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Research paper

Physicochemical stream response to diurnal, seasonal, and synoptic drivers on sub-Antarctic Marion Island

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The hyper-oceanic climate of sub-Antarctic Marion Island renders its freshwater systems highly sensitive to meteorological drivers. The physicochemical dynamics of stream water were determined by analysing high-frequency (5-min) data collected over a 2-year period (May 2015 – April 2017) in the perennial Soft Plume River, which drains the largest catchment on the island. Diurnal, seasonal, and synoptic-scale variations in stream temperature, pH, dissolved oxygen (DO), and specific conductivity (EC) were examined in relation to rainfall and air-surface temperature. Distinct diurnal patterns were evident, with stream temperature, pH, and DO reaching their highest levels around midday, while EC peaked at midnight. Seasonally, summer conditions produced higher stream temperatures, pH, and EC, but lower DO concentrations compared to winter, reflecting the influence of elevated air temperatures and increased evaporation during the warmer months. Four significant synoptic weather events were identified, each characterised by distinct physicochemical responses in the river. In general, increased precipitation produced a dilution effect on solutes, resulting in reduced pH and EC. DO consistently exhibited a strong negative correlation with stream temperature, which itself showed a delayed peak following maximum rainfall. An exception occurred after an extended dry period, when the first rainfall event triggered a sharp rise in EC. Such responses were associated with specific synoptic patterns that are reportedly becoming more frequent under current climate change. Overall, the findings indicate that the physicochemical characteristics of Marion Island's streams are strongly influenced by both short-term weather events and long-term climatic shifts, particularly rising mean annual temperatures and declining precipitation.

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INTRODUCTION

Sub-Antarctic islands are remote, ecologically sensitive regions that serve as key indicators for monitoring the effects of global climate change (Boelhouwers, 2003). Positioned within the strong westerly wind belt and influenced by major oceanic frontal systems, these hyper-oceanic environments are experiencing rapid climatic shifts, including significant warming and altered precipitation patterns (Thompson and Solomon, 2002; Nel et al., 2023). Understanding the response of these freshwater ecosystems to these changes is essential, as rivers and streams integrate atmospheric and terrestrial inputs, providing a direct measure of environmental health and stability (e.g., Williamson et al., 2008; Carpenter et al., 2011). Marion Island (46° 54' S, 37° 45' E), part of the Prince Edward Islands group, is a prime example of such an environment. Located 2 160 km southeast of South Africa, this volcanic island of approximately 293 km^2 is situated between the sub-Antarctic Polar Front (SAF) and the Antarctic Polar Front (APF) (Fig. 1). Its hyper-oceanic climate is characterised by cool, wet, and windy conditions, driven by the frequent passing of mid-latitude cyclones, frontal systems, and migratory anticyclones (Rouault et al., 2005). The island's geology consists of pre-glacial Pleistocene grey basaltic lavas overlain by post-glacial Holocene black lavas (Rudolph et al., 2021), which exhibit high porosity and water absorption rates (Boelhouwers et al., 2003). As a result, most streams on the island are non-perennial; however, the Soft Plume River (SPR) is the only perennial stream, draining a catchment of 7.29 km^2 (Stowe et al., 2018).

The Soft Plume River (SPR) is located on the eastern, leeward side of the island, and its perennial nature makes it an ideal system for investigating the long-term physicochemical dynamics of sub-Antarctic stream water. Like other freshwater bodies on the island, the SPR is characterised by low productivity and bacterial activity rates, making it a suitable site for isolating abiotic influences on water chemistry (Stowe et al., 2018). Moreover, its water chemistry is primarily controlled by precipitation, enriched with ions from the surrounding ocean, rather than by the underlying geology (Grobbelaar, 1978; Stowe et al., 2019).

Physicochemical characteristics of stream water are highly responsive to environmental drivers and important indicators of aquatic ecosystem health. Key parameters, including stream water temperature, pH, dissolved oxygen (DO), and specific conductivity (EC), fluctuate in response to climatic and hydrological processes (Stowe et al., 2018). High-frequency monitoring of these parameters is crucial for assessing both short-term responses to events associated with precipitation and long-term shifts associated with climate change. Stream water temperature is a fundamental driver of biological and chemical processes in aquatic systems (Smith, 1981), controlled mainly by

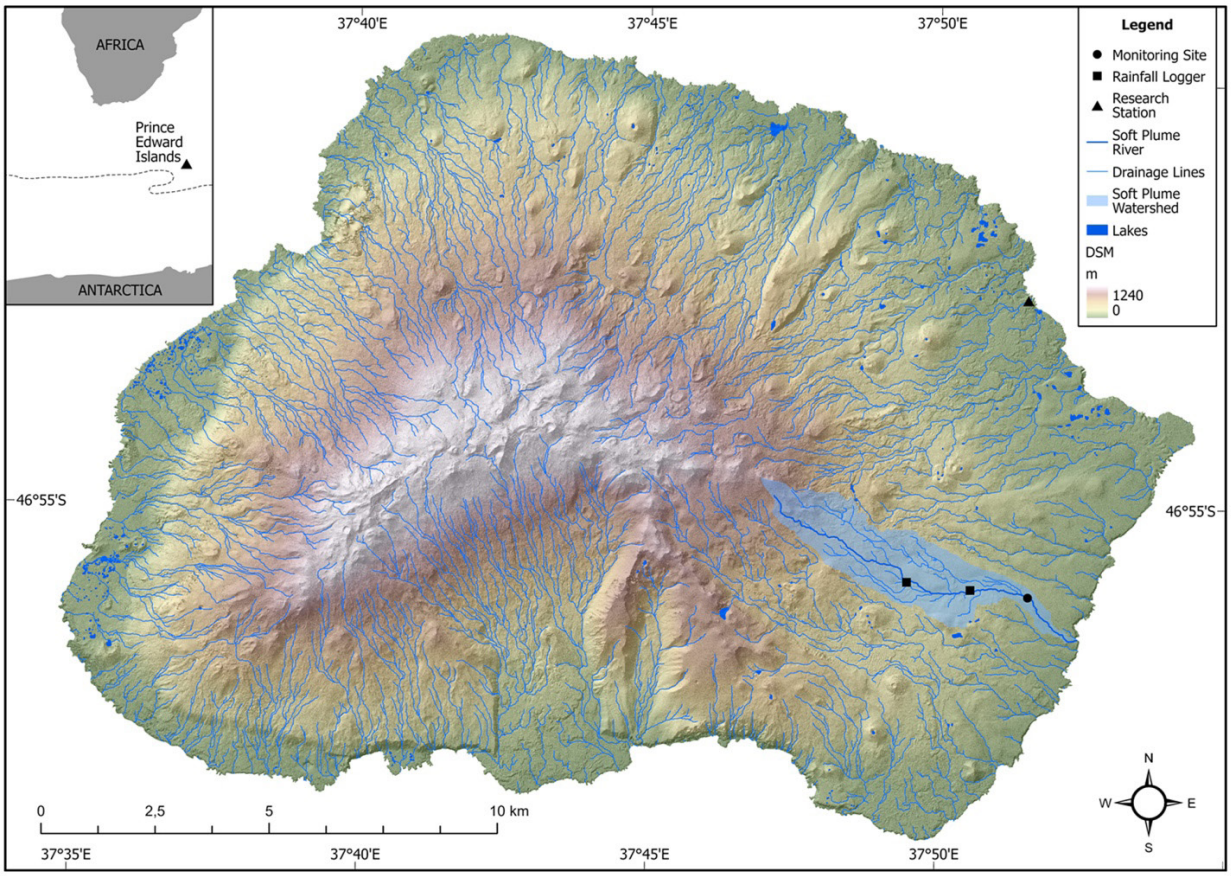


Figure 1. Location map of sub-Antarctic Marion Island. Note the location of the catchment for the Soft Plume River. The dashed line in the inset map provides a generalised position of the Antarctic Polar Front.

