (TMG) sandstones, South Africa. *Water SA* 40: 263-272.

Lin, L, & Lin, H (2019) Determination of groundwater sustainable yield using a numerical modelling approach for the Table Mountain Group sandstone aquifer, Rawsonville, South Africa. *Hydrogeology Journal* 27: 841-855.

Liu, J, Fu, G, Song, X, Charles, SP, Zhang, Y, Han, D, & Wang, S (2010) Stable isotopic compositions in Australian precipitation. *Journal of Geophysical Research: Atmospheres* 115.

Lomberg, CR, Rosewarne, PN, Raymer, DA, & Devey, DG (1996) Research into groundwater abstraction in the Port Elizabeth municipal area. Water Research Commission WRC Report No 515/1/97. *Report to the Water Research Commission SRK Report No 191472/4*

MacDonald, A, & Davies, J (2000) A brief review of groundwater for rural water supply in sub-Saharan Africa. BGS Technical Report WC/00/33.

Maclear, LGA (2001) The hydrogeology of the Uitenhage Artesian Basin with reference to the Table Mountain Group Aquifer. *Water SA* 27: 499-506.

Mahlalela, PT, Blamey, RC, Hart, NCG, & Reason, CJC (2020) Drought in the Eastern Cape region of South Africa and trends in rainfall characteristics. *Climate Dynamics* 55: 2743-2759.

Malherbe, H, Gebel, M, Pauleit, S, & Lorz, C (2018) Land use pollution potential of water sources along the southern coast of South Africa. *Change and Adaptation in Socio-Ecological Systems* 4: 7-20.

Mandiola, SR, Grundling, AT, Grundling, P-L, Van der Plicht, J, Van der Waal, BC, & Grootjans, AP (2021) Ecohydrological analysis of a South African through-flow mire: Vankervelsvlei revisited. *Mires and Peat* 27: 1-14.

Mekiso, F, & Ochieng, G (2014) Stable water isotopes as tracers at the Middle Mohlapitsi catchment/Wetland, South Africa. *International Journal of Engineering and Technology* 6: 1728-1736.

Meyer, PS (1998) An explanation of the 1: 500 000 general hydrogeological map Port Elizabeth 3324. Department of Water Affairs and Forestry.

Meyer, R (2008) Geological and Geohydrological Report: Part of the permit application for the development of a regional general and hazardous waste disposal facility on the farm Grassridge 190 Remainder near Addo, Eastern Cape. CES Report No. 015/08.

Michelsen, N, Van Geldern, R, Roßmann, Y, Bauer, I, Schulz, S, Barth, JAC, & Schüth, C (2018) Comparison of precipitation collectors used in isotope hydrology. *Chemical Geology* 488: 171-179.

Miller, JA, Dunford, AJ, Swana, KA, Palcsu, L, Butler, M, & Clarke, CE (2017) Stable isotope and noble gas constraints on the source and residence time of spring water from the Table Mountain Group Aquifer, Paarl, South Africa and implications for large scale abstraction. *Journal of Hydrology* 551: 100-115.

Millham, NP, & Howes, BL (1994) Freshwater flow into a coastal embayment: Groundwater and surface water inputs. *Limnology and Oceanography* 39: 1928-1944.

Mohuba, SC, Abiye, TA, Demlie, MB, & Modiba, MJ (2020) Hydrogeological characterization of the Thyspunt area, Eastern Cape Province, South Africa. *Hydrology* 7: 49.

Mokua, RA, Glenday, J, Nel, J, & Butler, M (2020) Combined use of stable isotopes and hydrochemical characteristics to determine streamflow sources in the Jonkershoek catchment, South Africa. *Isotopes in Environmental and Health Studies* 56: 238-259.

Murray, R, Goedhart, M, & Baron, J (2008) High-yielding groundwater areas around the Nelson Mandela Bay Municipality. Water Research Commission WRC Report no. TT327/08.

Naidoo, N, Pearce, D, Visser, W, Crafford, J, Maila, D, & Harris, K (2016) Implementation of effective wastewater charges by municipalities in South Africa: An investigation into the barriers and enablers. WRC Report No. TT 673/16.

