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Geochemistry of contrasting stream types, Taylor Valley, Antarctica

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ABSTRACT

The McMurdo Dry Valley region is the largest ice-free area of Antarctica. Ephemeral streams flow here during the austral summer, transporting glacial meltwater to perennially ice-covered, closed basin lakes. The chemistry of 24 Taylor Valley streams was examined over the two-decade period of monitoring from 1993 to 2014, and the geochemical behavior of two streams of contrasting physical and biological character was monitored across the seven weeks of the 2010–2011 flow season. Four species dominate stream solute budgets: HCO_3^-, Ca^{2+}, Na^+, and Cl^-, with SO_4^{2-}, Mg^{2+}, and K^+ present in significantly lesser proportions. All streams contain dissolved silica at low concentrations. Across Taylor Valley, streams are characterized by their consistent anionic geochemical fingerprint of $HCO_3 > Cl > SO_4$, but there is a split in cation composition between 14 streams with $Ca > Na > Mg > K$ and 10 streams with $Na > Ca > Mg > K$.

Andersen Creek is a first-order proglacial stream representative of the 13 short streams that flow <1.5 km from source to gage. Von Guerard is representative of 11 long streams 2–7 km in length characterized by extensive hyporheic zones. Both streams exhibit a strong daily cycle for solute load, temperature, dissolved oxygen, and pH, which vary in proportion to discharge. A well-expressed diurnal co-variation of pH with dissolved oxygen is observed for both streams that reflects different types of biological control. The relative consistency of Von Guerard composition over the summer flow season reflects chemostatic regulation, where water in transient storage introduced during times of high streamflow has an extended opportunity for water-sediment interaction, silicate mineral dissolution, and pore-water exchange.

INTRODUCTION

Located at 76°30′ to 78°30′ S latitude and 160° to 164° E longitude in the central Transarctic Mountains between the East Antarctic Ice Sheet and the Ross Sea coast of Victoria Land in Antarctica (Fig. 1A), the McMurdo Dry Valley region is a polar desert on the western edge of McMurdo Sound that comprises the largest ice-free area of Antarctica. Here, a set of E-W–trending valleys extends across an area of ~4800 km^2 as a mosaic of Paleozoic–Mesozoic bedrock outcrops, glaciers, mostly closed basin lakes, and open expanses of barren, frozen patterned ground covered by Quaternary glacial, lacustrine, and alluvial deposits (McKelvey and Webb, 1959; Green et al., 1988). This landscape lacks vascular plants but, despite its unusually harsh hyper-arid polar climate, supports robust aquatic ecosystems dominated by microbial mats and phytoplankton with soil ecosystems hosting a variety of microscopic organisms (Powers et al., 1998).

The U.S. National Science Foundation established a McMurdo Long-Term Ecological Research site (the MCM-LTER project) at Taylor Valley in 1993 that has the long-term objective of understanding the terrestrial and aquatic processes operating in this polar desert ecosystem. Taylor Valley (Fig. 1B) extends some 35 km in a NE-SW orientation from the Ross Sea coast to the terminus of the Taylor Glacier at the southwestern edge of the polar plateau. Numerous ephemeral streams develop here each austral summer, where they transport glacial meltwater across expanses of barren ground to three perennially ice-covered, closed basin lakes.

Since the inception of the MCM-LTER project, there have been major climate changes in the McMurdo Dry Valley region that have driven large, inter-annual variations in streamflow. Measurement of flow for the Onyx River, the longest river in the McMurdo Dry Valley region located in Wright Valley (Fig. 1A), began in 1970 and today is the longest environmental record of the region (Fig. 1C). The beginning of the MCM-LTER project in 1993 coincided with a period of sustained summer cooling and low streamflows that were associated with the effect of the Antarctic ozone hole on atmospheric dynamics over the continent (Doran et al., 2002; Walsh, 2009). This period of cooling was interrupted by warm, sunny conditions in the summer of 2001–2002, when substantial flooding occurred throughout the McMurdo Dry Valley region. That summer marked the end of the cooling trend and a return to the previous pattern of strong inter-annual variation in streamflow observed during the 1970s (Gooseff et al., 2017a).

