Hydrochemical dynamics on sub-Antarctic Marion Island

by

M-J Stowe

Minor dissertation submitted
in partial fulfilment of the requirements for the degree of Master of Science

In the Department of Environmental and Geographical Sciences

University of Cape Town

February 2017

Acknowledgements

I am grateful for the support and comments of my supervisor, Prof. Frank Eckardt, and co-supervisor, Prof. Werner Nel. Furthermore, I would like to thank them for providing me with the opportunity to experience Marion Island.

I acknowledge the contributions of the following members of the Landscape and Climate Interactions project to this research: Prof. David Hedding, for sharing his data and knowledge of Marion Island, as well as contributing to discussions surrounding my research; Abuyiselwe Nguna for assisting me in the field.

The research presented here is part of the project Landscape and Climate Interactions in a Changing Sub-Antarctic Environment (grant no. 93075). The analytical costs of this study were covered by this grant. This research received logistical support from the South African Department of Environmental Affairs. This project would not have been possible without funding provided through the National Research Foundation, by the South African Department of Science and Technology under the auspices of the South African National Antarctic Program.

Contents

List of Figures

List of Tables

Abstract

Although sub-Antarctic maritime environments are some of the most sensitive regions to climate change, investigations into isotopic and hydrochemical dynamics on sub-Antarctic islands are limited. To address this, the Soft Plume River on sub-Antarctic Marion Island was sampled daily along an altitudinal gradient during an intense high-resolution 16-day field campaign in April/May 2015. Samples were analysed for stable isotopes (δ^2H and $\delta^{18}O$) and major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}, NO_3^-). In addition, stream water physicochemistry (pH, water temperature, dissolved oxygen and total dissolved solids) was monitored *in situ* at a single site in the stream at 5 minute resolution for the duration of the field campaign. Monthly precipitation δ^2H and $\delta^{18}O$ had mean values of -27.51‰ and -4.67‰ respectively. Stream water δ^2H and $\delta^{18}O$ values were significantly different to that of precipitation, with values ranging from -48.0‰ to -33.6‰ and from -7.6‰ to -5.6‰, respectively. Major ion concentrations were dominated by Na^+ and Cl^-, reflecting the overwhelming influence of the surrounding ocean on the island's stream water chemistry. This finding is consistent with previous studies on Marion Island and other maritime sub-Antarctic islands. Temporal variability in stream chemistry was assessed through daily sampling. Findings show that variation was predominantly controlled by precipitation. Following high precipitation amounts low stream water δ^2H and $\delta^{18}O$ values were recorded. This was likely the result of the "amount effect". Similarly, a decrease in ion concentrations was also observed following high rainfall amounts. This was because of stream dilution. Sampling along the stream revealed that variation in δ^2H and $\delta^{18}O$ and most major ions was largest at the highest site. This pattern is likely the result of an altitudinal precipitation gradient, with higher amounts of precipitation falling at the highest altitude site. High-frequency monitoring of stream water physicochemistry revealed the presence of diel oscillations. Stream pH, temperature and dissolved oxygen concentrations all exhibited diel cycles. Stream pH and temperature were characterised by afternoon maxima and night time minima, with dissolved oxygen following an inverse cycle. These results are the first time diel cycles have been observed for stream water on Marion Island. Taken together, results from this study revealed that the Soft Plume River exhibited a noticeable degree of variability and complexity, especially as results only represent stream water chemical dynamics over a limited range of annual hydroclimatic variation.

Keywords: Stream chemistry, isotope hydrology, major ions, diurnal, high-resolution

Chapter 1: Introduction

1.1 Hydrochemical research in a changing sub-Antarctic environment

There is now unequivocal evidence showing that anthropogenic activities have altered the earth's climate (IPCC, 2013) by changing the atmosphere's composition and land surface cover (Pielke et al., 2002; Karl and Trenberth, 2003). Increased concentrations of greenhouse gases in the atmosphere and reduced planetary albedo have resulted in a positive total radiative forcing (Mann et al., 1998; IPCC, 2013). This has led to a combined ocean and surface temperature rise of 0.85 (0.65 to 1.06) °C, over the period 1880 – 2012 (IPCC, 2013). Along with the general linear trend of surface temperature increase, there is also the likelihood of increased frequency and intensity of extreme climatic events (Easterling et al., 2000; Frich et al., 2002). In addition, there has been a strengthening of the westerly winds over the Southern Ocean by 15-20% since the 1970s (Turner and Marshall, 2011). Subsequently, this has resulted in a poleward shift in the westerly storm track by 1-2º latitude (Turner et al., 2014).

In the Southern Hemisphere, the atmosphere has undergone major changes over recent decades (Thompson and Solomon, 2002; Shindell and Schmidt, 2004). While climate and oceanographic changes have been substantial (Boning et al., 2008), the spatial and temporal trends over decadal time scales are highly heterogeneous (Jones and Briffa, 1992; Kwok and Comiso, 2002). Sub-Antarctic islands are extremely sensitive to climatic change and can therefore be considered early identifiers of large scale climate change (Turner et al., 2014). While many of the sub-Antarctic islands have climatic and terrestrial similarities, the islands differ from each other in ways that offer advantages for understanding the impacts of global environmental change (Selkirk, 2007; Chown and Froneman, 2008).

Positioned at the interface between the sub-Antarctic Front (SAF) and Antarctic Polar Front (APF), the Prince Edward Islands (PEIs; Fig. 1.1) are ideally placed to contribute to the understanding environmental change in the sub-Antarctic region (Ansorge and Lutjeharms, 2002). Therefore, climatic and hydrological observations from the PEIs can provide valuable information pertaining to the nature of regional environmental change in the sub-Antarctic.

In this context, hydrological systems on remote maritime islands are regarded as sentinels because they integrate multiple physical, biological and chemical processes that are influenced by climate forcing (Milner et al., 2009). Hydrochemical changes could alter nutrient and solute budgets and thus, modify physicochemical conditions of freshwater on the island (Hannah et al., 2007). Despite low aquatic species diversity and abundance in stream water on Marion Island, these changes could nevertheless influence freshwater organisms and affect overall rates of ecosystem functioning in the island’s freshwater (Prowse et al., 2006; Woodward et al., 2010).

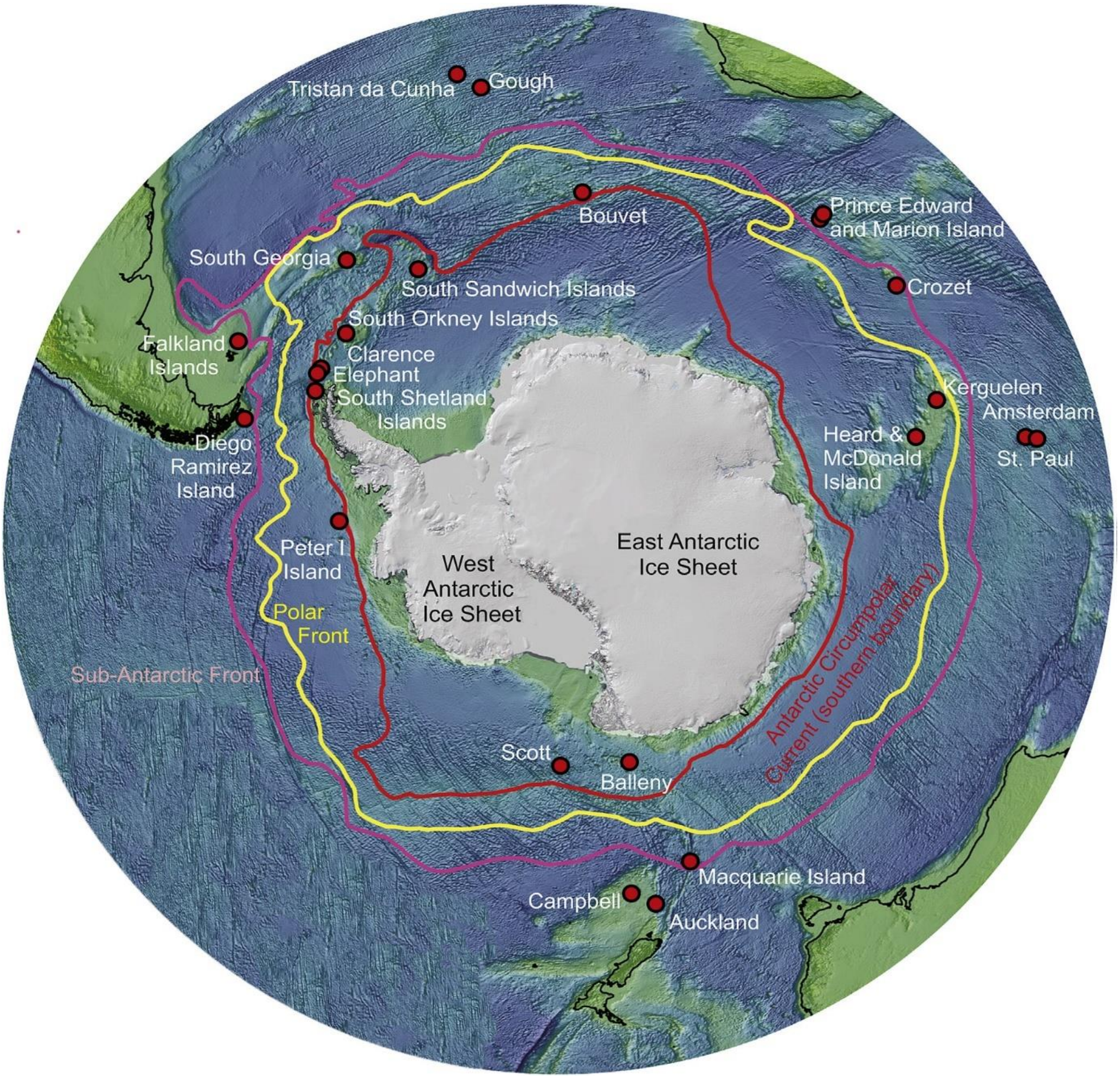


Figure 1.1. Map of maritime and sub-Antarctic Islands, adapted from Hodgson et al. (2014). Islands are displayed in relation to the position of the southern boundary of the Antarctic Circumpolar Current (ACC; red line), Antarctic Polar Front (APF; yellow line), and sub-Antarctic Front (SAF; pink line).

The thesis presented here aims to contribute to this understanding, by providing insight into contemporary hydrochemical dynamics on sub-Antarctic Marion Island. Specific aims and objectives are presented below.

1.2 General aims and objectives

There is a need for more hydrochemical datasets from remote and isolated maritime sub-Antarctic islands. Hydrological systems on maritime islands often exhibit a strong coupling with oceanic and atmospheric systems which, in turn, regulate various hydrochemical processes. Given the documented climatic change on Marion Island, investigation into current atmospheric, terrestrial and hydrological conditions are necessary. This will allow for a clearer picture of how hydrochemical systems on Marion Island might respond to future climatic change. The overarching aim of this study is to characterize Marion Island's hydrochemistry and assess variability on multiple time scales.

For this thesis, three main objectives were identified:

1. Establish the isotopic composition of precipitation and stream water on Marion Island, and investigate the mechanisms responsible for variability on multiple time scales (Chapter 2).
2. Determine the ionic composition of stream water on Marion Island, as well assess any temporal and spatial variation (Chapter 3).
3. Monitor stream physicochemistry *in situ* at high-resolution and identify the extent of diel variability and response to storm events (Chapter 3).

1.3 Format of thesis

This thesis is divided into 4 chapters. Chapters 2 and 3 of this thesis are structured as scientific papers relating to hydrochemical dynamics on Marion Island. These chapters make use of various techniques at different spatial and temporal resolutions to establish an understanding of the island's hydrochemistry. Chapter 2 is entitled *Isotopic composition of precipitation and stream water on sub-Antarctic Marion Island*, and is primarily focussed on the isotope hydrology of the island. This chapter makes use of hydrogen and oxygen isotopes in monthly precipitation over the period 1961 – 2013, and stream water collected during a single sampling campaign in April/May 2015. Chapter 3, *Hydrochemical characteristics of stream water on sub-Antarctic Marion Island*, focusses primarily on stream water chemistry.

This chapter utilizes major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^- , SO_4^{2-}, NO_3^-) and high-frequency physicochemical measurements (pH, water temperature, dissolved oxygen and total dissolved solids) to characterize stream chemical variability at diel (i.e. 24 h period), day-to-day and event time scales. Combined, Chapters 2 and 3 provide valuable insight into spatial and temporal hydrochemical dynamics on Marion Island.

The structure of these two chapters as scientific papers, with separate abstracts, acknowledgments and references, has been preserved. Given the nature and location of this study, there exists some similarity of material between certain sub-sections. This gives rise to some degree of repetition that would otherwise not have been included. However, where overlap does exist, effort has been made to modify the material to support and substantiate the results and findings of the relevant chapter.

Chapter 4 presents a synthesis of the main findings of this thesis and discusses them in relation to the aims and objectives identified in this introductory chapter. Furthermore, challenges associated with carrying out research in a harsh sub-Antarctic environment are identified. Lastly, limitations and challenges encountered in this study as well as possible future research opportunities are commented on.

References

Ansorge, I.J., Lutjeharms, J.R.E., 2002. The hydrography and dynamics of the ocean environment of the Prince Edward Islands (Southern Ocean). Journal of Marine Systems 37, 107-127.

Böning, C.W., Dispert, A., Visbeck, M., Rintoul, S.R., Schwarzkopf, F.U., 2008. The response of the Antarctic Circumpolar Current to recent climate change. Nature Geoscience 1, 864-869.

Chown, S.L., Froneman, P.W., 2008. The Prince Edward Islands. Land-sea interactions in a changing ecosystem. Sun Press, Stellenbosch, South Africa.

Easterling, D.R., Meehl, G.A., Parmesan, C., Changnon, S.A., Karl, T.R., Mearns, L.O., 2000. Climate extremes: observations, modeling, and impacts. Science 289, 2068-2074.

Frich, P., Alexander, L.V., Della-Marta, P., Gleason, B., Haylock, M., Tank, A.K., Peterson, T., 2002. Observed coherent changes in climatic extremes during the second half of the twentieth century. Climate Research 19, 193-212.

Hannah, D.M., Brown, L.E., Milner, A.M., Gurnell, A.M., McGregor, G.R., Petts, G.E., Smith, B.P., Snook, D.L., 2007. Integrating climate–hydrology–ecology for alpine river systems. Aquatic Conservation: Marine and Freshwater Ecosystems 17, 636-656.

Hodgson, D.A., Graham, A.G., Roberts, S.J., Bentley, M.J., Cofaigh, C.Ó., Verleyen, E., Vyverman, W., Jomelli, V., Favier, V., Brunstein, D., Verfaillie, D., Colhoun, E.A., Saunders, K.M., Selkirk, P.M., Mackintosh, A., Hedding, D.W., Nel, W., Hall, K., McGlone, M.S., van der Putten, N., Dickens, W.A., Smith, J.A., 2014. Terrestrial and submarine evidence for the extent and timing of the Last Glacial Maximum the onset of deglaciation on the maritime-Antarctic and sub-Antarctic islands. Quaternary Science Reviews 100, 137-158.

IPCC., 2013. Climate Change 2013: The physical science basis. contribution of working Group I to the fifth assessment report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Jones, P.D., Briffa, K.R., 1992. Global surface air temperature variations during the twentieth century: Part 1, spatial, temporal and seasonal details. The Holocene 2, 165-179.

Karl, T.R., Trenberth, K.E., 2003. Modern global climate change. Science 302, 1719-1723.

Kwok, R., Comiso, J.C., 2002. Southern Ocean climate and sea ice anomalies associated with the Southern Oscillation. Journal of Climate 15, 487-501.

Mann, M.E., Bradley, R.S., Hughes, M.K., 1998. Global-scale temperature patterns and climate forcing over the past six centuries. Nature 392, 779-787.

Milner, A.M., Brown, L.E., Hannah, D.M., 2009. Hydroecological response of river systems to shrinking glaciers. Hydrological Processes 23, 62-77.

Pielke, R.A., Marland, G., Betts, R.A., Chase, T.N., Eastman, J.L., Niles, J.O., Running, S.W., 2002. The influence of land-use change and landscape dynamics on the climate system: relevance to climate-change policy beyond the radiative effect of greenhouse gases. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences 360, 1705-1719.

Prowse, T.D., Wrona, F.J., Reist, J.D., Gibson, J.J., Hobbie, J.E., Lévesque, L.M., Vincent, W.F., 2006. Climate change effects on hydroecology of Arctic freshwater ecosystems. AMBIO: A Journal of the Human Environment 35, 347-358.

Selkirk, P.M., 2007. The nature and importance of the sub-Antarctic. In Papers and Proceedings of the Royal Society of Tasmania 141, 1-6.

Shindell, D.T., Schmidt, G.A., 2004. Southern Hemisphere climate response to ozone changes and greenhouse gas increases. Geophysical Research Letters 31.

Thompson, D.W., Solomon, S., 2002. Interpretation of recent Southern Hemisphere climate change. Science 296, 895-899.

Turner, J., G.J. Marshall. 2011. Climate change in the polar regions. Cambridge, Cambridge University Press.

Turner, J., Barrand, N.E., Bracegirdle, T.J., Convey, P., Hodgson, D.A., Jarvis, M., Jenkins, A., Marshall, G., Meredith, M.P., Roscoe, H., Shanklin, J., 2014. Antarctic climate change and the environment: an update. Polar Record 50, 237-259.

Woodward, G., Perkins, D.M., Brown, L.E., 2010. Climate change and freshwater ecosystems: impacts across multiple levels of organization. Philosophical Transactions of the Royal Society B: Biological Sciences 365, 2093-2106.

Chapter 2: Isotopic composition of precipitation and stream water on sub-Antarctic Marion Island

Abstract

Hydrological systems on remote and isolated maritime sub-Antarctic islands are important indicators of early and subtle signals in response to climatic change. Small sub-Antarctic watersheds are characterized by a high degree of sensitivity, making them valuable research environments. This study reports on the δ^2H and $\delta^{18}O$ isotope composition of precipitation and stream water from sub-Antarctic Marion Island, South Africa. δ^2H and $\delta^{18}O$ values of monthly research stationfor the period 1961 - 2013 were extracted from the Global Network of Isotopes in Precipitation database. Stream water samples were collected over a 16-day sampling campaign from the Soft Plume River, Marion Island. Precipitation weighted reduced major axis regression yielded a local meteoric water line (LMWL) defined by the compositional variation of precipitation has the equation $\delta^2H = 8.35\delta^{18}O + 11.49$. Comparison of precipitation δ^2H and $\delta^{18}O$ from other sub-Antarctic islands suggest that although local factors influence the isotopic composition of precipitation on each island, differences between islands are defined by their latitudinal position. Stream water $\delta^{18}O$ was lower than monthly averaged precipitation $\delta^{18}O$ and exhibited less variability. Stream water δ^2H and $\delta^{18}O$ values range from -48.0‰ to -33.6‰ and from -7.6 ‰ to – 5.6‰, respectively. Samples along the length of the stream showed no statistically significant difference in δ^2H and $\delta^{18}O$ values. However, variability in stream water δ^2H and $\delta^{18}O$ was largest at the highest altitude site in response to rainfall inputs. This seems to be driven by the "amount effect" associated with an altitudinal precipitation gradient, with higher rainfall amounts falling at the highest site compared to the lower site. Together, the results provide insight into the influence of remote and local processes on precipitation and stream water δ^2H and $\delta^{18}O$ on Marion Island.

Keywords: Hydrogen and oxygen isotopes, isotope hydrology, local meteoric water line, "amount effect"

2.1 Introduction

Islands in the sub-Antarctic are some of the most pristine remaining places in the world, where human activities and impacts are often limited to research stations. Few areas of the world still exhibit comparably undistrubed hydrology, enhancing the worth of this locality for the investigation of various topics, especially those related to natural processes occurring in the environment (Lecomte et al., 2016).

Hydrological systems (i.e. streams and lakes) in the sub-Antarctic are important indicators for identifying early and subtle signals in response to climatic change (Convey et al., 2009). This is because numerous terrestrial and hydrological processes respond to even small changes in climate (Prowse et al., 2006). Small watersheds are characterized by a high degree of sensitivity, making them valuable and unique research environments (Yde et al., 2016).

Given the observed warming and drying trends in air surface temperature and precipitation on Marion Island (Smith and Steenkamp, 1990; Smith, 2002; Rouault et al., 2005; Le Roux and McGeoch, 2008), coupled with changes in the relative intensity and frequency of mid-latitude synoptic systems (Turner et al., 2014), there is a need to examine past and current hydrochemical conditions. Findings ought to provide information on how these systems may potentially respond to future climatic change (van Geldern et al., 2014).

The stable isotope (δ^2H and δ^{18}O) composition of precipitation can provide valuable insight into processes in climate and hydrology (Stumpp et al., 2014). The isotopic composition of precipitation is regarded as an effective proxy for large-scale climatic patterns (Klaus et al., 2015), as both δ^2H and δ^{18}O vary spatially and temporally, depending on various geographic, environmental and atmospheric conditions (Ingraham, 1998). These factors (see Table 2.1), or isotope effects, are responsible for the fractionation of isotope ratios in precipitation and surface water (Callow et al., 2014).

Based on equilibrium and kinetic fractionation processes in the atmosphere, there is a strong correlation between δ^2H and δ^{18}O in precipitation (Dansgaard, 1964), and in a plot of δ^2H vs δ^{18}O , the line of best fit is referred to as the Global Meteoric Water Line (hereafter, GMWL; Craig, 1961; $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$). This relationship has since been refined by Rozanksi et al. (1993) using the results from the IAEA/WMO Global Network of Isotopes in Precipitation (GNIP) database: $\delta^2\text{H} = (8.20 \pm 0.07)\ \delta^{18}\text{O} + (11.27 \pm 0.65)$. Local meteoric water lines (LMWLs) deviate from the GMWL in both slope and intercept because of different climatic and geographic influences (Clark and Fritz, 1997). The slope of a LMWL differs depending on the temperature of condensation, which changes during rain out. Additionally, shallower slopes of the LMWL may be the result of sub-cloud evaporation that occurs after condensation (Liebminger et al., 2006).

Additional insight into water vapour source region and evaporative processes can be retrieved from deuterium excess (*d*), where, for a single sample, $d = \delta^2H - 8\delta^{18}O$ (Dansgaard, 1964). Deuterium excess varies in response to environmental changes that cannot be inferred from δ^2H and $\delta^{18}O$ alone (Liebminger et al., 2006). Physical conditions at the moisture source of precipitation determine the degree of kinetic fractionation that occurs with processes such as evaporation from the ocean to the atmosphere (Merlivat and Jouzel, 1979; Uemura et al., 2008).

The δ^2H and $\delta^{18}O$ composition of precipitation on oceanic islands usually display a weak relationship with both temperature and precipitation amount as they are close to the moisture source (Dansgaard, 1964; Aggarwal et al., 2012; Hughes and Crawford, 2012). Islands in the maritime sub-Antarctic are strongly influenced by synoptic low-pressure or mid-latitude cyclonic systems, embedded in the Southern Hemisphere Westerly Winds (Shulmeister et al., 2004; Hodgson et al., 2014). The dominance of westerly air flow and mid-latitude cyclonic (low-pressure) systems at these locations creates a relationship between the proportion of rain-out and rainfall intensity (Treble et al., 2005; Barras and Simmonds, 2008). Low δ^2H and $\delta^{18}O$ values have been observed in mid-latitude low-pressure cyclonic systems (Gedzelman et al., 1987; Gedzelman and Lawrence, 1990; Lawrence and Gedzelman, 1996; Callow et al., 2014), due to isotopic distillation occurring in these systems. In cyclonic systems, water condensed at high altitudes incorporates surrounding water vapour, which may already have low isotope values due to prior condensation, into the system (Dansgaard, 1964; Treble et al., 2005). The lowest δ^2H and $\delta^{18}O$ values tend to occur in the centre of a well-developed low pressure system (Gedzelman and Arnold, 1994). As a result, the δ^2H and $\delta^{18}O$ of precipitation measured at a single site is strongly associated with the proximity of the mid-latitude cyclonic system in relation to it (Lawrence et al., 1982; Gedzelman and Lawrence, 1990).

Coupled with precipitation, δ^2H and $\delta^{18}O$ in stream water provide complementary information that enables a more thorough understanding of hydrological systems in a specific environment (Lachniet and Patterson, 2009). The isotopic composition of surface water often matches that of precipitation, with the additional benefit of stream water δ^2H and $\delta^{18}O$

considered a spatially and temporally integrated isotopic signal that can reflect multiple environmental and hydrological processes (Kendall and Coplen, 2001). However, this is not always the case as there can be differences between the isotopic composition of stream water and precipitation because of numerous environmental and geographical factors (Dutton et al., 2005).

Water in most streams comprise of two main components, namely, recent precipitation that reaches the stream by surface runoff or subsurface paths, and groundwater (Kendall and Coplen, 2001). Depending on the size and geomorphological characteristics of the catchment, a variety of hydrological processes may affect the catchment and river water flow (Halder et al., 2015). Variations in stream water $\delta^{2}H$ and $\delta^{18}O$ is strongly dependent on elevation within a catchment, with high-elevation headwaters generally having low $\delta^{2}H$ and $\delta^{18}O$ values compared to lower elevation sections of a river, except under altitudinal gradients of less than 200 m (e.g. Longinelli and Edmond, 1983; Ramesh and Sarin, 1992; Pawellek et al., 2002; Dutton et al., 2005).

Streams with low residence times in smaller catchments are generally affected more directly by recent precipitation events when compared with large river catchments (Salati et al., 1979; Bershaw et al., 2012). Variations in moisture source origins or synoptic types are reflected in river water $\delta^{2}H$ and $\delta^{18}O$ (Kendall and Coplen, 2001; Lachniet and Patterson, 2009; Darling and Bowes, 2016). The isotopic composition of stream water in small catchments is, therefore, able to provide information pertaining to specific climatic processes that directly and rapidly influence the hydrology of the catchment.

This study reports $\delta^{2}H$ and $\delta^{18}O$ values of both precipitation and stream water from sub-Antarctic Marion Island, South Africa. The aim of this research is to gain insight into the variability and controls on the $\delta^{2}H$ and $\delta^{18}O$ composition of precipitation and stream water on sub-Antarctic Marion Island. To achieve this, this study draws on data extracted from the Global Network of Isotopes in Precipitation (GNIP) database and the results of stream water sampling over a single field campaign in April/May 2015. Precipitation and stream water $\delta^{2}H$ and $\delta^{18}O$ values from this study highlight key mechanisms that influence the isotope hydrology on Marion Island.

Table 2.1. Details of select physical processes or isotope effects that influence the isotopic composition of precipitation.

Isotope effect	Description	References
Amount	An apparent anticorrelation between the amount of precipitation and its isotopic composition. Initial rainfall will have the lowest isotope values because of preferential rainout out of the heavy isotope and thereafter become progressively higher.	Dansgaard (1964), Rozanski et al. (1993), Lee and Fung (2008)
Altitude	When air masses are lifted orographically, they cool and as a result, the isotopic composition of the subsequent rainfall is preferentially enriched with heavier isotopes. Because of this, precipitation at a higher altitude will have relatively lower isotope values.	Ambach et al. (1968), Siegenthaler and Oeschger (1980), Gonfiantini et al. (2001), Poage and Chamberlain (2001), Vreca et al. (2006), Liebminger et al. (2006)
Latitude	Generally, isotope values in precipitation become lower as water vapour moves towards the poles. Poleward transfer of water vapour associated with rain-out, which results in the low isotope values.	Dansgaard (1964), Rozanski et al. (1993), Bowen and Revenaugh (2003), Feng et al. (2009).
Temperature	Empirical relationship observed between annual averages of isotopes in precipitation and mean air surface temperature. This relationship is based on temperature distillation processes in the atmosphere.	Craig (1961), Dansgaard (1964), Rozanski et al. (1993), Kohn and Welker (2005).

2.2 Study area

2.2.1 Regional setting

Marion Island (46°54′S and 37°51′E) is a sub-Antarctic island, part of the Prince Edward Islands (PEI) (Fig. 2.1), consisting of a peak of a shield volcano situated in the Indian sector of the Southern Ocean (Verwoerd, 1971). The island has an area of ± 290 km^2 with peak elevation (Mascarin peak) at 1240 m above mean sea level (hereafter, a.m.s.l) (McDougall et al., 2001). From the central plateau, the eastern and northern sectors slope gently towards an undulating coastal plain, ~5 km wide. On the western and southern sectors of the island, the coastal plain is narrower (~900 m wide) and is met by a steep escarpment that rises to the interior (Conradie and Smith, 2012). The island consists primarily of basaltic lava (le Roex et al. 2012).

2.2.2 Climate

Marion Island's hyper-maritime position within the Polar Frontal Zone (PFZ) results in a distinct climatic regime (Schulze, 1971; Smith, 1987). Synoptic climate for the island is characterized by mid-latitude cyclones, frontal systems and anti-cyclones (Appendix Figure A1, 2; Vowinkel, 1954; Rouault et al., 2005). Mid-latitude cyclones that influence the islands climate develop and propagate in the South Atlantic under strong meridional oceanic and atmospheric temperature gradients (Petterssen and Smebye, 1971; Nel, 2012). These cyclones make their way from west to east, embedded in the westerly storm track (Ansorge et al., 2005). An approaching cyclone brings with it pre-cyclonic weather conditions that are characterized by an increase in strength in winds from the north-westerly direction, more dense cloud cover and an influx of warm sub-tropical air that results in an increase in temperature. In the post-cyclonic stage, the island experiences a shift in wind direction to the south-west, clearer skies and an influx of cool, dry air that tends to decrease the temperature (Nel, 2012).

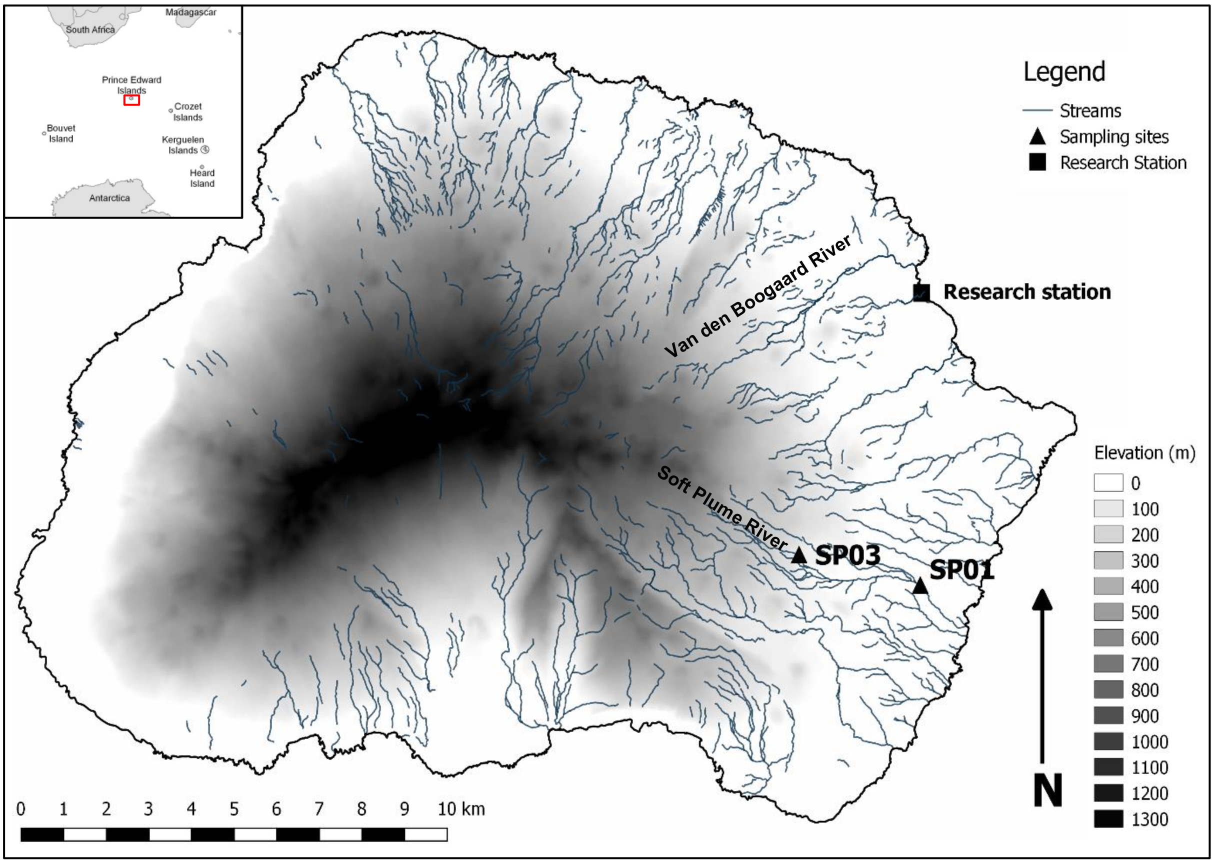


Figure 2.1. Map of sampling locations (SP03, ~255 m a.m.s.l; SP01, ~105 m a.m.s.l) along the Soft Plume River (SPR) on Marion Island. All streams (perennial and non-perennial) are included for reference. Inset: location of the Prince Edward Islands (PEI) in relation to other sub-Antarctic Islands and major landmasses.