Nakwafila, AN (2015) Salinisation source(s) and mechanism(s) in shallow alluvial aquifers along the Buffels River, Northern Cape Province, South Africa. Stellenbosch University. MSc dissertation

Natali, S, Doveri, M, Giannecchini, R, Baneschi, I, & Zanchetta, G (2022) Is the deuterium excess in precipitation a reliable tracer of moisture sources and water resources fate in the western Mediterranean? New insights from Apuan Alps (Italy). *Journal of Hydrology* 614: 128497.

NMBM (2022) Nelson Mandela Bay Municipality Water Outlook Report – Version 003.

Oehler, T, Ramasamy, M, George, ME, Babu, SDS, Dähnke, K, Ankele, M, Böttcher, ME, Santos, IR, & Moosdorf, N (2021) Tropical beaches attenuate groundwater nitrogen pollution flowing to the ocean. *Environmental Science and Technology* 55: 8432-8438.

Oude Essink, GHP, Van Baaren, ES, & de Louw, PGB (2010) Effects of climate change on coastal groundwater systems: A modeling study in the Netherlands. *Water resources research* 46.

Parsons, R (2009) Is Groenvlei really fed by groundwater discharged from the Table Mountain Group (TMG) Aquifer? *Water SA* 35: 657-662.

Peel, MC, Finlayson, BL, & McMahon, TA (2007) Updated world map of the Köppen-Geiger climate classification. *Hydrology and Earth System Sciences* 11: 1633-1644.

Perissinotto, R, Bornman, T, Steyn, P-P, Miranda, NAF, Dorrington, RA, Matcher, GF, Strydom, N, & Peer, N (2014) Tufa stromatolite ecosystems on the South African south coast. *South African Journal of Science* 110: 89-96.

Petersen, RM (2012) A conceptual understanding of groundwater recharge processes and surface-water/ groundwater interactions in the Kruger National Park. University of the Western Cape. MSc dissertation

Pfahl, S, & Sodemann, H (2014) What controls deuterium excess in global precipitation? *Climate of the Past* 10: 771-781.

Pietersen, K (2021) Post-Drought and Emergency Interventions: Towards Higher Water Security. WRC Report No. 3005/1/21.

Pohl, B, Rouault, M, & Roy, SS (2014) Simulation of the annual and diurnal cycles of rainfall over South Africa by a regional climate model. *Climate Dynamics* 43: 2207-2226.

Prinsloo, S (2013) The distribution and diversity of macroalgae in selected estuaries along the Eastern Cape coast of South Africa. Port Elizabeth, South Africa: Nelson Mandela Metropolitan University. MSc dissertation

Putman, AL, Fiorella, RP, Bowen, GJ, & Cai, Z (2019) A global perspective on local meteoric water lines: meta-analytic insight into fundamental controls and practical constraints. *Water resources research* 55: 6896-6910.

Rabalais, NN (2002) Nitrogen in aquatic ecosystems. *AMBIO: A Journal of the Human Environment* 31: 102-112, 111.

Raymer, D (2008) *Streams of Life – The Water Supply of Port Elizabeth and Uitenhage.* : The South African Institution of Civil Engineering.

Riding, R (2011) The nature of stromatolites: 3,500 million years of history and a century of research. *Advances in Stromatolite Geobiology*. Reitner, J, Quéric, N-V, & Arp, G (eds). Berlin Heidelberg, Germany: Springer, pp. 29-74.

Rishworth, GM, Perissinotto, R, & Bird, MS (2016a) Coexisting living stromatolites and infaunal metazoans. *Oecologia* 182: 539-545.

Rishworth, GM, Van Elden, S, Perissinotto, R, Miranda, NAF, Steyn, P-P, & Bornman, TG (2016b) Environmental influences on living marine stromatolites: insights from benthic microalgal communities. *Environmental Microbiology* 18: 503-513.

Rishworth, GM, Perissinotto, R, Bornman, TG, & Lemley, DA (2017) Peritidal stromatolites at the convergence of groundwater seepage and marine incursion: patterns of salinity, temperature and nutrient variability. *Journal of Marine Systems* 167: 68-77.