The MCM-LTER project has monitored the water quality of many streams in Taylor Valley over an extended period that covers the full range in flow conditions observed over the entire 50-year record of the Onyx River (Fig. 1C). For this reason, it is timely to analyze that valuable geochemical record to obtain a more detailed understanding of the chemical dynamics of Antarctic streams, which will also serve as a baseline against which to compare future changes. Because the ecological structure and function of the lakes and coastal ocean into which McMurdo Dry Valley region streams discharge depend on the hydrological connectivity between glaciers and permanent closed basin lakes (Gooseff et al., 2011), it is also essential to understand the geochemistry of these seasonal streams at different temporal scales. Therefore, this study examined the long-duration/low-frequency stream chemistry record of streams of contrasting character in Taylor Valley and made higher frequency measurements of two streams of contrasting character over the summer of 2010–2011 to obtain a detailed temporal record for a single flow season. Thus, data from this study contribute to the temporal and spatial understanding of the geochemical dynamics of McMurdo Dry Valley region streams that is required to establish a baseline against which to assess the impacts of global climate change going forward. As the climate in Antarctica continues to warm and glacial ice melts more

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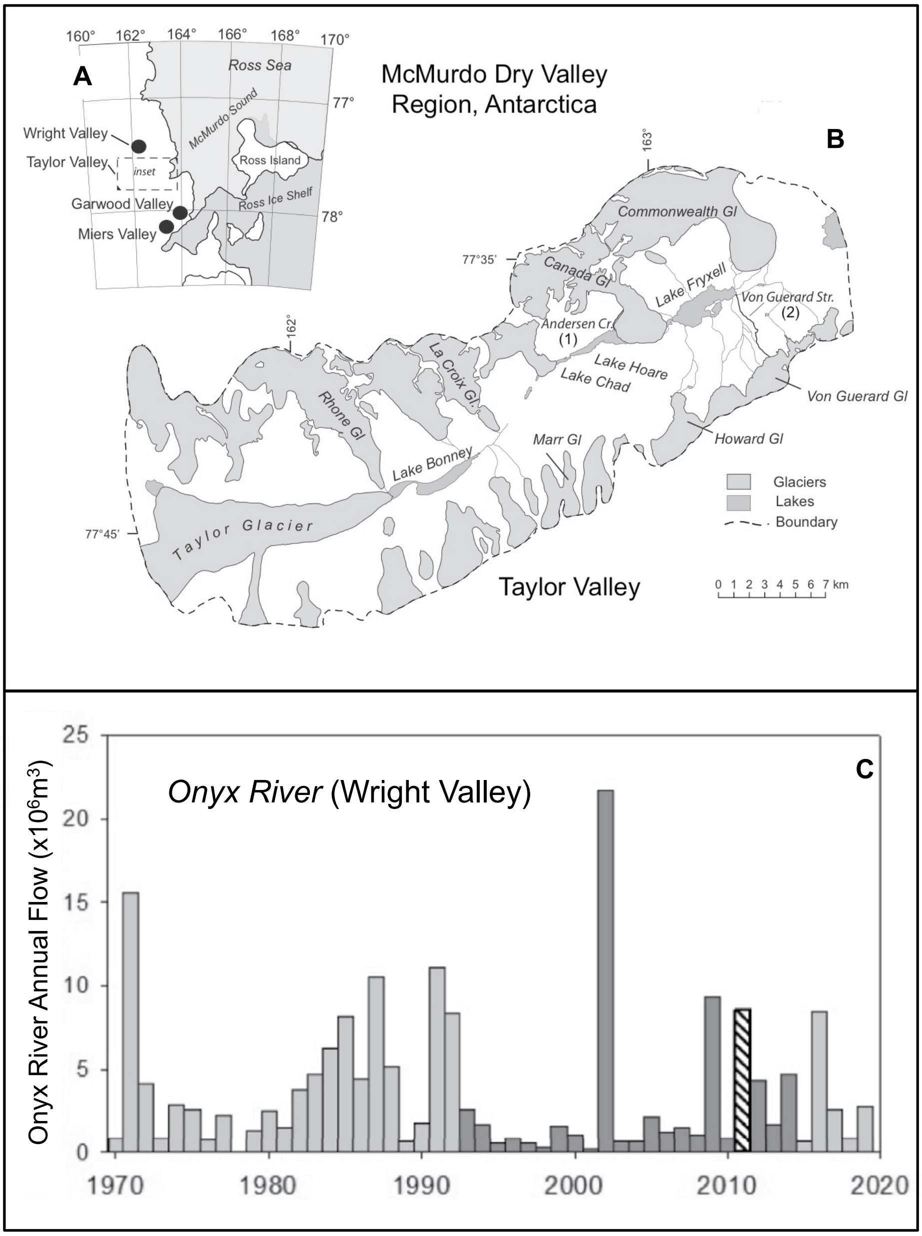

Figure 1. (A) Location map of the McMurdo Dry Valley region of Antarctica. (B) Map of Taylor Valley showing the positions of major glaciers, central closed basin lakes, and the two streams that are the focus of this study: (1) Andersen Creek and (2) Von Guerard. (C) Histogram of total annual flow of the Onyx River in Wright Valley, the longest river in the McMurdo Dry Valley region and on the Antarctic continent. The dark gray bars indicate the years of the long-term geochemical analysis presented in this study; the light gray bars indicate the years prior to the McMurdo Long-Term Ecological Research (MCM-LTER) program, when flow measurements were made by the New Zealand Antarctic program, and the years subsequent to the record analyzed in this study when flow measurements were made by the MCM-LTER program; and the hashed bar denotes the austral summer of 2010–2011, when the seasonal and diurnal sampling was conducted.