Table 1. Physicochemical parameters reported for streams on Marion Island across different studies (mean ± 1 standard deviation; ranges in brackets where available). The final column (Stowe et al., 2018) presents minimum–maximum values only.

Physicochemical parameters	Grobbelaar (1974)	Van Staden (2011)	Dartnall and Smith (2012)	Stowe et al. (2018)	Stowe et al. (2018) Mid-latitude cyclone range (15:00–21:00)
N (number of measurements)	26	28	19	120*	120*
Air-surface temperature (°C)	Not measured	Not measured	Not measured	8.2 (14.2)	2.0 – 9.2
Stream water temperature (°C)	Not measured	Not measured	Not measured	5.0 ± 1.94 (8.15)	4.6 – 7.5
pH (unit)	6.8 ± 0.3 (1.2)	6.9 ± 0.5 (1.8)	6.8 ± 0.8 (2.4)	7.2 ± 0.2 (1.3)	6.4 – 7.4
Dissolved Oxygen (DO; mg/L)	Not measured	Not measured	Not measured	12.1 ± 1.7 (2.0)	11.5 – 12.5
Specific conductivity (EC; µS/cm)	62.5 ± 22.1 (120.3)	53.4 ± 13.5 (44.0)	66.9 ±15.0 (59.0)	61.7 ±5.6 (27.7)	38.8 – 64.7

*Total number of hourly measurements over a 6-day period

heat exchange between the stream and its surroundings through advective processes (e.g., air mass movement) and non-advective mechanisms such as solar radiation, evaporation, and conduction (Webb and Zhang, 2004; Łaszewski, 2013).

Research on the physicochemical properties of Marion Island's streams has been sparse, historically relying on low-frequency, point-based measurements. The work of Grobbelaar (1978) established that the ionic composition of the island's freshwater is similar to that of the surrounding ocean ($Na^+ > Mg^{2+} > Ca^{2+} > SO_4^{2-} > HCO_3^-$). This finding, later substantiated by Van Staden (2011), Dartnell and Smith (2012), and Stowe et al. (2019), indicates that sea spray, rather than weathering of the island's basaltic lavas, is the dominant control on stream water chemistry. Until recently, continuous high-frequency data were absent. The first such investigation was conducted by Stowe et al. (2018), where the SPR was monitored for 16 days, including 6 days of continuous 5-min measurements. This study by Stowe et al. (2018) provided the first detailed insights into the diurnal physicochemical dynamics of the SPR (summarised in Table 1).

Although Stowe et al. (2018) provided valuable baseline data on diurnal variations and event-scale responses, the short duration of their study limited insights into longer-term dynamics. The influence of climatic drivers on stream physicochemistry over seasonal and multi-year timescales on Marion Island, therefore, remains poorly understood. Addressing this gap is essential, given the documented climatic shifts in the sub-Antarctic (see Nel et al., 2023). To this end, the present study analyses a 2-year, high-frequency (5-min interval) physicochemical dataset for the Soft Plume River (SPR). The objectives were to: (i) characterise the physicochemical properties of the SPR across diurnal, seasonal, and synoptic timescales; (ii) identify the climatic drivers regulating physicochemical fluxes in stream water; and (iii) examine the synoptic air circulation patterns associated with these drivers to evaluate their implications for understanding climate change impacts in the sub-Antarctic region.

METHODS

Data collection

Physicochemical stream water data

The current study analysed high-frequency physicochemical and meteorological data collected over a 2-year period, from May 2015 to April 2017, to determine the hydro-climatological dynamics of stream water on Marion Island. The physicochemical monitoring took place in the lower reaches of the SPR (Fig. 1). Physicochemical data were recorded in situ using an Eureka Manta multiprobe (Eureka Environmental Engineering, Austin, TX, USA) and programmed to record measurements every 5 minutes continuously for the 2-year period. The following physicochemical parameters were measured:

- Stream water temperature (°C)
- pH (pH units)
- Dissolved oxygen (DO, mg/L)
- Specific conductivity (EC, µS/cm)

Calibration of the multiprobe took place in water-saturated air before use and after data collection during the sampling process. Data were manually downloaded in the field at approximately 5-day intervals. Data are missing from September 2015 and from mid-April 2016 to May 2016 due to power supply issues with the multiprobe.

Meteorological data

Meteorological data were provided by the South African Weather Service (SAWS) from the research station on Marion Island (Fig. 1), which included monthly average air-surface temperatures and synoptic weather charts. Precipitation in the SPR catchment was measured using a tipping bucket rain gauge with a resolution of 0.2 mm, while rainfall data were monitored with Pace Scientific sensors (Mooresville, NC, USA) and recorded on Pace Scientific XR5 data loggers. To capture local spatial variability within the catchment, rainfall was measured in the upper and lower reaches of the SPR (Fig. 1).

Data analysis

The data analysis was structured to characterise physicochemical properties at diurnal and seasonal scales, assess the influence of distinct climatic drivers during 4 significant weather events, and evaluate the associated synoptic air circulation patterns.

Statistical approach and pre-testing

Prior to statistical analysis, all data were tested for normality using the Kolmogorov-Smirnov test and for homogeneity of variance using Levene's test. The data for the seasonal trend analysis met the assumptions for both normality ($p > 0.05$) and homogeneity of variance ($p > 0.05$). The data for diurnal trend analysis met the assumption of normality ($p > 0.05$) but did not meet the assumption of homogeneity of variance ($p < 0.05$). The subsequent selection of parametric or non-parametric tests was based on these results. For all statistical analyses, significance was determined at the 95% confidence level ($p < 0.05$).

Diurnal and seasonal trend analysis

For diurnal trends, measurements taken at 12:00 (noon) and 00:00 (midnight) were extracted for comparison. The non-parametric Mann-Whitney U test was applied to assess statistical significance. For seasonal trends, seasons were defined as Summer (December, January, February) and Winter (June, July, August). A parametric paired-sample t-test was used to determine if variations between the seasons were statistically significant.

Synoptic event and pattern analysis

Four significant weather events were identified based on their deviations from normative physicochemical conditions. The duration of each event was defined by the onset of rain (start) and the time when the stream temperature returned to its approximate pre-event baseline (end). Using the calculated mean stream temperature for the respective calendar month as a reference (e.g., the average for May 2015), the end of the event was determined by visual inspection of the time-series data. The event was considered concluded when the stream temperature trace no longer showed a trend related to the rainfall and stabilised around the monthly mean value.

RESULTS

Analysis of the 2-year high-frequency dataset from the SPR was conducted using Microsoft Excel 360 and IBM SPSS Statistics 21. The results are presented in 3 sections: (i) diurnal and seasonal trends, (ii) physicochemical responses to 4 significant weather events, and (iii) a synthesis of correlation trends.

Diurnal physicochemical trends

A non-parametric Mann-Whitney U test confirmed that all parameters exhibited statistically significant differences between the two selected time points. A significant contrast was observed between noon and midnight stream temperatures ($U = 90\ 996.000$, $Z = -13.933$, $p < 0.001$). Noon temperatures were consistently higher, with a mean of 6.57°C, compared to a mean midnight temperature of 5.18°C. Similarly, stream pH was significantly higher at noon than at midnight ($U = 87\ 531.000$, $Z = -14.010$, $p < 0.001$). The average noon pH was 7.10, while the average midnight pH was 6.74. DO concentrations were also significantly higher at noon ($U = 143\ 911.500$. $Z = -4.075$, $p < 0.001$), with a mean of 11.92 mg/L compared to the mean midnight concentration of 11.73 mg/L. In contrast to the other parameters, EC was significantly lower at noon and higher at midnight ($U = 113\ 629.000$, $Z = -9.411$, $p < 0.001$), with a mean noon value of 63.32 µS/cm compared to 65.64 µS/cm at midnight.