Over the period of this study, weather conditions were typical for mean winter conditions on the island (Schulze, 1971). Precipitation fell on 12 out of 16 days with an hourly mean amount of 0.7 mm h^{-1} (Fig. 2.2). The longest duration where no rainfall fell was 59 hours (~2.5 days) and occurred between 22/04/2015 22:00 GMT + 3 and 25/04/2015 08:00 GMT + 3. Rainfall with the highest intensity (6.2 mm h^{-1}) fell at 17:00 GMT + 3 on 22/042015. Rainfall with maximum intensity coincided with mean sea level pressure (hereafter, MSLP) of 994.6 hPa. The decrease in MSLP with rainfall indicates that most rainfall was associated with mid-latitude low-pressure cyclonic systems, with lower MSLP associated with more intense cyclones passing directly over the island (Appendix Figure A1, 2; Sinclair, 1995).

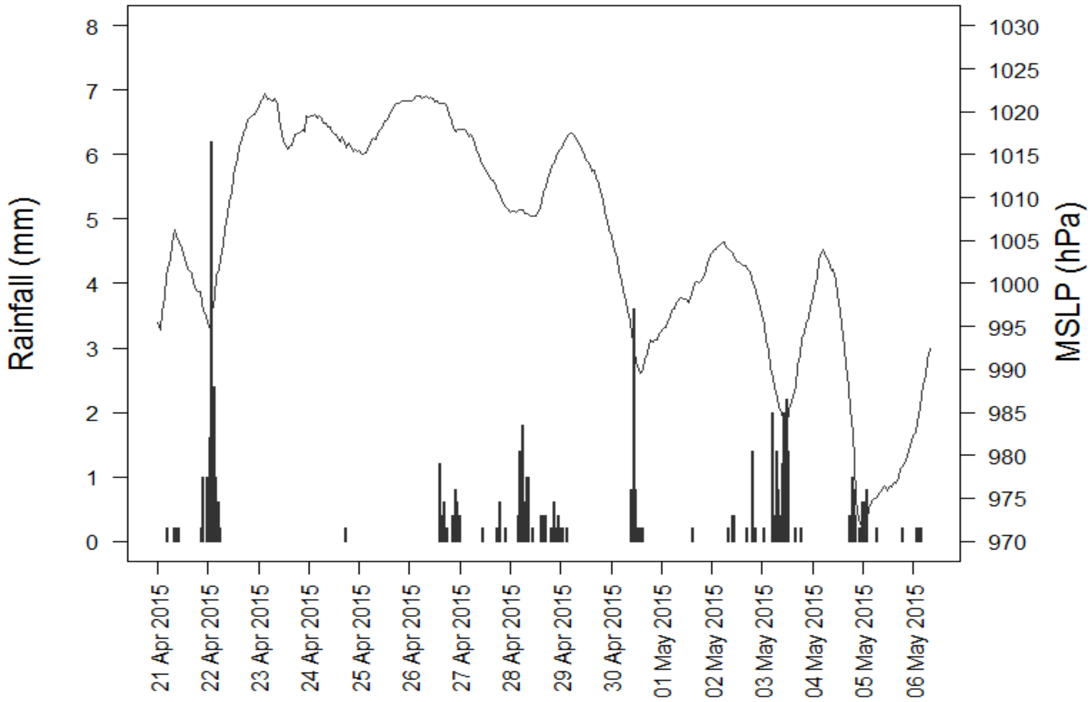


Figure 2.2. Hourly recordings of rainfall (bars) and mean sea level pressure (MSLP; line) over the period 21/04/2015 – 06/05/2016. All data were recorded at the research station on Marion Island.

2.2.2 Soft Plume River

The catchment of the Soft Plume River (hereafter, SPR) is small (~5.26 km^2) and located on the eastern side of Marion Island (Fig. 2.1). Elevation in the catchment varies between ~650 m a.m.s.l. at the lava peaks and ~15 m a.m.s.l where the river enters the ocean. Perennial streams are uncommon on the island as the precipitation infiltrates the porous lavas and reaches the sea as ground water (Verwoerd, 1971; Dartnall and Smith, 2012). Where streams flow, they are often intermittent with only a few exceptions. The SPR is only one of two perennial rivers (the other being Van den Boogaard River) present on the island (Grobbelaar, 1978), although, Dartnall and Smith (2012), suggest non-perennial flow of the Van den Boogaard River has been observed. The upper reaches of the SPR is characterized by narrow channels with banks of low-gradient. At lower reaches the river channel becomes increasingly incised with more turbulent, higher velocity flow. The vegetation along the banks of the river is dominated by the alien grass *Poa annua*, which often grows submerged together with filamentous algae (Gremmen and Smith, 2004).

2.3 Methods and Data

2.3.1 Precipitation δ^2H and δ^{18}O

The δ^2H and δ^{18}O values of precipitation were extracted from The Global Network of Isotopes in Precipitation (GNIP) database. The GNIP database comprises an electronic holding of precipitation isotope, associated geographical and precipitation data (Aggarwal et al., 2010).δ^2H and δ^{18}O values are available online, through the Water Isotope System for Data Analysis, Visualization and Electronic Retrieval (WISER) accessible at the IAEA web site: http://www.iaea.org/water (IAEA/WMO, 2016). All precipitation δ^2H and δ^{18}O data used in this study are presented as supplementary material (Appendix Table B).

As part of the GNIP programme, precipitation samples collected at the research station on Marion Island (Fig. 2.1), have been analysed for their δ^2H and δ^{18}O composition. The research station is operated by the South African Weather Service (SAWS) and is situated on the eastern side of Marion Island (46 °53′S, 37°52′E, 24 m a.m.s.l; Fig. 2.1). Precipitation is collected manually in a standard rain gauge following the IAEA/GNIP protocol. The rain gauge is situated 1.2 m above the ground, with no structures nearby. The collector is emptied manually daily at 05:45 GMT + 3. The collected water is emptied into a HPDE bottle containing the composite monthly sample and stored in a dark, cool place. Since the beginning of the GNIP program on the island, precipitation samples have been analyzed by various laboratories (see raw dataset, accessible at: http://www.iaea.org/water) using different analytical methods. Therefore, the analytical uncertainty of measurements for each sample is not known, but can be assumed to be on the order 2.0‰ and 0.2‰ for δ^2H and δ^{18}O respectively (Halder et al., 2015). Only 7.5% of the 199 samples had d-excess values less than 0‰, suggesting that samples have not undergone significant secondary evaporation (Puntsag et al., 2016).

Over the period 1961 to 2013, missing values resulted in a differing number of data for δ^2H and δ^{18}O. Only samples where both δ^2H and δ^{18}O were available for a single sample were retained ($n = 185$). In addition, all samples with a d-excess less the 3 ‰ ($n = 23$) were removed from the data set. This value is the equivalent value of evaporating ocean water at 20-30 °C and 95% relative humidity (Merlivat and Jouzel, 1979) and has been used elsewhere as a conservative cut-off point (e.g. Hughes and Crawford, 2012). However, it should be noted that selective removal of data can have a considerable influence on the slope and intercept of LMWLs (Hughes and Crawford, 2012).

2.3.2 Meteorological data

All climate data used in this study was recorded at the research station on the islands and provided for use by SAWS. For long term data (1961 – 2013), daily temperature data (determined from hourly recordings) were used to calculate monthly means. Similarly, daily total precipitation amounts (measured from 06:00 GMT + 3 to 06:00 GMT + 3 the following day) were used to determine monthly averages. Precipitation is suggested to comprise mostly of rainfall (Smith, 2002). However, it is possible that limited amounts of snow and hail may contribute to precipitation measurements (Le Roux and McGeoch, 2008). Over the period of this study (21/04/2015 – 06/05/2015), weather conditions were established using hourly recordings of total daily rainfall and MSLP.

2.3.3 Stream water sample collection

Daily sampling was conducted over a 16-day period (April 21 – May 6 2015) at two locations along the SPR (Fig. 2.1; SP03 and SP01). SP03 and SP01 are at altitudes of ~255 m and ~105 m a.m.s.l respectively and ~ 2.9 km apart. Sampling took place at approximately the same time each day (SP03, ~10:00 GMT + 3; SP02, 10:30 GMT + 3; SP01, 11:00 GMT + 3). All stream-water samples for stable isotope analysis were collected as grab samples. Samples were collected in 60 ml glass bottles. Sample bottles were rinsed three times with sample water before final collection. The rinsed bottles were filled to the brim to ensure that no air space was present and sealed tightly. Samples were returned immediately to the lab on Marion Island where they were given an additional seal of Parafilm® (Bemis Flexible Packaging, Neenah, WI 54956, USA) to prevent any potential evaporation. Water samples were stored in the dark, at 4 °C to avoid any potential contamination or isotopic fractionation through evaporation and gas-diffusion.

2.3.4 Stream water sample analysis

All samples were analysed for oxygen and hydrogen stable isotopes at the Geological Science Laboratory, University of Cape Town, according to protocol of Harris et al. (2010). Oxygen was analysed using the CO_2 equilibration method of Socki et al. (1992) with pre-evacuated glass vials (7 ml). Hydrogen was analysed using the closed-tube-Zn-reduction method, whereby sample water was converted to H_2 using disposable aliquots of Zn in individual reaction vessels (Coleman et al., 1982). A microcapilliary tube containing 2 mg of water was placed into a Pyrex containing 100 mg of Indiana Zn (Schimmelman and DeNiro, 1993). The Pyrex tube was then attached to the vacuum line, frozen in liquid nitrogen, evacuated and then sealed using a torch. Once a sufficient number of samples had been prepared, the batch was placed in a furnace at 450 °C, allowing the sample to reduce to H_2. Isotope ratios of CO_2 and H_2 were measured using a ThermoFinnigan DELTA^{plus} XP mass spectrometer in dual inlet mode. A fractionation factor of 1.0412 between CO_2 and water was used to convert raw CO_2 $\delta^{18}O$ values to those of water (Coplen, 1993).

The isotope ratios are expressed in the δ notation, where:

$$\delta X = [(Rsample / Rstandard) – 1] \times 10^3 ‰$$

X is ^{18}O or ^{2}H and Rsample and Rstandard are the ratios of heavy to light isotope in the sample and standard respectively. All δ^2H and $\delta^{18}O$ values are reported relative to SMOW. Two internal standards were analysed in duplicate (O) or triplicate (H) with each batch of samples. These standards, CTMP2010 and RMW have calibrated δ^2H and $\delta^{18}O$ values of -7.4 and -2.74‰, and -131.4 and – 17.38‰, respectively, and the values obtained were used to convert raw data to the SMOW scale and to correct for scale compression. The precision of analyses, determined by repeat measurements of standard materials, was better than 2.0‰ and 0.2‰ for δ^2H and $\delta^{18}O$, respectively.

2.4 Results

2.4.1 Precipitation δ^2H and $\delta^{18}O$

2.4.1.1 Time series and seasonal cycle

To provide an understanding of the seasonal variation in rainfall $\delta^{18}O$ values and associated meteorology, statistical analysis of GNIP data and climatological data from the research station on Marion Island was carried out. A time series (1961 – 2013) of bulk monthly precipitation and mean monthly average and maximum air surface temperature is plotted in Figure 2.3a. Mean monthly precipitation is 183.6 ± 13.48 mm, with average maxima (204.13 mm) and minima (163.25 mm) occurring in May and October respectively. There is a relatively small annual range (40.88 mm). Average and maximum air temperatures exhibit a distinct seasonal cycle with maxima and minima occurring in summer and winter respectively (Fig.

2.3a). The annual range for both average (4.30 °C) and maximum (4.7 °C) air temperature is relatively small.

Seasonal variability of monthly precipitation $\delta^{18}O$ is plotted in Figure 2.3b. There is inter-annual variability in $\delta^{18}O$ values present over the entire time series. Trends in $\delta^{18}O$ were not identified due to the large uncertainties associated with substantial amounts of missing data (see Section 2.3.1). A time series of $\delta^{2}H$ over the same period (not plotted here) shows a similar pattern of inter-annual variability with more frequent and larger periods of missing data. The tendency for $\delta^{2}H$ to be less frequently measured has been observed for other GNIP stations (Lachniet and Patterson, 2009). Figure 2.3b illustrates $\delta^{18}O$ peaks are more depleted from the beginning of the record up until ~1990. Following this, peaks in $\delta^{18}O$ become progressively dampened through time.

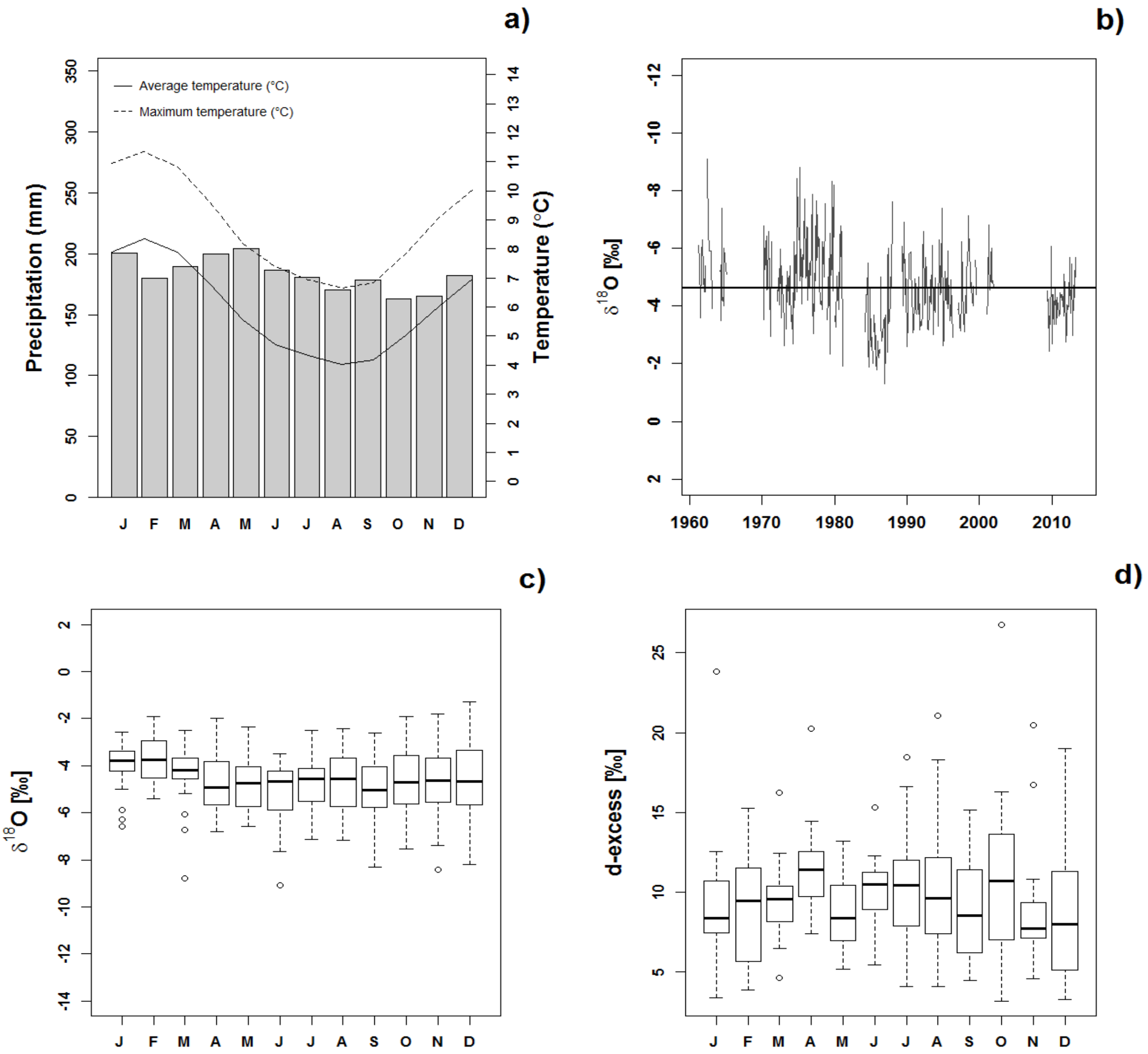


Figure 2.3. a) Total monthly precipitation (bars), average monthly surface temperature (solid line) and average monthly maximum surface temperature (dashed line). Climate data are from the period 1961 – 2013. b) Time series of monthly averaged $\delta^{18}O$ values of precipitation from Marion Island. Samples are from the period 1961-2013. The solid horizontal line represents the mean (-4.61‰; n = 177) calculated over the available period. c) Boxplots of seasonal variation in $\delta^{18}O$. d) Boxplots of d-excess seasonal variation. The boxes for all boxplots are bounded by lower and upper quartile limits, with the central line within the box representing the median values. Whiskers extend to the most extreme values within 1.5 times the interquartile range. Outliers are displayed by open dots.

A time series of $\delta^{18}O$ and *d*-excess is presented in Figures 2.3c and d respectively. Generally, $\delta^{18}O$ values for spring and early summer precipitation are more variable. There is no obvious seasonality present in precipitation $\delta^{18}O$ at Marion Island. Higher median $\delta^{18}O$ values tend to occur in some summer months. The annual range for $\delta^{18}O$ is 1.53‰. The unweighted *d*-excess values for the yearly cycle are plotted in Figure 2.3d. The distribution of *d*-excess values is relatively uniform throughout the entire yearly cycle. The pattern of variability in d-excess is similar to that of $\delta^{18}O$ (Fig. 2.3c), with a larger degree of variability occurring in spring and early summer months.

2.4.1.2 Local meteoric water lines

Local meteoric water lines (LMWLs) for Marion Island were determined using three regression models: ordinary least squares regressions (OLSR) (IAEA, 1992), major axis ordinary least squares regression (MA) and reduced major axis regression (RMA) (Argiriou and Lykoudis, 2006). In addition, weighting of each of the regression models was done to account for the potential influence of smaller precipitation amounts (Hughes and Crawford, 2012). Precipitation weighted regressions (PWLSR, PMA and PWLSR) were determined following Hughes and Crawford (2012) and Crawford et al. (2014). The slopes and intercepts of the LMWLs, using the different weighted and unweighted regression models, are presented in Table 2.2. The average root mean sum of standard errors ($rmSSE_{avg}$) was also calculated for each regression model following the equation of Crawford et al. (2014), with results presented in Table 2.1. The $rmSSE_{avg}$ is a relative error, with values closer to 1.0 considered a more accurate regression for a data set.

There is an overall agreement between weighted and unweighted regressions. Weighting by precipitation results in a minor increase in both slope and intercept for all of the regression models, with the exception being the slope of the PWLSR. For unweighted (weighted) regression models there was a general trend whereby the smallest slope was produced by the OLSR (PWLSR), followed by the RMA (PWRMA), with the MA (PWMA) producing the largest slope. A similar pattern was observed with the intercepts.

Table 2.2. The slopes and errors, with standard errors for unweighted and weighted regressions. SD; standard deviation, rmSSEavg ; root mean sum of standard errors (averaged) calculated according to Crawford et al. (2014).

Regression	**Slope ± SD**	**Intercept ± SD**	**rmSSE$_{avg}$**
OLSR	7.58 ± 0.26	7.84 ± 1.26	1.04
RMA	8.34 ± 0.26	11.39 ± 1.26	1.02
MA	9.15 ± 0.29	15.18 ± 1.38	1.04
PWLSR	7.56 ± 0.27	7.74 ± 1.31	1.04
PWRMA	8.35 ± 0.27	11.49 ± 1.34	1.02
PWMA	9.2 ± 0.3	15.52 ± 1.44	1.04

Precipitation δ^2H and δ^{18}O data is plotted in Figure 2.4. The unweighted mean δ^2H for monthly averaged precipitation from Marion Island over the period 1961 – 2013 is -27.51‰ ± 9.33‰ and ranged from -64.50‰ to -4.00‰ (n = 177). Mean δ^{18}O is -4.67‰ ± 1.12 with a range from -9.10‰ to -2.43‰ (n = 177).

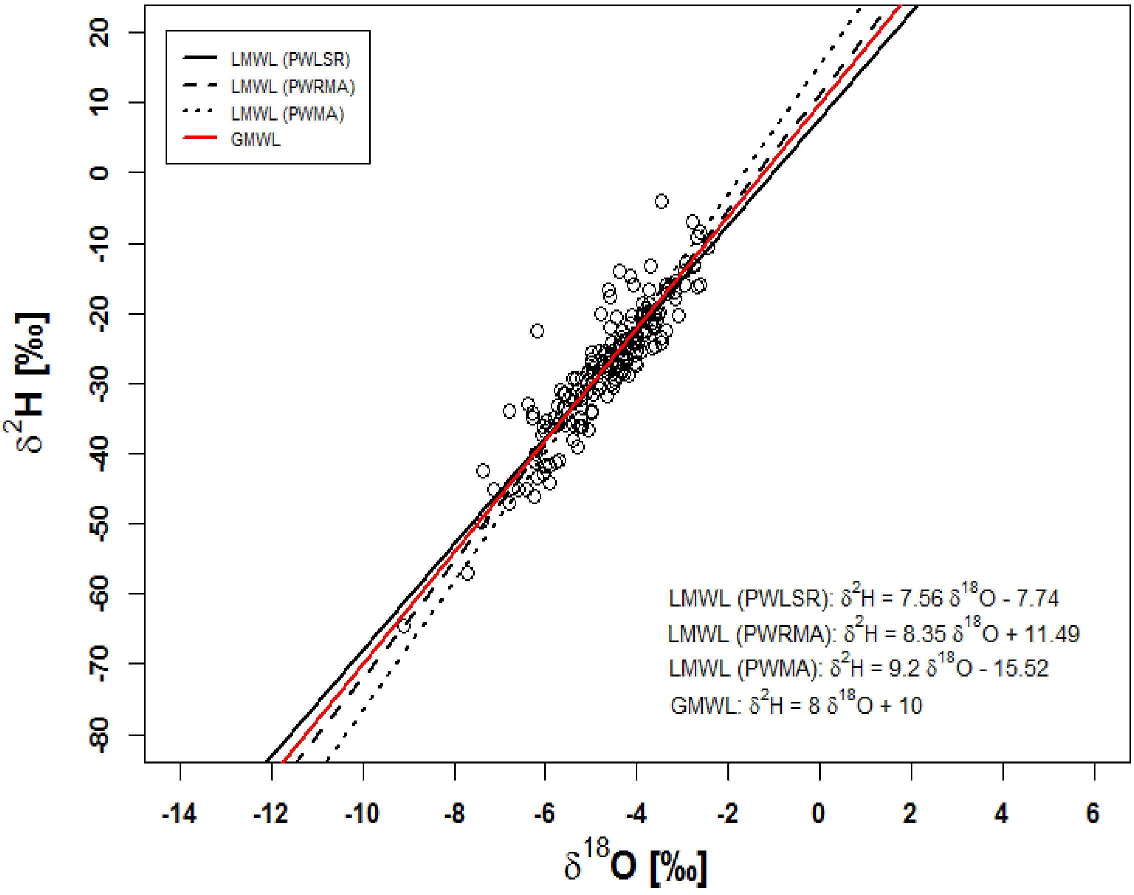


Figure 2.4. Monthly averaged δ^2H vs δ^{18}O values of precipitation from Marion Island. Samples cover the period 1961-2013. Local meteoric water line; LMWL, Global meteoric water line; GMWL. The weighted LMWLs were calculated after Crawford et al. (2014). The GMWL follows the equation determined by Craig (1961).

2.4.1.3 Relationship with meteorological parameters

Figure 2.5a – d illustrates the relationship of unweighted δ^{18}O with different climatic parameters. The strongest correlation is found between δ^{18}O and mean air surface temperature ($r = 0.39$, $p < 0.001$). There is a moderate positive correlation between δ^{18}O and mean monthly maximum surface temperature ($r = 0.37$, $p < 0.001$) air surface temperatures with δ^{18}O. A weak negative correlation exists between δ^{18}O and rainfall ($r = -0.24$, $p < 0.05$).

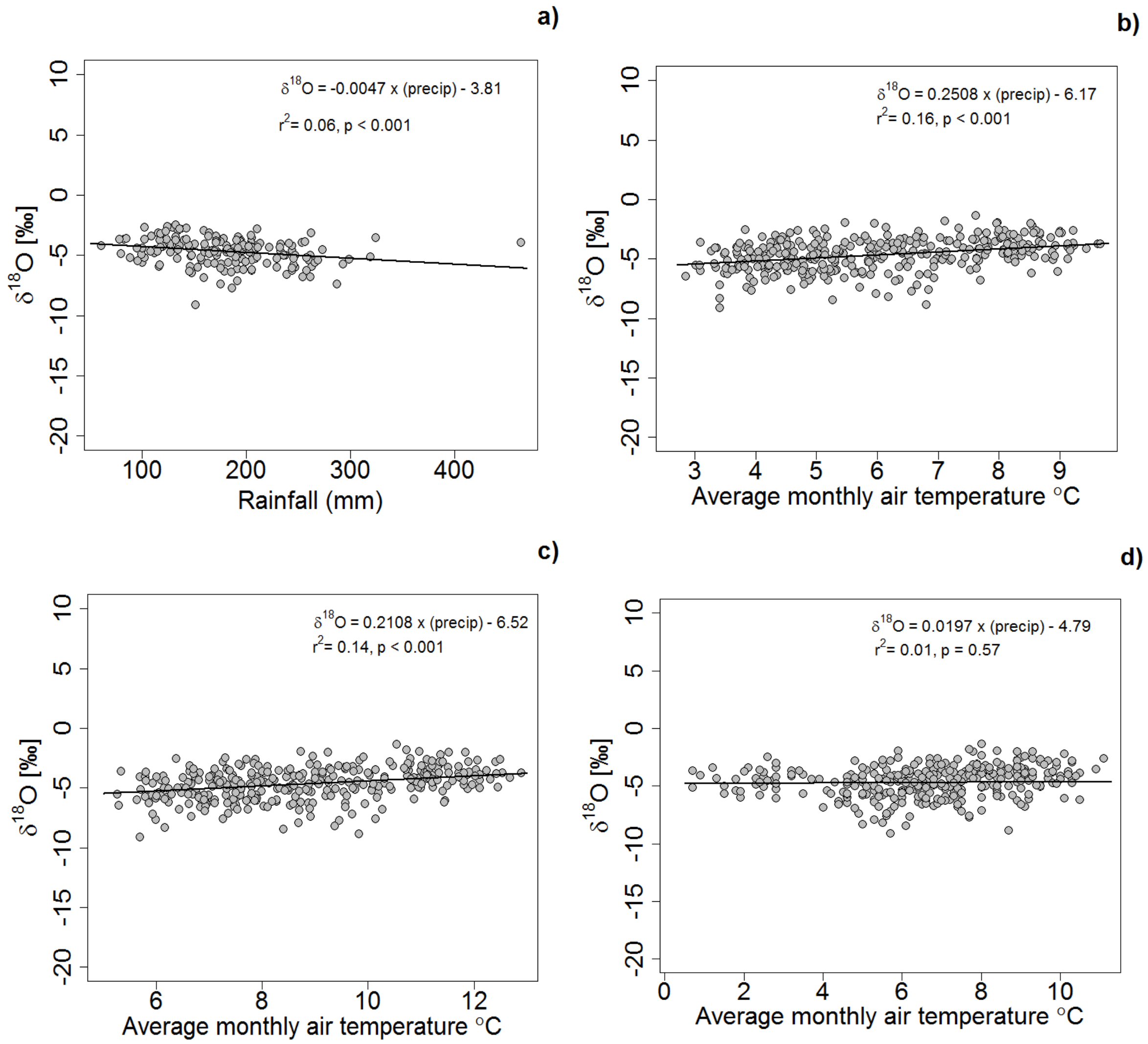


Figure 2.5. Bivariate plot of monthly averaged δ^{18}O against a) total monthly rainfall (mm), b) average monthly air surface temperature (°C), c) average monthly maximum air surface temperature (°C), and d) average monthly minimum air surface temperature (°C).

2.4.1.4 Relation to islands in the maritime sub-Antarctic

Precipitation δ^{2}H and δ^{18}O ((accessible at: http://www.iaea.org/water)) from Marion Island (46.77° S 37.85° E), Gough Island (40.32° S 9.94° W) and Falkland Islands (51.7° S 57.85° W) are plotted in Figure 2.6. Local meteoric water lines for each respective island are also shown on Figure 2.6. Marion Island had weighted mean δ^{2}H and δ^{18}O values of -27.8‰ and -4.5‰. Weighted mean values on Gough Island were -20.5‰ and -3.8‰ for δ^{2}H and δ^{18}O respectively. On Falklands Islands, weighted mean δ^{2}H and δ^{18}O was -58.2‰ and -8.1‰.

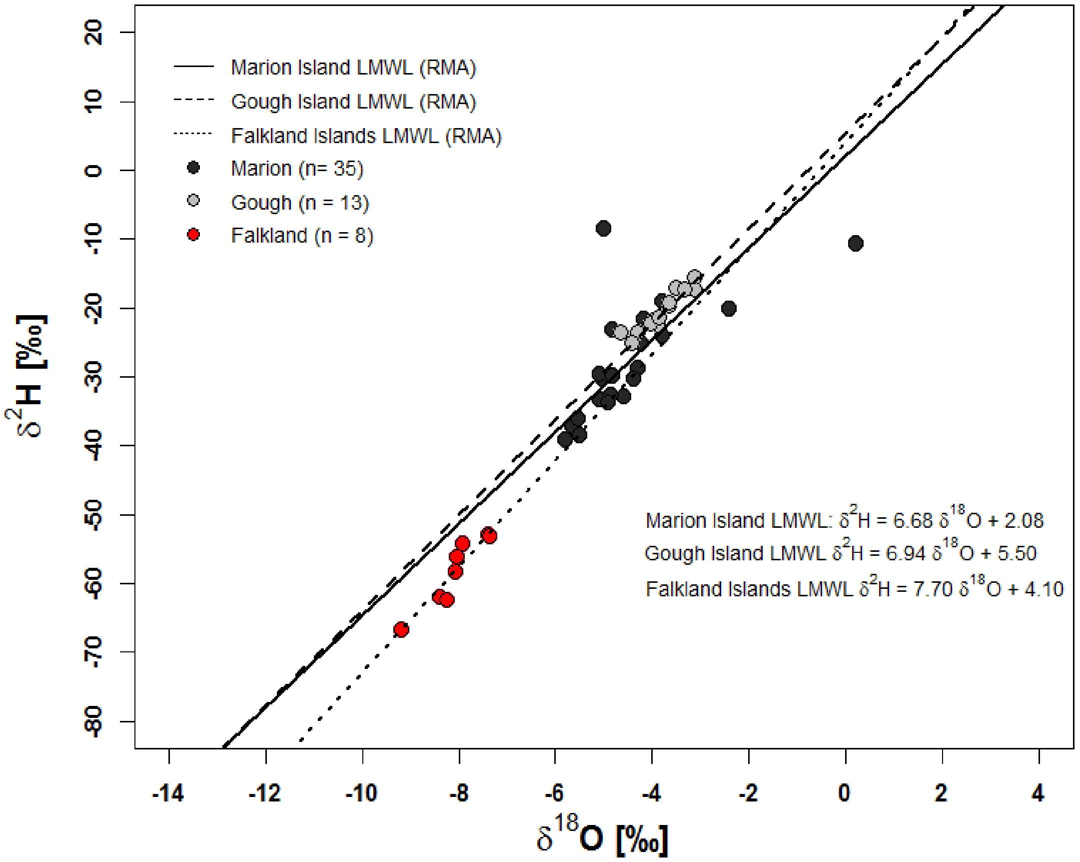


Figure 2.6. Bivariate plot of mean annual precipitation weighted δ^2H and δ^{18}O. Data for Marion Island (1961 – 2013; n = 35), Gough Island (1961 – 2013; n = 13) and Falkland Islands (1961 – 1979). Raw data were extracted from the GNIP database and reduced to precipitation-amount-weighted, mean annual values after Bowen and Wilkinson (2002), to allow for meaningful comparison. Local meteoric water lines (LMWLs) for all islands were determined using reduced major axis (RMA) regressions.