rapidly than at present (Chapman and Walsh, 2007; Turner et al., 2014), streamflow is likely to exceed the flood events recorded in the recent past. The consequences of higher streamflow volumes will affect solute fluxes through hyporheic zone expansion and consequent enhanced salt mobilization and chemical weathering. Understanding the processes and dynamics controlling stream geochemistry and stream interactions with the alluvial soils and subsurface flows that determine solute accumulation is necessary to predict future behavior.

BACKGROUND

The McMurdo Dry Valley region's climate is characterized by a mean annual air temperature in valley bottoms varying from –21 °C to –18 °C, which during the summer can rise daily to 10 °C at some locations, and between 2–50 cm annual precipitation that falls mostly as snow (Doran et al., 2002; Fountain et al., 2010). There is a slight climate gradient inland from cloudy, wetter, and colder conditions near the coast toward drier and warmer conditions inland. Most McMurdo Dry Valley region glaciers are polar alpine glaciers, but a few like Taylor Glacier at the southwestern end of Taylor Valley are outlet glaciers of the East Antarctic Ice Sheet. The largest alpine glaciers descend only short distances into the valley from the surrounding mountains because sublimation and melting exceed snow accumulation below 1500 m in all seasons (Chinn, 1985).

Local relief within the McMurdo Dry Valley region is <3000 m, and the landscape is considered to have been geomorphologically stable over the past few million years (Denton et al., 1993). Exposed lithologies consist of a pre-Ordovician metasedimentary basement sequence composed of schists, hornfels, and marble; a younger group of granite and granite gneiss intrusions of lower Paleozoic age; and the overlying mid-Paleozoic to mid-Mesozoic Beacon Sandstones that have been intruded by the Jurassic Ferrar Dolerites (McKelvey and Webb, 1959). Valley floors are covered with moraines and a thin patchy cover of Quaternary glacial, lacustrine, and alluvial sediments that are remarkably similar across the region and occasional cinder cones of the McMurdo Volcanic Group (McKelvey and Webb, 1959; Denton et al., 1989). A texturally coarse and heterogeneous alluvial soil derived from marine sediments, paleo-lake beds, valley wall colluvium, and the weathering of bedrock glacial till covers ~95% of valley floors (McCraw, 1967; Bockheim, 2002). This soil, mapped as about half shallowly ice-cemented and half dry-frozen (Bockheim et al., 2007), is strongly cryoturbated (Bockheim and McLeod, 2008).

Bordered to the northwest by the Asgard Range and to the southeast by the Kukri Hills, Taylor Valley (Fig. 1B) comprises an area of ~400 km^2, about one-third of which is covered with glacial drift, moraine, and Quaternary lacustrine sediments (Denton et al., 1989). Typical of the McMurdo Dry Valley region, alluvial soils across Taylor Valley have a coarse, gravelly-sandy texture and extremely low contents