Seasonal physicochemical trends

A multi-season comparison was conducted to identify inter-annual variations in hydro-climatological conditions in the SPR.

Inter-annual winter comparison (2015 vs. 2016)

Rainfall and spatial variation: A notable spatial difference in rainfall distribution was observed in both winters, with significantly higher precipitation recorded at the upper reaches of the SPR compared to the lower reaches. In Winter 2015, the upper reaches received 772.4 mm of rainfall, while the lower reaches received 320.8 mm. A similar pattern occurred in Winter 2016, with 771.0 mm recorded at the upper and 488.6 mm at the lower reaches. However, a paired-sample t-test indicated no statistically significant difference in the total rainfall quantity between the two winter seasons ($t = 0.358$, $p > 0.05$), suggesting that the observed physicochemical shifts were likely driven by factors other than total precipitation volume.

Physicochemical trends: A paired-sample t-test revealed statistically significant differences between Winter 2015 and Winter 2016 for all measured physicochemical parameters ($p < 0.001$ for all). The mean stream temperature was slightly higher in Winter 2016 (4.76°C) compared to Winter 2015 (4.36°C; $t = -41.39$), with observed temperatures ranging from 1.41–8.24°C in Winter 2015 and 1.14–8.43°C in Winter 2016, indicating greater temperature variability and a broader range of extreme values (Fig. 2A). Mean pH decreased from 7.10 in Winter 2015 to

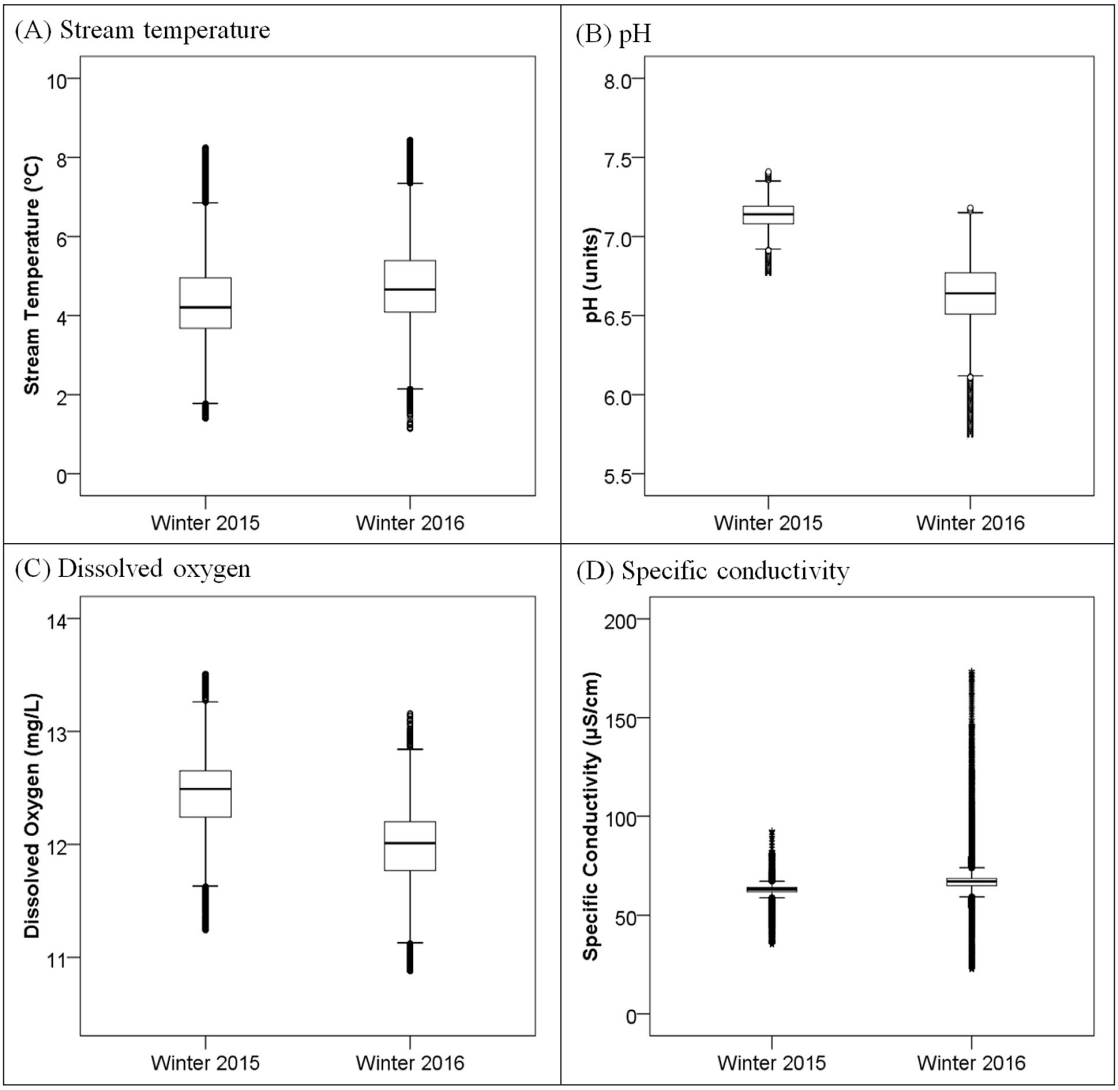


Figure 2. Statistical comparison of physicochemical parameters during the winters of 2015 and 2016. Box plots illustrate the median, interquartile range, and outliers for each parameter. Panels show comparisons of (A) stream temperature, (B) pH, (C) dissolved oxygen (DO), and (D) specific conductivity (EC).

6.61 (t = 259.690) in Winter 2016, with pH ranges of 6.28–7.41 and 5.56–7.18, respectively (Fig. 2B). Mean DO concentration also showed a slight decline from 12.43 mg/L in Winter 2015 to 11.96 mg/L (t = 138.20) in Winter 2016, with DO values ranging from 11.24–13.51 mg/L and 10.88–13.16 mg/L, respectively (Fig. 2C). Conversely, mean EC levels increased significantly between the two winters, increasing from 62.16 µS/cm in Winter 2015 to 67.58 µS/cm (t = –63.53) in Winter 2016. EC values ranged from 35.2–92.8 µS/cm in Winter 2015 and 22.6–173.7 µS/cm in Winter 2016, with the variability and range also substantially greater in Winter 2016 (Fig. 2D).

Inter-annual summer comparison (2016 vs. 2017)

Rainfall and spatial variation: Rainfall data collection was challenging in Summer 2016 due to a substantial number of missing data points; in contrast, the Summer 2017 dataset was mostly complete. Consequently, a definitive statistical comparison between the two seasons is not possible. The total recorded rainfall for Summer 2016 was 224.2 mm at the upper reaches and 12.4 mm at the lower reaches. In Summer 2017, total recorded rainfall was 473.8 mm and 185.6 mm at the upper and lower reaches, respectively.