2.4.2 Stream water δ^2H and δ^{18}O

2.4.2.1 Isotopic composition of the Soft Plume River

The δ^2H and δ^{18}O composition of stream water from the SPR is given in Table 2.3. The value of sample SP 24/04/15 020 (-12.05‰; Table 2.3) was omitted due to analytical error, indicated by a shifted δ^{13}C value of the CO_2 gas used for equilibration. Additionally, the δ^2H value (-20.4‰) of sample SP 30/04/15 038 (Table 2.3) was identified as an outlier (2 sigma-criterium; IAEA, 1992) and therefore, removed. Mean δ^2H for all stream water samples is -37.1 ± 3.2‰, with a range from -48.0‰ to -33.6‰ (n = 31). For δ^{18}O, the mean is -6.0 ± 0.41‰ and values range from -7.6 ‰ to – 5.6‰ (n = 31).

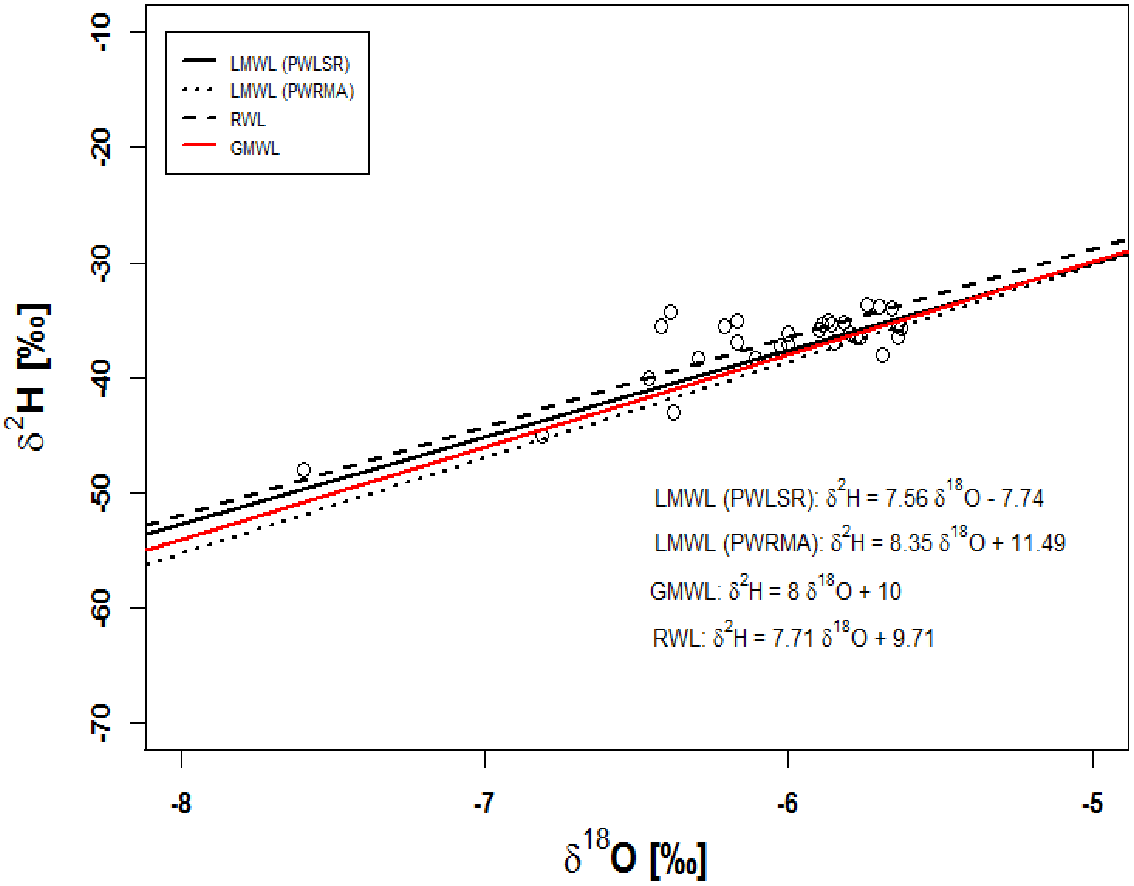


Figure 2.7. δ^2H vs δ^{18}O (‰) of stream water from the Soft Plume River (SPR). Samples (n = 30) were collected daily, over the period 21/04/2015 – 06/05/2015. Local meteoric water line; LMWL, Global meteoric water line; GMWL. The weighted regression LMWL follows the method used by Crawford et al. (2014). The GMWL follows the equation determined by Craig (1961).

The river water line (RWL), sometimes referred to as the surface water line (SWL) (Rock and Mayer, 2007; Lachniet and Patterson, 2009; Timsic and Patterson, 2014), was determined using an unweighted reduced major axis linear regression model (RMA) and an ordinary least squares regression (OLSR). The results of the RMA regression model provided for a RWL equation calculated as $\delta^2H = 7.71\delta^{18}O + 9.71$, whereas for an OLSR it was $\delta^2H = 6.21\delta^{18}O + 0.52$.

Table 2.3. δ^2H and $\delta^{18}O$ (‰) values of stream water from the Soft Plume River (SPR). Sampling sites (SP03, SP01) are indicated on Figure 2.1. "NA" indicates data that has been removed. "/" indicates that the parameter could not be calculated due to missing values.

Site	Date	Sample name	δ^2H	$\delta^{18}O$	d-excess
SP03	21/04/2015	SP 21/04/15 012	-33.8	-5.7	11.8
SP03	22/04/2015	SP 22/04/15 015	-35.4	-5.64	9.72
SP03	23/04/2015	SP 23/04/15 017	-43	-6.38	8.04
SP03	24/04/2015	SP 24/04/15 020	-38.2	NA	/
SP03	25/04/2015	SP 25/04/14 023	-37	-6.17	12.36
SP03	26/04/2015	SP 26/04/15 026	-35.6	-6.21	14.08
SP03	27/04/2015	SP 27/04/15 029	-36.9	-5.85	9.9
SP03	28/04/2015	SP 28/04/15 032	-35.2	-5.82	11.36
SP03	29/04/2015	SP 29/04/15 035	-38	-5.69	7.52
SP03	30/04/2015	SP 30/04/15 038	NA	-5.86	/
SP03	01/05/2015	SP 01/05/15 041	-36.4	-5.64	8.72
SP03	02/05/2015	SP 02/05/15 044	-36.4	-5.78	9.84
SP03	03/05/2015	SP 03/05/15 047	-34	-5.66	11.28
SP03	04/05/2015	SP 04/05/15 050	-48	-7.6	12.8
SP03	05/05/2015	SP 05/05/15 053	-45.1	-6.81	9.38
SP03	06/05/2015	SP 07/05/15 057	-34.3	-6.39	16.82
SP01	21/04/2015	SP 21/04/15/ 014	-33.6	-5.74	12.32
SP01	22/04/2015	SP 22/04/15 016	-35	-6.17	14.36
SP01	23/04/2015	SP 23/04/15 019	-38.4	-6.11	10.48
SP01	24/04/2015	SP 24/04/15 022	-35.4	-5.86	11.48
SP01	25/04/2015	SP 25/04/14 025	-35.7	-5.63	9.34
SP01	26/04/2015	SP 26/04/15 028	-37.2	-6.03	11.04
SP01	27/04/2015	SP 27/04/15 031	-35.8	-5.9	11.4
SP01	28/04/2015	SP 28/04/15 034	-36.1	-5.8	10.3
SP01	29/04/2015	SP 29/04/15 037	-37.1	-6	10.9
SP01	30/04/2015	SP 30/04/15 040	-36.2	-6	11.8
SP01	01/05/2015	SP 01/05/15 043	-35.1	-5.87	11.86
SP01	02/05/2015	SP 02/05/15 046	-35.3	-5.89	11.82
SP01	03/05/2015	SP 03/05/15 049	-36.4	-5.76	9.68
SP01	04/05/2015	SP 04/05/15 052	-40.1	-6.46	11.58
SP01	05/05/2015	SP 05/05/15 055	-38.3	-6.3	12.1
SP01	06/05/2015	SP 07/05/15 059	-35.6	-6.42	15.76

2.4.2.2 Time series

A daily time series of stream water δ^{2}H and δ^{18}O is presented in Figure 2.8a – d. Small variations, often within the range of analytical error associated with δ^{18}O and δ^{2}H, are seen at both sites through the time series.

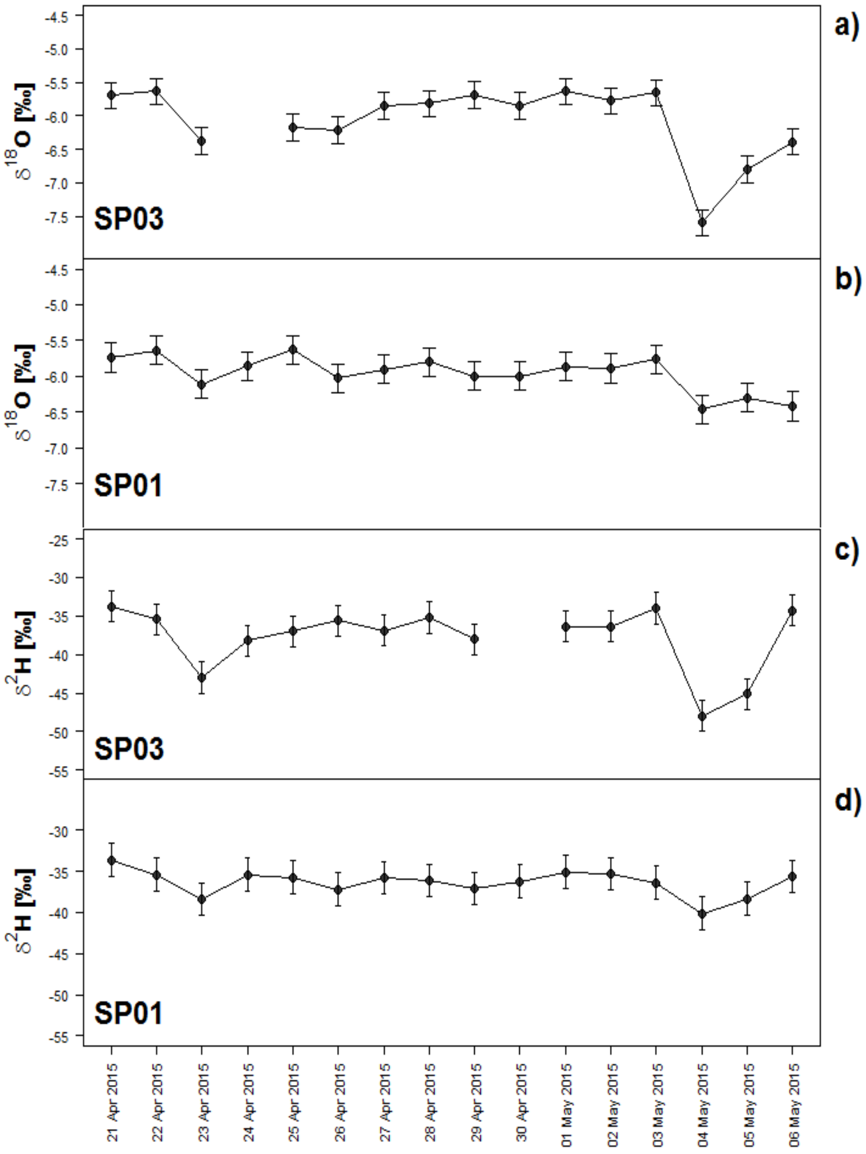


Figure 2.8. Daily time series of δ^{2}H and δ^{18}O in the Soft Plume River (SPR) collected over the period 21/04/2015 – 06/05/2015. a) δ^{18}O at SP03, b) δ^{18}O at SP01, c) δ^{2}H at SP03 and d) δ^{2}H at SP01. Error bars indicate range of analytical error associated with δ^{2}H (2.0 ‰) and δ^{18}O (0.2 ‰).

δ^{2}H and δ^{18}O showed similar patterns at SP03 and SP01. There is a strong positive correlation ($r = 0.79$, $p < 0.0005$) between the δ^{18}O values of SP03 and SP01. For δ^{2}H, the relationship was slightly weaker ($r = 0.85$, $p < 0.0005$) at the two sites. At both sites there are two noticeable dips in δ^{2}H and δ^{18}O on 23/04/2015 and 04/04/2015 respectively. However, the magnitude of change was larger at the highest altitude site. On 23/04/2015, δ^{2}H decreased by 7.6‰ at SP03 and 3.0‰ at SP01. For δ^{18}O there was a decrease of 0.74‰ and 0.57‰ at SP03 and SP01 respectively. On 04/05/2015, the amount δ^{2}H and δ^{18}O decreased was considerably more than 23/04/2015. δ^{2}H decreased by 14‰ at SP03 and 3.7‰ at SP01. A similar pattern was found in δ^{18}O, with a decreases of 1.94‰ at SP03 and 1.0‰ at SP01.

2.4.2.3 Variation along the stream

Boxplots of δ^{2}H and δ^{18}O values of stream water at SP03 and SP01 is plotted in Figure 2.8a and b respectively. At SP03, δ^{2}H has a mean of -37.82 ± 4.23‰, with a range from -48.00‰ to -33.80‰ (n = 15). For δ^{2}H for SP01 the mean -36.36 ± 1.57‰, ranging from -40.10‰ to -33.60‰ (n = 16). At SP03, the mean δ^{18}O is -6.1 ± 0.55‰. δ^{18}O ranges from -7.6‰ to -5.64‰ (n = 15). The mean of δ^{18}O at SP01 is -5.96 ± 0.25‰ with a range from -6.40‰ to -5.63‰ (n = 15).

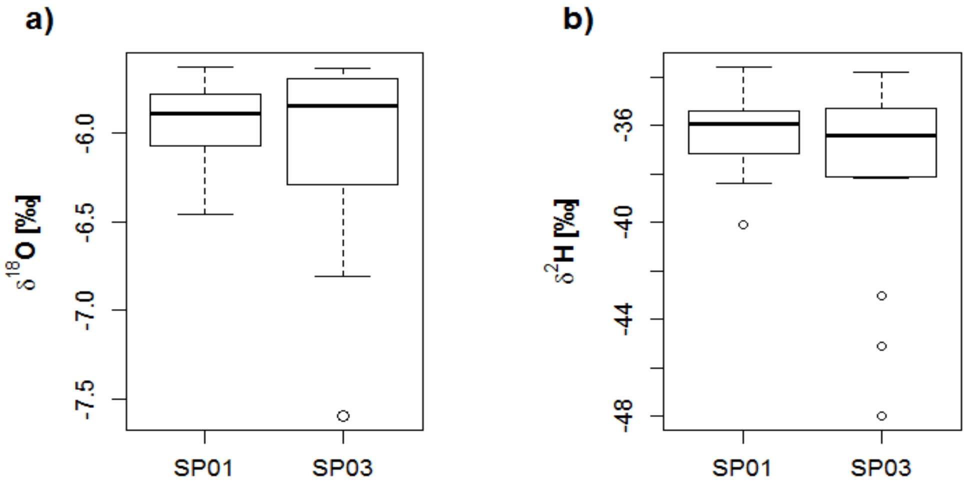


Figure 2.9. Box and whisker plots for all stream water sampled at SP03 and SP01 on the Soft Plume River (SPR) where a) is δ^{18}O and b) is δ^{2}H for SP03 and SP01 respectively. The boxes are bounded by lower and upper quartile limits, with the central line within the box representing the median values. The whiskers extend to the most extreme values within 1.5 times the interquartile range. Outliers are displayed by open dots.

A Wilcoxon-Mann-Whitney (WMW) test (Wilcoxon, 1945; Mann and Whitney, 1947) was applied to determine if there are any significant differences in δ^2H and δ^{18}O between the two sampling sites. For δ^2H, there was no significant difference between SP03 and SP01 (Mann-Whitney *Z*-value = 0.5, p = 0.7). A similar pattern was observed for δ^{18}O, with no significant difference between the two sites. (Mann-Whitney *Z*-value = -0.2, p = 0.8).

2.5 Discussion

2.5.1 Isotopic composition of precipitation

The climatology of Marion Island is well established (e.g. Schulze, 1971; Smith and Steenkamp, 1999; Smith, 2002; Rouault et al., 2005; Le Roux and McGeoch, 2008). All months (winter and summer) receive similar precipitation amounts and accounts for lack of seasonality in precipitation δ^{18}O (Fig. 2.3c). This pattern is in contrast to that found by Feng et al. (2009) in their analysis of GNIP data, whereby lower precipitation δ^{18}O values were found in winter months. The lack of isotopic seasonality results in there being no pronounced "amount effect" as there are several large amount rainfall months that show little depletion in δ^{18}O values (Bowen, 2008). This absence of an "amount effect" is further supported by the weak negative correlation (r = -0.24 p < 0.05,) between monthly averaged δ^{18}O and precipitation amount (Dansgaard, 1964). Observations from other islands (e.g. Sao Tome and Gough Island) exhibit similar patterns, as they are close to the moisture source (Aggarwal et al., 2012; Hughes and Crawford, 2012).

It is also unlikely that the "temperature effect" (Table 2.1; Dansgaard, 1964; Kohn and Welker, 2005) has a substantial influence on the isotopic composition of precipitation on Marion Island given weak positive correlations with average (r = 0.39, p < 0.0001) and maximum air surface temperature (r = 0.37, p < 0.0001). Bowen (2008) notes that, while there exists a significant correlation of precipitation δ^{18}O with air surface temperature above 30º N/S latitude, exceptions are found at maritime stations with low temperature seasonality. Hendricks et al. (2000) found that the sensitivity of precipitation δ^{18}O to local air surface temperature changes was low at coastal sites. This supports the weak relationship between temperature and precipitation δ^{18}O relationship on Marion Island with its low seasonal range (Fig. 2.3a).

2.5.2 Local meteoric water lines

While some studies use ordinary least squares regression to determine the line of best fit (Jouzel and Merlivat, 1984; Benjamin et al., 2005), RMA and MA regressions are theoretically more suited because the regression models do not assume a dependence on both variables (Carr, 2012). This is because measurements of both δ^2H and δ^{18}O are subject to error, and as a result, violate the assumptions of an ordinary least squares regression (OLSR) (Carr, 2012). Although a RMA fit involves a very specific pattern of error variance, prioritizing the presence versus the absence of error is preferred rather than the pattern of error in selecting between methods (Smith, 2009). Where there is a high correlation between δ^2H and δ^{18}O, an OLSR fit is very similar to the RMA regression line for the same data (Harris et al., 2010).

More robust determinations of LMWLs can also be achieved by weighting the various regressions (Crawford and Hughes, 2012; Crawford et al., 2014). Crawford et al. (2014) found, through an analysis of GNIP data that weighted RMA regressions tend to be more accurate estimators of the slope and intercept of an LWML than weighted OSLR and therefore better suited for the development of a LMWL. However, different and unweighted regressions lines have value for particular hydrological applications under certain circumstances.

The OLSR LMWL ($\delta^2H = (7.58 \pm 0.26)\delta^{18}O + (7.84 \pm 1.26)$) and PWLSR ($\delta^2H = (7.56 \pm 0.27)\delta^{18}O + (7.84 \pm 1.26)$) for Marion Island both have a smaller slope and intercept compared with the Craig (1961) GMWL ($\delta^2H = 8\delta^{18}O + 10$). The GMWL was developed using the OLSR regression technique (Craig, 1961) and therefore it is more appropriate to compare OLSR LMWLs with the GMWL (Crawford et al., 2016). Smaller slopes of LMWLs have been observed elsewhere, mainly on islands and some coastal sites (Crawford et al., 2014). This is supported by Gat (2005), who found that in maritime settings where the precipitation is often an initial stage condensate, a bivariate plot of δ^2H and δ^{18}O results in the data being distributed within an ellipse as opposed to directly along the LMWL. The degree of deviation from the GMWL largely reflects the latitudinal and oceanic position of Marion Island (Rozanski et al., 1993; Bowen and Wilkinson, 2002; Bowen and Revenaugh, 2003).

Both the RMA (PWRMA) and MA (PMA) produced larger slopes and intercepts than the OLSR (PWLSR). Crawford et al. (2014) found that the largest differences in slopes and intercepts between the different regressions was present on islands and some coastal sites. From the calculated values of rmSSEav (Table 2.2), it appears that the RMA and PRMA is better suited to the development of a LMWL for Marion Island. This is consistent with the findings of Crawford et al. (2014) who suggest that PWRMA regressions are most suited for island sites.

There is no considerable difference in the slope and intercepts of the weighted and unweighted regressions. This is expected, as at stations where relatively high amounts of rainfall occur throughout the yearly cycle, precipitation weighted and unweighted averages are similar (Stumpp et al., 2014). Nevertheless, precipitation weighted regressions generally provide for a more robust and accurate determination of LMWLs as they account for the potential influence of small rainfall amounts (Dansgaard, 1964) and sampling method bias (Froehlich et al., 2002).

2.5.3 Comparison within the maritime sub-Antarctic

Marion Island, Gough Island and Falkland Islands are isolated from landmasses (Convey and Lebouvier, 2009), with their climates regulated by the surrounding Southern Ocean and associated frontal zones (Fig. 1.1; Pendlebury and Barnes-Keoghan, 2007). Each of these islands experience relatively high amounts of rainfall through the yearly cycle. Mean annual precipitation ranges from ~600 mm on the Falkland Islands to ~3000 on Gough Island, with ~2000 mm on Marion Island (Jones et al., 2003; Bokhorst et al., 2007). The rain-bearing systems that affect the islands are strongly influenced by the Southern Hemisphere Westerly Winds, which regulate moisture supply and the passage of synoptic systems (Hodgson et al., 2014).

At high-latitude coastal areas the precipitation “amount” and “temperature effects” are not pronounced (Table 2.1; Rozanski et al., 1993; Bowen and Revenaugh, 2003; Kohn and Welker, 2005; Aggarwal et al., 2012). Given that coastal islands are close to the initial moisture source (Aggarwal et al., 2012), the differences in precipitation δ^2H and δ^{18}O between the sub-Antarctic islands (Fig. 2.6) are consistent with the “latitude effect” (Dansgaard, 1964; Table 2.1). This effect results in the Falkland Islands (highest latitude) having the lowest δ^2H and δ^{18}O values and Gough Island (lowest latitude) the highest (Fig. 2.6). This pattern is further supported by the agreement between the isotopic composition of precipitation on each respective island and the map of interpolated global precipitation δ^{18}O produced by Bowen and Revenaugh (2003).

2.5.4 δ^2H and $\delta^{18}O$ in the Soft Plume River

Stream water may comprise of precipitation and/or groundwater, depending on the amount of recent rainfall, size and physical characteristics of the catchment. Subsequently, in small catchments that respond rapidly to precipitation, the isotopic composition of rainfall is closely related to that of stream water (Dutton et al., 2005). There is, however, uncertainty in the spatial and temporal distribution of precipitation represented in stream water (Bershaw et al., 2012). Nevertheless, δ^2H and $\delta^{18}O$ in small shallow streams can be used to investigate physiographic and meteorological processes affecting the isotopic composition of stream water (Durand et al., 1993; Kendall and Coplen, 2001; Machavaram et al., 2006).

Variability of δ^2H and $\delta^{18}O$ in the SPR appears to be driven primarily by precipitation. This is illustrated by the two clear dips at both sites in stream water δ^2H and $\delta^{18}O$ on 23/04/2015 and 04/05/2015, which coincide with maximum rainfall intensity (6.2 mm h^{-1}) and the longest period of uninterrupted rainfall (9-hours) respectively (Fig. 2.2). Various precipitation-related processes might explain these decreases. Increased flow associated with precipitation induced surface runoff has been shown to result in lower stream δ^2H and $\delta^{18}O$ (e.g. Machavaram et al., 2006). In addition, decreases in the stream might be reflecting the low δ^2H and $\delta^{18}O$ in rainfall associated with intense, low-pressure cyclonic systems (Barras and Simmonds, 2008; Baldini et al., 2010; Callow et al., 2014; Timsic and Patterson, 2014). This suggestion is supported by the findings of McCartney et al. (1998), who found that under wetter conditions (high amounts of antecedent moisture) the isotopic signal in rainfall is transferred more directly to stream water compared with rainfall under drier conditions. However, more data are needed to further investigate the mechanisms driving the decreases in stream δ^2H and $\delta^{18}O$.

Variability along the stream is likely a result of the "amount effect" (Table 2.1), driven by an altitudinal precipitation gradient whereby more rainfall occurs at the higher site compared with the lower. A similar situation was found by Dalai et al. (2002) in the Yamanua catchment in the Himalaya mountain range. The same pattern was also observed by Ogrinc et al. (2008) in the River Slava, Slovenia, where lower reaches of the river received less rainfall and subsequently had higher δ^2H and $\delta^{18}O$ values. While there are no significant difference between the sites for δ^2H (Mann-Whitney Z-value = 0.5, p = 0.7) and $\delta^{18}O$ (Mann-Whitney Z-value = -0.2, p = 0.8), the isotopic composition of stream water at the highest site SP03 is more variable and exhibits a larger response to precipitation inputs compared with the lowest site SP01. Higher rainfall amounts at SP03 would have resulted in lower δ^2H and $\delta^{18}O$ values at SP03 compared with SP01. Although rainfall was not measured along an altitudinal gradient in this study, the explanation is supported by Blake (1996). Blake (1996) found higher total monthly rainfall amounts at ~550 m a.m.s.l (4653 mm) to be substantially more than at 34 m a.m.s.l (2837 mm).

Furthermore, there is the possibility of snow-melt contributing to stream water and altering the isotopic composition of stream water with the addition of melt water depleted in $\delta^{18}O$ (Dalai et al., 2002; Taylor et al., 2002; Meier et al., 2013). While snow quantities, accumulation and ablation rates have not previously been determined, observations from the sampling period suggest that when it does snow, it only stands for a few days, predominantly in winter. Peng et al. (2015) found similar patterns of snow accumulation and suggest that limited amounts of snowfall that stands for a relatively short period of time only makes a trivial contribution to stream water.

2.5.5 Comparison between $\delta^{18}O$ in precipitation and stream water

Stream water $\delta^{18}O$ (or $\delta^{2}H$) in a drainage basin should reflect the amount and altitude weighted precipitation (Rowley and Garzione, 2007). This coherence between the isotopic composition of precipitation and stream water has been shown for many areas around the world, such as, the USA (Kendall and Coplen, 2001), northern Sweden (Jonsson et al., 2009) and subcontinental catchments in India (Lambs et al., 2005). However, large differences between precipitation and stream water $\delta^{18}O$ value have also been shown. In areas of western USA complex hydro-meteorological patterns result in lower $\delta^{18}O$ values in stream water relative to precipitation (Kendall and Coplen, 2001; Dutton et al., 2005). The slopes of river water lines (RWLs, or surface water lines; SWL) have been shown to be higher than their associated LMWLs (e.g. Rock and Mayer, 2007; Yi et al., 2010; Maurya et al., 2011).

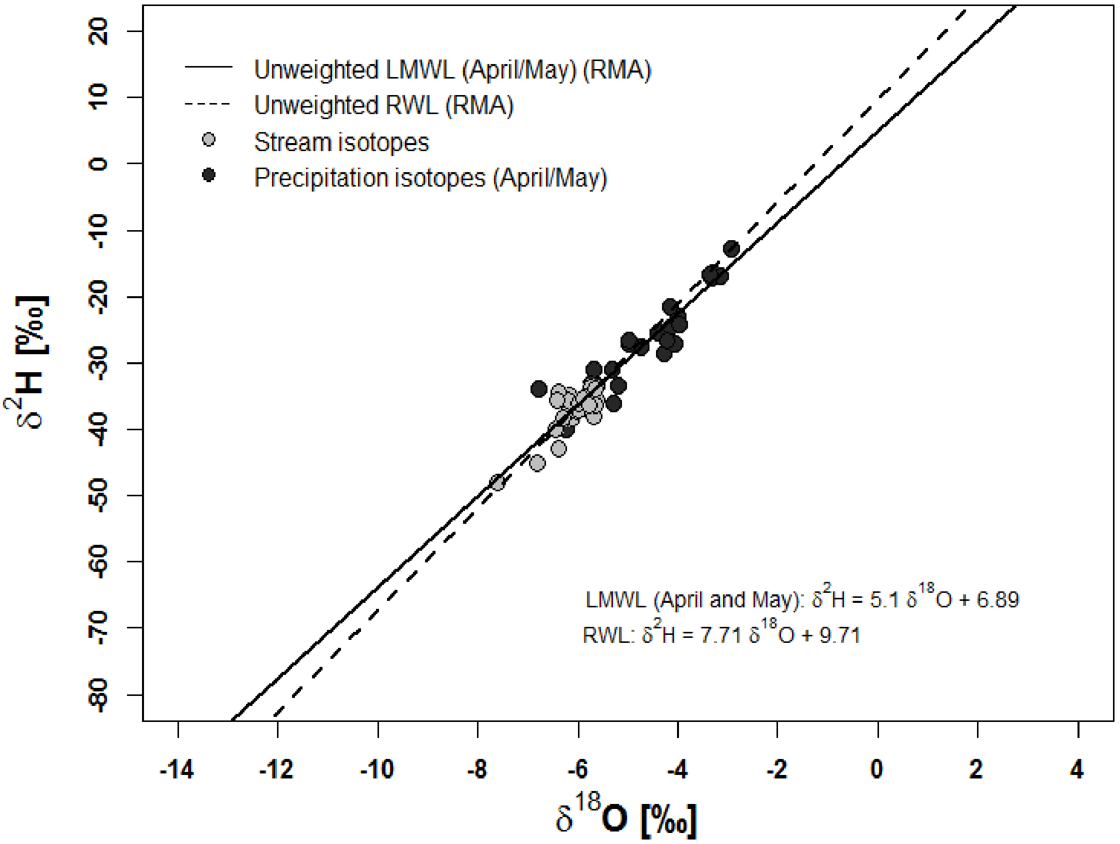


Figure 2.10. δ^2H vs δ^{18}O of monthly precipitation (April and May; n = 25) and stream water (n = 30) on Marion Island. Precipitation samples are from the research station and stream water samples are from the Soft Plume River.

To minimize the influence of any seasonal differences between precipitation and stream water δ^{18}O, only precipitation from April and May was considered as this overlapped with the stream water sampling period. Mean stream water δ^{18}O for the SPR is -6.04 ± 0.41‰ (n = 30) whereas the mean for April and May precipitation is -4.64 ± 1.04‰ (n = 25). There is a significant difference in monthly averaged precipitation (April/May) and stream water δ^{18}O (Mann-Whitney *Z*-value = 5.01, $p < 0.001$), with stream water δ^{18}O being lower (Fig. 2.10). These differences might be explained by the isotopic averaging of the precipitation sample. Whereas stream sampling might represent a signature associated with an event, a composite precipitation sample might comprise of smaller rainfall events with relatively enriched δ^{18}O (Hughes and Crawford, 2013; Zhou et al., 2014). In addition, differences between stream and precipitation isotopes might relate to the spatial differences between sampling sites. While the both the research station and SPR are situated on the eastern side of the island, topographical differences, and subsequently weather conditions, may be responsible for the differences.

2.6 Conclusion

δ^2H and $\delta^{18}O$ values in precipitation and surface water enable us to develop a better understanding of atmospheric and hydrological processes on Marion Island, providing valuable insight in to how these systems might respond to future climatic change. The overall δ^2H and $\delta^{18}O$ composition of bulk monthly precipitation is not significantly correlated with monthly precipitation amount and average air surface temperature, consistent with findings from other maritime islands. Differences in precipitation $\delta^{18}O$ between other maritime islands, with similar climatic conditions, follow a latitudinal trend with decreasing values towards the poles..

The precipitation weighted reduced major axis (PWRMA) local meteoric water line (LMWL) was calculated to be $\delta^2H = 8.35\delta^{18}O + 11.49$ for Marion Island. For comparison with the global meteoric water line (GMWL), the ordinary least squares regression (OLSR)-derived LMWL was $\delta^2H = 7.58\delta^{18}O + 7.84$. The relative error for each regression model, calculated as the $rmSSE_{avg}$, was smallest for the RMA and PWRMA. Consistent with the findings of Crawford et al. (2014) for coastal islands, results from this study suggest that the PWRMA is most suitable for the development of a LMWL on Marion Island.