TABLE 1. OVERVIEW OF STREAM CHEMISTRY ACROSS TAYLOR VALLEY OVER THE TWO DECADES OF MCM-LTER MONITORING FROM 1993 TO 2014

Stream	Drainage	Length (km)	TDS (mg/L)	Sampling Interval	Geochemical Character		Description
Taylor Valley							
Commonwealth	to coast	0.7	34	1993–2014	$HCO_3 > Cl >> SO_4$	Na > Ca >> Mg > K	Drains the east side of Commonwealth Glacier to New Harbor
Fryxell Watershed							
Mariah	to Lake Fryxell	0.3	32	1993–2014	$HCO_3 >> Cl >> SO_4$	Na >> Ca >> K > Mg	Drains the southeast corner of Canada Glacier
Andrews	to Lake Fryxell	0.4	20	1993–2008	$HCO_3 >> Cl >> SO_4$	Na > Ca >> Mg > K	Drains the lower east side of Canada Glacier
Bowles	to Lake Fryxell	0.4	51	1993–2014	$HCO_3 >> Cl >> SO_4$	Na > Ca >> Mg > K	Drains multiple flows from tongue of Canada Glacier
Green	to Lake Fryxell	1.2	30	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca > Na >> Mg > K	Drains multiple flows from tongue of Canada Glacier
Canada	to Lake Fryxell	1.4	21	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca > Na >> Mg > K	Drains the upper east side of Canada Glacier
McKnight	to Lake Fryxell	2.2	84	1993–2014	$HCO_3 >> Cl >> SO_4$	Na >> Ca >> Mg > K	Drains the south face of Commonwealth Glacier
Lost Seal	to Lake Fryxell	2.3	77	1993–2014	$HCO_3 > Cl >> SO_4$	Na > Ca >> Mg > K	Drains the upper east side of Commonwealth Glacier
Huey	to Lake Fryxell	2.4	115	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca > Na >> Mg > K	Drains a small glacier in a steep-sided hollow
Von Guerard	to Lake Fryxell	4.9	109	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca > Na >> Mg > K	Drains the glaciers of the Kukri Hills
Harnish	to Lake Fryxell	5.0	164	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca~Na >> Mg > K	Drains the glaciers of the Kukri Hills
Crescent	to Lake Fryxell	5.7	147	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca > Na >> Mg > K	Drains the Crescent Glacier in the Kukri Hills
Delta	to Lake Fryxell	6.5	109	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca > Na >> Mg >> K	Drains the Howard Glacier in the Kukri Hills
Aiken	to Lake Fryxell	6.9	116	1993–2014	$HCO_3 >> Cl >> SO_4$	Na >> Ca > Mg > K	Drains Many Glaciers Pond fed by flows from the Kukri Hills
Hoare Watershed							
Wharton	to Lake Chad	0.2	51	1993–2013	$HCO_3 >> Cl >> SO_4$	Ca >> Na >> Mg > K	Drains the Suess Glacier into Lake Chad
McKay	to Lake Chad	0.3	40	1993–2013	$HCO_3 >> Cl >> SO_4$	Ca >> Na >> Mg > K	
House	to Lake Chad	0.5	52	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca >> Na >> K >> Mg	Drains the east side of the Suess Glacier to Lake Chad
Andersen Creek	to Lake Hoare	1.4	49	1993–2014	$HCO_3 > Cl > SO_4$	Ca > Na > K>Mg	Drains the west side of Canada Glacier
Bonney Watershed							
Lawson	to Lake Bonney	0.6	28	1993–2014	$HCO_3 \sim Cl >> SO_4$	Na >> Ca > Mg > K	Drains the Rhone Glacier
Vincent	to Lake Bonney	0.9	55	1993–2009	$HCO_3 >> Cl >> SO_4$	Ca > Na > Mg > K	Drains the eastern edge of the toe of the Hughes Glacier
Mason	to Lake Bonney	1.0	86	1993–2008	$HCO_3 >> Cl >> SO_4$	Ca > Na >> Mg > K	Drains the Rhone Glacier
Bartlette	to Lake Bonney	0.9	51	1993–2009	$HCO_3 > Cl > SO_4$	Na > Ca > K>Mg	Drains the northwest sector of the toe of the Hughes Glacier
Bohner	to Lake Bonney	2.7	129	1993–2014	$Cl > HCO^3 > SO_4$	Na > Ca > K>Mg	Drains the Sollas Glacier
Priscu	to Lake Bonney	3.2	117	1993–2014	$HCO_3 > Cl >> SO_4$	Ca~Na >> K > Mg	Drains the LaCroix Glacier and Sollas Glaciers
Fryxell Watershed Average			83	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca >> Na >> Mg > K and Na > Ca >> Mg > K	
Hoare Watershed Average			48	1993–2014	$HCO_3 >> Cl >> SO_4$	Ca >> Na >> Mg > K	
Bonney Watershed Average			78	1993–2014	$HCO_3 >> Cl >> SO_4$	Na > Ca >> Mg > K and Ca >> Na >> Mg > K	
Taylor Valley Average			***70***	***1993–2014***	$\boldsymbol{HCO_3\ Cl\ SO_4}$	***Na > Ca Mg > K***	
Wright Valley Average			***128***	***1993–2014***	$\boldsymbol{HCO_3 > Cl\ SO_4}$	***Na > Ca Mg > K***	
Miers Valley Average			***107***	***1993–2014***	$\boldsymbol{HCO_3 > Na\ SO_4}$	***Na > Ca K > Mg***	
Garwood Valley Average			***287***	***1993–2014***	$\boldsymbol{HCO_3 > Cl\ SO_4}$	***Na > Ca Mg K***	

Note: Source: http://www.mcmlter.org/streams-data. MCM-LTER—McMurdo-Long-Term Ecological Research. TDS—total dissolved solids.

of clay and organic material but contain an abundance of eolian dust and soluble salts (McCraw, 1967; Bockheim, 1997). Marine aerosol and atmospheric dust of local origin are considered to be responsible for as much as 40% by volume of the salt content of soils across the McMurdo Dry Valley region landscape (Claridge and Campbell, 1977).