Physicochemical trends: Paired-sample t-tests confirmed significant and consistent variations in all measured physicochemical parameters between the two summers (p < 0.001 for all). Mean stream temperature increased slightly from 7.21°C in Summer 2016 to 7.30°C in Summer 2017 (t = –10.58), with temperatures ranging from 3.72–14.78°C in Summer 2016 and 3.19–14.45°C in Summer 2017, although both summers displayed a similar temperature central spread (Fig. 3A). A notable shift was observed in stream pH, which decreased from a mean of 7.32 in Summer 2016 to 7.02 in Summer 2017 (t = 59.14), with pH ranges of 3.54–8.84 and 4.51–9.80, respectively (Fig. 3B). Mean DO concentration also decreased from 11.85 mg/L in Summer 2016 to 11.20 mg/L (t = 73.91) in Summer 2017. DO values ranged from 9.72–16.82 mg/L in Summer 2016 and 9.46–12.47 mg/L in Summer 2017, with the Summer 2017 distribution showing less variability than the preceding summer (Fig. 3C). EC levels were higher in Summer 2017, increasing from 63.62 µS/cm in Summer 2016 to 65.61 µS/cm (t = –21.61) in Summer 2017, with ranges from 22.4–70.2 µS/cm in Summer 2016 and 21.0–82.0 µS/cm in Summer 2017, showing greater variability and a broader range of values in Summer 2017 (Fig. 3D).

Physicochemical responses to synoptic weather events

To investigate the direct impact of short-term weather patterns on stream physicochemistry, 4 significant and distinct synoptic rainfall events were isolated from the 2-year dataset for detailed analysis (Table 2).

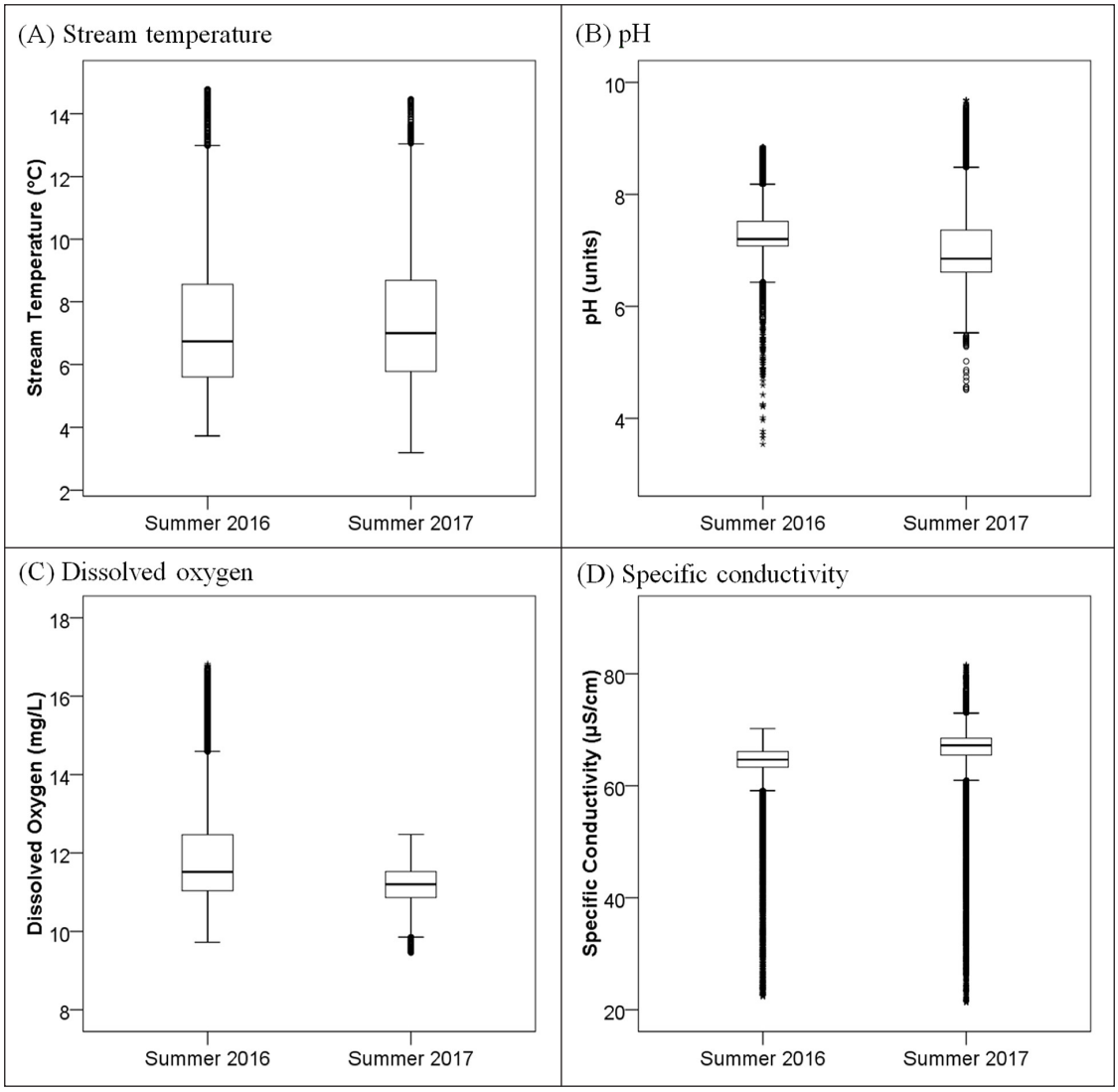


Figure 3. Statistical comparison of physicochemical parameters during the summers of 2016 and 2017. Box plots illustrate the median, interquartile range, and outliers for each parameter. Panels show comparisons of (A) stream temperature, (B) pH, (C) dissolved oxygen (DO), and (D) specific conductivity (EC).

Table 2. Summary of key meteorological drivers, antecedent conditions, and the key physicochemical responses observed during synoptic-scale events

Event	Date	Synoptic driver	Antecedent condition	Key physicochemical response	Main finding
1	May 2015	Mid-latitude cyclone	Normal	Pronounced dilution (↓ pH, ↓ EC)	Typical dilution response
2	July 2015	Successive cold fronts	Wet/primed	Dilution, especially on the second pulse	System priming enhances responses
3	October 2015	Cut-off low system	Normal	Strong dilution; temp ↑ from warm rain	Thermal response causes lag responses
4	November 2016	Cold front after a dry period	6-day dry period	'First flush' EC spike, then dilution	Antecedent conditions can reverse the response

Event 1 (26–27 May 2015)

This 17-hour event was characterised by 60.4 mm of rainfall in the upper reaches and a mean air-surface temperature of 6.10°C. Stream temperature peaked at 7.15°C approximately 3 hours after the maximum rainfall, demonstrating a delayed thermal response (Fig. 4A). Stream pH decreased rapidly from a pre-event high of 7.24 to a minimum of 6.29, showing a near-simultaneous response to rainfall (Fig. 4B). DO concentration decreased to a minimum of 11.53 mg/L, corresponding with a period of elevated stream temperature (Fig. 4C). EC exhibited a pronounced dilution effect, decreasing to a minimum of 20.10 µS/cm approximately 9 hours after the event began (Fig. 4D).

Correlation analysis for this event showed that stream temperature exhibited strong to very strong negative correlations with all parameters: pH ($r = -0.829$, $p < 0.001$), DO ($r = -0.888$, $p < 0.001$), and EC ($r = -0.799$, $p < 0.001$). A very strong positive linear relationship was observed between pH and EC ($r = 0.982$, $p < 0.001$), while a strong positive correlation between pH and DO was observed ($r = 0.678$, $p < 0.001$).