This paper also presents the first dataset of δ^2H and $\delta^{18}O$ in stream water for Marion Island. Stream water δ^2H and $\delta^{18}O$ was shown to respond rapidly and directly to rainfall inputs into the stream. Low stream water δ^2H and $\delta^{18}O$ values were found to coincide with maximum intensity rainfall, amount and longest duration of uninterrupted rainfall. There were no significant difference in δ^2H and $\delta^{18}O$ along the stream. However, the highest altitude site exhibited a larger magnitude of change and lower δ^2H and $\delta^{18}O$ in response to rainfall inputs compared with the lower site. This difference between sites suggests the presence of an altitudinal precipitation gradient with more rainfall falling at higher altitudes along the stream. Precipitation had significantly higher $\delta^{18}O$ compared with stream water $\delta^{18}O$, however, sampling at different times and locations limited the interpretation of this pattern.

The stream water data are a valuable addition to the Global Network of Isotopes in Rivers (GNIR). Results also serve as important, preliminary findings that will inform the current longer term monitoring program on Marion Island that is investigating inter-seasonal and intra-seasonal dynamics.

Acknowledgements

The research presented here is part of the project Landscape and Climate Interactions in a Changing Sub-Antarctic Environment (grant no. 93075). This research received logistical support from the South African Department of Environmental Affairs. Funding was provided through the National Research Foundation, by the South African Department of Science and Technology under the auspices of the South African National Antarctic Program. Climate data from the research station on Marion Island were provided by the South African Weather Services. Prof. Werner Nel (Department of Geography and Environmnetal Science, University or Fort Hare, South Africa), Prof. Dave Hedding (Department of Geography, University of South Africa, South Africa) Abuyiselwe Nguna (University of Fort Hare) assisted with sample collection in the field. Dr. Catherine Hughes of the Australian Nuclear Science and Technology Organisation provided the code for calculation of the PWRMA and PWMA meteoric water lines. Dr. Janine Halder of the International Atomic Energy Agency (IAEA) provided valuable comments on GNIP data used in this chapter. Sherissa Roopnarain of the Department of Geological Science at the University of Cape Town provided the stream water isotope analysis.

References

Ambach, W., Dansgaard, W., Eisner, H., Møller, J., 1968. The altitude effect on the isotopic composition of precipitation and glacier ice in the Alps. Tellus 20, 595-600.

Aggarwal, P. K., Araguas-Araguas, L. J., Groening, M., Kulkarni, K. M., Kurttas, T., Newman, B. D., Vitvar, T., 2010. Global hydrological isotope data and data networks. In: West, J.B., Boweb, G.J., Dawson, T.E., Tu, K.P. (Eds.) Isoscapes – Understanding Movement, Pattern, and Process on Earth Through Isotope Mapping. Springer, the Netherlands.

Aggarwal, P.K., Alduchov, O.A., Froehlich, K.O., Araguas-Araguas, L.J., Sturchio, N.C., Kurita, N., 2012. Stable isotopes in global precipitation: A unified interpretation based on atmospheric moisture residence time. Geophysical Research Letters 39, L11705. http://dx.doi.org/10.1029/2012GL051937.

Ansorge, I.J., Speich, S., Lutjeharms, J.R.E., Goni, G.J., Rautenbach, C.J., Froneman, P.W., Rouault, M. and Garzoli, S.L., 2005. Monitoring the oceanic flow between Africa and Antarctica: Report of the first GoodHope cruise. South African Journal of Science 101, 29-35.

Argiriou, A.A., Lykoudis, S., 2006. Isotopic composition of precipitation in Greece. Journal of Hydrology 327, 486-495.

Baldini, L.M., McDermott, F., Baldini, J.U., Fischer, M.J., Möllhoff, M., 2010. An investigation of the controls on Irish precipitation $\delta^{18}O$ values on monthly and event timescales. Climate Dynamics 35, 977-993.

Barras, V.J., Simmonds, I., 2008. Synoptic controls upon $\delta^{18}O$ in southern Tasmanian precipitation. Geophysical Research Letters 35, L02707. http://dx.doi.org/10.1029/2007GL031835.

Benjamin, L., Knobel, L.L., Hall, L.D., Cecil, L.D., Green, J.R., 2005. Development of a Local Meteoric Water Line for Southeastern Idaho. USGS: Western Wyoming, and south-central Montana USGS 17.

Bershaw, J., Penny, S.M., Garzione, C.N., 2012. Stable isotopes of modern water across the Himalaya and eastern Tibetan Plateau: Implications for estimates of paleoelevation and paleoclimate. Journal of Geophysical Research: Atmospheres 117, D2. http://dx.doi.org/10.1029/2011JD016132

Bokhorst, S., Huiskes, A., Convey, P., Aerts, R., 2007. Climate change effects on organic matter decomposition rates in ecosystems from the Maritime Antarctic and Falkland Islands. Global Change Biology 13, 2642-2653.

Bowen, G.J., Wilkinson, B., 2002. Spatial distribution of $\delta^{18}O$ in meteoric precipitation. Geology 30, 315-318.

Bowen, G.J., Revenaugh, J., 2003. Interpolating the isotopic composition of modern meteoric precipitation. Water Resources Research 39, 1299.

Bowen, G.J., 2008. Spatial analysis of the intra-annual variation of precipitation isotope ratios and its climatological corollaries. Journal of Geophysical Research: Atmospheres 113. http://dx.doi.org./10.1029/2007JD009295.

Callow, N., McGowan, H., Warren, L., Speirs, J., 2014. Drivers of precipitation stable oxygen isotope variability in an alpine setting, Snowy Mountains, Australia. Journal of Geophysical Research: Atmospheres 119, 3016-3031.

Carr, J.R., 2012. Orthogonal regression: a teaching perspective. International Journal of Mathematical Education in Science and Technology 43, 134-143.

Clark, D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers, Boca Roton, Florida.

Coleman, M.L., Shepherd, T.J., Durham, J.J., Rouse, J.E., Moore, G.R., 1982. Reduction of water with zinc for hydrogen isotope analysis. Analytical Chemistry 54, 993-995.

Conradie, E.C., Smith, V.R., 2012. Spatial variation in soil chemistry on a sub-Antarctic island. Open Journal of Soil Science 2, 111-115.

Convey, P., Lebouvier, M., 2009. Environmental change and human impacts on terrestrial ecosystems of the sub-Antarctic islands between their discovery and the mid-twentieth century. Papers and Proceedings of the Royal Society of Tasmania 143, 33-44.

Convey, P., Bindschadler, R., Di Prisco, G., Fahrbach, E., Gutt, J., Hodgson, D.A., Mayewski, P.A., Summerhayes, C.P., Turner, J., 2009. Antarctic climate change and the environment. Antarctic Science 21, 541-563.

Coplen, T.B., 1993. Uses of environmental isotopes. Regional Ground-Water Quality. Van Nostrand Reinhold, New York.

Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702-1703.

Crawford, J., Hughes, C.E., Parkes, S.D., 2013. Is the isotopic composition of event based precipitation driven by moisture source or synoptic scale weather in the Sydney Basin, Australia?. Journal of Hydrology 507, 213-226.

Crawford, J., Hughes, C.E., Lykoudis, S., 2014. Alternative least squares methods for determining the meteoric water line, demonstrated using GNIP data. Journal of Hydrology 519, 2331-2340.

Crawford, J., Hollins, S.E., Meredith, K.T., Hughes, C.E., 2016. Precipitation stable isotope variability and sub-cloud evaporation processes in a semi-arid region. Hydrological Processes. http://dx.doi.org./doi/10.1002/hyp.10885.

Dalai, T.K., Bhattacharya, S.K., Krishnaswami, S., 2002. Stable isotopes in the source waters of the Yamuna and its tributaries: seasonal and altitudinal variations and relation to major cations. Hydrological Processes 16, 3345-3364.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16, 436-468.

Darling, W.G., Bowes, M.J., 2016. A long-term study of stable isotopes as tracers of processes governing water flow and quality in a lowland river basin: the upper Thames, UK. Hydrological Processes 30, 2178-2195.

Dartnall, H.J., Smith, V.R., 2012. Freshwater invertebrates of sub-Antarctic Marion Island. African Zoology 47, 203-215.

Durand, P., Neal, M., Neal, C., 1993. Variations in stable oxygen isotope and solute concentrations in small submediterranean montane streams. Journal of Hydrology 144, 283-290.

Dutton, A., Wilkinson, B.H., Welker, J.M., Bowen, G.J., Lohmann, K.C., 2005. Spatial distribution and seasonal variation in 18O/16O of modern precipitation and river water across the conterminous USA. Hydrological Processes 19, 4121-4146.

Feng, X., Faiia, A.M., Posmentier, E.S., 2009. Seasonality of isotopes in precipitation: a global perspective. Journal of Geophysical Research: Atmospheres, 114. http://dx.doi.org./10.1029/2008JD011279.

Froehlich, K., Gibson, J.J, Aggarwal, P.K., 2002. Deuterium excess in precipitation and its climatological significance. In: Proceedings of Study of Environmental Change Using Isotope Techniques, IAEA, Vienna, IAEA-CSP-13/P.

Gat, J.R., 2005. Some classical concepts of isotope hydrology. In: Aggarwal, P.K., Gat, J.R., Froehlich, K.F.O. (Eds.), Isotope in the Water Cycle: Past, Present and Future of a Developing Science, International Atomic Energy Agency, Vienna.

Gedzelman, S.D., Lawrence, J.R., White, J.W., Smiley, D., 1987. The isotopic composition of precipitation at Mohonk Lake, New York: the “amount effect”. Journal of Geophysical Research: Atmospheres 92, 1033-1040.

Gedzelman, S.D., Lawrence, J.R., 1990. The isotopic composition of precipitation from two extratropical cyclones. Monthly Weather Review 118, 495-509.

Gedzelman, S.D., Arnold, R., 1994. Modeling the isotopic composition of precipitation. Journal of Geophysical Research: Atmospheres 99, 10455-10471.

Gedzelman, S., Lawrence, J., Gamache, J., Black, M., Hindman, E., Black, R., Dunion, J., Willoughby, H., Zhang, X., 2003. Probing hurricanes with stable isotopes of rain and water vapor. Monthly Weather Review 131, 1112-1127.

Gonfiantini, R., Roche, M.A., Olivry, J.C., Fontes, J.C., Zuppi, G.M., 2001. The altitude effect on the isotopic composition of tropical rains. Chemical Geology 181, 147-167.

Gremmen, N., Smith, V., 2004. The flora of Marion and Prince Edward Islands. Data Analyse Ecologie, Diever.

Grobbelaar, J.U., 1978. Mechanisms controlling the composition of freshwaters on the sub-Antarctic island Marion. Archiv für Hydrobiologie 83, 145-157.

Halder, J., Terzer, S., Wassenaar, L.I., Araguás-Araguás, L.J., Aggarwal, P.K., 2015. The Global Network of Isotopes in Rivers (GNIR): integration of water isotopes in watershed observation and riverine research. Hydrology and Earth System Sciences 19, 3419-3431.

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.

Hendricks, M.B., DePaolo, D.J., Cohen, R.C., 2000. Space and time variation of $\delta^{18}O$ and δD in precipitation: Can paleotemperature be estimated from ice cores?. Global Biogeochemical Cycles 14, 851-861.

Hodgson, D.A., Graham, A.G., Roberts, S.J., Bentley, M.J., Cofaigh, C.Ó., Verleyen, E., Vyverman, W., Jomelli, V., Favier, V., Brunstein, D., Verfaillie, D., Colhoun, E.A., Saunders, K.M., Selkirk, P.M., Mackintosh, A., Hedding, D.W., Nel, W., Hall, K., McGlone, M.S., van der Putten, N., Dickens, W.A., Smith, J.A., 2014. Terrestrial and submarine evidence for the extent and timing of the Last Glacial Maximum the onset of deglaciation on the maritime-Antarctic and sub-Antarctic islands. Quaternary Science Reviews 100, 137-158.

Hughes, C.E., Crawford, J., 2012. A new precipitation weighted method for determining the meteoric water line for hydrological applications demonstrated using Australian and global GNIP data. Journal of Hydrology 464, 344-351.

Hughes, C.E., Crawford, J., 2013. Spatial and temporal variation in precipitation isotopes in the Sydney Basin, Australia. Journal of Hydrology 489, 42-55.

IAEA., 1992. Statistical treatment of data on environmental isotopes in precipitation, Technical Reports Series No. 331, IAEA, Vienna, 781.

IAEA/WMO., 2016. Global Network of Isotopes in Precipitation. The GNIP Database. Accessible at: http://www.iaea.org/water.

Ingraham, N.L., 1998. Isotopic variation in precipitation. In: Kendall, C., McDonnell, J.J. (Eds.), Isotope Tracers in Catchment Hydrology. Elsevier, New York.

Jones, A.G., Chown, S.L., Ryan, P.G., Gremmen, N.J.M., Gaston, K.J., 2003. A review of conservation threats on Gough Island: a case study for terrestrial conservation in the Southern Oceans. Biological Conservation 113, 75-87.

Jonsson, C.E., Leng, M.J., Rosqvist, G.C., Seibert, J., Arrowsmith, C., 2009. Stable oxygen and hydrogen isotopes in sub-Arctic lake waters from northern Sweden. Journal of Hydrology 376, 143-151.

Jouzel, J., Merlivat, L., 1984. Deuterium and oxygen 18 in precipitation: Modeling of the isotopic effects during snow formation. Journal of Geophysical Research: Atmospheres 89, 11749-11757.

Kendall, C., Coplen, T.B., 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. Hydrological Processes 15, 1363-1393.

Klaus, J., McDonnell, J.J., Jackson, C.R., Du, E., Griffiths, N.A., 2015. Where does streamwater come from in low-relief forested watersheds? A dual-isotope approach. Hydrology and Earth System Sciences 19, 125-135.

Kohn, M.J., Welker, J.M., 2005. On the temperature correlation of $\delta^{18}O$ in modern precipitation. Earth and Planetary Science Letters 231, 87-96.

Lachniet, M.S., Patterson, W.P., 2009. Oxygen isotope values of precipitation and surface waters in northern Central America (Belize and Guatemala) are dominated by temperature and “amount effect”s. Earth and Planetary Science Letters 284, 435-446.

Lambs, L., Balakrishna, K., Brunet, F., Probst, J.L., 2005. Oxygen and hydrogen isotopic composition of major Indian rivers: a first global assessment. Hydrological Processes 19, 3345-3355.

Lawrence, J.R., Gedzelman, S.D., White, J.W., Smiley, D. and Lazov, P., 1982. Storm trajectories in eastern US D/H isotopic composition of precipitation. Nature 296, 638–640.

Lawrence, R.J., Gedzelman, D.S., 1996. Low stable isotope ratios of tropical cyclone rains. Geophysical Research Letters 23, 527-530.

Lecomte, K.L., Vignoni, P.A., Córdoba, F.E., Chaparro, M.A., Chaparro, M.A., Kopalová, K., Gargiulo, J.D., Lirio, J.M., Irurzun, M.A., Böhnel, H.N., 2016. Hydrological systems from the Antarctic Peninsula under climate change: James Ross archipelago as study case. Environmental Earth Sciences 75, 1-20.

Lee, J.E., Fung, I., 2008. "Amount effect" of water isotopes and quantitative analysis of post-condensation processes. Hydrological Processes 22, 1-8.

Le Roex, A.P., Chevallier, L., Verwoerd, W.J., Barends, R., 2012. Petrology and geochemistry of Marion and Prince Edward Islands, Southern Ocean: Magma chamber processes and source region characteristics. Journal of Volcanology and Geothermal Research 223, 11-28.

Le Roux, P.C., McGeoch, M.A., 2008. Changes in climate extremes, variability and signature on sub-Antarctic Marion Island. Climatic Change 86, 309-329.

Liebminger, A., Haberhauer, G., Papesch, W., Heiss, G., 2006. Correlation of the isotopic composition in precipitation with local conditions in alpine regions. Journal of Geophysical Research: Atmospheres 111. D05104, http://dx.doi.org./10.1029/2005JD006258.

Longinelli, A., Edmond, J.M., 1983. Isotope geochemistry of the Amazon basin: a reconnaissance. Journal of Geophysical Research: Oceans 88, 3703-3717.

Machavaram, M.V., Whittemore, D.O., Conrad, M.E., Miller, N.L., 2006. Precipitation induced stream flow: An event based chemical and isotopic study of a small stream in the Great Plains region of the USA. Journal of Hydrology 330, 470-480.

Mann, H.B., Whitney, D.R., 1947. On a test of whether one of two random variables is stochastically larger than the other. The Annals of Mathematical Statistics, 50-60.

Maurya, A.S., Shah, M., Deshpande, R.D., Bhardwaj, R.M., Prasad, A., Gupta, S.K., 2011. Hydrograph separation and precipitation source identification using stable water isotopes and conductivity: River Ganga at Himalayan foothills. Hydrological Processes 25, 1521-1530.

McCartney, M.P., Neal, C., Neal, M., 1998. Use of deuterium to understand runoff generation in a headwater catchment containing a dambo. Hydrology and Earth System Sciences Discussions 2, 65-76.

McDougall, I.A.N., Verwoerd, W., Chevallier, L.U.C., 2001. K–Ar geochronology of Marion Island, Southern Ocean. Geological Magazine, 138, 1-17.

Meier, C., Knoche, M., Merz, R., Weise, S.M., 2013. Stable isotopes in river waters in the Tajik Pamirs: regional and temporal characteristics. Isotopes in Environmental and Health Studies 49, 542-554.

Merlivat, L., Jouzel, J., 1979. Global climatic interpretation of the deuterium-oxygen 18 relationship for precipitation. Journal of Geophysical Research: Oceans 84, 5029-5033.

Nel, W., 2012. A preliminary synoptic assessment of soil frost on Marion Island and the possible consequences of climate change in a maritime sub-Antarctic environment. Polar Research 31.

Pawellek, F., Frauenstein, F., Veizer, J., 2002. Hydrochemistry and isotope geochemistry of the upper Danube River. Geochimica et Cosmochimica Acta 66, 3839-3853.

Pendlebury, S., Barnes-Keoghan, I.P., 2007. Climate and climate change in the sub-Antarctic. Papers and Proceedings of the Royal Society of Tasmania 141, 67-81.

Peng, T.R., Chen, K.Y., Zhan, W.J., Lu, W.C., Tong, L.T.J., 2015. Use of stable water isotopes to identify hydrological processes of meteoric water in montane catchments. Hydrological Processes 29, 4957-4967.

Poage, M.A., Chamberlain, C.P., 2001. Empirical relationships between elevation and the stable isotope composition of precipitation and surface waters: considerations for studies of paleoelevation change. American Journal of Science 301, 1-15.

Prowse, T.D., Wrona, F.J., Reist, J.D., Gibson, J.J., Hobbie, J.E., Lévesque, L.M., Vincent, W.F., 2006. Climate change effects on hydroecology of Arctic freshwater ecosystems. AMBIO: A Journal of the Human Environment 35, 347-358.

Puntsag, T., Mitchell, M.J., Campbell, J.L., Klein, E.S., Likens, G.E., Welker, J.M., 2016. Arctic Vortex changes alter the sources and isotopic values of precipitation in northeastern US. Scientific Reports 6.

Ramesh, R., Sarin, M.M., 1992. Stable isotope study of the Ganga (Ganges) river system. Journal of Hydrology 139, 49-62.

Rock, L., Mayer, B., 2007. Isotope hydrology of the Oldman River basin, southern Alberta, Canada. Hydrological Processes 21, 3301-3315.

Rouault, M., Melice, J-L., Reason, C.J.C., Lutjeharms, J.R.E., 2005. Climate variability at Marion Island, Southern Ocean, since 1960. Journal of Geophysical Research 110, C05007.1- C05007.9.

Rowley, D.B., Garzione, C.N., 2007. Stable isotope-based paleoaltimetry. Annual Review of Earth and Planetary Sciences 35, 463-508.

Rozanski, K., Sonntag, C., Münnich, K.O., 1982. Factors controlling stable isotope composition of European precipitation. Tellus 34, 142-150.

Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: Swart, P.K., McKenzie, K.C.I.J., Savin, S. (Eds.), Climate Change in Continental Isotopic Records. American Geophysical Union, Washington, D. C.

Salati, E., Dall'Olio, A., Matsui, E., Gat, J.R., 1979. Recycling of water in the Amazon basin: an isotopic study. Water Resources Research 15, 1250-1258.

Schulze, B.R., 1971. The climate of Marion Island. In: Van Zinderen Bakker, E.M., Winterbottom, J.M., Dyer, R. A. (Eds.), Marion and Prince Edward Islands. Report on the South African biological and geological expedition 1965–1966. A. A. Balkema.

Schimmelmann, A., DeNiro, M.J., 1993. Preparation of organic and water hydrogen for stable isotope analysis: effects due to reaction vessels and zinc reagent. Analytical Chemistry 65, 789-792.

Shulmeister, J., Goodwin, I., Renwick, J., Harle, K., Armand, L., McGlone, M.S., Cook, E., Dodson, J., Hesse, P.P., Mayewski, P., Curran, M., 2004. The Southern Hemisphere westerlies in the Australasian sector over the last glacial cycle: a synthesis. Quaternary International 118, 23-53.

Siegenthaler, U., Oeschger, H., 1980. Correlation of 18O in precipitation with temperature and altitude. Nature 285, 314-317.

Sinclair, M.R., 1995. A climatology of cyclogenesis for the Southern Hemisphere. Monthly Weather Review 123, 1601-1619.

Smith, V.R., 2002. Climate change in the sub-Antarctic: an illustration from Marion Island. Climatic Change 52, 345-357.

Smith, V.R., Steenkamp, M., 1990. Climatic change and its ecological implications at a sub-Antarctic Island. Oecologia 85, 14-24.

Smith, R.J., 2009. Use and misuse of the reduced major axis for line-fitting. American Journal of Physical Anthropology 140, 476-486.

Socki, R.A., Karlsson, H.R., Gibson Jr, E.K., 1992. Extraction technique for the determination of oxygen-18 in water using preevacuated glass vials. Analytical Chemistry 64, 829-831.

Stumpp, C., Klaus, J., Stichler, W., 2014. Analysis of long-term stable isotopic composition in German precipitation. Journal of Hydrology 517, 351-361.

Taylor, S., Feng, X., Williams, M., McNamara, J., 2002. How isotopic fractionation of snowmelt affects hydrograph separation. Hydrological Processes 16, 3683-3690.

Timsic, S., Patterson, W.P., 2014. Spatial variability in stable isotope values of surface waters of Eastern Canada and New England. Journal of Hydrology 511, 594-604.

Treble, P.C., Budd, W.F., Hope, P.K., Rustomji, P.K., 2005. Synoptic-scale climate patterns associated with rainfall $\delta^{18}O$ in southern Australia. Journal of Hydrology 302, 270-282.

Turner, J., Barrand, N.E., Bracegirdle, T.J., Convey, P., Hodgson, D.A., Jarvis, M., Jenkins, A., Marshall, G., Meredith, M.P., Roscoe, H., Shanklin, J., 2014. Antarctic climate change and the environment: an update. Polar Record 50, 237-259.

Uemura, R., Matsui, Y., Yoshimura, K., Motoyama, H., Yoshida, N., 2008. Evidence of deuterium excess in water vapor as an indicator of ocean surface conditions. Journal of Geophysical Research: Atmospheres 113, L13216, http://dx.doi.org./10.1029/2004GL019954.

van Geldern, R., Kuhlemann, J., Schiebel, R., Taubald, H., Barth, J.A., 2014. Stable water isotope patterns in a climate change hotspot: the isotope hydrology framework of Corsica (western Mediterranean). Isotopes in Environmental and Health Studies 50, 184-200.

Verwoerd, W.J., 1971: Geology. In: Van Zinderen Bakker, E.M., Winterbottom, J.M., Dyer, R.A. (Eds.), Marion and Prince Edward Islands. Balkema, Cape Town.

Vowinckel, E., 1954. Synotische Klimotologie vom gebiet Marion Island. (Synoptic climatology of the Marion Island area). Notos 3, 12-21.

Vreča, P., Bronić, I.K., Horvatinčić, N., Barešić, J., 2006. Isotopic characteristics of precipitation in Slovenia and Croatia: Comparison of continental and maritime stations. Journal of Hydrology 330, 457-469.

Wilcoxon, F., 1945. Individual comparisons by ranking methods. Biometrics Bulletin 1, 80-83.

Yde, J.C., Knudsen, N.T., Steffensen, J.P., Carrivick, J.L., Larsen, N.K., Mernild, S.H., Roberts, D.H., Russell, A.J., 2016. Stable oxygen isotope variability in two contrasting glacier river catchments in Greenland. Hydrology and Earth System Sciences 20, 1197-1210.

Yi, Y., Gibson, J.J., Hélie, J.F., Dick, T.A., 2010. Synoptic and time-series stable isotope surveys of the Mackenzie River from Great Slave Lake to the Arctic Ocean, 2003 to 2006. Journal of Hydrology 383, 223-232.

Zhou, S., Wang, Z., Joswiak, D.R., 2014. From precipitation to runoff: stable isotopic fractionation effect of glacier melting on a catchment scale. Hydrological Processes, 28, 3341-3349.

Chapter 3: Hydrochemical characteristics of stream water on sub-Antarctic Marion Island

Abstract

Hydrological systems on remote and isolated maritime islands respond rapidly to climate-induced environmental changes. It is therefore important to understand current hydrological conditions in environments that are particularly sensitive to climate change. This research gap was addressed by using major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^- , SO_4^{2-}, NO_3^-) and high-resolution physicochemical (pH, water temperature, dissolved oxygen and total dissolved solids) measurements from the Soft Plume River to better understand contemporary hydrochemical dynamics on Marion Island. Samples were collected at three sites along the stream and physicochemistry monitored *in situ* at a single site. The chemical composition of the stream is dominated by Na^+ and Cl^-, consistent with previous studies from Marion Island and other maritime sub-Antarctic islands. Concentrations of most solutes decrease rapidly in response to high rainfall amounts. This decrease was largest at the highest altitude site, suggesting that more rainfall fell at this site. High-resolution monitoring of physicochemical parameters revealed the presence of diel cycles in stream water for the first time on Marion Island. Diel cycles were generally of low amplitude and strongly coupled with prevailing hydrometeorological conditions. These findings provide insight into mechanisms that underpin variability in stream chemistry and illustrate the importance of high-frequency monitoring for accurate characterisation of processes operating on multiple temporal scales.

Keywords: Stream water chemistry, high-frequency monitoring, diel cycles

3.1 Introduction

Pristine watersheds in remote regions of the world are valuable and informative environments for the detection of climatological changes (Cantonati & Ortler, 1998). Small catchments, such as those found on many sub-Antarctic islands, have been invaluable, providing the basis for detailed investigation and understanding of various systems, especially those related to natural processes occurring in the environment (Sidle, 2006; Lecomte et al., 2016). Hydrological systems on oceanic islands often exhibit a strong coupling with climatic phenomena which regulate various biogeochemical processes (Blaen et al., 2014). Terrestrial and hydrological systems respond to even small changes in climate, making these systems important indicators for identifying early and subtle signals in response to climatic change (Prowse et al., 2006; Convey et al., 2009).

Stream water chemistry is sensitive to climate, in particular to changes in precipitation and air temperature (Dalai et al., 2002; Millot et al., 2002). Consequently, changes and fluctuations in stream chemistry can be strong indicators of climate change impacts at the scale of whole watersheds (Holmes, 2013). However, processes that drive fluctuations in stream chemistry are highly dynamic and spatially complex at hourly, daily, seasonally and storm event time scales. Subsequently, elucidating specific processes and drivers regulating stream water chemistry can be challenging (Holloway and Dahlgren, 2001). Given this, there is a need for an improved understanding of current hydrochemical dynamics at various spatial and temporal scales in environments that are particularly sensitive to climatic change.

This study reports on the major ion chemistry (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-}) and high-resolution physicochemical (pH, water temperature, dissolved oxygen and total dissolved solids) dynamics of the Soft Plume River, Marion Island. These data provide insight into stream hydrochemical dynamics on diurnal, sub-daily and storm event time scales. Results from this study complement previous studies on stream chemistry on the island (Grobbelaar 1974; 1978a), providing an enhanced perspective on the mechanisms controlling spatiotemporal variations in stream chemistry. High-resolution monitoring conducted here provides important, and never before recorded, information on diel cycles in stream water. Challenges associated with *in situ* high-frequency monitoring in a harsh sub-Antarctic environment are considered. In addition, the limitations of point-based sampling measurements and implications for understanding temporal stream dynamics are discussed.

3.1.1 Previous stream chemical research

The chemistry of lotic water on Marion Island has been discussed in detail by Grobbelaar (1974, 1975, 1978a, b), with more recent research expanding his initial findings (Smith, 2008; van Staden, 2011; Dartnall and Smith, 2012). In general, the streams are characterized by an ionic dominance of $Na^+ > Mg^{2+} > Ca^+ > K^+ : Cl^- > HCO_3^- > SO_4^{2-}$ (Grobbelaar, 1974; 1978a; van Staden, 2011). The dominance of sea-salts (Na^+ and Cl^-) reflect the island's maritime and latitudinal position. According to Grobbelaar (1978), the island's stream water chemistry is predominantly controlled by the high amounts of rainfall throughout the year and enrichment due to sea-spray. The dominance of westerly and north-westerly winds force substantial amounts on sea-salt particles into the atmosphere, which is then often deposited as sea-spray and condensation nuclei in raindrops on the terrestrial environment (Fig. 3.2c; Schulze, 1971; Rouault et al., 2005). Together, these factors exhibit variable influence on stream water chemistry depending on the prevailing climatic conditions and landscape position of the stream (Grobbelaar, 1975).

Higher resolution investigations into stream water chemistry on the island are rare. Grobbelaar (1974) provides the only continuous, daily time series of stream water chemistry. Samples were taken at six locations along the van den Boogaard River (hereafter, VDBR; Fig. 3.1) and also over a 27-day period (08/02/1972 – 05/03/1972) at a single site approximately 250 m above mean sea level (hereafter, a.m.s.l). The VDBR is a perennial stream situated on young black basaltic lava on the eastern side of the island, similar to that of the Soft Plume River (hereafter, SPR; Fig. 3.1). The results showed that sea-salts (Na^+ and Cl^-) were the most abundant at all sites with a small increase in ionic content along the course of the river. Temporal variation in stream Na^+ and Cl^- concentrations were observed through the time series. Strong negative correlations were found between daily rainfall amount and Na^+ ($r = -0.74$) and Cl^- ($r = -0.54$) in streams, suggesting that rainfall amount has a significant influence on stream chemistry (Grobbelaar, 1974).

Physicochemical parameters such as pH, stream water temperature, dissolved oxygen and total dissolved solids have never been continuously monitored in stream water on Marion Island. As a result, understanding of the island's stream physicochemical dynamics is based entirely on discrete point-based measurements that have been recorded concomitantly with water sample collection. These low-frequency hydrochemical data provide necessary information on the mean state of stream physicochemistry (Burt et al., 2011). However, it has been shown that hydrological and biological processes influence variations in stream water chemistry on sub-daily timescales (Hodgson and Evans, 1997; Nimick et al., 2005; Moraetis et al., 2010; Neal et al., 2012). Therefore, point-based grab sample measurements are often prone to high uncertainties associated with under representation of high-discharge and short duration events that may result in significant changes in stream dynamics (Jordan and Cassidy, 2011; Sherson et al., 2015).

In addition, diel (i.e., 24 h period) variability in stream chemistry is also not accounted for by discrete measurement at low frequencies (Halliday et al., 2012). Diel variation in stream chemistry may arise in response to any physical, biological or chemical process that operates on a day-night cycle (Nimick et al., 2011; Gammons et al., 2015). To date, no studies on diel oscillations in stream water chemistry have been carried out on Marion Island.

3.2 Study area

3.2.1 Regional setting

Prince Edward Island and Marion Island (46°54′S and 37°51′E), the larger or the two, comprise the Prince Edward Islands (PEI) group (Fig. 3.1). The PEI are located in the Indian sector of the Southern Ocean some 2000 km southeast of South Africa (Fig. 1.1; Lutjeharms and Ansorge, 2008). The PEI have been managed as a Special Nature Reserve under the South African Environment Conservation Act (Act No. 73 of 1989) since 1995 and were declared a Marine Protected Area in 2013 under the Marine Living Resources Act (Act No. 18 of 1998) (PEIMPWG, 1996; DEA, 2013).