The primary water source within Taylor Valley is melting of alpine glaciers below 1500 m elevation during the warmest months of the austral summer, when continuous solar radiation can elevate air temperatures above a threshold of about −5 °C to generate glacial melting. The little snow that falls typically sublimates before making a hydrologic contribution (Clow et al., 1988).

Glacial meltwater generates ephemeral streams that flow for periods of 6–12 weeks each year between late November to early February (Chinn, 1981) and exhibit a large inter-annual variability in total flow volume (Conovitz et al., 1998). Over the course of an austral summer, streamflow commences at low amounts as glacial melting begins, grows to a mid-season high, and then diminishes as winter approaches. Superimposed on this annual trend is diurnal fluctuation in streamflow produced by the daily freeze-thaw cycle. Because glacial surface temperatures are typically near the ice melting point throughout the summer, a fine balance exists where small changes in radiant energy, temperature, and snowfall control the melting of glacial ice (Dana et al., 1998; Fountain et al., 2010) and, consequently, determine the daily volume of glacial meltwater. Thus, streamflow within Taylor Valley is quite flashy (Hoffman et al., 2008) and exhibits large diurnal variation, with the timing of the daily discharge peak for each stream determined by the solar trajectory, the orientation of its source glacier, and the stream slope and length (Conovitz et al., 1998; Wlostowski et al., 2016). Most streams experience several days of no flow during the summer because of differential cloud cover across Taylor Valley (Von Guerard et al., 1995).

In contrast to the other valleys of the McMurdo Dry Valley region (Wright, Garwood, and Miers) that have long streams flowing down their central valley axis, surface streams within Taylor Valley are short and, with one exception, discharge into ice-covered lakes on the central valley floor: Lake Bonney, Lake Chad/Hoare, and Lake Fryxell (Fig. 1B). The exception is the Commonwealth Stream that flows from the east side of the Commonwealth Glacier to the Ross Sea coast. These Taylor Valley streams range up to 7 km in length, with half <1.5 km long (Table 1), and in sections can display three different morphologies: (1) narrow, bouldery channels cut through moraines, (2) channels of intermediate width in front of glaciers that contain boulders set in a matrix of alluvium, and (3) wide, shallow braided channels on alluvial flood plains (McGraw, 1967). Lake Fryxell is the easternmost lake of Taylor Valley and receives glacial meltwater input from 13 streams, combined Lake Chad/Hoare is located in the central portion of Taylor Valley and receives meltwater input from four streams, and Lake Bonney is the westernmost lake in Taylor Valley and receives meltwater input from six streams (Table 1).

The deep, ice-cemented permafrost of the region precludes a groundwater contribution to McMurdo Dry Valley region lakes. However, thawing of the near-surface permafrost at elevations below 300 m during the summer months creates an active layer of thawed soil (Campbell et al., 1998; Bockheim et al., 2007). This active layer develops at the surface as summer warming commences and air temperatures rise above the freezing point, and throughout the summer it expands progressively downward within the alluvial soil profile to a depth of no more than a meter (Conovitz et al., 2006). It is within this active layer that the near-surface movement of fluid occurs and hyporheic zones can develop around stream channels. Streams and lakes may also receive a minor input of water from shallow seeps within the active layer that develop from the localized melting of snow patches, frozen precipitation accumulated in the subsurface, permafrost, and buried ice (Harris et al., 2007; Levy et al., 2011), particularly during summer episodes of higher than normal temperature. The interaction of such interstitial meltwater with particulate dry-frozen soil at the top of the permafrost zone causes such subsurface seeps to have elevated solute contents compared to glacial meltwater and hyporheic zone water (Harris et al., 2007).

METHODOLOGY

Since the establishment of the MCM-LTER in 1993, more than 20 Taylor Valley streams and their tributaries have been gaged for flow, with their compositions and ecological properties monitored over the course of each austral summer. Stream discharge, temperature, and specific conductance are recorded at 15 min intervals. Some streams have been sampled for chemistry on a regular basis several times each year with others only opportunistically sampled on an intermittent basis.

For this study, samples for anion, cation, and H_4SiO_4 analyses were collected and filtered using 47 mm, 0.4 µm polycarbonate membrane filters into high-density polyethylene bottles. Samples from the routine stream sampling were filtered within hours of collection, whereas those from the diurnal sampling were filtered at the time of sampling. Cation samples were filtered into bottles that had been soaked with 1% or 10% HCl solution and then rinsed five times with ultrapure water. Bottles for anion and H_4SiO_4 samples were rinsed five times with ultrapure water before use.