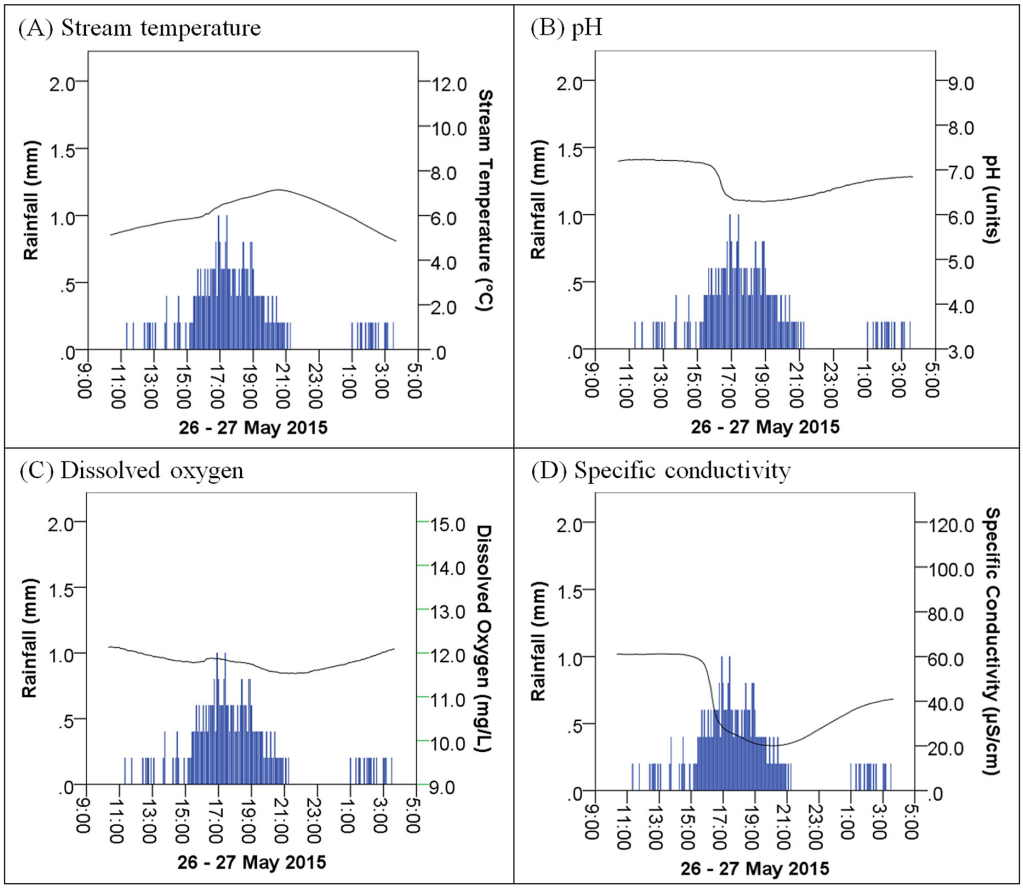


Figure 4. Physicochemical responses (black line) to rainfall (blue bars) during synoptic Event 1 (26–27 May 2015). This event, driven by a mid-latitude cyclone, demonstrates an apparent dilution response in the stream. Panels display the changes in (A) stream temperature, (B) pH, (C) dissolved oxygen (DO), and (D) specific conductivity (EC).

Event 2 (08–11 July 2015)

This extended event consisted of 2 distinct, successive rainfall periods (Events 2.1 and 2.2) spanning a total of 74.5 hours and delivering a cumulative amount of 62.8 mm of rain in the upper reaches, with a mean air-surface temperature of 0.46°C. When analysed together, the event showed a peak stream temperature of 5.34°C early in the event, followed by a minimum of 1.41°C approximately 40 hours after the initial rainfall (Fig. 5A). Stream pH fluctuated significantly, reaching a minimum of 6.31 during the first rainfall pulse and a maximum of 7.27 during the brief lull between the pulses (Fig. 5B). DO responded inversely to temperature, reaching a minimum of 12.02 mg/L during the initial temperature peak, and a maximum of 13.51 mg/L during the coldest period (Fig. 5C). EC largely mirrored the pH trend, decreasing during periods of high rainfall (Fig. 5D).

The combined correlation analysis for Event 2 revealed several significant relationships between the measured parameters. Rainfall quantity exhibited weak yet significant negative correlations with pH ($r = -0.384$, $p < 0.001$), EC ($r = -0.227$, $p < 0.001$), and DO ($r = -0.101$, $p < 0.001$), alongside a very weak positive correlation with stream temperature ($r = 0.114$, $p < 0.001$). Stream temperature indicated a very strong negative correlation with DO ($r = -0.974$, $p < 0.001$) and a strong positive correlation with EC ($r = 0.680$, $p < 0.001$). Among the physicochemical variables, pH was very strong and positively correlated with EC ($r = 0.909$, $p < 0.001$), while DO was strongly and negatively correlated with pH ($r = -0.692$, $p < 0.001$).

Event 3 (06–08 October 2015)

This 38-hour event was driven by a substantial rainfall of 82 mm in the upper reaches of the SPR, with a mean air-surface temperature of 1.78°C. Stream temperature showed a pronounced increase, peaking at 10.86°C approximately 14 hours after the onset of rain and coinciding with the maximum air temperature of 4.80°C (Fig. 6A). A strong dilution effect was observed for pH, which dropped to a minimum of 5.91 shortly after the event began (Fig. 6B). DO concentration decreased significantly to 10.41 mg/L, coinciding with the peak in stream temperature (Fig. 6C). EC also decreased due to dilution, reaching a minimum of 25.20 µS/cm (Fig. 6D).

Correlation analysis for Event 3 revealed several distinct relationships. Rainfall quantity had no statistically significant impact on stream temperature ($r = -0.027$, $p = 0.552$) but showed a strong negative correlation with pH ($r = -0.610$, $p < 0.001$), a weak negative correlation with EC ($r = -0.269$, $p < 0.001$), and a weak positive correlation with DO ($r = 0.169$, $p < 0.001$). Stream temperature was once again a dominant driver, exhibiting a very strong negative correlation with DO ($r = -0.985$, $p < 0.001$), a strong negative correlation with EC ($r = -0.701$, $p < 0.001$), and a moderately negative correlation with pH ($r = -0.407$, $p < 0.001$). Furthermore, pH had a very strong positive correlation with EC ($r = 0.864$, $p < 0.001$) and a weak positive correlation with DO ($r = 0.287$, $p < 0.001$).

Event 4 (03–05 November 2016)

This 33-hour event received 46.8 mm of rain in the upper reaches, with a mean air-surface temperature of 9.66°C. Unlike previous events, stream temperature remained consistently higher than the monthly average throughout, peaking at 9.39°C (Fig. 7A). The pH showed a significant drop to a minimum of 5.52 (Fig. 7B). DO decreased as the temperature rose, reaching a minimum of 10.57 mg/L (Fig. 7C). A key distinction in this event was the response of EC, which showed a rapid and pronounced increase at the onset of the event, peaking at 114.10 µS/cm before subsequently decreasing (Fig. 7D). This atypical response was linked to a preceding dry period.