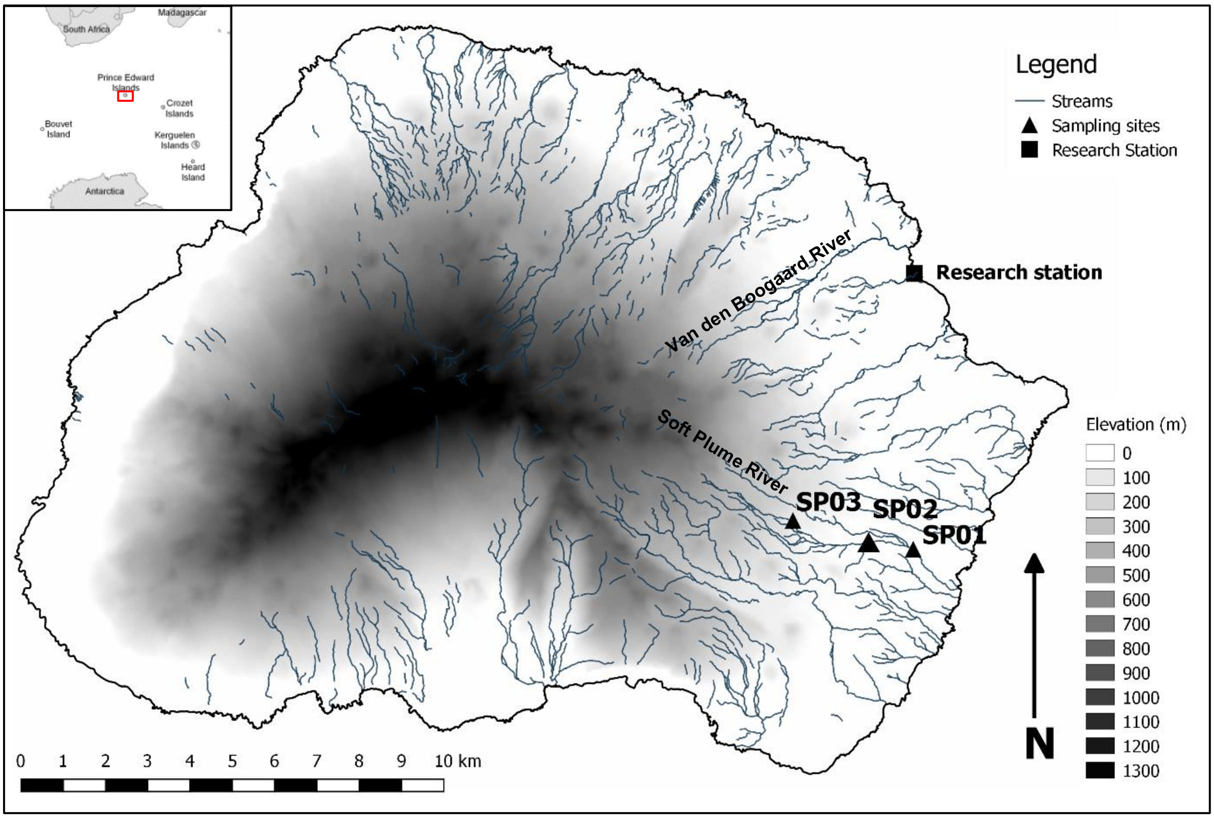


Figure 3.1. Map of Marion Island indicating sampling sites (SP03, ~253 m a.m.s.l; SP02, ~179 m a.m.s.l; SP01, ~ 103 m a.m.s.l) along the Soft Plume River (SPR). All streams (perennial and non-perennial) are included for reference. Inset: location of the Prince Edward Islands (PEI) in relation to other sub-Antarctic islands and major landmasses.

3.2.2 Climate

Marion Island's hyper-oceanic and latitudinal position results in a distinct climatic regime (Boelhouwers et al., 2003). The island experiences high precipitation amounts that is approximately evenly distributed throughout the yearly cycle, with minima occurring in February, October and November (Fig. 3.2a). Mean annual precipitation (1949-2014) was 2243 mm. As with other sub-Antarctic islands, the Southern Ocean moderates diurnal and annual temperature variations due to its high thermal inertia (Schulze, 1971; Bonan, 2002). The island has a mean daily temperature range of less than 2 °C and 3 °C in winter and summer respectively (Le Roux, 2008). Seasonal differences in mean air temperature are approximately 4 °C depending on the base period used (Smith, 2002; Le Roux and McGeoch, 2008). Coupled with these conditions are high humidity, cloud-cover and strong (> 15 m sec $^{-1}$) westerly – to - north-westerly winds (Schulze, 1971; Rouault et al., 2005).

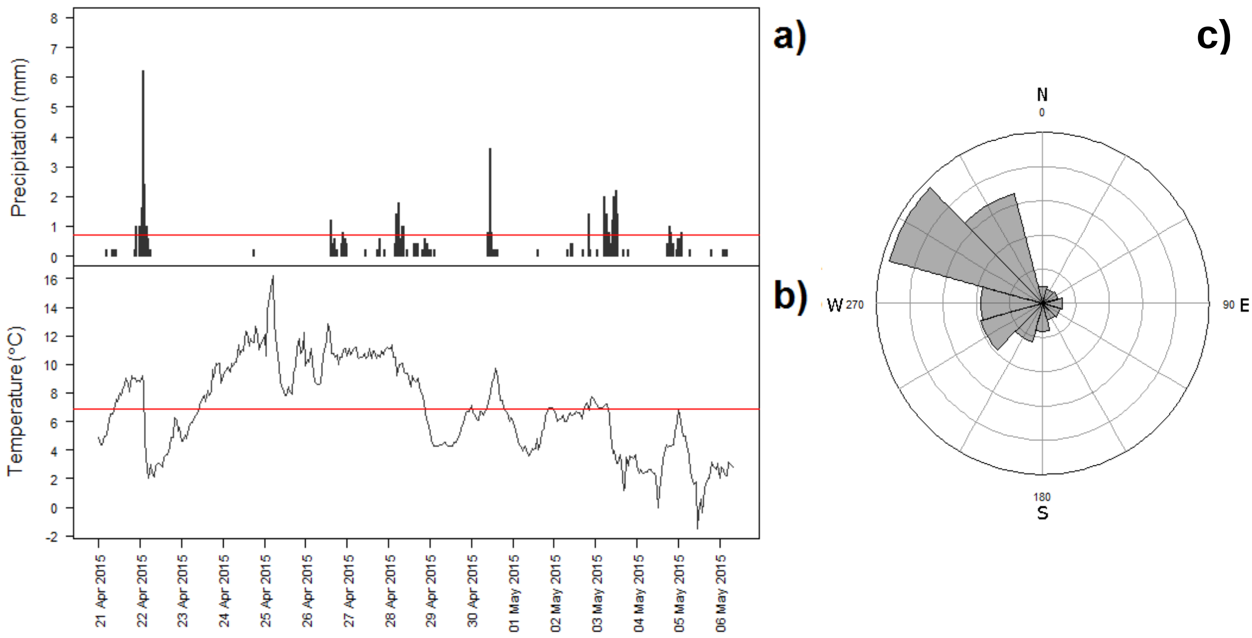


Figure 3.2. a) Hourly precipitation (bars) over the period. Horizontal line (red) indicates the mean (0.71 mm). b) Hourly air surface temperature. Horizontal line (red) indicates the mean temperature (6.9 ºC). c) Count of hourly wind direction recordings. All data are from the period 21/04/2015 15:00 GMT – 06/05/2015 and were recorded at the research station on Marion Island.

Weather conditions over the study period were consistent with the island’s climatic regime (Fig. 3.2a - c; Schulze, 1971). Rainfall fell on most days (Fig. 3.2a; n = 12). Maximum hourly rainfall was 6.2 mm (22/04/2015 17:00 GMT + 3) which contributed to the highest daily rainfall amount of 14.4 mm on 22/04/2015. The longest duration of consecutive rainfall was nine hours (03/05/2015 20:00 GMT + 3 – 04/05/2015 04:00 GMT + 3). Over this nine-hour period a total of 11.8 mm was recorded. Mean air surface temperature was 6.9 ± 3.17 °C and ranged from -1.5 to 16.2 °C (Fig. 3.2b). Temperature exhibited diurnal variation consistent with mean amplitudes measured on the island (Boelhouwers et al.,2003). Wind direction through the time series was predominantly north-west with a smaller westerly component through the study period (Fig. 3.2c).

Marion Island experiences considerable spatial variability in climate. (Schulze 1971; Chown and Avenant 1992; Blake 1996; Le Roux, 2008). While weather conditions are known to vary with topography, altitude and recording height a detailed understanding of islands spatial climatic variability is yet to emerge (Bonan, 2002; Beggs et al., 2004; Le Roux, 2008). Climatic conditions are modified by the islands topography and as a result, microclimate may vary significantly from conditions measured at the research station (46 °53′S, 37°52′E, 24 m a.m.s.l; Fig. 3.1; Nyakatya and McGeoch, 2008). Blake (1996) found total monthly rainfall at mid-altitude (4653 mm; ~550 m a.m.s.l) to be considerably higher than a lower site (2873 mm; 34 m a.m.s.l). While a clear altitudinal precipitation gradient exists, the nature of the gradient may vary depending on topographical differences (Le Roux, 2008).

3.2.3 Topography and geology

The PEI represent the tip of an oceanic intraplate volcano (Verwored, 1971; Chevallier, 1986). Marion Island has a surface area of ± 290km^2 and a circumference of ~72 km (Hedding, 2008). Topographically, the island's low lying areas are characterized by an undulating coastal plain. On the western and southern sides of the island the coastal plain is narrow, varying from ~ 400 – 900 m wide. Whereas, on the eastern side the plain is much wider (~3 – 5 km) (Conradie and Smith, 2012). A steep escarpment rises from the lower lying areas to the interior with peak elevation (Mascarin peak) at 1240 m a.m.s.l (McDougall et al., 2001).

The island's geological evolution is relatively recent with K-Ar dating identifying at least five glacial-interglacial periods and sporadic volcanic activity during the last 450 000 years (McDougall et al., 2001; Boelhouwers et al., 2008). The first main volcanic period was during the Pleistocene. This period produced grey lavas which showed signs of glaciation (Hall, 1978; 2002). The second period was during the Holocene, and is represented by post-glacial black lava and scoria cones that show no sign of glaciation.

3.3 Study site

Perennial streams are uncommon on the island. Porous lavas dominate much of the island's topography and as a result precipitation infiltrates rapidly with the majority reaching the sea via underground recharge (Verwoerd, 1971; Grobbelaar, 1974, 1975). The SPR and VDBR are the only two perennial streams on the island, although recently the latter has been observed flowing intermittently (Fig. 3.1; Dartnall and Smith, 2012). The SPR is located on the eastern side of the island and flows through one of the larger catchments of the island (~ 5.2 km^2; Fig. 3.1). The upper reaches of the stream are shallow, with stream banks of varying gradient that depend on topography. The banks of the SPR are usually steep in the lower reaches owing to fluvial erosion and consist mainly of peat. Filamentous algae is often present in stream where erosion is absent (Smith and Froneman, 2008). The stream bottom varies in composition. In the upper reaches of the stream, rocky and more granular substrate dominate, whereas, along the lower reaches peat is predominantly found (Grobbelaar, 1975).

The SPR provides an opportunity to investigate temporal and spatial stream chemical dynamics of the only continuously flowing lotic water on the island. In addition, no continuous and systematic study of the SPR has previously been carried out. To address this knowledge gap, three locations along the SPR were identified to better understand spatial and temporal stream dynamics. The three study sites span an altitudinal range of ~150 m. The highest site, SP03 is at ~253 m a.m.s.l, while the lower sites SP02 and SP01 are located at ~179 and ~103 m a.m.s.l respectively (Fig. 3.1).

3.3 Materials and Methods

3.3.1 Data collection

Data were obtained over a 16-day period (21 April – 06 May) in 2015 as part of the South African Nation Antarctic Programme (SANAP) research campaign on Marion Island. A Eureka^{TM} Manta multiprobe was set up at SP01 (Fig. 3.1). The multiprobe continuously logged the following physicochemical parameters *in situ* at five minute intervals; pH, water temperature (°C), dissolved oxygen (DO, mg/L) and total dissolved solids (TDS, mg/L). All probes were calibrated in water-saturated air prior to deployment in the field. Data was downloaded manually in the field on 24/04/2015, 04/05/2015 and 06/05.2016. Continuous river stage height (m) was gauged using a levellogger (Solinist levellogger model 3001) and barometrically calibrated with a pressure transducer (Solinist levellogger model 3001).

3.3.2 Sample collection

Sampling was conducted over a 16-day period (21/04/2015 – 06/05/2015) at three locations along the SPR (Fig. 3.1; SP03, SP02, SP01). Sampling took place at approximately the same time each day (~10:00 GMT + 3, SP03; ~10:30 GMT + 3, SP02; ~11:00 GMT + 3, SP01) to ensure that any diurnal variation in solute concentrations were evenly accounted for over the sampling period (Neal et al., 2012). All water samples for major ion analysis were collected in 250 ml polyethelene (HDPE) bottles. Prior to departure into the field, sample bottles were acid washed with dilute HNO_3 and rinsed three times with distilled-deionized water. Sample water was filtered on site using cellulose acetate 0.45µm membrane syringe filters. Given the low ambient temperatures present on the island no preservative was added to the filtered sample (Grobbelaar, 1978a). All water samples were stored for the duration of the study at 4 °C at the research base on Marion Island.

3.3.3 Sample Analysis

All major elements were analysed at the Central Analytical Facility (CAF) at the University of Stellenbosch, South Africa. The cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) were analysed by inductively coupled plasma – atomic emission spectrometry (ICP – AES; Thermo ICap 6200). The instrument was calibrated using NIST (National Institute of Standards and Technology, Gaithersburg MD, USA) traceable standards to quantify the cations. The analytical precision was within 10%; 94.3% for Ca, 96.7% for Mg, 96.5% for K, and 99.2% for Na.

Anions (Cl^-, SO_4^{2-}, NO_3^-) were analysed by ion chromatography (IC) with Waters IC Pak Anion column (4.5 x 50 mm) and a Waters 432 Conductivity detector, coupled to a Waters 717plus Auto sampler and an Agilent 1100 series binary pump. The gradient pump flow-rate was set at 1.1 ml/minute.

3.4 Results

3.4.1 Stream chemistry

A total of 47 samples were collected from three sampling sites along the SPR. All major ion data from the SPR are presented in Table 3.1, with the mean concentrations and standard deviations for each solute plotted in Figure 3.3. Cation abundances were typical for freshwater streams on maritime sub-Antarctic islands (Gorham and Cragg, 1960; Holdgate, 1961; Grobbelaar, 1974), with Na^+, Mg^{2+}, Ca^+, K^+. Anion abundances were Cl^-, SO_4^{2-}. Due to logistical and technical constraints bicarbonate (HCO_3^-) was not measured. However, Grobbelaar (1974; 1978a, b), found relatively low concentrations of HCO_3^- in other streams on Marion Island. Nitrate (NO_3^-) was present in low amounts (Table 3.1), with a number of samples below the detection limit ($n = 13$). Nitrate had a mean 0.6 ± 0.62 and a range of 0.2 to 3.6 mg/L, consistent with previous studies (Grobbelaar 1974, 1978a; van Staden, 2011).

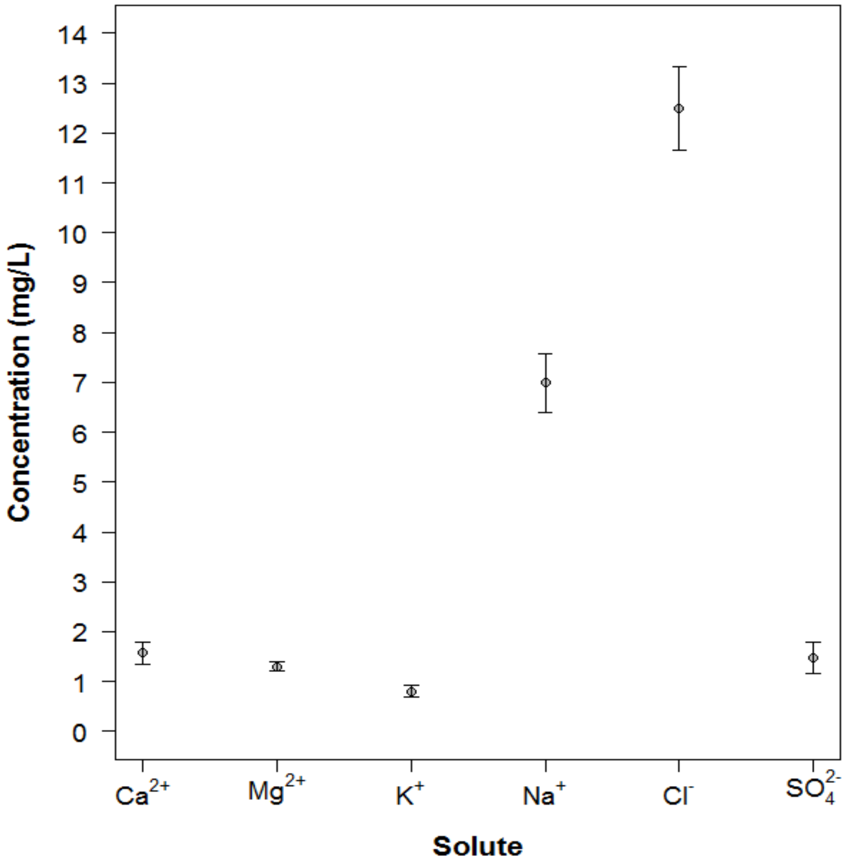


Figure 3.3. Average concentration of ions (mg/L) from the Soft Plume River (SPR). Means were determined from measurements from all three sites. Error bars indicate standard deviations.

The molar Na:Cl ratio for each sample is presented in Table 3.1. The mean molar Na:Cl ratio for all samples was 0.86 ± 0.04 and ranged from 0.71 to 0.99 ($n = 47$). There is a strong, significant positive correlation between Na^+ and Cl^- concentrations ($r = 0.80$; $p < 0.001$). Average concentrations of other major ions such as Ca^{2+}, Mg^{2+}, K^+ and SO_4^{2-} show moderate to high correlation with Cl^- ($r = 0.48$, $p < 0.05$; $r = 0.37$, $p < 0.05$; $r = 0.67$, $p < 0.0001$ and $r = 0.22$ respectively).

Na^+ had a mean of 7 ± 0.58 mg/L and a range from 4.8 to 8.1 mg/L ($n = 47$). The mean Cl^- concentration was 12.5 ± 0.84 mg/L, with a range from 9.7 to 13.8 mg/L ($n = 47$). Mean values for Ca^{2+} (mean = 1.6 ± 0.22 mg/L), Mg^{2+} (mean = 0.8 ± 0.13 mg/L), K^+ (mean = 1.3 ± 0.1 mg/L) and SO_4^{2-} (mean = 1.5 ± 0.3 mg/L) were all relatively similar, albeit considerably less than both Na^+ and Cl^- (Fig. 3.3).

Table 3.1. Major ions (mg/L) in the Soft Plume River. Na:Cl calculated as molar ratio.”–“ indicates below detection limit.

Site	Date	Sample name	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	SO$_4^{2-}$	NO$_3^{-}$	Na:Cl
SP03	21/04/2015	SP 21/04/15 012	1.67	1.44	0.93	7.04	12.5	1.3	3.6	0.87
SP03	/	/	NA	NA	NA	NA	NA	NA	NA	/
SP03	23/04/2015	SP 23/04/15 017	0.95	1.03	0.44	5.57	10.7	1.7	0.5	0.8
SP03	24/04/2015	SP 24/04/14 020	1.31	1.22	0.65	6.24	11.3	1.3	-	0.85
SP03	25/04/2015	SP 25/04/15 023	1.7	1.35	0.81	6.71	11.9	0.9	0.6	0.87
SP03	26/04/2015	SP 26/04/15 026	1.83	1.45	0.88	6.93	12	1.9	0.6	0.89
SP03	27/04/2015	SP 26/04/15 029	1.91	1.45	0.84	6.77	11.9	1.3	-	0.88
SP03	28/04/2015	SP 28/04/15 032	1.87	1.48	0.8	6.86	11.9	1.7	0.4	0.89
SP03	29/04/2015	SP 29/04/15 035	1.69	1.43	0.69	6.67	11.5	1.4	0.7	0.89
SP03	30/04/2015	SP 30/04/15 038	1.69	1.4	0.7	6.38	11.6	1.9	-	0.85
SP03	01/05/2015	SP 01/05/15 041	1.47	1.26	0.57	5.9	12.8	1.1	0.2	0.71
SP03	02/05/2015	SP 02/05/15 044	1.7	1.38	0.74	6.39	12.8	1.6	0.3	0.77
SP03	03/05/2015	SP 03/05/15 047	1.75	1.41	0.74	6.51	11.6	1.7	0.5	0.87
SP03	04/05/2015	SP 04/05/15 050	0.79	0.91	0.39	4.84	9.7	1.4	-	0.77
SP03	05/05/2015	SP 05/05/15 053	1.16	1.21	0.48	6.16	11.4	1.5	0.3	0.83
SP03	06/05/2015	SP 06/05/15 057	1.45	1.34	0.68	6.84	12.7	0.9	0.3	0.83
SP02	21/04/2015	SP 21/04/15 013	1.67	1.3	0.96	7.5	13.1	2	1.9	0.88
SP02	22/04/2015	SP 22/04/15 015	1.73	1.28	0.95	7.47	13.5	1.3	0.8	0.85
SP02	23/04/2015	SP 23/04/15 018	1.24	1.12	0.85	7.12	12.3	1.9	0.7	0.89
SP02	24/04/2015	SP 24/04/15 021	1.66	1.29	0.94	7.28	12.9	1.3	-	0.87
SP02	25/04/2015	SP 25/04/15 024	1.72	1.36	0.79	6.72	11.8	1.3	0.6	0.88
SP02	26/04/2015	SP 26/04/15 027	1.72	1.31	0.92	7.39	12.5	1.2	-	0.91
SP02	27/04/2015	SP 26/04/15 030	1.75	1.33	0.97	7.33	12.6	0.9	0.2	0.9
SP02	28/04/2015	SP 28/04/15 033	1.39	1.2	0.94	7.31	12.2	1.5	0.7	0.92
SP02	29/04/2015	SP 29/04/15 036	1.7	1.31	0.94	7.32	12.9	1.6	0.7	0.88
SP02	30/04/2015	SP 30/04/15 039	1.69	1.3	0.92	7.22	13.2	1.4	0.3	0.84
SP02	01/05/2015	SP 01/05/15 042	1.63	1.27	0.86	7.03	13	1.7	-	0.83
SP02	02/05/2015	SP 02/05/15 045	1.71	1.31	0.91	7.21	12.8	1.4	0.3	0.87
SP02	03/05/2015	SP 03/05/15 048	1.7	1.29	0.89	7.01	12.7	1.7	0.4	0.85
SP02	04/05/2015	SP 04/05/15 051	1.34	1.16	0.74	6.37	12	1.4	0.5	0.82
SP02	05/05/2015	SP 05/05/15 054	1.65	1.32	0.93	7.43	12.8	1.3	0.5	0.9
SP02	06/05/2015	SP 06/05/15 058	1.65	1.3	0.92	7.46	13.1	1.4	-	0.88
SP01	21/04/2015	SP 21/04/15 014	1.72	1.35	0.85	7.7	13.8	1.7	1.3	0.86
SP01	22/04/2015	SP 22/04/15 016	1.58	1.29	0.82	7.47	12.9	2	0.8	0.89
SP01	23/04/2015	SP 23/04/14 019	1.33	1.29	0.74	7.06	13.2	1.6	0.5	0.82
SP01	24/04/2015	SP 24/04/15 022	1.58	1.32	0.83	7.47	13.2	1.8	0.4	0.87
SP01	25/04/2015	SP 25/04/15 025	1.58	1.3	0.81	7.44	13.1	1.7	0.5	0.88
SP01	26/04/2015	SP 26/04/15 028	1.62	1.31	0.81	7.28	13.8	2	-	0.81
SP01	27/04/2015	SP 27/04/15 031	1.62	1.32	0.81	7.39	13.1	1.5	0.3	0.87
SP01	28/04/2015	SP 28/04/15 034	1.69	1.29	0.81	7.25	13	1.3	-	0.86

SP01	29/04/2015	SP 29/04/15 037	1.6	1.31	0.85	7.31	13	0.8	-	0.87
SP01	30/04/2015	SP 30/04/15 040	1.6	1.31	0.78	7.18	11.2	1.1	-	0.99
SP01	01/05/2015	SP 01/05/15 043	1.54	1.28	0.78	6.99	11.7	1.7	-	0.92
SP01	02/05/2015	SP 02/05/15 046	1.62	1.3	0.89	7.29	13.1	1.4	0.6	0.86
SP01	03/05/2015	SP 03/05/15 049	1.65	1.35	0.86	7.35	13.2	1.4	0.3	0.86
SP01	04/05/2015	SP 04/05/15 052	1.27	1.2	0.67	6.87	12.5	1.3	0.4	0.85
SP01	05/05/2015	SP 05/05/15 055	1.51	1.31	0.84	7.41	13.3	1.1	0.3	0.86
SP01	06/05/2015	SP 06/05/15 059	1.63	1.38	0.94	8.05	13.4	1.8	0.6	0.93

3.4.2 Time series of major ions

A daily time series of major ions is presented in Figure 3.4a – f. Low amplitude diurnal variation was observed at all sites through the sampling period. Superimposed on the diurnal variation are two distinct dips in the concentrations of all ions, except for SO_4^{2-}, on 23/04/2015 and 04/05/2015 respectively (Fig. 3.4a – f). Depletion of solute concentrations is observed following highest total rainfall amount (14.4 mm) on 22/04/2015 and longest duration of consecutive rainfall hours between 03/05/2015 and 04/05/2015 (Fig. 3.2a). Except for SO_4^{2-}, the lowest concentrations for Ca^{2+} (0.79 mg/L), Mg^{2+} (0.39 mg/L), K^+ (0.91 mg/L), Na^+ (4.84 mg/L) and Cl^- (9.7 mg/L) were experienced on 04/05/2015, following the longest duration of rainfall.

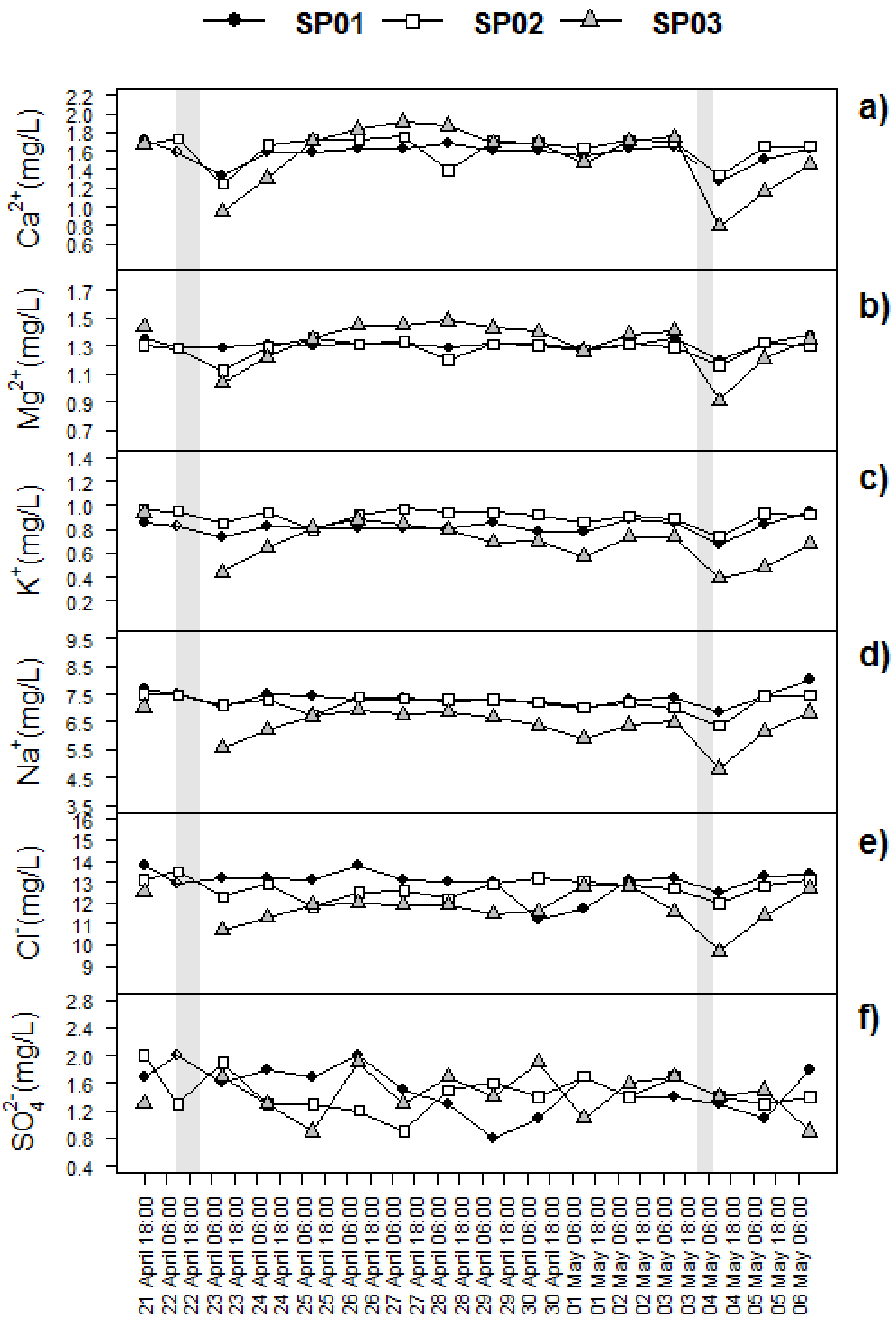


Figure 3.4. Time series of a) Ca^{2+}, b) Mg^{2+}, c) K^{+}, d) Na^{+}, e) Cl^{-} and f) SO_4^{2-} over the period 21/04/2015 – 06/05/2015, measured at three sites along the Soft Plume River. Grey bars indicate the duration of rainfall between 12:00 – 21:00 GMT + 3 on 22/04/2015 (14.4 mm) and 20:00 GMT +3 03/05/2015 to 04:00 GMT +3 04/05/2015 (11.8 mm) respectively.

3.4.3 Variation along the stream

The ionic composition of the SPR exhibited identifiable, and in some cases, significant differences between SP03, SP02 and SP01 for each ion respectively (Fig. 3.6a – f; Table 3.2). Figure 3.6 illustrates that site at the highest altitude site SP03 exhibits the largest amount of variability for each ion, with the exception of SO_4^{2-}, which displays a similar degree of variability at all three sites (Fig. 3.6f). Sea-salt concentrations are also most variable at SP03, with a range of 4.8 to 7.0 mg/L (n = 15) and 9.7 to 12.8 mg/L (n = 15) for Na^+ and Cl^- respectively. Na^+ and Cl^- concentrations are lower at SP03 and both exhibit an increasing trend downstream (Fig. 3.6d, e).