Typically, samples for chemical analyses were transported to the Crary Laboratory at the McMurdo Station within a month of collection, and major element composition was determined by ion chromatography using a Dionex DX-120 dual-channel instrument following the procedure described in Welch et al. (2010). Cation measurement precision is 5.1% for Na, 2.0% for K, 2.6% for Mg, and 6.9% for Ca whereas anion precision is 1.5% for Cl and 2.8% for SO_4 by relative standard deviation determination. Estimates of error are obtained by analysis of USGS Standard Reference Samples from an ongoing "round-robin" interlaboratory comparison study. The average percent difference of the measured concentrations compared to the most probable value (MPV) is Ca <6%, Mg <5%, Cl and SO_4 ~4%, Na and silica ~2%, and K ~1%. Total alkalinity is assumed to be carbonate alkalinity present as bicarbonate (HCO_3^-), given the pH range typical of Taylor Valley streams examined in this study, and then estimated from the measured cation-anion difference by subtracting the total anion equivalents from cation equivalents following Lyons et al. (2005). Previous work suggests that bicarbonate determined in this manner has an average difference of ± 5% compared to alkalinity determined by titration (Welch et al., 2010). Analysis of reactive dissolved silica was measured on the anion aliquot later at Ohio State University using a colorimetric method based on Mullin and Riley (1955). Most of these analyses over the period of LTER monitoring have been done manually; however, in recent years, this has been done using an automated method with a Skalar SAN ++ CFA or Lachat FIA analyzer. Precision of replicate Si measurements is 0.2%–4.6%. Because it is not usually ionized at the near-neutral pH values of Taylor Valley streams, dissolved Si is expressed here as H_4SiO_4, which typically comprises <10% of the total anion [alkalinity + (Cl^- +SO_4^{2-}) + silica] budget.

For the diurnal studies, temperature (°C), electrical conductivity (µS/cm), dissolved oxygen (DO in mg/L), and pH were measured in situ using a Yellow Springs Instrument multi-parameter probe calibrated according to the manufacturer's instructions. The probe was immersed in water at each site and measurements were recorded after readings stabilized, while water samples for later laboratory analysis were collected downstream of the probe as described by Lyons et al. (2013). Temperature and electrical conductivity values at Von Guerard and Andersen Creek gage stations are very strongly correlated in samples for which chemical composition was determined and with values measured by the multiprobe instrument (r^2 >0.98), so the 15 min gage records were used in the discussion that follows.

For the summer of 2010–2011, observed flow at Andersen Creek commenced on 7 December 2010 and continued until 26 January 2011, whereas that for Von Guerard began on 8 December 2010 and continued until 8 February 2011. Both streams were sampled routinely over the 7-week flow season, ~6:00 p.m. at Andersen Creek and ~9:30 p.m. for Von Guerard, both to place the compositions of these streams in an interannual context and provide a seasonal context for the two diurnal studies. Diurnal variations were examined at two different temporal scales, hourly at Von Guerard on 8–9 December and at Andersen Creek on 10–11 December and then 4-hourly for both streams from 31 December to 3 January at Von Guerard and from 3 to 7 January at Andersen Creek. Both streams were sampled synoptically at four to five upstream-downstream locations twice during the flow season, first in December and then again in January. The hyporheic zones around both streams were sampled weekly over the flow season using piezometers constructed from 6 mm, teflon-tipped polytetrafluoroethylene tubing with perforations on the tip to act as a screen. The depth/extent of the hyporheic zone was not measured, but following Gooseff et al. (2003) and Cozzetto et al. (2013) it was assumed to extend in the stream channel to the top of the active layer at a depth ≥40 cm so that piezometers were placed to 20 cm depth within the stream channel and also perpendicular to the channel at near stream (<1 m) and distal stream (>1 m) locations (Leslie et al., 2017). Hyporheic sampling occurred in conjunction with streamflow collection and was prioritized to locations of saturated sediment to ensure sample collection.

Seasonal monitoring data for gaged McMurdo Dry Valley region streams and stream chemical analyses are publicly available at the MCM-LTER website: www.mcmlter.org/streams-data. The compositional data from our study of the Andersen Creek and Von Guerard streams over the course of the 2010–2011 summer flow season are provided in the supplementary material[1] accompanying this article.

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[1] Supplemental Material. Compositional data for Von Guerard and Andersen Creek streams over the 2010–2011 flow season. Please visit https://doi.org/10.1130/GSAB.S.12344183 to access the supplemental material, and contact editing@geosociety.org with any questions.