Rishworth, GM, Perissinotto, R, & Bornman, TG (2019) Box 3. South African peritidal stromatolites. *South African National Biodiversity Assessment 2018: Technical Report Volume 5: Coast*. Harris, LR, Sink, KJ, Skowno, AL, & Van Niekerk, L (eds). South African National Biodiversity Institute, Pretoria.

Rishworth, GM, Cawthra, HC, Dodd, C, & Perissinotto, R (2020a) Peritidal stromatolites as indicators of stepping-stone freshwater resources on the Palaeo-Agulhas Plain landscape. *Quaternary Science Reviews* 235: 105704.

Rishworth, GM, Dodd, C, Perissinotto, R, Bornman, TG, Adams, JB, Anderson, CR, Cawthra, HC, Dorrington, RA, du Toit, H, Edworthy, C, Gibb, R-LA, Human, LRD, Isemonger, EW, Lemley, DA, Miranda, NAF, Peer, N, Raw, JL, Smith, AM, Steyn, P-P, Strydom, NA, Teske, PR, & Welman, S (2020b) Modern supratidal microbialites fed by groundwater: functional drivers, value and trajectories. *Earth-Science Reviews* 210: 103364.

Roets, W, Xu, Y, Raitt, L, & Brendonck, L (2008a) Groundwater discharges to aquatic ecosystems associated with the Table Mountain Group (TMG) aquifer: A conceptual model. *Water SA* 34: 77-88.

Roets, W, Xu, Y, Raitt, L, El-Kahloun, M, Meire, P, Calitz, F, Batelaan, O, Anibas, C, Paridaens, K, Vandenbroucke, T, Verhoest, NEC, & Brendonck, L (2008b) Determining discharges from the Table Mountain Group (TMG) aquifer to wetlands in the Southern Cape, South Africa. *Hydrobiologia* 607: 175-186.

Rogers, G (2021a) Metro to inject groundwater into Churchill Dam supply. *The HeraldLive*.

Rogers, G (2021b) Nelson Mandela Metro looking to harvest coastal springs. *The HeraldLive*.

Rosewarne, PN (2002) Case Study: Port Elizabeth Municipal Area. *A Synthesis of the Hydrogeology of the Table Mountain Group – Formation of a Research Strategy WRC Report No TT 158/01* Pietersen, K, & Parsons, R (eds), pp. 205-211.

Rossouw, L (2012) Phase 1 Palaeontological Impact Assessment of a proposed water pipeline between Cannon Rocks and Kenton-on-Sea and between Cannon Rocks and Alexandria, EC Province. CES Report.

Rouault, M, Roy, SS, & Balling, RC (2013) The diurnal cycle of rainfall in South Africa in the austral summer. *International Journal of Climatology* 33: 770-777.

Rozanski, K, Araguás-Araguás, L, & Gonfiantini, R (1993) Isotopic Patterns in Modern Global Precipitation. *Climate Change in Continental Isotopic Records*, pp. 1-36.

Rust, IC (1991) Environmental geology of the coastal zone: a South African perspective. *South African Journal of Marine Science* 10: 397-405.

Santos, IR, Chen, X, Lecher, AL, Sawyer, AH, Moosdorf, N, Rodellas, V, Tamborski, J, Cho, H-M, Dimova, N, Sugimoto, R, Bonaglia, S, Li, H, Hajati, M-C, & Li, L (2021) Submarine groundwater discharge impacts on coastal nutrient biogeochemistry. *Nature Reviews Earth & Environment* doi:10.1038/s43017-021-00152-0.

Schachtschneider, K, & February, EC (2013) Impact of *Prosopis* invasion on a keystone tree species in the Kalahari Desert. *Plant Ecology* 214: 597-605.

Schael, DM, & Gama, PT (2019) Ecosystem process and function of temporary wetlands: baseline data for climate change predictions. Report to the Water Research Commission WRC Report No. 2348/1/19.

Schneider, RL, Negley, TL, & Wafer, C (2005) Factors influencing groundwater seepage in a large, mesotrophic lake in New York. *Journal of Hydrology* 310: 1-16.

Scholl, MA, Shanley, JB, Zegarra, JP, & Coplen, TB (2009) The stable isotope amount effect: New insights from NEXRAD echo tops, Luquillo Mountains, Puerto Rico. *Water resources research* 45.