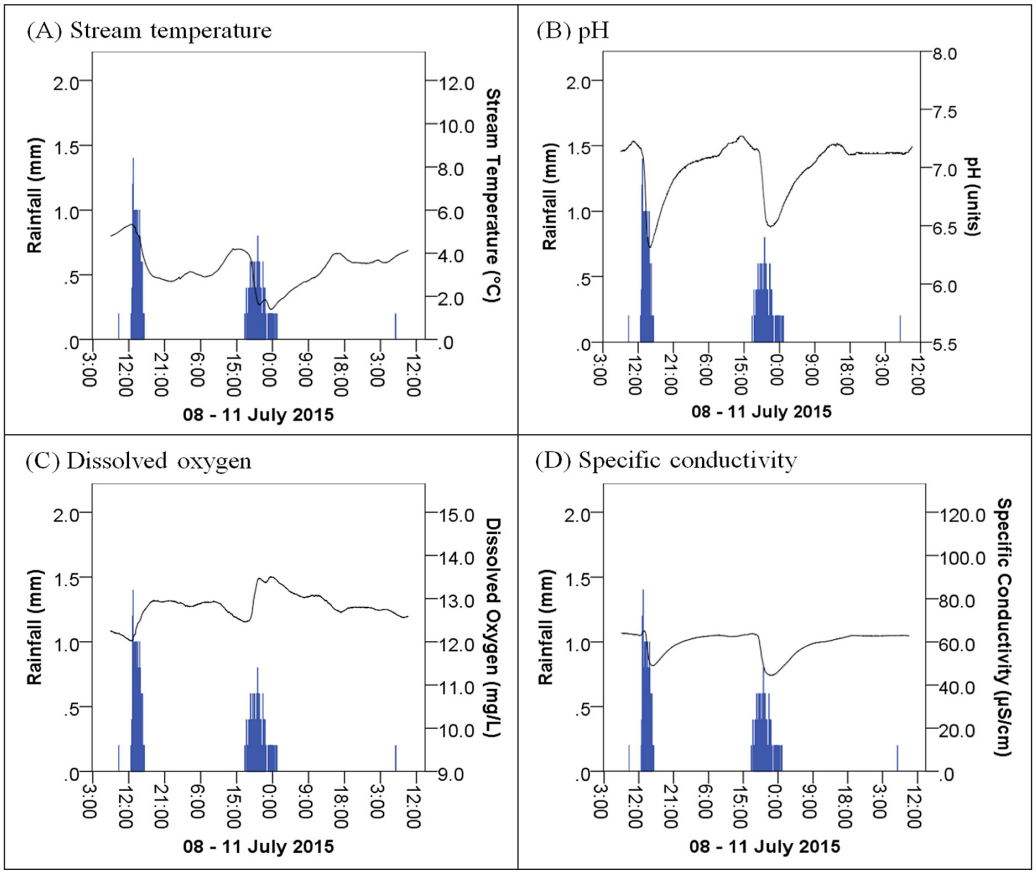


Figure 5. Physicochemical responses (black line) to rainfall (blue bars) during synoptic Event 2 (08–11 July 2015). This event was characterised by 2 successive cold fronts, showing a strong dilution effect during both rainfall pulses. Panels display the changes in (A) stream temperature, (B) pH, (C) dissolved oxygen (DO), and (D) specific conductivity (EC).

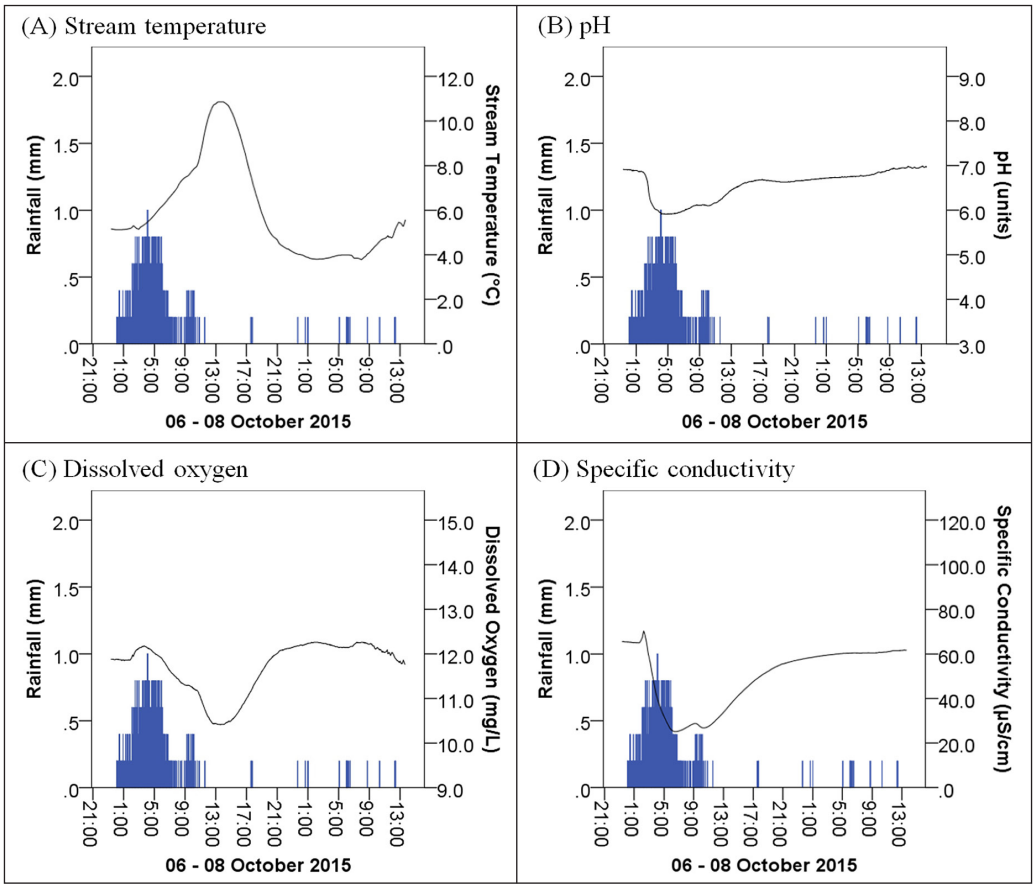


Figure 6. Physicochemical responses (black line) to rainfall (blue bars) during synoptic Event 3 (06–08 October 2015). Driven by an intense cut-off low-pressure system, this event shows a dilution effect together with a thermal increase from possible warm sector rain. Panels display the changes in (A) stream temperature, (B) pH, (C) dissolved oxygen (DO), and (D) specific conductivity (EC).