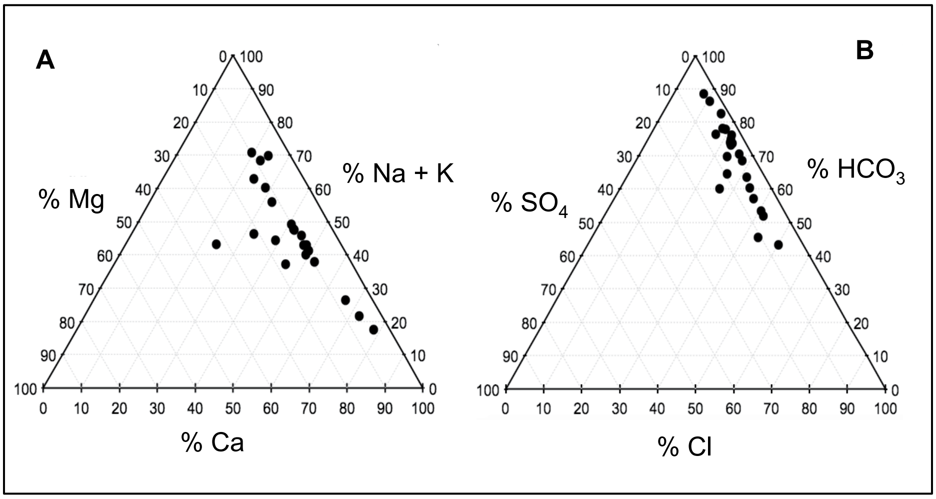

Figure 2. Ternary plots of sodium-calcium-magnesium (A) and bicarbonate-chloride-sulfate (B) for the seasonally ephemeral streams of Taylor Valley.

OVERVIEW

Table 1 summarizes the average chemical composition of the 24 Taylor Valley streams included in this study over the period of LTER monitoring from 1993 to 2014. As illustrated in Figure 2, four dissolved species dominate stream solute budgets—HCO_3^-, Cl^-, Ca^{2+}, and Na^+, with Mg^{2+}, SO_4^{2-}, and K^+ present in significantly lesser proportions. All streams contain dissolved silica at low concentrations. Overall, the geochemical fingerprint of streams in Taylor Valley is comparable to that of the other three valleys of the McMurdo Dry Valley region but at lower overall solute loading. Within Taylor Valley, streams are characterized by their consistent anionic geochemical fingerprint of $HCO_3 > Cl > SO_4$ but split between two cation compositional trends—those 14 streams with $Ca > Na > Mg > K$ and the other 10 streams having $Na > Ca > Mg > K$. Streams of both compositional types are present within the Lake Bonney and Lake Fryxell watersheds, whereas streams of the Lake Chad/Hoare basin are restricted to the $Ca > Na > Mg > K$ type.

Taylor Valley stream hydrochemistry can be understood in terms of hydrologic connectivity, i.e., the concept that movement of water is the mechanism by which mass and energy transfer takes place between and among discrete units of a landscape (Stieglitz et al., 2003). Lyons et al. (1998) first described the source-to-sink processes that move glacial meltwater across the polar desert landscape of the McMurdo Dry Valley region to its closed basin central valley lakes and discussed the multiple processes that contribute to spatial differences in stream chemistry. Gooseff et al. (2002, 2003) then recognized hyporheic zones as the principal domain of chemical weathering in the dry valley environment and characterized the hyporheic zone exchange that modulates stream hydrochemical character and regulates biogeochemical processes, and McKnight et al. (2004) described the nutrient element dynamics and uptakes in streams containing benthic algal communities.

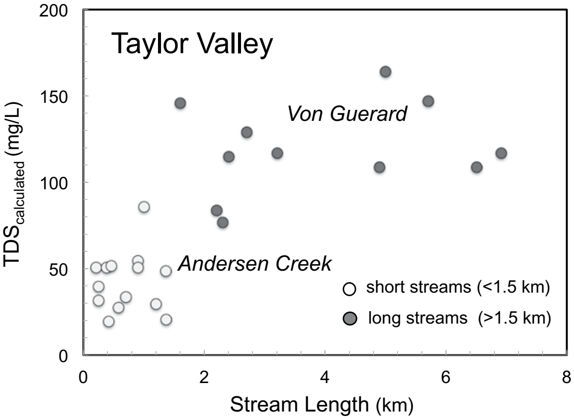

Figure 3. Plot of calculated total dissolved solids versus stream length of 24 seasonally ephemeral streams of Taylor Valley, Antarctica, with the Andersen Creek and Von Guerard streams identified (data from Table 2). Streams with longer travel length from glacial source to stream gage are characterized by higher dissolved solute loads than streams having shorter source to gage distances.