Stowe, MJ, Harris, C, Hedding, D, Eckardt, F, & Nel, W (2018) Hydrogen and oxygen isotope composition of precipitation and stream water on sub-Antarctic Marion Island. *Antarctic Science* 30: 83-92.

Taylor, A, Atkins, F, & Jack, C (2023) Governing Groundwater in City Regions : Water Metabolism and Actor Networks in the Cases of Capte Town and Nelson Mandela Bay. Report to the Water Research Commission WRC Report No. 3066/1/23.

Van Aardt, T (2018) Boreholes could affect quality of PE's water. Bizcommunity.

Van Deventer, C (2021) The fore-laws of boreholes – handy tips before drilling. Van Deventer & Van Deventer.

Vegter, J (1990) Groundwater regions and subregions of South Africa. Directorate of Geohydrology Technical Report No. GH 3697.

Vogel, JC, Talma, AS, Heaton, THE, & Kronfeld, J (1999) Evaluating the rate of migration of an uranium deposition front within the Uitenhage Aquifer. *Journal of Geochemical Exploration* 66: 269-276.

Wanke, H, Gaj, M, Beyer, M, Koeniger, P, & Hamutoko, JT (2018) Stable isotope signatures of meteoric water in the Cuvelai-Etosha Basin, Namibia: Seasonal characteristics, trends and relations to southern African patterns. *Isotopes in Environmental and Health Studies* 54: 588-607.

Webb, GE, & Kamber, BS (2011) Trace Element Geochemistry as a Tool for Interpreting Microbialites. *Earliest Life on Earth: Habitats, Environments and Methods of Detection*. Golding, SD, & Glikson, M (eds). Dordrecht: Springer Netherlands, pp. 127-170.

Weitz, J, & Demlie, M (2014) Conceptual modelling of groundwater-surface water interactions in the Lake Sibayi Catchment, Eastern South Africa. *Journal of African Earth Sciences* 99: 613-624.

West, AG, Dawson, TE, February, EC, Midgley, GF, Bond, WJ, & Aston, TL (2012) Diverse functional responses to drought in a Mediterranean-type shrubland in South Africa. *New Phytologist* 195: 396-407.

West, AG, February, EC, & Bowen, GJ (2014) Spatial analysis of hydrogen and oxygen stable isotopes ("isoscapes") in ground water and tap water across South Africa. *Journal of Geochemical Exploration* 145: 213-222.

Winter, TC, Harvey, JW, Franke, OL, & Alley, WM (1998) Ground water and surface water: A single resource. *Circular*: Survey, USG.

Wurtsbaugh, WA, Paerl, HW, & Dodds, WK (2019) Nutrients, eutrophication and harmful algal blooms along the freshwater to marine continuum. *WIREs Water* 6: e1373.

Yin, L, Hou, G, Su, X, Wang, D, Dong, J, Hao, Y, & Wang, X (2011) Isotopes (δD and $\delta^{18}O$) in precipitation, groundwater and surface water in the Ordos Plateau, China: implications with respect to groundwater recharge and circulation. *Hydrogeology Journal* 19: 429-443.

Zengeni, R, Kakembo, V, & Nkongolo, N (2016) Historical rainfall variability in selected rainfall stations in Eastern Cape, South Africa. *South African Geographical Journal* 98: 118-137.

Zhang, Y, Santos, IR, Li, H, Wang, Q, Xiao, K, Guo, H, & Wang, X (2020) Submarine groundwater discharge drives coastal water quality and nutrient budgets at small and large scales. *Geochimica et Cosmochimica Acta* 290: 201-215.