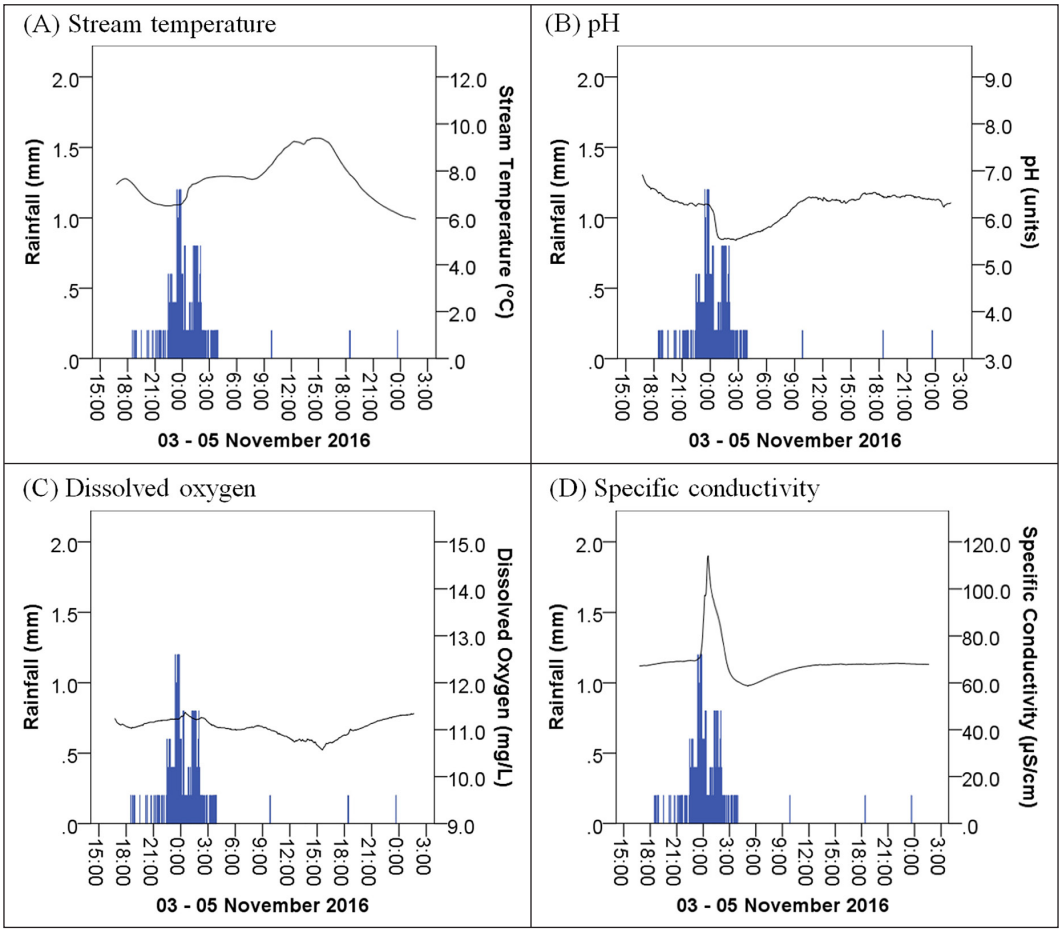


Figure 7. Physicochemical responses (black line) to rainfall (blue bars) during synoptic Event 4 (03–05 November 2016). This event, following a 6-day dry period, demonstrates a distinct 'first flush' phenomenon. The sharp initial increase in specific conductivity (D) contrasts with the dilution effect seen in other events. Panels display the changes in (A) stream temperature, (B) pH, (C) dissolved oxygen (DO), and (D) specific conductivity (EC).

Correlation analysis for Event 4 highlighted several patterns that were distinct from the other events, particularly the influence of rainfall. Rainfall quantity showed a moderate positive correlation with EC ($r = 0.511$, $p < 0.001$), while also exhibiting weak negative relationships with stream temperature ($r = -0.205$, $p < 0.001$) and pH ($r = -0.301$, $p < 0.001$). Stream temperature maintained its strong negative correlation with DO ($r = -0.920$, $p < 0.001$) but showed only a very weak negative correlation with EC ($r = -0.159$, $p < 0.001$) and no statistically significant relationship with pH. Another deviation from previous trends was pH, which displayed very weak negative correlations with both DO ($r = -0.227$, $p < 0.001$) and EC ($r = -0.160$, $p < 0.001$).

Synthesis of correlation trends across events

A comprehensive examination of correlations across all events revealed several consistent and overarching relationships (refer to Table 3).

- **Stream temperature and DO**: A very strong and statistically significant negative correlation was present in all events, highlighting the dominant control of temperature on oxygen solubility.
- **Rainfall and pH**: A consistent pattern of negative correlation was observed, indicating that increased rainfall consistently led to decreased stream pH. The strength of this relationship varied from weak to strong, depending on the event.
- **Rainfall and EC**: In most events, rainfall was weakly to moderately negatively correlated with EC, demonstrating a dilution effect. Event 4 was a notable exception, showing a moderate positive correlation.
- **pH and EC**: A very strong positive correlation was observed in 4 of the 5 events, indicating that decreases in pH were closely associated with decreases in EC. Event 4 was again the exception, displaying a very weak negative correlation.

DISCUSSION

This study provides the longest continuous high-frequency analysis of stream water physicochemical properties on a sub-Antarctic island to date. The results reveal a system strongly influenced by atmospheric drivers across diurnal, seasonal, and synoptic timescales. The findings confirm established diurnal patterns, provide the first multi-year assessment of seasonality for the SPR, and directly link physicochemical responses to specific, recurring synoptic weather systems.

Interpretation of diurnal and seasonal dynamics

Diurnal trends

The statistically significant differences between noon and midnight physicochemical values highlight the dynamic nature of the stream system, which is strongly influenced by the island's meso-climate. The consistently higher stream temperatures at noon compared to midnight align with the diurnal cycle of air-surface temperature, which is driven by solar radiation (Schulze, 1971). This confirms the direct thermal linkage between the atmosphere and the stream, as previously noted in a shorter-term study by Stowe et al. (2018).

The corresponding noon peaks in pH and DO are also primarily driven by this thermal cycle. The average noon pH is consistent

Table 3. Pearson correlation coefficients (*r*) for physicochemical and meteorological parameters across all measured synoptic events

Correlation pair	Event 1	Event 2.1	Event 2.2	Event 3	Event 4
Correlation with stream temperature					
Stream temperature vs. rainfall	0.349***	0.455***	−0.347***	−0.027	−0.205***
Stream temperature vs. pH	−0.829***	0.137	0.917***	−0.407***	0.014
Stream temperature vs. dissolved oxygen	−0.888***	−0.979***	−0.975***	−0.985***	−0.920***
Stream temperature vs. specific conductivity	−0.797***	0.234***	0.936***	−0.701***	−0.159***
Correlation with rainfall					
Rainfall vs. pH	−0.444***	−0.354***	−0.433***	−0.610***	−0.301***
Rainfall vs. dissolved oxygen	−0.046	0.297***	0.169***	0.169***	0.316***
Rainfall vs. specific conductivity	−0.303***	−0.106*	−0.394***	−0.269***	**0.511*****
Correlation with pH					
pH vs. dissolved oxygen	0.678***	−0.206***	−0.879***	0.287***	−0.227***
pH vs. specific conductivity	0.982***	0.940***	0.972***	0.864***	−0.160***
Correlation with dissolved oxygen					
Dissolved oxygen vs. specific conductivity	−0.717***	−0.305***	−0.925***	0.626***	0.325***

Notes: Significance levels are denoted as: *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$. All non-significant correlations ($p \geq 0.05$) are shown without an asterisk. Value in bold highlights the anomalous positive correlation during the 'first flush' event.

with the daily pattern of increasing pH after sunrise observed by Stowe et al. (2018). The higher DO concentrations at noon were further supported by the diurnal pattern reported by Stowe et al. (2018). While biological activity (photosynthesis and respiration) can influence diurnal pH and DO cycles (Grobbelaar, 1975; Grobbelaar et al., 1987), primary production in Marion Island streams is minimal. Therefore, the observed patterns are predominantly controlled by physical processes. The strong inverse relationship between stream temperature and oxygen solubility is the key driver; as the stream water warms during the day, its capacity to hold DO decreases, though this effect is moderated by atmospheric exchange.

Conversely, EC was consistently higher at midnight, aligning with the diurnal EC variations reported by Stowe et al. (2018), who noted peak concentrations at midnight. This pattern likely reflects a relative concentration of solutes during periods of lower streamflow and reduced influences from surface runoff or precipitation, which are more common during daylight hours. The confirmation of these strong diurnal trends highlights the need for high-frequency monitoring to understand baseline stream dynamics on Marion Island.

Seasonal trends and hydro-climatic controls

This study provides the first multi-year assessment of seasonal physicochemical trends on Marion Island. The comparison between Winter 2015 and Winter 2016 revealed a significant increase in stream temperature and EC in the subsequent winter, accompanied by a decrease in pH and DO. The higher mean stream temperature in Winter 2016 can be inferred to result from higher mean air-surface temperatures, a known climatic trend on the island (Nel et al., 2009). The corresponding increase in EC is likely a consequence of higher evaporation rates driven by these warmer conditions, resulting in increased solute concentration (Hayek et al., 2020; Fai et al., 2023). The decrease in pH and DO is consistent with established principles: warmer water holds less DO, and changes in temperature and precipitation influence pH (Kelly, 1996; Stowe et al., 2018).