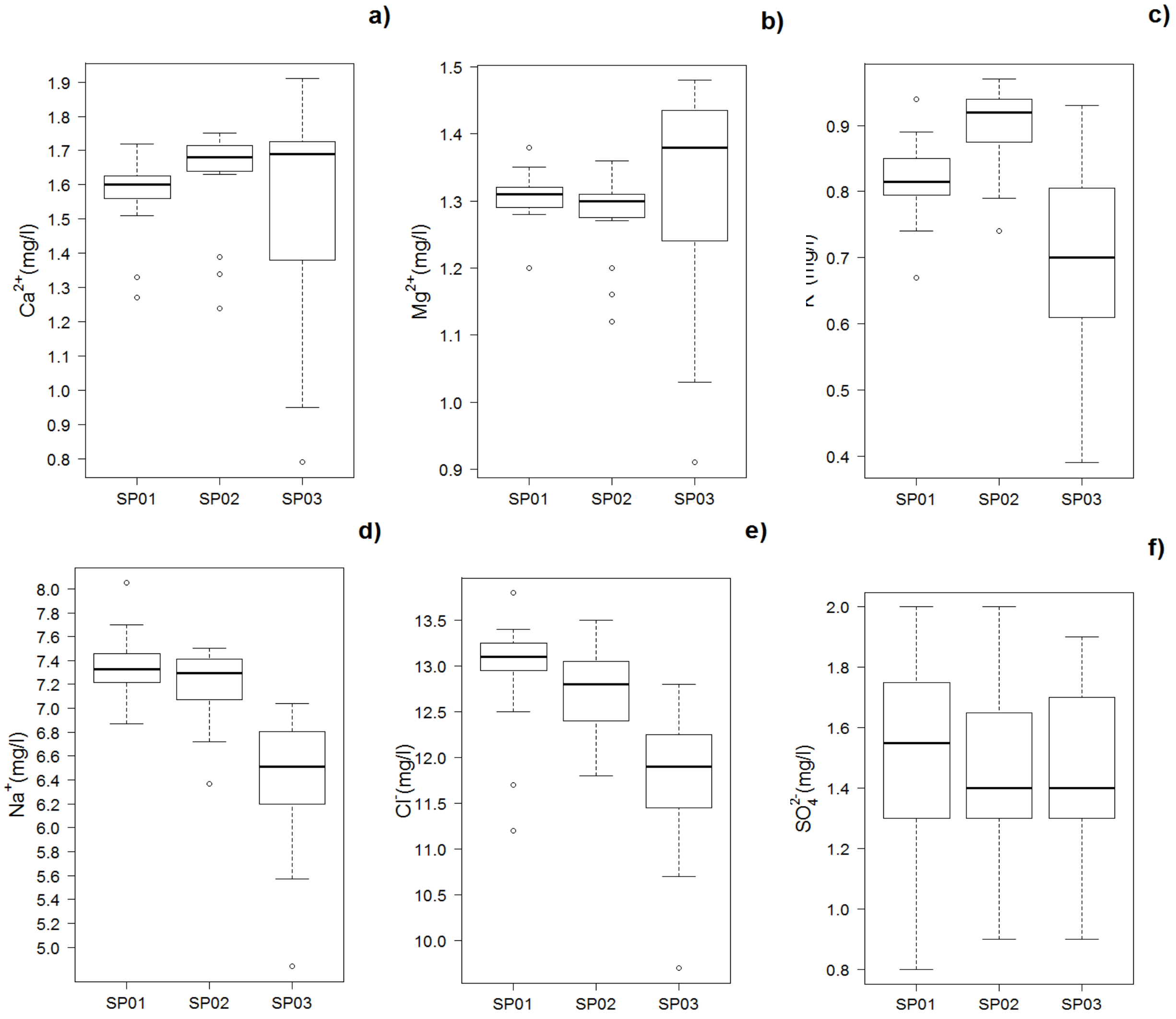


Figure 3.5. Box and whisker plots for all major ions, except NO_3^-, sampled at SP03, SP02 and SP01 on the Soft Plume River where a) Ca^{2+}, b) Mg^{2+}, c) K^+, d) Na^+, e) Cl^- and f) SO_4^{2-}. The boxes are bounded by lower and upper quartile limits, with the central line within the box representing the median values. The whiskers extend to the most extreme values within 1.5 times the interquartile range. Outliers are displayed by open dots.

A Wilcoxon-Mann-Whitney (WMW) test (Wilcoxon, 1945; Mann and Whitney, 1947) was applied to determine if there are any significant differences between sites. The results are presented in Table 3.2. Significantly lower concentrations of Na^+ and Cl^- are found at SP03 compared with the lower altitude sites SP02 and SP01 (Table 3.2). K^+ concentrations are significantly lower at SP03 than SP02 and SP01. Concentrations of both K^+ and Ca^{2+} are higher at SP02 than SP01. No significant differences were found for the rest of the major ions between any of the sampling sites.

Table 3.2. Wilcoxon-Mann-Whitney test results for differences in major ions between sampling sites SP03, SP02 and SP01. P-values represent the probability that the two datasets are derived from the same distribution. Significantly different values are in bold.

	SP01-SP02		**SP01-SP03**		**SP02-SP03**	
Ion	**Mann-Whitney *Z***	**p-value**	**Mann-Whitney *Z***	**p-value**	**Mann-Whitney *Z***	**p-value**
Ca2+	-3.00	**0.001**	-0.80	0.40	0.20	0.80
Mg2+	1.00	0.20	-1.00	0.10	-1.90	0.06
K+	-3.00	**0.001**	3.00	0.01	4.00	**0.00005**
Na+	0.90	0.40	5.00	**0.00005**	4.00	**0.00005**
Cl-	2.00	0.04	4.00	**0.0005**	3.50	**0.0002**
SO42-	0.70	0.50	0.70	0.50	0.00	1.00

3.4.4 Stream physicochemical characteristics

Mean daily physicochemical measurements are presented in Table 3.3. All measurements were recorded by the multi-parameter sonde (5 minute interval) at SP01 and converted to daily averages to determine mean values (Table 3.3). Problems with power-supply to the multi-parameter sonde resulted in a substantial amount of missing data (Table 3.3).

Daily means of pH, stream water temperature, DO and TDS were similar through the time series. Stream pH was close to neutral (mean = 7.2 ± 0.22) and ranged from 6.24 to 7.77 (n = 2139). Mean stream temperature was 5.0 ± 1.94 ºC and ranged from 1.71 to 9.86 °C (n = 2139). DO had a mean of 97.6 ± 1.7 mg/L and a range from 94.1 to 102.8 mg/L (n = 2139). TDS had a mean of 39.5 ± 3.19 mg/L and ranged from 24.6 to 42.8 mg/L (n = 2139).

Table 3.3. Daily (00:00-24:00 GMT + 3) averages of physicochemical variables recorded at SP01.

Date	pH	Temperature (°C)	Dissolved oxygen (mg/L)	Total dissolved solids (mg/L)	River stage (m)
21/04/2015	7.3 ± 0.11	4.7 ± 0.50	12.3 ± 0.10	42.0 ± 0.51	0.6 ± 0.01
22/04/2015	7.1 ± 0.39	5.7 ± 1.26	12.1 ± 0.42	37.5 ± 6.25	0.6 ± 0.20
23/04/2015	7.1 ± 0.22	4.12 ± 0.76	12.7 ± 0.24	37.2 ± 3.19	0.6 ± 0.01
24/04/2015	7.2 ± 0.1	5.8 ± 1.35	12.2 ± 0.37	40.6 ± 0.56	0.6 ± 0.01
25/04/2015	7.3 ± 0.11	7.7 ± 1.31	11.6 ± 0.35	40.8 ± 0.69	0.6 ± 0.01
26/04/2015	7.3 ± 0.13	7.2 ± 0.76	11.8 ± 0.18	40.7 ± 0.39	0.6 ± 0.01
27/04/2015	-	-	-	-	-
28/04/2015	-	-	-	-	-
29/04/2015	-	-	-	-	-
30/04/2015	-	-	-	-	-
01/05/2015	-	-	-	-	-
02/05/2015	-	-	-	-	-
03/05/2015	-	-	-	-	-
04/05/2015	7.2 ± 0.03	3.6 ± 0.44	12.6 ± 0.11	39.4 ± 1.14	0.6 ± 0.12
05/05/2015	7.0 ± 0.22	3.7 ± 0.33	12.5 ± 0.48	38.6 ± 2.34	0.5 ± 0.13
06/05/2015	7.2 ± 0.14	2.4 ± 0.42	12.8 ± 0.13	40.9 ± 1.23	0.5 ± 0.02

3.4.6 Time series of stream physicochemistry

A time series of pH, stream water temperature, dissolved oxygen (DO), total dissolved solids (TDS) and river stage (m) for the period 21/04/2015 to 06/05/2015 is presented in Figure 3.6a - e. All measurements responded rapidly to high rainfall amounts. The response coincided with maximum rainfall intensity and the longest period of sustained rainfall on 22/04/2015 (14.8 mm; 6.2 mm h^{-1}) and 03/05/2015 – 04/05/2015 (9 hours; 11.2 mm) (Fig. 3.2a).

The largest response from all measurements was to the rainfall event on 22/04/2015 (Fig. 3.6a - f). Over this period, there was a sharp decrease in pH (1.3), stream temperature (3.9 °C) and TDS (16 mg/L) between 17:00 – 21:00 GMT + 3, coinciding with the most intense period of rainfall (Fig. 3.2a; 6.2 mm h^{-1}; 17:00 GMT + 3). DO concentrations and river stage height increased by 1.5 mg/L and 0.69 m respectively over the same period. A similar and consistent, but lower amplitude response was observed for all measurements on 05/04/2015 compared with the rainfall event on 22/04/2015. Unfortunately, due to missing data it was not possible to examine the response of measurements to the longest duration of rainfall (Fig. 3.2a; 03/05/2015 20:00 GMT + 3 – 04/05/2015 04:00 GMT + 3).

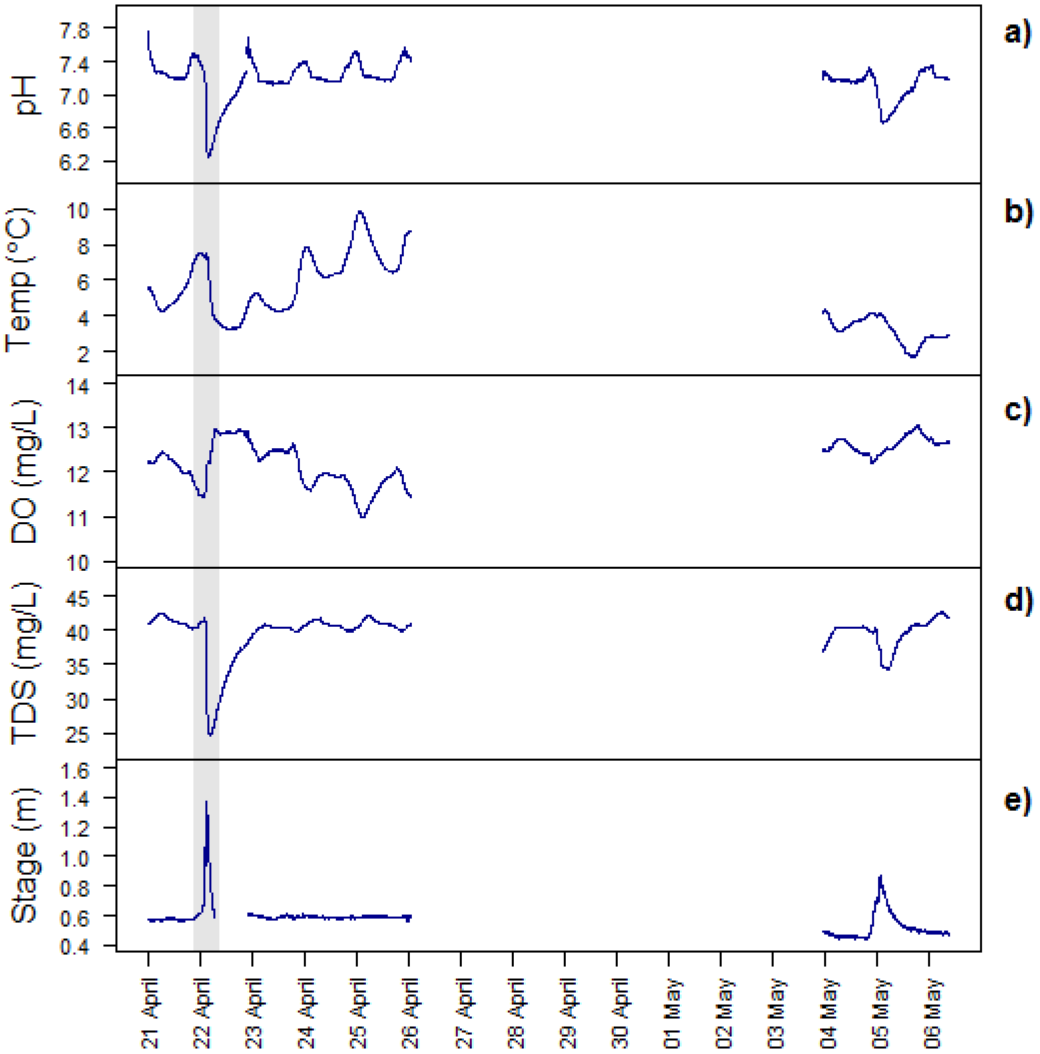


Figure 3.6. Time series (5 minute interval) of a) pH, b) temperature (°C), c) dissolved oxygen (DO; mg/L), d) total dissolved solids (TDS; mg/L) and e) river stage height (m) in the Soft Plume River at SP01 from 21/04/2015 to 26/04/2015. The grey bar indicates the highest total daily rainfall (Fig. 3.2a; 14.4 mm).

3.4.7 Diel variability

To further investigate diel cycles in stream physicochemistry, measurements from the original data set were extracted to exclude the period of missing data and converted to hourly averages to generate a new hourly data set that covered the period 21/04/2015 to 26/04/2015 (Figure 3.7a – d). All measurements, except for river stage height (m) exhibited diel oscillations (Fig. 3.6a - f).

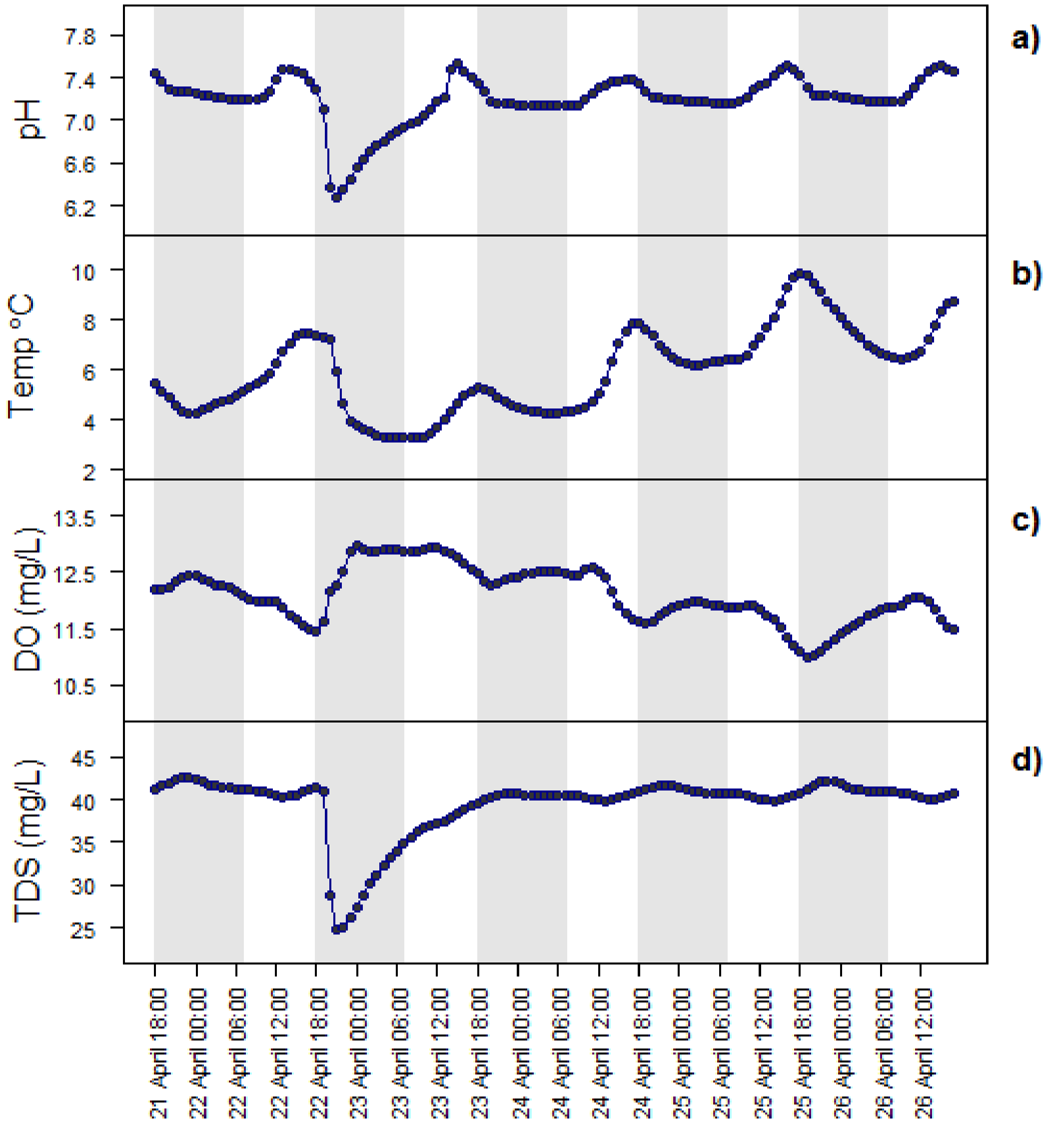


Figure 3.7. Time series of hourly measurements of a) pH, b) stream temperature (ºC), c) dissolved oxygen (DO; mg/L) and d) total dissolved solids (TDS; mg/L) in the Soft Plume River at SP01 from 21/04/2015 to 26/04/2015. Grey bars indicate approximate night time hours (18:00 – 07:00 GMT + 3).

Diel cycles of pH and stream temperature followed similar trends (Fig. 3.7a, b). Both increased during the day with maxima around during the afternoon, followed by a decrease and minima during night time. Stream pH maximum precedes stream water temperature maximum. The time-lagged relationship is further explained by the results of a cross-correlation function (ccf; R Development Core Team, 2016). The ccf identifies dominant and significant positive cross correlations at lags of 2-3 hours. This is seen in Figure 3.7a, b, where peak pH precedes stream temperature maxima by 2-3 hours. Diel changes in pH are on average 0.5 pH units, with maxima occurring between 13:00 – 15:00 GMT + 3. Stream water temperature minima and maxima occurred between 00:00-04:00 and 15:00 – 18:00 GMT + 3 respectively. Diel stream water temperature changes were on average 2.7 °C. Stream water temperature displayed a significant, positive linear trend between 21/04/2015-26/04/2015 ($r^2 = 0.39$; $p < 0.0001$).

There was a significant negative correlation between stream water temperature and DO concentrations ($r =-0.96$, $p < 0.0001$), suggesting a causal relationship. DO concentrations begin to decrease during the morning as stream water is warmed and oxygen solubility decreases. DO exhibited diel cycles characterized by night time maxima and day time minima. While diel cycles were present the range was low (mean = 0.7 mg/L). A significant, negative linear trend was identified for DO concentrations over the period 21/04/2015 – 26/04/2015 ($r^2 = 0.28$; $p < 0.0001$).

TDS exhibits a small mean range of diurnal variability (mean = 2.1 mg/L), but responds rapidly to the rainfall event on the 22/04/2015, whereby concentrations dropped from 40.9 mg/L at 17:00 GMT + 3 to 30.1 mg/L by 00:00 GMT + 3 (Fig. 3.7d). TDS increased during the night time and decreased during the day time. Maxima and minima were observed during night and day time hours respectively. Similar patterns have been reported elsewhere for electrical conductivity (EC), which is often used as a proxy for TDS because of their strong correlation (Thomas, 1986; Hayashi et al., 2012). For river stage there is no clear and consistent amplitude or timing of daily minimum and maximum values throughout the sampling period.

3.5 Discussion

3.5.1 Chemical composition of stream water

The major mechanisms controlling the chemical composition of stream water have broadly been identified as, atmospheric precipitation, rock dominance and evaporation-crystallization processes (Clarke, 1924; Gibbs, 1970). On oceanic islands, freshwaters receive most of their ions from precipitation (Tyler, 1972; Buckney and Tayler, 1974; Smith, 1987). This results in the chemical composition of freshwater closely resembling that of seawater (Gorham and Cragg, 1960). Major ion concentrations in the SPR highlight the substantial influence Marion Island's hyper-maritime location and prevailing climatic conditions on its stream water chemical composition.

Consistent with previous studies, ion concentrations in the SPR were low and same relative proportions as that of seawater (Grobbelaar, 1974, 1975, 1978a; van Staden, 2011). Na^+ and Cl^- were the most abundant ions with mean concentrations of 7 ± 0.58 mg/L and 12.5

± 0.84 mg/L respectively. The ionic dominance order of $Cl^- > Na^+ > SO_4^{2-} > Mg^{2+} > Ca^{2+} > K^+$ found in the SPR is identical to that of seawater. Furthermore, the mean molar Na:Cl ratio (0.86), is virtually the same as that of seawater (0.87; Likens et al., 1987). On islands and for coastal regions, Na:Cl ratios of this order indicate that atmospheric inputs, enriched in sea-salts derived from the surrounding ocean, are the dominant control on precipitation and surface water chemistry (Gaillardet et al., 1999).

Results are also consistent with studies from other sub-Antarctic islands. For example, on Macquarie Island, Iles Kerguelen and sub-Antarctic Campbell Island (Fig. 1.1) the chemical composition of freshwater is dominated by Na^+ and Cl^- with the authors attributing the abundance of these ions to the influence ocean surrounding the respective islands (Tyler, 1972; Taylor, 1974). In addition, studies from maritime Antarctica also found a similar pattern. Na^+ and Cl^- were the most abundant ions in freshwaters on Signy Island (Caulkett and Ellis-Evans, 1997), Livingston Island (Toro et al., 2007) and King George Island (Vinocur & Unrein, 2000) (Fig. 1.1). Nedzarek et al. (2015) concluded that this pattern is typical for small streams on oceanic islands that have relatively damp climates.

Comparison between the SPR and VDBR offers insight into the influence of wind-direction, precipitation amounts and landscape position on stream chemistry. Samples from the VDBR have significantly higher concentrations of Na^+ (Mann-Whitney Z-value = -3, $p < 0.05$) and Cl^- (Mann-Whitney Z- value = -4, $p < 0.001$) compared to samples from the SPR. Greater proximity to the coastline and more direct exposure to the north-westerly winds would result in higher concentrations of Na^+ and Cl^- in stream water (Grobbelaar, 1974; Smith, 1987; Neal and Kirchner, 2000). As the VDBR is situated on the north-eastern side of the island it is more exposed to northwesterly winds enriched in sea-salts. In addition, weather conditions during the time of sampling could have influenced the concentrations of Na^+ and Cl^-. However, given that the SPR and VDBR were sampled at different times, with presumably different weather conditions, it is not possible to identify the dominant factors responsible for the differences between the streams. Nevertheless, such differences in Na^+ and Cl^- concentrations between the VDBR and SPR warrant a detailed future study.

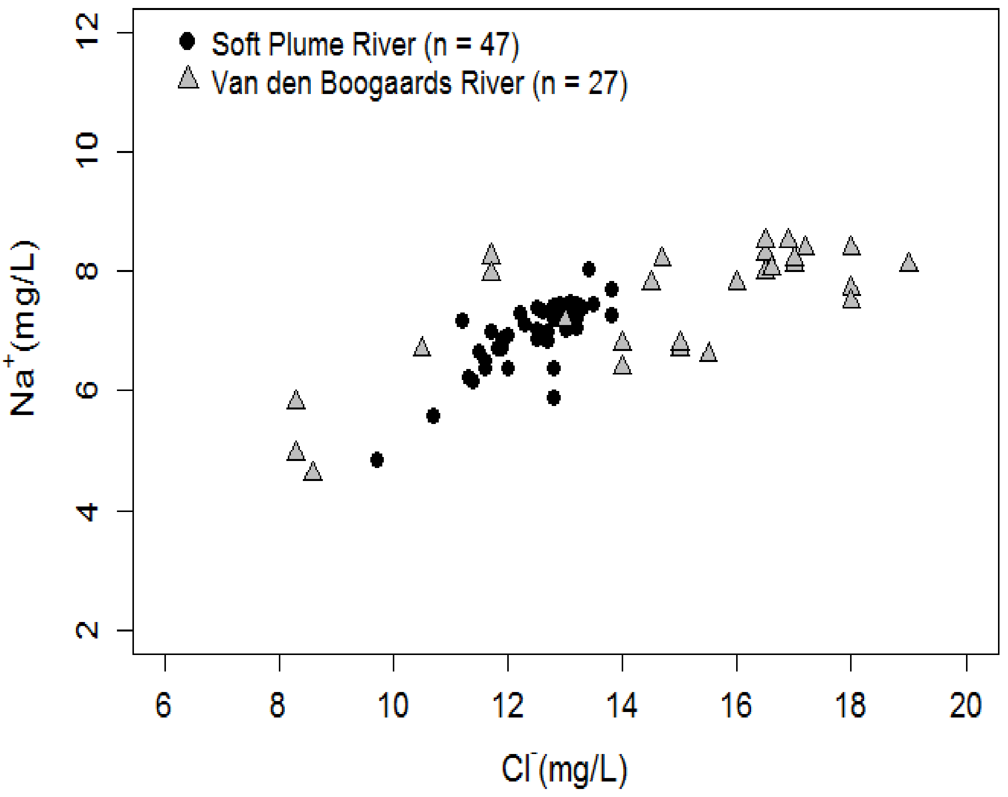


Figure 3.8. Bivariate plot of Na^+ and Cl^- from the Soft Plume River (SPR) and van den Boogaard River (VDBR) (Fig. 3.1). Samples from the SPR are from this study (21/04/2015 – 06/05/2015). Data for the VDBR are from Grobbelaar (1974), collected daily between 08/02/1972 – 05/03/1972.

3.5.2 Temporal and spatial variation along the stream

Stream solute concentrations have been shown to vary on multiple temporal scales (Neal and Kirchner, 2000; Kirchner et al., 2004; Nimick et al., 2011; Neal et al., 2012). At all sampling sites, most solutes tend to co-vary and remain stable at low concentrations through the time series. The average magnitude of diurnal variation shown by each solute is similar to that found in the VDBR (Grobbelaar, 1974).

Superimposed on the diurnal variation are two clear dips in the concentration of most solutes, except SO_4^{2-}, observed at all sites on 22/04/2015 and 04/05/2015 respectively (Fig. 3.4). These dips coincide with maximum rainfall intensity (Fig. 3.2a; 6.8 mm h^{-1}; 22/04/2015) and the longest duration of consecutive rainfall (9 hours; 03/05/2015 20:00 GMT + 3 – 04/05/2015 04:00 GMT + 3). This suggests that rainfall amount, intensity and duration all influence the dilution of most stream solute concentrations in the SPR (Walling and Foster, 1975). Lee et al. (2015) found a similar response from solutes in the Haean Basin, between

South and North Korea, whereby dilution of stream ions varied relative to rainfall intensity, duration and antecedent moisture conditions.

Although the three sampling sites lie within ~3 km of each other and drain a common lithology, spatial differences in stream chemistry were observed. A similar pattern was found by Hindshaw et al. (2011) for a glacial catchment in Switzerland. The highest altitude site SP03 tends to exhibit the largest response in all solutes, except SO_4^{2-}, compared with the lower sites SP02 and SP01. This could be explained by possible altitudinal precipitation gradients whereby more rainfall at SP03 would result in a greater dilution of solute concentrations. Although not recorded in this study, altitudinal precipitation gradients that have previously been observed on Marion Island (Blake, 1996), would account for the larger response observed at SP03. These findings are further supported by the concentration-discharge relationship whereby concentrations of major ions generally tend to decrease with increasing discharge (Johnson et al., 1969; House and Warwick, 1998). The dilution effect is characterized by the dilution of baseflow stream solutes by surface run-off, predominantly derived directly from precipitation, with increasing discharge (House and Warwick, 1998). However, in catchments where precipitation is frequent and relatively evenly distributed throughout the year, such as on Marion Island, it is extremely difficult to determine definite baseflow conditions (Tetzlaff et al., 2007). Nevertheless, it is still possible to identify a response in stream chemistry to high rainfall inputs.

Concentrations of Na^+ and Cl^- are significantly lower at SP03 compared with SP02 and SP01 throughout the time series. Although only based on a single day of sampling (31/01/1972), Grobbelaar (1974) found a similar altitudinal relationship for Na^+ and Cl^- in the VDBR, where the lowest concentration of stream Na^+ and Cl^- were found at the highest site (~ 350 m a.m.s.l) and gradually increased downstream. Again, an altitudinal precipitation gradient would also explain the significantly lower concentrations of Na^+ and Cl^- at SP03 compared with SP02 and SP01 observed through the time series (Table 3.2.; Fig. 3.4). Smith (1987) found there to be a significant negative correlation between major ions and total ionic content in precipitation with amount of precipitation ($r = -0.66$, $p < 0.05$) on Marion Island. Assuming that under the very wet conditions the signal of sea-salts in rainfall is transferred more directly to a stream (Neal et al., 2012), it is expected that if more rainfall fell at SP03 then stream Na^+ and Cl^- concentrations would be higher at SP03 compared with SP02 and SP01.

3.5.3 Stream physicochemistry

The physicochemical characteristics of the SPR are similar to that of other streams on the island and typical for streams on undisturbed oceanic islands (Gorham and Cragg, 1960; Holdgate, 1961; Grobbelaar, 1974, 1978a; Grobbelaar et al., 1987; van Staden, 2011; Dartnall and Smith, 2012). Mean stream pH is neutral, similar to what was observed in the VDBR (Grobbelaar, 1974). Mean stream temperature mirrors air surface temperature, as shown by the significant positive correlation ($r = 0.79$, $p < 0.001$). This relationship is expected as both air and stream surface temperatures are ultimately heated by net solar radiation (Blaen et al., 2013; Arismendi et al., 2014). DO concentrations in the SPR were similar to those measured in various other streams on the island (Grobbelaar et al., 1987). The range of DO in the SPR is similar to that found in the Ro´balo River on sub-Antarctic Navarino Island (Contador et al., 2015). TDS commonly correlates well with major ion concentrations (Nimick et al., 2003), with low mean TDS concentrations in the SPR supporting previous findings of low stream solute concentrations on the island (Grobbelaar, 1975).

Stream chemistry can respond significantly to storm events (Holloway and Dahlgren, 2001). The physicochemistry of the SPR responded rapidly to a short and intense rainfall event on 22/04/2015 (14.4 mm; Fig. 3.6). Following this, stream pH, temperature and TDS all decreased sharply due to dilution (Hayashi et al., 2012). In contrast, DO concentrations increased. A similar pattern for DO was found by Feller and Kimmins (1979) in an undisturbed stream in British Columbia. For pH, a decrease following high rainfall is consistent with studies of streams draining small basins (Feller and Kimmins, 1979; Langan, 1989; Caissie et al., 1996). Stream temperature in the SPR decreased by 4 ºC following the rainfall event on 22/04/2016. Brown and Hannah (2007) found there to be a significant relationship between total precipitation amount and temperature change, with higher rainfall storms resulting in greater stream temperature depression. Additionally, no significant relationship was found between temperature change and rainfall duration, mean and max intensity or start time of the rainfall.

3.5.4 Diel cycles

Streams on Marion Island are oligotrophic with low rates of primary productivity, typical of unenriched, maritime island freshwaters (Grobbelaar, 1974, 1975; Grobbelaar et al., 1987; Cooper et al., 1992). The low biological activity of streams on the island suggests that diel cycles driven by aquatic organisms would be small and that external drivers, such as net solar radiation will exert greater influence (Nimick et al., 2003; Neal et al., 2012). Of the various processes that control stream physicochemistry, sunlight is considered the primary driver of diurnal cycles (Poole and Berman, 2001). Air temperature, relative humidity, cloud cover and wind speed all influence the heat exchange between the stream and the atmosphere (Nimick et al., 2011). As a result, sunny and cloudless conditions promote larger diel cycles, particularly in temperature, in streams that are not shaded (Gammons et al., 2015).

Changes in stream pH occur on a daily basis as a result of various processes. The mean diurnal variation in pH (0.5) is consistent with other studies which have found diurnal pH variation to be below one pH unit (Nimick et al., 2005; Nimick et al., 2011). Stream pH generally varies as a result of changing concentrations of dissolved CO_2 caused by aquatic organisms producing or consuming CO_2 through photosynthesis and respiration respectively (Nimick et al., 2011). However, in oligotrophic streams absent of macrophytes, such as the SPR, other processes are responsible for fluctuations in stream pH (Parker et al., 2007). Diurnal changes in temperature can be responsible for small diurnal changes in pH (Nimick et al., 2011). For example, the pH of neutrality and the solubility of dissolved CO_2 increases with decreasing temperature, resulting in high pH at lower temperatures (Bäckström et al., 2002). In the SPR, stream pH begins to rise after sunrise and increases throughout the day, a pattern has been observed by other authors (Drysdale et al., 2003; Moraetis et al., 2010). In addition, late-afternoon maxima and night time minima in stream pH was found by other studies that attributed the pH cycles to photosynthesis (Fuller and Davis, 1989; Nimick et al., 2003; Gammons et al., 2007).