7. Supplementary information

Table S 1. *Hillingdon station (315 mamsl) isotopic data for rainfall samples collected between March 2022 and March 2023. Values are expressed as ‰ relative to the Vienna Standard Oceanic Meteoric Water (VSMOW). SD = standard deviation of two separate sample runs of a single sample (each run consisting of nine injections of which the last five measurements are averaged).*

Month	δ^2H (‰)	SD	$\delta^{18}O$ (‰)	SD	d-excess (‰)	Rainfall (mm)
Apr '22	-12.4	0.3	-4.24	0.13	21.6	47.0
May '22	-10.5	0.1	-3.76	0.09	19.6	45.5
Jun '22	-23.5	0.7	-5.80	0.01	22.9	86.0
Jul '22	3.7	0.1	-1.92	0.01	19.0	31.5
Aug '22	-10.9	0.7	-4.60	0.05	25.9	78.5
Sept '22	-14.5	0.1	-4.72	0.02	23.2	77.0
Oct '22	6.5	0.3	-2.03	0.03	22.7	28.0
Nov '22	0.7	0.3	-2.69	0.04	22.2	18.5
Dec '22	-14.1	0.0	-3.79	0.01	16.2	87.0
Jan '23	-4.0	0.1	-3.31	0.03	22.5	27.5
Feb '23	-13.4	0.4	-4.37	0.10	21.6	57.5
Mar'23	-0.8	0.3	-2.99	0.03	23.1	85.5

Table S 2. *Melkhoutboom station (566 mamsl) isotopic data for rainfall samples collected between March 2022 and March 2023. Values are expressed as ‰ relative to the Vienna Standard Oceanic Meteoric Water (VSMOW). SD = standard deviation of two separate sample runs of a single sample (each run consisting of nine injections of which the last five measurements are averaged).*

Month	δ^2H (‰)	SD	$\delta^{18}O$ (‰)	SD	d-excess (‰)	Rainfall (mm)
Apr '22	-6.2	0.7	-3.20	0.28	19.4	44.0
May '22	-11.9	0.2	-4.53	0.12	24.3	58.0
Jun '22	-21.5	0.1	-5.28	0.01	20.7	38.0
Jul '22	-2.1	0.2	-3.13	0.02	22.9	25.0
Aug '22	-15.4	0.1	-5.11	0.02	25.5	49.0
Sept '22	-26.5	0.1	-6.11	0.01	22.4	26.0
Oct '22	7.4	0.2	-1.78	0.02	21.7	8.0
Nov '22	9.0	0.4	-2.98	0.03	32.8	14.0
Dec '22	-9.2	0.0	-3.32	0.02	17.4	32.0
Jan '23	0.0	0.1	-2.34	0.11	18.7	32.0
Feb '23	-15.7	0.4	-4.61	0.08	21.2	67.0
Mar'23	-1.2	0.2	-2.63	0.04	19.8	16.0

Table S 3. *Loerie Ruskamp station (224 mamsl) isotopic data for rainfall samples collected between March 2022 and March 2023. Values are expressed as ‰ relative to the Vienna Standard Oceanic Meteoric Water (VSMOW). SD = standard deviation of two separate sample runs of a single sample (each run consisting of nine injections of which the last five measurements are averaged).*

Month	δ^2H (‰)	SD	$\delta^{18}O$ (‰)	SD	d-excess (‰)	Rainfall (mm)
Apr '22	-0.4	0.3	-2.73	0.15	21.4	30.0
May '22	-7.8	0.2	-3.82	0.07	22.8	62.0
Jun '22	-18.2	0.4	-5.09	0.08	22.5	46.0
Jul '22	-0.2	0.2	-3.06	0.07	24.3	31.0
Aug '22	-11.7	0.7	-4.49	0.06	24.3	39.0
Sept '22	-19.7	0.2	-5.41	0.01	23.6	29.0
Oct '22	9.7	0.5	-0.98	0.02	17.6	14.0
Nov '22	4.5	0.1	-2.13	0.03	21.6	12.7
Dec '22	-22.7	0.1	-4.94	0.04	16.8	77.0
Jan '23	-7.7	0.2	-3.28	0.04	18.6	52.0
Feb '23	-16.4	0.5	-4.74	0.09	21.5	83.0
Mar'23	-5.9	0.2	-3.01	0.06	18.1	63.0

Table S 4. *Cape St Francis station (12 mamsl) isotopic data for rainfall samples collected between March 2022 and March 2023. Values are expressed as ‰ relative to the Vienna Standard Oceanic Meteoric Water (VSMOW). SD = standard deviation of two separate sample runs of a single sample (each run consisting of nine injections of which the last five measurements are averaged).*