The comparison of Summer 2016 and Summer 2017 revealed similar trends, but with greater extremes. All physicochemical parameters followed the same trajectory as the winter-to-winter comparison: stream temperature and EC increased, while pH and DO decreased. The values recorded during the summers were generally more extreme than in the winters, reflecting the higher energy input and more dynamic atmospheric conditions of the summer season. An intra-annual comparison between the winter and summer of 2016 further elucidated these controlling factors, highlighting a dynamic balance between temperature-driven evaporation and precipitation-driven dilution. The notable increase in mean stream temperature from winter to summer was directly mirrored by a reduction in DO concentration, reinforcing the temperature-dependence of DO. However, pH and EC showed opposite trends to those observed in the seasonal year-on-year comparisons, with pH increasing while EC decreased from winter to summer.

The observed seasonal trends likely reflect a complex interaction between multiple hydro-climatic and biochemical processes operating across both inter-annual and intra-annual timescales. Increased sunshine and higher air-surface temperatures during summer may enhance evaporation and promote solute concentration, contributing to elevated EC values (Hayek et al., 2020). Conversely, precipitation-driven dilution may reduce EC and alter pH dynamics during high-flow conditions (Rodríguez Castro et al., 2016; Stowe et al., 2018). Variations in DO and pH may additionally reflect interactions between temperature-dependent solubility, hydrological conditions, and biological processes within the stream system. Collectively, these findings suggest that physicochemical variability in the SPR is governed by multiple interacting environmental controls, rather than a single dominant mechanism.

Overall, the observed physicochemical ranges across the 2015–2017 monitoring period indicate substantial natural temporal variability within the SPR system. Stream temperature, pH, DO, and EC values varied in response to seasonal hydro-climatic conditions, with notable inter-seasonal differences observed across parameters. These findings provide important context for interpreting historical observations from Marion Island and demonstrate that previously reported values are generally consistent with the variability observed during this study.

Interpretation of synoptic events

The analysis of 4 significant weather events provides direct evidence of the mechanisms controlling physicochemical fluctuations, with each event linked to specific synoptic patterns identified by Nel et al. (2020).

Event 1 (26–27 May 2015)

Event 1 was driven by the island being in the warm sector of a mid-latitude cyclone (Cluster 7) (Nel et al., 2020), followed by the passage of a cold front (transition to Cluster 3). This synoptic

sequence explains the observed results: elevated air-surface and stream temperatures followed by a pronounced dilution of pH and EC due to the 60.4 mm of associated rainfall. Furthermore, the timing of the physicochemical minimums (1 to 1.5 hours before the stream temperature maximum) highlights the different response times of solute chemistry versus thermal inertia.

Event 2 (08–11 July 2015)

Event 2 was characterised by 2 successive cold fronts passing over the island during winter, associated with weather Clusters 3 and 4. This explains the overall decrease in air-surface and stream temperatures. The dilution effect was evident across both sub-events, with pH and EC decreasing in response to rainfall. The fact that the strongest correlations between physicochemical parameters occurred during the second sub-event (Event 2.2) suggests that the system was already primed by the first front, leading to an exaggerated response to the second pulse of rainfall.

Event 3 (06–08 October 2015)

Event 3 was dominated by an intense cut-off low-pressure system (Cluster 2 from Nel et al., 2020). This system placed the island in a warm sector on the morning of 07 October, where most of the 82 mm of rain fell, before the cold front passed. This explains the seemingly contradictory observation of decreasing air-surface temperature but increasing stream temperature. The increase in stream temperature was likely due to the influx of warmer rainwater from the warm sector. The subsequent decrease in DO was a direct consequence of this thermal increase, with both parameters exhibiting a delayed response relative to rainfall, highlighting the stream's thermal inertia. The pronounced decrease in pH and EC was a clear and direct result of dilution from the intense rainfall.

Event 4 (03–05 November 2016)

Event 4 provides the most compelling evidence for antecedent conditions influencing physicochemical response. This event was driven by the passage of a cold front (Cluster 4) followed by a low-pressure system (Cluster 3 from Nel et al., 2020). The key finding was the rapid and substantial increase in EC at the onset of rain, a direct contrast to the dilution effect seen in previous events. This atypical 'first flush' response is explained by the extended dry period that preceded the event (minimal rainfall for 6 days). During this time, solutes concentrated in the stream and the surrounding catchment due to evaporation. The initial rainfall rapidly mobilised these accumulated solids, causing the observed spike in EC before the system reverted to a dilution-dominated state (Lake, 2003). This event demonstrates that the hydro-climatological context preceding a rainfall event is as important as the event itself in determining the physicochemical response.

Across all events, 3 patterns were remarkably consistent. First, there was a delayed thermal response, with maximum or minimum stream temperatures occurring several hours after the peak rainfall. Second, a very strong negative correlation was observed between stream temperature and DO in every event, confirming the significance of this relationship regardless of the synoptic driver. Finally, pH consistently decreased with rainfall across all events, validating dilution as the primary mechanism controlling stream pH during synoptic-scale events.

Climate change implications

The synoptic weather events analysed in this study are not random occurrences, but are associated with defined atmospheric circulation patterns (clusters) that have known long-term frequency trends defined by Nel et al. (2020). The events in this study were predominantly associated with Clusters 2, 3, 4, and 7 described by Nel et al. (2020). According to Nel et al. (2020), the frequencies of Clusters 2, 3, and 7 increased between 1960 and 2009, while the frequency of Cluster 4 decreased. These trends are directly linked to documented climate change on Marion Island, namely increasing mean annual air-surface temperatures and decreasing precipitation (Boelhouwers, 2003; Hedding and Greve, 2018; Nel et al., 2023).

This study's findings provide a link between long-term climatic shifts and stream water quality for sub-Antarctic Marion Island. The increasing frequency of weather clusters that cause significant physicochemical fluctuations suggests that Marion Island's streams will experience these dynamic conditions more often. The warming trend is expected to lead to higher average stream temperatures and consequently lower baseline DO concentrations, potentially stressing aquatic ecosystems. Furthermore, the trend of decreasing overall precipitation (Sumner et al., 2004; Hedding and Greve, 2018) suggests that periods of low flow and drought-like conditions may become more common. This is particularly significant for Marion Island, given that most streams are already non-perennial. The results from Event 4 are particularly relevant in this context. If extended dry periods followed by intense rainfall become more frequent, the 'first flush' phenomenon, characterised by sharp spikes in EC, could become a more regular feature of the island's physicochemistry. This would lead to a system defined by greater extremes, including long periods of solute concentrations offset by intense, short-lived dilution and flushing events. This shift from a dilution-dominated system to one with more frequent evaporative concentration has significant implications for the ecological functioning and water quality of sub-Antarctic Marion Island.

CONCLUSION

This study demonstrated that the physicochemical characteristics of the SPR on sub-Antarctic Marion Island are intricately linked to climatic drivers across multiple timescales. Clear diurnal cycles are driven by solar radiation, while seasonal trends reflect a complex interaction between temperature-driven evaporation and precipitation-driven dilution. The analysis of synoptic events provides a direct causal link between specific weather systems and distinct, predictable physicochemical responses, with antecedent conditions playing a crucial role. The weather patterns associated with the most significant fluctuations are increasing in frequency as a result of regional climate change. These findings suggest a future trajectory for Marion Island's streams characterised by higher temperatures, lower DO, and more extreme fluctuations in solute concentrations, affecting pH and EC, providing a baseline for understanding the future of vulnerable sub-Antarctic freshwater ecosystems.

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AUTHOR CONTRIBUTIONS

Kayla Cassandra Schoenknecht: Formal analysis, investigation, visualisation, writing (original draft).

David William Hedding: Project conceptualisation, data curation, writing (reviewing and editing).

Werner Nel: Supervision, data curation, project administration, writing (reviewing and editing).

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon request.

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