Stream water and air temperatures are both primarily heated through solar radiation. Their relationship therefore is able to provide insight into physical processes that regulate stream thermal regimes (Mohseni and Stefan, 1999; Lisi et al., 2015). The prevailing climatic conditions drive the small diurnal stream temperature variations (Boelhouwers et al., 2003). Despite this, stream temperatures in the SPR mimic the air temperature regime cycle with maxima and minima in the late afternoon and night time respectively. The relationship between stream and air temperature is widely recognised (Crisp and Howson, 1982; Webb, 1987). In the SPR with a strong, significant positive relationship with air temperature measured at the research station ($r = 0.78$, $p < 0.0001$). However, stream temperatures were also on average lower than air surface temperatures and generally lag air surface maxima as a result of the streams thermal inertia (Webb, 1987; Erickson et al., 2000). Moraetis et al. (2010) found such a lag to be between two to five hours for the Koiliaris River, Greece, with a similar relationship observed by other authors (Webb et al., 2003; Dominnguez-Villar et al., 2008).

Stream water temperature is the dominant control on DO concentrations in the SPR. The temperature dependent solubility of oxygen is illustrated in Figure 3.7 where DO responds directly to water temperature (Guasch et al., 1998). DO concentrations decrease as stream water is warmed and oxygen solubility decreases (Nimick et al., 2003). In addition, there is a strong, significant negative relationship between DO concentrations and stream water temperature ($r = -0.96$, $p < 0.0001$). This strong correlation further emphasizes the dominant control stream temperature has on DO concentrations. Such a relationship is consistent with small, shallow and impoverished streams (Rajwa-Kuligiewicz et al., 2015). The night time maxima and day time minima in DO observed in the SPR is also found in oligotrophic mountain streams with steep gradients (Nimick et al., 2011). Similar patterns have been observed elsewhere in streams that are not biologically productive with the opposite pattern observed in streams with substantial photosynthetic activity (Nimick et al., 2003; Loperfido et al., 2009). Generally, DO concentrations decrease at night time as respiration of aquatic organisms increase the dissolved CO_2 in water and decrease stream pH (Simonsen and Harremoës, 1978; Drysdale, 2003). This night time pattern is absent in the SPR, highlighting the low biological activity of the stream.

3.5.4 Implications for understanding stream physicochemical dynamics

From the results of the high-frequency monitoring of the SPR it is clear that all measurements respond rapid to high amounts of rainfall. In addition, most measurements also exhibited diel cycles. Tomlinson and De Carlo (2003), suggest that in watersheds that experience short but intense rainfall and subsequently exhibit a flashy response in stream chemistry, high-resolution monitoring is essential for accurate characterization of stream dynamics. The results from this study illustrate how point-based measurements might under represent short duration events (Fig. 3.6), depending on when and where the measurement is made.

Spot measurements have been used to identify the mean state of stream water on the island (Grobbelaar, 1974, 1975, 1978; van Staden, 2011), however such measurements mask sub-daily variation and misrepresent “true" conditions (Wilby et al., 2014). High-frequency measurement schemes will not always be necessary but should rather be guided by what is primarily being investigated and the research questions being asked (Burt et al., 2011; Halliday et al., 2012).

3.6 Conclusion

The chemical composition of the Soft Plume River was typical for streams on Marion Island and consistent with previous studies from the island and other maritime sub-Antarctic islands. Na^+ and Cl^- dominated the overall composition of the stream with the remaining ions present in low concentration. The mean Na:Cl ratio (0.86) was nearly identical to that of seawater (0.87), indicating that precipitation enriched in marine ions controls the chemical composition of the SPR. The time series revealed that temporal variation in stream chemistry was the result of stream dilution associated with high rainfall amounts. Along the stream there were significant differences in Na^+ and Cl^- concentrations. Na^+ and Cl^- concentrations were significantly lower at the highest site SP03 compared with SP02 and SP01. It is likely that this pattern was the result of an altitudinal precipitation gradient.

This study also presents the first ever *in situ* high-resolution investigation into stream physicochemical dynamics on Marion Island. The high-frequency data revealed that the Soft Plume River exhibits a noticeable degree of variability and complexity, especially as the data only represent stream dynamics over a limited range of annual climatic variation. Stream pH, temperature, dissolved oxygen, total dissolved solids and stage height all responded rapidly to high rainfall amounts. In addition, all measurements, except for stage height, exhibited diel oscillations. Diel cycles in pH were small. Stream temperature followed the daily insolation cycle and was the dominant control of DO cycles with a significant inverse relationship between the two. Together, findings highlight the limitations of discontinuous point-based measurements. High-frequency monitoring provided valuable insight into variability in stream water chemistry that would otherwise not be accounted for at a lower temporal resolution.

Acknowledgements

This work is undertaken as part of the National Research Foundation/South African National Antarctic Programme project: Landscape and Climate Interactions in a Changing Sub-Antarctic Environment (grant no. 93075). Climate data from the research station on Marion Island were provided by the South African Weather Services. Prof. Werner Nel (Department of Geography and Environmental Science, University or Fort Hare, South Africa), Prof. Dave Hedding (Department of Geography, University of South Africa, South Africa) Abuyiselwe Nguna (University of Fort Hare) assisted with sample collection. Riana Rossouw and Meryl Patience of the Central Analytical Facility at Stellenbosch University provided the analysis of cations and anions respectively.

References

Arismendi, I., Safeeq, M., Dunham, J.B., Johnson, S.L., 2014. Can air temperature be used to project influences of climate change on stream temperature?. Environmental Research Letters 9, 1-12.

Bäckström, M., Börjesson, E., Karlsson, S., 2002. Diurnal variations of abiotic parameters in a stream, recipient for drainage water in Ranstad, southwest Sweden. Journal of Environmental Monitoring 4, 772-777.

Beggs, P.J., Selkirk, P.M., Kingdom, D.L., 2004. Identification of von Karman vortices in the surface winds of heard island. Boundary-Layer Meteorology 113, 287-297.

Blaen, P.J., Hannah, D.M., Brown, L.E., Milner, A.M., 2013. Water temperature dynamics in High Arctic river basins. Hydrological Processes 27, 2958-2972.

Blaen, P.J., Hannah, D.M., Brown, L.E., Milner, A.M., 2014. Water source dynamics of high Arctic river basins. Hydrological Processes 28, 3521-3538.

Blake, B. J.,1996. Microclimate and prediction of photosynthesis at Marion Island. M.Sc. thesis, University of the Free State, Bloemfontein, South Africa.

Boelhouwers, J., Holness, S., Sumner, P., 2003. The maritime Subantarctic: a distinct periglacial environment. Geomorphology 52, 39-55.

Boelhouwers, J., Meiklejohn, I., Holness, S., Hedding, D., 2008. Geology, Geomorphology and Climate Change: land-sea interactions in a changing ecosystem. In: Chown, S.N., Froneman, W. (Eds.), The Prince Edward Islands: land-sea interactions in a changing ecosystem. Stellenbosch, African Sun Media.

Bonan, G., 2015. Ecological climatology: concepts and applications. Cambridge University Press.

Brown, L.E., Hannah, D.M., 2007. Alpine stream temperature response to storm events. Journal of Hydrometeorology 8, 952-967.

Buckney, R.T., Tyler, P.A., 1974. Reconnaissance limnology of Sub-Antarctic islands. II. Additional features of the chemistry of Macquarie Island lakes and tarns. Marine and Freshwater Research 25, 89-95.

Burt, T.P., Howden, N.J.K., Worrall, F., McDonnell, J.J., 2011. On the value of long-term, low-frequency water quality sampling: avoiding throwing the baby out with the bathwater. Hydrological Processes 25, 828-830.

Caissie, D., Pollock, T.L., Cunjak, R.A., 1996. Variation in stream water chemistry and hydrograph separation in a small drainage basin. Journal of Hydrology 178, 137-157.

Cantonati, M., Ortler, K., 1998. Using spring biota of pristine mountain areas for long-term monitoring. In Hydrology, Water resources and Ecology in headwaters (Proceedings of the Head-Water'98 Conference held at Meran/Merano, Italy). IAHS Publishing. 248, 379–385.

Caulkett, A.P., Ellis-Evans, J.C., 1997. Chemistry of streams of Signy Island, maritime Antarctic: sources of major ions. Antarctic Science 9, 3-11.

Chevallier, L., 1986. Tectonics of Marion and Prince Edward volcanoes (Indian Ocean): result of regional control and edifice dynamics. Tectonophysics 124, 155-175.

Chown, S.L., Avenant, N., 1992. Status of Plutella xylostella at Marion Island six years after its colonization. South African Journal of Antarctic Research 22, 37–40.

Clarke, F.W., 1924 Data of geochemistry. US Geological Survey Bulletin 770.

Conradie, E.C., Smith, V.R., 2012. Spatial variation in soil chemistry on a sub-Antarctic island. Open Journal of Soil Science 2, 111-115.

Contador, T., Kennedy, J.H., Rozzi, R., Villarroel, J.O., 2015. Sharp altitudinal gradients in Magellanic Sub-Antarctic streams: patterns along a fluvial system in the Cape Horn biosphere reserve (55 S). Polar Biology 38, 1853-1866.

Convey, P., Bindschadler, R., Di Prisco, G., Fahrbach, E., Gutt, J., Hodgson, D.A., Mayewski, P.A., Summerhayes, C.P., Turner, J., 2009. Antarctic climate change and the environment. Antarctic Science 21, 541-563.

Cooper, J., Crafford, J.E., Hecht, T., 1992. Introduction and extinction of brown trout (Salmo trutta L.) in an impoverished subantarctic stream. Antarctic Science 4, 9-14.

Crisp, D.T., Howson, G., 1982. Effect of air temperature upon mean water temperature in streams in the north Pennines and English Lake District. Freshwater Biology 12, 359-367.

Dalai, T.K., Bhattacharya, S.K., Krishnaswami, S., 2002. Stable isotopes in the source waters of the Yamuna and its tributaries: seasonal and altitudinal variations and relation to major cations. Hydrological Processes 16, 3345-3364.

Dartnall, H.J., Smith, V.R., 2012. Freshwater invertebrates of sub-Antarctic Marion Island. African Zoology 47, 203-215.

Department of Environmental Affairs (DEA)., 2013. Prince Edward Islands declared a Marine Protected Area.

https://www.environment.gov.za/mediarelease/princeedwardislands_declaredmarineprotectedarea. Accessed 28 November 2015.

Domínguez-Villar, D., Arteaga, C., García-Giménez, R., Smith, E.A., Pedraza, J., 2008. Diurnal and seasonal water variations of temperature, pH, redox potential and conductivity in gnammas (weathering pits): Implications for chemical weathering. Catena 72, 37-48.

Drysdale, R., Lucas, S., Carthew, K., 2003. The influence of diurnal temperatures on the hydrochemistry of a tufa-depositing stream. Hydrological Processes 17, 3421-3441.

Dutton, A., Wilkinson, B.H., Welker, J.M., Bowen, G.J., Lohmann, K.C., 2005. Spatial distribution and seasonal variation in 18O/16O of modern precipitation and river water across the conterminous USA. Hydrological Processes 19, 4121-4146.

Erickson, T.R., Stefan, H.G., 2000. Linear air/water temperature correlations for streams during open water periods. Journal of Hydrologic Engineering 5, 317-321.

Feller, M.C., Kimmins, J.P., 1979. Chemical characteristics of small streams near Haney in southwestern British Columbia. Water Resources Research 15, 247-258.

Fuller, C.C., Davis, J.A., 1989. Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters. Nature 340, 52.

Gaillardet, J., Dupré, B., Allègre, C.J., 1999. Geochemistry of large river suspended sediments: silicate weathering or recycling tracer?. Geochimica et Cosmochimica Acta, 63, 4037-4051.

Gammons, C.H., Grant, T.M., Nimick, D.A., Parker, S.R., DeGrandpre, M.D., 2007. Diel changes in water chemistry in an arsenic-rich stream and treatment-pond system. Science of the Total Environment 384, 433-451.

Gammons, C.H., Nimick, D.A., Parker, S.R., 2015. Diel cycling of trace elements in streams draining mineralized areas—a review. Applied Geochemistry 57, 35-44.

Gibbs, R.J., 1970. Mechanisms controlling world water chemistry. Science 170, 1088-1091.

Gorham, E., Cragg, J.B., 1960. The chemical composition of some bog waters from the Falkland Islands. The Journal of Ecology, 175-181.

Grobbelaar, J.U., 1974. A contribution to the limnology of the sub-Antarctic island Marion. Ph.D. thesis, University of the Orange Free State, Bloemfontein, South Africa.

Grobbelaar, J.U., 1975. The lentic and lotic freshwater types of Marion Island (sub-Antarctic): a limnological study. Verhandlungen Internationale Vereinigung Limnologie 19, 949-951.

Grobbelaar, J.U., 1978a. Mechanisms controlling the composition of freshwaters on the sub-Antarctic island Marion. Archiv für Hydrobiologie 83, 145-157.

Grobbelaar, J.U., 1978b. Factors limiting the algal growth on the sub-Antarctic island Marion. Verhandlungen Internationale Vereinigung für Limnologie 20, 1159-1164.

Grobbelaar, J.U., Jarvis, A.C., Robarts, R.D., Sephton, L.M., Steenkamp, M., Cawood, M.E., 1987. A diel study of carbon flow in the pelagic zone of a small lava-lakelet on Marion Island (sub-Antarctic). Polar Biology 7, 115-124.

Guasch, H., Armengol, J., Martí, E., Sabater, S., 1998. Diurnal variation in dissolved oxygen and carbon dioxide in two low-order streams. Water Research 32, 1067-1074.

Halliday, S.J., Wade, A.J., Skeffington, R.A., Neal, C., Reynolds, B., Rowland, P., Neal, M., Norris, D., 2012. An analysis of long-term trends, seasonality and short-term dynamics in water quality data from Plynlimon, Wales. Science of the Total Environment 434, 186-200.

Hall, K.J., 1978. Quaternary glacial geology of Marion Island. Ph.D Thesis. University of the Orange Free State, Bloemfontein, South Africa.

Hall, K., 2002. Review of Present and Quaternary periglacial processes and landforms of the maritime and sub-Antarctic region. South African Journal of Science 98, 71-81.

Hayashi, M., Vogt, T., Mächler, L., Schirmer, M., 2012. Diurnal fluctuations of electrical conductivity in a pre-alpine river: effects of photosynthesis and groundwater exchange. Journal of Hydrology 450, 93-104.

Hedding, D.W., 2008. Spatial inventory of landforms in the recently exposed central highland of sub-Antarctic Marion Island. South African Geographical Journal 90, 11-21.

Hensley, R.T., Cohen, M.J., 2016. On the emergence of diel solute signals in flowing waters. Water Resources Research. http://dx.doi.org/10.1002/2015WR017895.

Hindshaw, R.S., Tipper, E.T., Reynolds, B.C., Lemarchand, E., Wiederhold, J.G., Magnusson, J., Bernasconi, S.M., Kretzschmar, R., Bourdon, B., 2011. Hydrological control of stream water chemistry in a glacial catchment (Damma Glacier, Switzerland). Chemical Geology 285, 215-230.

Hodgson, P., Evans, J.G., 1997. Continuous pH, electrical conductivity and temperature measurement at Plynlimon: towards an integrated, reliable and low maintenance instrument system. Hydrology and Earth System Sciences Discussions 1, 653-660.

Holdgate, M.W., 1961, April. The fresh water fauna of Gough island (South Atlantic). In Proceedings of the Linnean Society of London 172, 8-24.

Holloway, J.M., Dahlgren, R.A., 2001. Seasonal and event-scale variations in solute chemistry for four Sierra Nevada catchments. Journal of Hydrology 250, 106-121.

Holmes, R.M., Coe, M.T., Fiske, G.J., Gurtovaya, T., McClelland, J.W., Shiklomanov, A.I., Spencer, R.G., Tank, S.E. and Zhulidov, A.V., 2013. Climate change impacts on the hydrology and biogeochemistry of Arctic rivers. In: Goldman, C. R., Kumagi, M., Robarts, R.D. (Eds.), Climatic Change and Global Warming of Inland Waters: Impacts and Mitigation for Ecosystems and Societies, John Wiley and Sons.

House, W.A., Warwick, M.S., 1998. Hysteresis of the solute concentration/discharge relationship in rivers during storms. Water Research 32, 2279-2290.

Johnson, N.M., Likens, G.E., Bormann, F.H., Fisher, D.W., Pierce, R.S., 1969. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resources Research 5,1353-1363.

Jordan, P., Cassidy, R., 2011. Technical Note: Assessing a 24/7 solution for monitoring water quality loads in small river catchments. Hydrology and Earth System Sciences 15, 3093-3100.

Kirchner, J.W., Feng, X., Neal, C., Robson, A.J., 2004. The fine structure of water-quality dynamics: the (high-frequency) wave of the future. Hydrological Processes 18, 1353-1359.

Langan, S.J., 1989. Sea-salt induced streamwater acidification. Hydrological Processes 3, 25-41.

Lecomte, K.L., Vignoni, P.A., Córdoba, F.E., Chaparro, M.A., Chaparro, M.A., Kopalová, K., Gargiulo, J.D., Lirio, J.M., Irurzun, M.A., Böhnel, H.N., 2016. Hydrological systems from the Antarctic Peninsula under climate change: James Ross archipelago as study case. Environmental Earth Sciences 75, 1-20.

Le Roux, P.C., 2008. Climate and climate change. In: Chown, S.N., Froneman, W. (Eds.), The Prince Edward Islands: land-sea interactions in a changing ecosystem. Stellenbosch: African Sun Media.

Le Roux, P.C., McGeoch, M.A., 2008. Changes in climate extremes, variability and signature on sub-Antarctic Marion Island. Climatic Change 86, 309-329.

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

Lisi, P.J., Schindler, D.E., Cline, T.J., Scheuerell, M.D., Walsh, P.B., 2015. Watershed geomorphology and snowmelt control stream thermal sensitivity to air temperature. Geophysical Research Letters 42, 3380-3388.

Loperfido, J.V., Just, C.L., Schnoor, J.L., 2009. High-frequency diel dissolved oxygen stream data modeled for variable temperature and scale. Journal of Environmental Engineering 135, 1250-1256.

Lutjeharms, J.R.E., Ansorge, I.J., 2008. Oceanographic setting of the Prince Edward Islands. In: Chown, S.L., Froneman, P.W. (Eds.), The Prince Edward Islands: land-sea interactions in a changing ecosystem. African Sun Media, Stellenbosch, South Africa.

Lyons, W.B., Welch, K.A., Welch, S.A., Camacho, A., Rochera, C., Michaud, L., Dewit, R., Carey, A.E., 2013. Geochemistry of streams from Byers Peninsula, Livingston Island. Antarctic Science 25, 181-190.

Mann, H.B., Whitney, D.R., 1947. On a test of whether one of two random variables is stochastically larger than the other. The Annals of Mathematical Statistics, 50-60.

McDougall, I.A.N., Verwored, W., Chevallier, L.U.C., 2001. K–Ar geochronology of Marion Island, Southern Ocean. Geological Magazine 138, 1-17.

Millot, R., Gaillardet, J., Dupré, B., Allègre, C.J., 2002. The global control of silicate weathering rates and the coupling with physical erosion: new insights from rivers of the Canadian Shield. Earth and Planetary Science Letters 196, 83-98.

Mohseni, O., Stefan, H.G., 1999. Stream temperature/air temperature relationship: a physical interpretation. Journal of Hydrology 218, 128-141.

Moraetis, D., Efstathiou, D., Stamati, F., Tzoraki, O., Nikolaidis, N.P., Schnoor, J.L. Vozinakis, K., 2010. High-frequency monitoring for the identification of hydrological and bio-geochemical processes in a Mediterranean river basin. Journal of Hydrology 389, 127-136.

Neal, C., Kirchner, J.W., 2000. Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls. Hydrology and Earth System Sciences Discussions 4, 295-310.

Neal, C., Reynolds, B., Rowland, P., Norris, D., Kirchner, J.W., Neal, M., Sleep, D., Lawlor, A., Woods, C., Thacker, S., Guyatt, H., 2012. High-frequency water quality time series in precipitation and streamflow: From fragmentary signals to scientific challenge. Science of the Total Environment 434, 3-12.

Nędzarek, A., Tórz, A., Podlasińska, J., 2015. Ionic composition of terrestrial surface waters in Maritime Antarctic and the processes involved in formation. Antarctic Science 27, 150-161.

Nimick, D.A., Gammons, C.H., Cleasby, T.E., Madison, J.P., Skaar, D., Brick, C.M., 2003. Diel cycles in dissolved metal concentrations in streams: occurrence and possible causes. Water Resources Research 39, 1247.

Nimick, D.A., Cleasby, T.E., McCleskey, R.B., 2005. Seasonality of diel cycles of dissolved trace-metal concentrations in a Rocky Mountain stream. Environmental Geology 47, 603-614.

Nimick, D.A., Gammons, C.H., Parker, S.R., 2011. Diel biogeochemical processes and their effect on the aqueous chemistry of streams: A review. Chemical Geology 283, 3-17.

Nyakatya, M.J., McGeoch, M.A., 2008. Temperature variation across Marion Island associated with a keystone plant species (Azorella selago Hook.(Apiaceae)). Polar Biology 31, 139-151.

Parker, S.R., Gammons, C.H., Poulson, S.R., DeGrandpre, M.D., 2007. Diel variations in stream chemistry and isotopic composition of dissolved inorganic carbon, upper Clark Fork River, Montana, USA. Applied Geochemistry 22, 1329-1343.

Prince Edward Islands Management Plan Working Group (PEIMPWG)., 1996. Prince Edward Islands Management Plan. Pretoria: Department of Environmental Affairs & Tourism.

Poole, G.C., Berman, C.H., 2001. An ecological perspective on in-stream temperature: natural heat dynamics and mechanisms of human-caused thermal degradation. Environmental Management 27, 787-802.

Prowse, T.D., Wrona, F.J., Reist, J.D., Gibson, J.J., Hobbie, J.E., Lévesque, L.M., Vincent, W.F., 2006. Climate change effects on hydroecology of Arctic freshwater ecosystems. AMBIO: A Journal of the Human Environment 35, 347-358.

R Development Core Team., 2016. R: A language and environment for statistical computing. In: R Foundation for Statistical Computing (Eds), R Development Core Team, Vienna, Austria.

Rajwa-Kuligiewicz, A., Bialik, R.J., Rowiński, P.M., 2015. Dissolved oxygen and water temperature dynamics in lowland rivers over various timescales. Journal of Hydrology and Hydromechanics 63, 353-363.

Rouault, M., Melice, J-L., Reason, C.J.C., Lutjeharms, J.R.E., 2005. Climate variability at Marion Island, Southern Ocean, since 1960. Journal of Geophysical Research 110.

Schulze, B.R., 1971. The climate of Marion Island. In: Van Zinderen Bakker, E.M., Winterbottom, J.M., Dyer, R. A. (Eds.), Marion and Prince Edward Islands. Report on the South African biological and geological expedition 1965–1966. A. A. Balkema.

Sherson, L.R., Van Horn, D.J., Gomez-Velez, J.D., Crossey, L.J., Dahm, C.N., 2015. Nutrient dynamics in an alpine headwater stream: use of continuous water quality sensors to examine responses to wildfire and precipitation events. Hydrological Processes 29, 3193-3207.

Sidle, R.C., 2006. Field observations and process understanding in hydrology: essential components in scaling. Hydrological Processes 20, 1439-1445.

Simonsen, J.F., Harremoës, P., 1978. Oxygen and pH fluctuations in rivers. Water Research 12, 477-489.

Smith, V.R., 1987. Chemical composition of precipitation at Marion Island (sub-Antarctic). Atmospheric Environment 21, 1159-1165.

Smith, V.R., 2002. Climate change in the sub-Antarctic: an illustration from Marion Island. Climatic Change 52, 345-357.

Smith, V.R., 2008. Terrestrial and freshwater primary production and nutrient cycling. In: Chown, S.L., Froneman, P.W. (Eds.), The Prince Edward Islands: land-sea interactions in a changing ecosystem. African Sun Media, Stellenbosch, South Africa.

Smith, V.R., Steenkamp, M., 1990. Climatic change and its ecological implications at a sub-Antarctic Island. Oecologia 85, 14-24.

Taylor, F.J., 1974. Chemical analyses of Campbell Island fresh waters. New Zealand Journal of Marine and Freshwater Research 8, 389-402.

Tetzlaff, D., Waldron, S., Brewer, M.J., Soulsby, C., 2007. Assessing nested hydrological and hydrochemical behaviour of a mesoscale catchment using continuous tracer data. Journal of Hydrology 336, 430-443.

Thomas, A.G., 1986. Specific conductance as an indicator of total dissolved solids in cold, dilute waters. Hydrological Sciences Journal 31, 81-92.

Tomlinson, M.S., De Carlo, E.H., 2003. The need for high resolution time series data to characterize Hawaiian Streams. Journal of the American Water Resources Association 39, 113–123.

Toro, M., Camacho, A., Rochera, C., Rico, E., Bañón, M., Fernández-Valiente, E., Marco, E., Justel, A., Avendaño, M.C., Ariosa, Y., Vincent, W.F., 2007. Limnological characteristics of the freshwater ecosystems of Byers Peninsula, Livingston Island, in maritime Antarctica. Polar Biology 30, 635-649.

Tyler, P.A., 1972. Reconnaissance Limnology of Sub-Antarctic Islands I. Chemistry of Lake Waters from Macquarie Island and the Iles Kerguelen. Internationale Revue der gesamten Hydrobiologie und Hydrographie 57, 759-778.

Van Staden, W., 2011. Limnoecology of the freshwater algal genera (excluding diatoms) on Marion Island (sub–Antarctic). M.Sc. thesis. North-West University, North-West, Province, South Africa.

Verwoerd, W.J., 1971: Geology. In: Van Zinderen Bakker, E.M., Winterbottom, J.M., Dyer, R.A. (Eds.), Marion and Prince Edward Islands. Balkema, Cape Town.

Vinocur, A., Unrein, F., 2000. Typology of lentic water bodies at Potter Peninsula (King George Island, Antarctica) based on physical-chemical characteristics and phytoplankton communities. Polar Biology 23, 858-870.

Wade, A.J., Palmer-Felgate, E.J., Halliday, S.J., Skeffington, R.A., Loewenthal, M., Jarvie, H.J., Bowes, M.J., Greenway, G.M., Haswell, S.J., Bell, I.M., Joly, E., 2012. Hydrochemical processes in lowland rivers: insights from in situ, high-resolution monitoring. Hydrology and Earth System Science 16, 4323-4342.

Walling, D.E., Foster, I.D.L., 1975. Variations in the natural chemical concentration of river water during flood flows, and the lag effect: some further comments. Journal of Hydrology 26, 237-244.

Webb, B.W., 1987. The relationship between air and water temperatures for a Devon river. Report of the Transactions of the Devonion Association for the Advancement of Science 119, 197-222.

Webb, B.W., Clack, P.D., Walling, D.E., 2003. Water–air temperature relationships in a Devon river system and the role of flow. Hydrological Processes 17, 3069-3084.

Wilby, R.L., Johnson, M.F., Toone, J.A., 2014. Nocturnal river water temperatures: spatial and temporal variations. Science of the Total Environment 482, 157-173.

Wilcoxon, F., 1945. Individual comparisons by ranking methods. Biometrics Bulletin 1, 80-83.

Chapter 4: General conclusion and synthesis

4.1 Introduction

Through the use of hydrogen and oxygen isotopes, major ions and high-frequency physicochemical measurements, this study revealed new information pertaining to hydrochemical conditions on Marion Island. Data generated from the Soft Plume River (SPR) are useful not only in identifying current processes operating on daily, sub-daily and storm event time scales, but may also provide valuable insight into how the island's hydrochemistry might respond to future climate change. This chapter summarizes and synthesizes the main findings of this study and concludes by commenting on limitations encountered and potential future research opportunities.

4.2 Summary of findings

To better understand hydrochemical dynamics on Marion Island, stream water from the SPR was analysed for the following: hydrogen (δ^2H) and oxygen ($\delta^{18}O$) isotope ratios, major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^- , SO_4^{2-}, NO_3^-) and high-frequency physicochemical measurements (pH, water temperature, dissolved oxygen and total dissolved solids). In addition, previously published precipitation and stream chemical data were used. Conclusions presented in this chapter are greatly simplified but are stated in a way that integrates the main findings of Chapters 2 and 3, providing a holistic understanding of the island's hydrochemical dynamics.

4.2.1 Isotopic, ionic and physicochemical characteristics of the Soft Plume River

Together, the isotopic, ionic and physicochemical composition of the SPR provide insight into both large and local scale processes affecting Marion Island. Results suggest that the chemical composition of the SPR is primarily derived from atmospheric inputs, which are ultimately a function of large-scale atmospheric and oceanic systems. These systems control the origin and isotopic composition of moisture that reaches the island (Rozanski et al., 1993; Aggarwal et al., 2012). Locally, weather conditions vary spatially and as a result, exert variable influence on the island's freshwater chemistry depending on landscape position (Schulze, 1971; Rouault et al., 2005).

Marion Island's latitudinal and hyper-oceanic position in the Indian sector of the Southern Ocean strongly influences the isotopic composition of precipitation that feeds the SPR. Precipitation δ^2H and δ^{18}O on the island is a function of latitude and the moisture source origin of synoptic weather systems that affect the island (Rozanski et al., 1993; Appendix Fig. B1, 2). Mid-latitude cyclonic systems originate in the south Atlantic Ocean between 30° - 40° S and migrate eastwards, embedded in the southern hemisphere westerlies (Sinclair, 1995; Simmonds and Keay, 2000). As a result of the island being close to the moisture, precipitation δ^2H and δ^{18}O do not undergo substantial fractionation during transport (Aggarwal et al., 2012). However, precipitation associated with low-pressure cyclonic systems are known to have low and variable δ^2H and δ^{18}O values that vary with storm intensity and rainout (Callow et al., 2014).

Precipitation δ^2H and δ^{18}O values are further modified by local factors such as rainfall amount, temperature and altitude (Rozanski et al., 1993; Kohn and Welker, 2005; Gonfiantini et al., 2001). As a result, mean stream water δ^2H and δ^{18}O values in the SPR were lower than that of bulk monthly precipitation collected at the research station (Table 4.1). Despite other studies finding a similar pattern (e.g. Kendal and Coplen, 2001; Dutton et al., 2005), for this study it was not possible to accurately identify the mechanisms responsible for the difference. This is because stream water and precipitation samples were collected at different times and locations on the island.

Table 4.1. Summary statistics for stream water δ^2H and δ^{18}O from the Soft Plume River. All precipitation statistics are based on unweighted values.

Site	**N**	**Variable**	**Mean (‰)**	**SD (‰)**	**Min (‰)**	**Max (‰)**	**Range (‰)**
SP03	15	δ^2H	-37.82	4.23	-48.00	-33.80	14.20
SP03	15	δ^{18}O	-6.08	0.55	-7.60	-5.64	1.96
SP01	16	δ^2H	-36.33	1.58	-40.10	-33.60	6.50
SP01	16	δ^{18}O	-6.00	0.24	-6.46	-5.63	0.83
All SPR sites^A	62	δ^2H	-37.05	3.19	-48.00	-33.60	14.4
All SPR sites^A	62	δ^{18}O	-6.04	0.41	-7.60	-5.63	1.97
Met. station^B	177	δ^2H_{precip}	-27.51	9.33	-64.50	-4.00	60.50
Met. station^B	177	$\delta^{18}O_{precip}$	-4.67	1.12	-9.10	-2.43	6.67

^{A} SP03 and SP01

^{B} Research station

Major ion concentrations in the SPR were typical for freshwater streams on maritime sub-Antarctic islands (Table 4.2; Gorham and Cragg, 1960; Holdgate, 1961; Grobbelaar, 1974). Samples had an ionic dominance order of $Na^+ > Mg^{2+} > Ca^+ > K^+$: $Cl^- > SO_4^{2-}$ and a Na:Cl ratio almost identical to that of seawater (0.86). Results support the findings of Grobbelaar (1974). Na^+ and Cl^- concentrations in SPR were significantly different to the Van den Boogaard River (Grobbelaar, 1974). While interesting, it was not possible to accurately explain this difference as the rivers were sampled at different times under different climatic conditions.

Table 4.2. Summary statistics of major ions in stream water samples from all sites along the Soft Plume River collected over the period 21/04/2015 – 06/05/2015. Na:Cl calculated as molar ratio.