Month	δ^2H (‰)	SD	$\delta^{18}O$ (‰)	SD	d-excess (‰)	Rainfall (mm)
Apr '22	-3.0	0.2	-3.18	0.13	22.4	82.5
May '22	-4.8	0.9	-3.45	0.18	22.8	107.5
Jun '22	-21.5	0.9	-5.58	0.05	23.2	103.0
Jul '22	-4.2	0.3	-3.43	0.04	23.3	65.0
Aug '22	-9.1	0.3	-4.17	0.01	24.3	101.0
Sept '22	-6.7	0.4	-3.83	0.05	24.0	41.0
Oct '22	15.2	0.0	-0.20	0.04	16.7	7.5
Nov '22	-1.7	0.3	-2.90	0.03	21.5	25.0
Dec '22	-12.1	0.0	-3.17	0.06	13.3	96.0
Jan '23	-5.7	0.0	-3.80	0.01	24.6	42.5
Feb '23	-7.2	0.4	-3.96	0.01	24.5	29.0
Mar'23	-0.9	0.1	-2.50	0.05	19.1	37.0

<u>Table S 5.</u> *Kini Bay station (35 mamsl) isotopic data for rainfall samples collected between March 2022 and March 2023. Values are expressed as ‰ relative to the Vienna Standard Oceanic Meteoric Water (VSMOW). SD = standard deviation of two separate sample runs of a single sample (each run consisting of nine injections of which the last five measurements are averaged).*

Month	δ^2H (‰)	SD	$\delta^{18}O$ (‰)	SD	d-excess (‰)	Rainfall (mm)
Apr ‘22	1.6	0.7	-2.45	0.16	21.2	47.0
May ‘22	-3.7	0.3	-3.31	0.18	22.8	78.0
Jun ‘22	-17.6	0.5	-5.12	0.43	23.3	59.8
Jul ‘22	-2.8	0.2	-2.90	0.08	20.4	49.8
Aug ‘22	-10.5	0.2	-4.46	0.01	25.2	85.0
Sept ‘22	-12.1	0.0	-4.58	0.01	24.5	77.5
Oct ‘22	8.4	0.2	-1.44	0.04	19.9	25.0
Nov ‘22	0.3	0.1	-2.45	0.04	19.9	28.5
Dec ‘22	-11.0	0.1	-3.67	0.02	18.3	102.0
Jan ‘23	-6.9	0.2	-3.52	0.05	21.2	36.0
Feb ‘23	-12.6	0.2	-3.97	0.05	19.1	40.0
Mar’23	-2.8	0.3	-3.29	0.01	23.5	55.5

<u>Table S 6.</u> *Gqeberha station (136 mamsl) isotopic data for rainfall samples collected between March 2022 and March 2023. Values are expressed as ‰ relative to the Vienna Standard Oceanic Meteoric Water (VSMOW). SD = standard deviation of two separate sample runs of a single sample (each run consisting of nine injections of which the last five measurements are averaged).*

Month	δ^2H (‰)	SD	$\delta^{18}O$ (‰)	SD	d-excess (‰)	Rainfall (mm)
Apr ‘22	0.3	0.3	-2.83	0.21	23.0	76.0
May ‘22	-6.7	0.3	-3.53	0.05	21.5	106.0
Jun ‘22	-20.6	0.1	-5.56	0.03	23.9	76.0
Jul ‘22	-1.4	0.1	-3.19	0.09	24.1	86.5
Aug ‘22	-18.9	0.3	-5.36	0.04	24.0	164.0
Sept ‘22	-23.4	0.4	-5.77	0.04	22.8	70.0
Oct ‘22	13.4	0.5	-1.62	0.03	26.3	45.0
Nov ‘22	10.4	0.3	-2.98	0.02	34.2	29.5
Dec ‘22	-11.2	0.0	-3.64	0.08	17.9	117.0
Jan ‘23	-6.8	0.1	-3.45	0.00	20.7	39.5
Feb ‘23	-15.3	0.8	-4.33	0.04	19.4	36.0
Mar’23	-1.2	0.2	-2.89	0.08	22.0	71.0

Table S 7. *Isotopic values of calibration and control standards used.*

Standard	**δ²H (‰)**	**δ¹⁸O (‰)**
LGR1 (calibration standard)	-161.3 ± 0.5	-20.72 ± 0.15
BIHS1 (QC)	-72.82 ± 0.60	-10.85 ± 0.15
BIHS2 (QC)	-19.94 ± 0.54	-4.91 ± 0.07
BIHS3 (calibration standard)	-12.20 ± 0.32	-2.76 ± 0.07

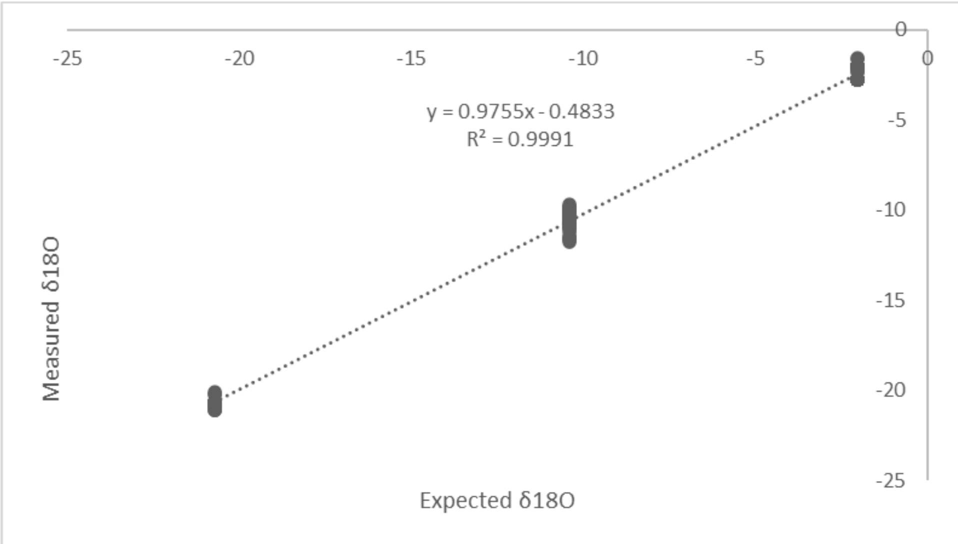


Figure S 1. *Calibration curve of the measured versus expected $\delta^{18}O$ values for the isotopic calibration standards for February 2022-August 2023.*

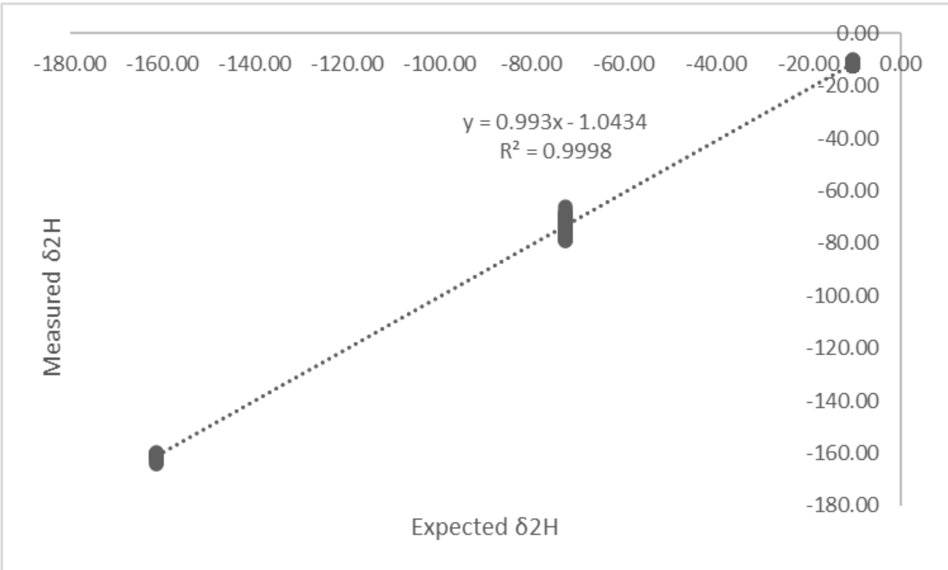


Figure S 2. *Calibration curve of the measured versus expected δ^2H values for the isotopic calibration standards for February 2022-August 2023.*

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