Variable	**N**	**Mean (mg/L)**	**SD (mg/L)**	**Min (mg/L)**	**Max (mg/L)**	**Range (mg/L)**
Ca^{2+}	47	1.58	0.22	0.79	1.91	1.12
Mg^{2+}	47	1.30	0.10	0.91	1.48	0.57
K^+	47	0.81	0.13	0.39	0.97	0.58
Na^+	47	6.99	0.58	4.84	8.05	3.21
Cl^-	47	12.49	0.84	9.70	13.80	4.10
SO_4^{2-}	47	1.47	0.31	0.80	2.00	1.20
NO_{3-}	34	0.64	0.62	0.20	3.60	3.40
Na:Cl	47	0.86	0.05	0.71	0.99	0.28

The physicochemistry of the SPR was indicative of Marion Island’s physiographic and climatic conditions. Stream pH was neutral, with average water temperature slightly lower than that of mean air surface temperature recorded at the research station. Mean dissolved oxygen concentrations reflected the prevailing weather conditions (low temperature, high cloud cover and limited sunshine hours), basin geomorphology and lack of biological activity in the SPR. Mean total dissolved solid concentrations were low, consistent with previous studies which reported small dissolved loads in various freshwater bodies on the island (Grobbelaar, 1974; van Staden, 2011). Overall, mean physicochemical characteristics of the SPR were similar to that of other lotic water bodies on Marion Island.

4.2.2 Variation on daily, sub-daily and storm event time scales

Results suggest that variation in stream water δ^2H and $\delta^{18}O$ (Chapter 2) and major ion concentrations (Chapter 3) was strongly influenced by precipitation amount and intensity (Fig.

4.1a-d). Stream water δ^2H, $\delta^{18}O$ and major ion concentrations all decrease in response to high amounts of rainfall on 22/04/2015 and 03-04/05/2015. Lower stream water isotope values following high rainfall were likely the result of the "amount effect" (Fig. 4.1c) High precipitation amounts are associated with lower δ^2H and $\delta^{18}O$ values due to preferential rainout of the heavy isotope ^2H and ^{18}O respectively (Dansgaard, 1964). In contrast, the decrease in major ion concentrations in the SPR was the result of dilution (Fig. 4.1a, b). This dilution-concentration relationship is widely acknowledged (e.g. Johnson et al., 1969; House and Warwick, 1998) and expected given the flashy nature of precipitation affecting the SPR.

In addition to the aforementioned fluctuations in stream chemistry, there was a difference in the amount of variation experienced at each sampling site. For stream water δ^2H and $\delta^{18}O$ and major ion concentrations, the stream response to precipitation inputs was largest at the highest altitude site SP03. Although precipitation was not directly measured in this study, the pattern in stream chemistry suggests that higher amounts of precipitation fell at the highest altitude site. The "amount effect" would again explain the lower stream water δ^2H and $\delta^{18}O$ recorded at SP03 (Dansgaard, 1964). Similarly, higher precipitation amounts at SP03 would have resulted in greater dilution and therefore account for the lower concentrations of most ions observed at SP03 following substantial rainfall.

As illustrated in Chapter 3, most stream physicochemical parameters exhibited diel variability over the sampling period. Stream pH and stream temperature followed diel cycles characterized by afternoon maxima and night time minima, with pH maxima preceding stream temperature maxima. Stream temperature fluctuations followed that of air surface temperature, albeit with a smaller range. Dissolved oxygen concentrations were inversely related to stream water temperature. Increases in stream temperature reduce oxygen solubility and as a result, decrease dissolved oxygen concentrations (Nimick et al., 2011). No noticeable diel cycles were observed for total dissolved solids and river stage height.

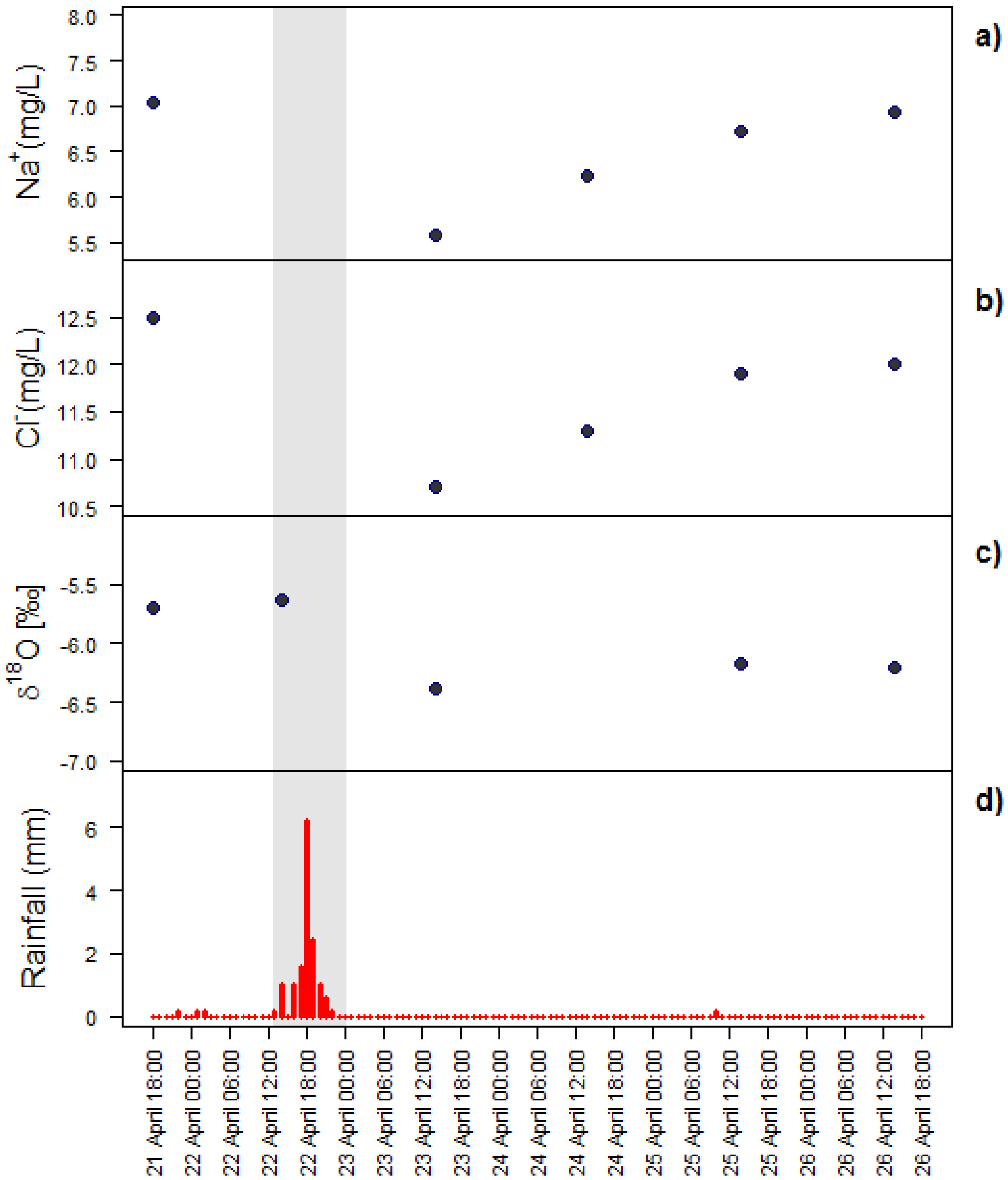


Figure 4.1. Time series of a) Na^+, b) Cl^- and c) $\delta^{18}O$ at SP03 on the Soft Plume River. d) Hourly precipitation measurements recorded at the research station. The grey bar indicates the duration of the highest amount of precipitation recorded through the time series.

4.3 Practicalities and constraints

The challenges experienced in this study are common to many on Marion Island (e.g. Berg, 2009; van Staden, 2011). For this study, results are based mostly on a single sampling campaign in April/May 2015 with additional data from Grobbelaar (1974) and Global Network of Isotopes in Precipitation database. Subsequently, results have inherent spatial and temporal limitations that restrict inferences that can be made from the findings. Additionally, because of these issues of scale and sampling frequency, findings may not be transferable to other sub-Antarctic island catchments of differing size and anthropogenic pressures.

While stream water δ^2H, δ^{18}O, major ion concentrations and physicochemistry were shown to respond to precipitation inputs, it was not possible to obtain a truly accurate understanding of the rainfall-runoff relationship. This is because rainfall amounts were recorded at the research station. Because of sampling site altitude, topography and landscape position of the SPR, rainfall recorded at the research station might not be representative of precipitation in the SPR catchment (Blake, 1996; Neal et al., 2004).

Furthermore, this study attempted to continuously monitor *in-situ* stream physicochemical parameters in the SPR. Unanticipated challenges developed as a result of inexperience with using the Eureka^{TM} Manta multiprobe in harsh climatic conditions. Equipment failure because of power supply failure resulted in missing data (Chapter 3). To account for the missing data, diel variation was examined by extracting data from the original data set, excluding the period of missing data and converted to hourly averages to generate a new hourly data set that covered the period 21/04/2015 to 26/04/2015.

4.4 Future research opportunities

Results from Chapters 2 and 3 highlighted the need for continual investigation into the islands hydrochemistry. Despite small sample numbers and limited spatial coverage, findings present a sound basis for understanding daily and sub-daily variability stream water chemistry. Furthermore, temporal and spatial constraints provide an opportunity for future research to address limitations and expand on key findings from this study.

Event-based and/or daily precipitation sampling would help to elucidate controls on δ^2H and δ^{18}O that are missed through the use of bulk monthly precipitation samples. For example, event-based precipitation samples from sites in eastern Puerto Rico were classified by Scholl et al. (2009) according to prevailing synoptic weather systems (e.g. low and high pressure systems, fronts and troughs). They found that there was an association between isotopically depleted precipitation and low-pressure and convective systems. Numerous other studies (Gedzelmen and Lawrence, 1990; Baldini et al., 2010) have found similar patterns whereby intense low-pressure systems were associated with precipitation depleted in δ^2H and δ^{18}O. Additionally, Callow et al. (2014) found relatively consistent depleted precipitation δ^2H and $\delta^{18}O$ values for cold fronts, where moisture was sourced from the Southern Ocean (between 31º - 49º S).

To address spatial heterogeneity in the islands freshwater chemistry, simultaneous sampling of the SPR and Van den Boogaard River would provide insight into spatial variability of $\delta^{2}H$ and $\delta^{18}O$ as well as major ion concentrations. While, results from Chapter 3 suggest that there are significant differences in Na^+ and Cl^- concentrations between the two rivers, it was not possible to determine mechanisms driving the differences between the streams because they were sampled at different times and under weather conditions (Grobbelaar, 1974). On Byers Peninsula, Livingston Island streams draining a similar lithology was shown to exhibit significant spatial variability in stream chemistry which was interpreted as being indicative of varying processes controlling stream ion concentrations (Toro et al., 2007; Lyons et al., 2013). On Marion Island, spatial variability in stream chemistry is likely to reflect the relative influence of meteorological variables such as precipitation amount, wind direction and speed.

This study also presented compelling evidence to suggest that there is an altitudinal precipitation gradient along the reaches of the SPR. To evaluate this, future studies could place automated weather stations or rainfall tipping buckets at various heights along the SPR. While Blake (1996), identified an altitudinal precipitation gradient, focussing rainfall collection along the reaches of the SPR will allow for an enhanced understanding of rainfall-runoff chemical dynamics (Neal and Kirchner, 2000). Investigation of microclimate dynamics would not only facilitate a better understanding of stream chemical processes in the SPR, but also complement studies that have examined other variables, such as temperature (e.g. Nyakata and McGeoch, 2008).

4.5 Conclusion

The study of Marion Island's hydrochemistry presented here has illustrated how the islands precipitation and stream water chemistry is intrinsically linked to large-scale atmospheric and oceanic systems, as well as local processes. Furthermore, this study illustrated that the SPR exhibits a considerable degree of variability and complexity, especially as sampling only represent stream dynamics over a limited range of annual climatic variation. In addition, this study also provides the first data set of stream water $\delta^{2}H$ and $\delta^{18}O$, as well as continuous *in situ* physicochemical measurements, from a sub-Antarctic island. This study has achieved its aims and has contributed to a deeper understanding of hydrochemical dynamics on Marion Island.

References

Aggarwal, P.K., Alduchov, O.A., Froehlich, K.O., Araguas-Araguas, L.J., Sturchio, N.C., Kurita, N., 2012. Stable isotopes in global precipitation: A unified interpretation based on atmospheric moisture residence time. Geophysical Research Letters 39, L11705. http://dx.doi.org/10.1029/2012GL051937.

Baldini, L.M., McDermott, F., Baldini, J.U., Fischer, M.J., Möllhoff, M., 2010. An investigation of the controls on Irish precipitation $\delta^{18}O$ values on monthly and event timescales. Climate Dynamics 35, 977-993.

Berg, O., 2009. Small scale spatial and temporal variability of microclimate in a fellfield landscape, Marion Island. M.Sc. thesis. Uppsala University, Sweden.

Blake, B. J.,1996. Microclimate and prediction of photosynthesis at Marion Island. M.Sc. thesis, University of the Free State, Bloemfontein, South Africa.

Callow, N., McGowan, H., Warren, L., Speirs, J., 2014. Drivers of precipitation stable oxygen isotope variability in an alpine setting, Snowy Mountains, Australia. Journal of Geophysical Research: Atmospheres 119, 3016-3031.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16, 436-468.

Dutton, A., Wilkinson, B.H., Welker, J.M., Bowen, G.J., Lohmann, K.C., 2005. Spatial distribution and seasonal variation in 18O/16O of modern precipitation and river water across the conterminous USA. Hydrological Processes 19, 4121-4146.

Gedzelman, S.D., Lawrence, J.R., 1990. The isotopic composition of precipitation from two extratropical cyclones. Monthly Weather Review 118, 495-509.

Gorham, E., Cragg, J.B., 1960. The chemical composition of some bog waters from the Falkland Islands. The Journal of Ecology, 175-181.

Gonfiantini, R., Roche, M.A., Olivry, J.C., Fontes, J.C., Zuppi, G.M., 2001. The altitude effect on the isotopic composition of tropical rains. Chemical Geology 181, 147-167.

Grobbelaar, J.U., 1974. A contribution to the limnology of the sub-Antarctic island Marion. Ph.D. thesis, University of the Orange Free State, Bloemfontein, South Africa.

Holdgate, M.W., 1961, April. The fresh water fauna of Gough island (South Atlantic). In Proceedings of the Linnean Society of London 172, 8-24.

House, W.A., Warwick, M.S., 1998. Hysteresis of the solute concentration/discharge relationship in rivers during storms. Water Research 32, 2279-2290.

Johnson, N.M., Likens, G.E., Bormann, F.H., Fisher, D.W., Pierce, R.S., 1969. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resources Research 5,1353-1363.

Kendall, C., Coplen, T.B., 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. Hydrological Processes 15, 1363-1393.

Kohn, M.J., Welker, J.M., 2005. On the temperature correlation of $\delta^{18}O$ in modern precipitation. Earth and Planetary Science Letters 231, 87-96.

Lyons, W.B., Welch, K.A., Welch, S.A., Camacho, A., Rochera, C., Michaud, L., Dewit, R., Carey, A.E., 2013. Geochemistry of streams from Byers Peninsula, Livingston Island. Antarctic Science 25, 181-190.

Neal, C., Kirchner, J.W., 2000. Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls. Hydrology and Earth System Sciences Discussions 4, 295-310.

Neal, C., Skeffington, R., Neal, M., Wyatt, R., Wickham, H., Hill, L., Hewitt, N., 2004. Rainfall and runoff water quality of the Pang and Lambourn, tributaries of the River Thames, south-eastern England. Hydrology and Earth System Sciences Discussions 8, 601-613.

Nimick, D.A., Gammons, C.H., Parker, S.R., 2011. Diel biogeochemical processes and their effect on the aqueous chemistry of streams: A review. Chemical Geology 283, 3-17.

Nyakatya, M.J., McGeoch, M.A., 2008. Temperature variation across Marion Island associated with a keystone plant species (Azorella selago Hook.(Apiaceae)). Polar Biology 31, 139-151.

Rouault, M., Melice, J-L., Reason, C.J.C., Lutjeharms, J.R.E., 2005. Climate variability at Marion Island, Southern Ocean, since 1960. Journal of Geophysical Research 110, C05007.1- C05007.9.

Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: Swart, P.K., McKenzie, K.C.I.J., Savin, S. (Eds.), Climate Change in Continental Isotopic Records. American Geophysical Union, Washington, D. C.

Scholl, M.A., Shanley, J.B., Zegarra, J.P., Coplen, T.B., 2009. The stable isotope “amount effect”: new insights from NEXRAD echo tops, Luquillo Mountains, Puerto Rico. Water Resources Research 45.

Schulze, B.R., 1971. The climate of Marion Island. In: Van Zinderen Bakker, E.M., Winterbottom, J.M., Dyer, R. A. (Eds.), Marion and Prince Edward Islands. Report on the South African biological and geological expedition 1965–1966. A. A. Balkema.

Simmonds, I., Keay, K., 2000. Mean Southern Hemisphere extratropical cyclone behavior in the 40-year NCEP–NCAR reanalysis. Journal of Climate 13, 873-885.

Sinclair, M.R., 1995. A climatology of cyclogenesis for the Southern Hemisphere. Monthly Weather Review 123, 1601-1619.

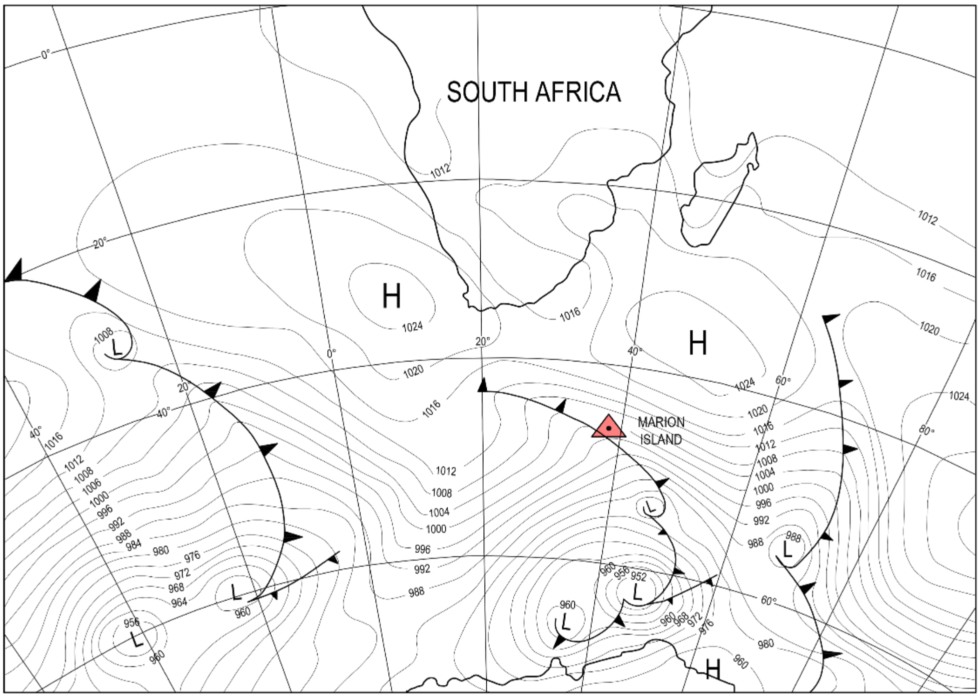
Toro, M., Camacho, A., Rochera, C., Rico, E., Bañón, M., Fernández-Valiente, E., Marco, E., Justel, A., Avendaño, M.C., Ariosa, Y., Vincent, W.F., 2007. Limnological characteristics of the freshwater ecosystems of Byers Peninsula, Livingston Island, in maritime Antarctica. Polar Biology 30, 635-649.

Van Staden, W., 2011. Limnoecology of the freshwater algal genera (excluding diatoms) on Marion Island (sub–Antarctic). M.Sc. thesis. North-West University, North-West, Province, South Africa.

Appendices

Figure A. Synoptic weather chart (surface pressure lines) of the Southern Ocean for 1) 22 April 2015 12:00 GMT + 3, 2) 04 May 2015 18:00 GMT + 3.

1)



2)

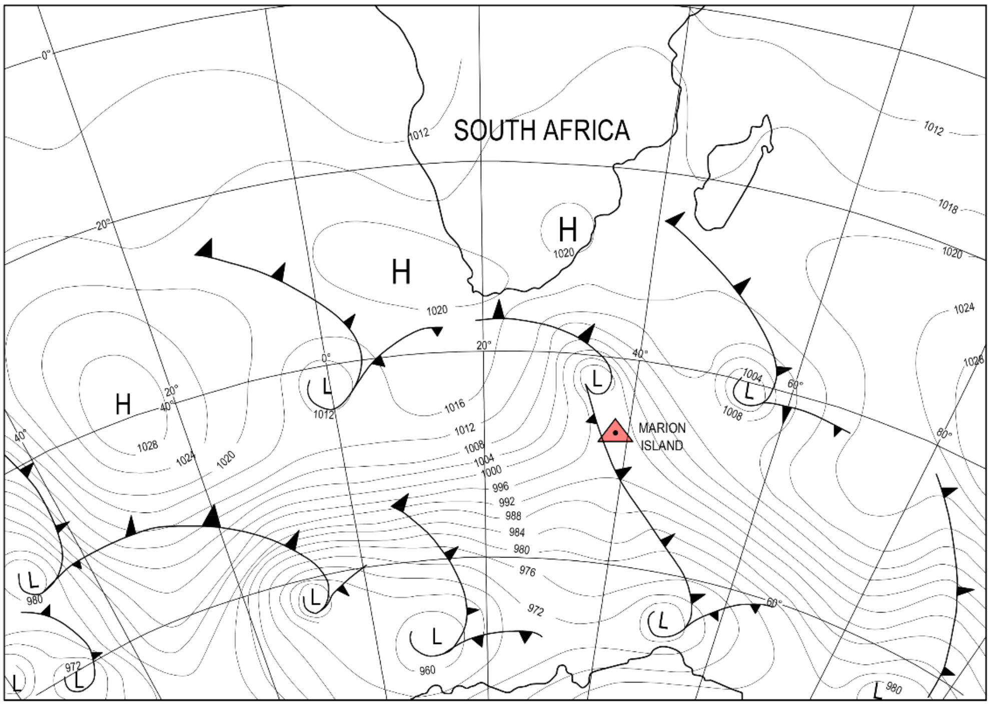


Table B. Monthly averaged δ^2H vs δ^{18}O (‰) values of precipitation from Marion Island used in this study. Samples are from the period 1961-2013. All data are from the Global Network of Isotopes in Precipitation (available at: http://www.iaea.org/water). All data with a d-excess value of less than 3‰ were removed from the data set, following Hughes and Crawford (2012). Precipitation amount is recorded at the research station.

Date	**Precipitation (mm)**	**δ^{18}O**	**δ^2H**	**d-excess**
Apr-1961	191	-6.1	-37.2	11.6
May-1961	100	-5.6	-31.6	13.2
Jun-1961	464	-3.9	-20.5	10.7
Jul-1961	178	-3.6	-19.9	8.9
Sep-1961	174	-5.8	-34.8	11.6
Oct-1961	179	-6.3	-34.1	16.3
Nov-1961	88	-5.2	-36	5.6
Dec-1961	261	-5	-34.1	5.9
Jan-1962	273	-4.5	-29.8	6.2
Feb-1962	260	-5.4	-29.2	14
Mar-1962	196	-4.5	-29.2	6.8
Jun-1962	151	-9.1	-64.5	8.3
Aug-1962	185	-6.4	-32.9	18.3
Sep-1962	197	-6.2	-43.4	6.2
Oct-1962	146	-5.9	-44	3.2
Jan-1963	263	-5.9	-41.6	5.6
Feb-1963	253	-3.9	-25.5	5.7
Mar-1964	258	-5.2	-31.6	10
Apr-1964	299	-5.3	-31	11.4
May-1964	324	-3.5	-19.9	8.1
Jun-1964	287	-7.4	-49.6	9.6
Jul-1964	181	-4.2	-23.6	10
Aug-1964	222	-4.3	-28	6.4
Sep-1964	194	-4	-27.3	4.7
Oct-1964	153	-6	-41.6	6.4
Nov-1964	293	-5.7	-41	4.6
Dec-1964	196	-5.3	-39.1	3.3
Feb-1965	319	-5.1	-28.6	12.2
Mar-1970	205	-3.52	-20	8.16
Apr-1970	254	-6.78	-34	20.24
May-1970	229	-5.27	-36	6.16
Jun-1970	209	-5.25	-35	7
Jul-1970	205	-6.26	-46	4.08
Aug-1970	244	-4.57	-30	6.56
Sep-1970	147	-6.41	-45	6.28

Oct-1970	196	-4.59	-22	14.72
Nov-1970	239	-6.59	-45	7.72
Mar-1971	159	-2.95	-14	9.6
Apr-1971	258	-6.23	-40	9.84
Mar-1972	244	-4.18	-28.8	4.64
Apr-1972	237	-4.98	-27.1	12.74
May-1972	233	-4.05	-27.2	5.2
Jun-1972	233	-4.66	-31.8	5.48
Jul-1972	247	-5.97	-35.4	12.36
Aug-1972	193	-3.6	-24.7	4.1
Sep-1972	157	-5.4	-38.1	5.1
Jan-1973	192	-3.46	-24.3	3.38
Feb-1973	102	-2.63	-15.9	5.14
May-1973	198	-4.28	-28.5	5.74
Jun-1973	102	-5.2	-29.3	12.3
Jul-1973	211	-4.13	-14.6	18.44
Aug-1973	171	-4.97	-31.5	8.26
Sep-1973	133	-4.05	-24.1	8.3
Oct-1973	181	-4.69	-25.4	12.12
Nov-1973	205	-5.4	-35.9	7.3
Dec-1973	167	-4.59	-17.7	19.02
Jan-1974	171	-3.48	-4	23.84
Mar-1974	140	-3.69	-13.3	16.22
Apr-1974	129	-2.68	-9.1	12.34
Jul-1975	266	-5.57	-35.9	8.66
Aug-1975	245	-5.79	-41.3	5.02
Sep-1975	191	-5	-33.8	6.2
Oct-1975	205	-6.17	-22.6	26.76
Dec-1975	186	-7.72	-57	4.76
Jan-1976	236	-4.99	-28.8	11.12
Feb-1976	210	-5.05	-36.5	3.9
Mar-1976	261	-6.74	-44.8	9.12
May-1994	163	-3.31	-16.3	10.18
Jun-1994	145	-6.28	-34.9	15.34
Jul-1994	181	-4.54	-24.3	12.02
Aug-1994	188	-4.38	-14	21.04
Sep-1994	100	-4.46	-20.5	15.18
Oct-1994	247	-4.99	-25.7	14.22
Nov-1994	175	-7.39	-42.4	16.72
Dec-1994	124	-2.62	-8.5	12.46
Jan-1995	195	-3.78	-19.8	10.44
Feb-1995	210	-2.77	-6.9	15.26
Mar-1995	115	-3.15	-15.5	9.7

Apr-1995	156	-5.19	-33.4	8.12
May-1995	172	-4.74	-27.5	10.42
Jun-1995	232	-4.34	-23.5	11.22
Jul-1995	127	-4.08	-16	16.64
Aug-1995	116	-5.9	-36.1	11.1
Sep-1995	204	-3.92	-20.6	10.76
Oct-1995	127	-4.72	-28.1	9.66
Nov-1995	162	-4.63	-16.6	20.44
Jan-1996	195	-3.79	-19.3	11.02
Feb-1996	99	-4.92	-28.5	10.86
Mar-1996	194	-3.88	-18.6	12.44
Apr-1996	134	-2.92	-12.7	10.66
Jan-1997	175	-3.87	-22.6	8.36
Feb-1997	256	-3.84	-22.9	7.82
Mar-1997	133	-4.09	-24.3	8.42
Apr-1997	204	-3.34	-17.1	9.62
May-1997	164	-3.15	-17	8.2
Jul-1997	206	-4.34	-28.3	6.42
Aug-1997	244	-6.22	-41.2	8.56
Oct-1997	132	-3.46	-23.5	4.18
Nov-1997	82	-3.62	-21.8	7.16
Dec-1997	262	-3.1	-20.4	4.4
Jan-1998	207	-4.37	-27.4	7.56
Mar-1998	171	-3.75	-19.9	10.1
Apr-1998	190	-4.99	-26.6	13.32
May-1998	176	-5.74	-33.1	12.82
Jun-1998	244	-6.05	-36.1	12.3
Jul-1998	191	-7.12	-45.1	11.86
Aug-1998	182	-5.58	-31.4	13.24
Sep-1998	199	-5.49	-32.1	11.82
Oct-1998	203	-4.74	-28.2	9.72
Nov-1998	191	-4.5	-25.2	10.8
Dec-1998	111	-4.8	-20.1	18.3
Jan-1999	197	-4.11	-20.3	12.58
Feb-1999	160	-4.69	-26	11.52
Mar-1999	121	-4.01	-23.5	8.58
Jun-1999	190	-5.58	-33.4	11.24
Jul-1999	190	-5.09	-29.8	10.92
Aug-1999	100	-4.4	-25	10.2
Jan-2001	190.1	-3.71	-21.47	8.21
Feb-2001	119.3	-4.25	-24.56	9.44
Mar-2001	112.1	-4.54	-25.91	10.41
Apr-2001	159.1	-6.81	-47.08	7.4

May-2001	162.7	-5.62	-33.41	11.55
Jun-2001	170	-4.54	-26.79	9.53
Jul-2001	146.4	-5.06	-28.44	12.04
Aug-2001	116.3	-5.76	-35.88	10.2
Sep-2001	229.1	-6	-36.81	11.19
Oct-2001	164.3	-4.82	-25.49	13.07
Nov-2001	79.3	-4.87	-29.96	9
Dec-2001	184.5	-4.66	-28.24	9.04
May-2009	135.2	-4.16	-24.75	8.53
Jun-2009	134.2	-4.51	-30.47	5.61
Jul-2009	150.5	-4.02	-25.35	6.81
Aug-2009	131.5	-2.43	-10.58	8.86
Sep-2009	101.7	-3.66	-24.82	4.46
Oct-2009	170.8	-3.38	-22.56	4.48
Nov-2009	133.6	-5.23	-36.07	5.77
Dec-2009	175.2	-6.06	-42.95	5.53
Jan-2010	136.6	-2.76	-13.33	8.75
Feb-2010	142.1	-2.69	-16.07	5.45
Mar-2010	145	-4.4	-28.72	6.48
Apr-2010	240.7	-4.01	-23.06	9.02
May-2010	108.5	-3.36	-16.64	10.24
Jun-2010	169	-4.64	-26.64	10.48
Jul-2010	170.3	-3.79	-22.52	7.8
Aug-2010	163.3	-3.36	-16.04	10.84
Sep-2010	160.7	-4.31	-25.94	8.54
Oct-2010	84.1	-3.58	-20.96	7.68
Nov-2010	144	-4.12	-23.58	9.38
Dec-2010	77.7	-3.64	-22.12	7
Jan-2011	123	-3.66	-21.34	7.94
Feb-2011	116.7	-3.73	-18.61	11.23
Mar-2011	181.8	-4.46	-27.64	8.04
Apr-2011	191.6	-4.39	-25.3	9.82
May-2011	60	-4.2	-26.63	6.97
Jun-2011	94.4	-4.4	-24.63	10.57
Jul-2011	117.1	-4.31	-26.53	7.95
Aug-2011	141.9	-3.65	-20.12	9.08
Sep-2011	209.8	-5.1	-31.17	9.63
Oct-2011	114.6	-4.66	-26.55	10.73
Nov-2011	184.8	-4.81	-30.79	7.69
Dec-2011	135.7	-2.76	-13	9.08
Jan-2012	117.2	-3.16	-17.9	7.38
Feb-2012	159.4	-4.04	-25.84	6.48
Mar-2012	170.7	-3.89	-20.37	10.75

Apr-2012	202.4	-4.16	-21.56	11.72
May-2012	212.7	-3.98	-24.18	7.66
Jun-2012	169.3	-5.67	-35.24	10.12
Jul-2012	147.3	-4.95	-27.79	11.81
Aug-2012	132	-3.75	-16.75	13.25
Sep-2012	268.9	-5.35	-29.33	13.47
Oct-2012	95.2	-5.45	-31.73	11.87
Nov-2012	122	-2.97	-16.04	7.72
Dec-2012	107.7	-4.68	-27.32	10.12
Jan-2013	202	-4.25	-23.65	10.35
Feb-2013	245.6	-5.22	-32.27	9.49
Mar-2013	211.2	-4.31	-22.52	11.96
Apr-2013	219.6	-5.67	-30.93	14.43