Several studies (e.g., Conovitz et al., 1998; Lyons et al., 1998; McKnight et al., 2004; Wlostowski et al., 2016; Gooseff et al., 2017b) have recognized stream length as a framework for studying and comparing streams across Taylor Valley. Singley et al. (2017) noted that the discharge of Taylor Valley streams is highly variable on both long and short timescales, described discharge-concentration relationships for selected streams, and observed that different hyporheic zone turnover rates control concentration-discharge (C-Q) patterns at daily to inter-annual timescales. Therefore, we follow this framework in our investigation of compositional controls on stream chemistry at three temporal scales—inter-annual, annual, and diurnal—for two contrasting Taylor Valley stream types. This comparison between Von Guerard, a stream with a well-developed hyporheic zone that contains a substantial benthic algal mat community, and Andersen Creek, a simple first-order stream lacking this complexity, offers the opportunity to gain new insights into the different processes that influence stream chemistry within Taylor Valley.

STREAM DESCRIPTIONS

The seasonally ephemeral streams of Taylor Valley can be divided into two groups from a geomorphological and hydrological perspective—short streams and long streams. The former are simple low-order streams that flow <1.5 km from their glacial source directly to their outlet gage. Some of these flow through steep rocky channels, while others have a gentler gradient and flow through alluvium. By contrast, the latter comprise a set of complex stream networks that flow between 2 km and 7 km in established channels. The longest streams meander for some portion of their distance across the alluvial valley floor, have spatially extensive hyporheic zones in those reaches, and contain benthic algal mat communities. Typically, longer streams exhibit higher solute loads than shorter streams (Fig. 3) and exhibit a progressive downstream increase in solute concentration (Gooseff et al., 2002; Wlostowski et al., 2016). Andersen Creek and Von Guerard are two readily accessible streams of contrasting physical and biological character. Located adjacent to the Lake Hoare and F6 camps, respectively (Fig. 1B), these two streams have been monitored and analyzed each year since 1993. Andersen Creek is the longest of the group of 13 short streams (Table 1) that are concentrated along the northwestern side of the middle section of Taylor Valley, whereas Von Guerard belongs to the group of 11 long streams (Table 1), most of which are located in the east-southeastern section lower Taylor Valley.

Von Guerard

The Von Guerard Stream is located on the southeastern side of the Fryxell basin (Fig. 1B), where it drains the northeast face of the Von Guerard Glacier in the Kukri Hills and flows northwestward with an average slope of 0.078 m/m into the east side of Lake Fryxell (Conovitz et al., 1998). It forms a complex stream network that exhibits pronounced changes in physical and ecological character during its 4.9 km course. Streamflow begins in three small channels that coalesce into a 5–8 m deep channel of steep gradient cut through glacial till. It then changes in its middle reach after flowing across sandy section of gentle slope that contains several ponds to a long segment of moderate gradient stream that flows in a wide, 3–6-m-deep channel within a stabilized stone pavement before again flattening out into a largely sandy stream channel in its lower reaches. Throughout most of its course, flow is over a bed of unconsolidated, sand-sized alluvium that contains boulders and cobbles comprised largely of diorite, schist, gneiss, and sandstone (Bockheim 1997). The stream has a well-developed and laterally expansive hyporheic zone in its middle to downstream reaches. Chemical weathering and water exchange between stream and soil have been well documented, with solute concentrations higher in the hyporheic zone than in the stream (Gooseff et al., 2002, 2003; McKnight et al., 2004). The intermediate reaches of the stream support abundant benthic algal mats in portions of the streambed that are stabilized by stone pavement (Alger et al., 1997; McKnight et al., 1998). The maximum discharge measured for Von Guerard is just below 500 L/s, with a factor of 10 daily flow variation common (http://mcm.lternet.edu/content/von-guerard-stream-gage-measurements). Gooseff et al. (2002) recorded an increase of 12%–66% in electrical conductivity and major ion concentrations at Von Guerard for three upstream-to-downstream samplings undertaken during the 1990 and 1992 flow seasons. Von Guerard is amongst the warmest streams in Taylor Valley and has the greatest probability of reaching daily water temperature >8 °C (Wlostowski et al., 2016).

Andersen Creek

Andersen Creek is a first-order, low-gradient proglacial stream of simple source to outlet hydrologic character located on the northwestern side of the Lake Chad/Hoare basin (Fig. 1B). It drains the west side of the Canada Glacier of the Asgard Range and flows southeastwards for 1.4 km along the edge of the glacier at a slope of 0.087 m/m into Lake Hoare. The stream runs in a narrow and shallow channel that is fed continuously throughout almost its entire length by supraglacial streams and meltwater from the glacier walls. This channel has been cut into bedrock of metasediments and dolerite that is overlain by glacial drift and lacustrine deposits (Hendy et al., 1979; Hall et al., 2000), and the stream is devoid of algal material throughout its length (Alger et al., 1997). The stream moves away from the base of the glacier in its lower reaches and flows across a flat, sandy deltaic area before discharging into Lake Hoare. The hyporheic zone around Andersen Creek is of minimal extent where observed. At base flow, Andersen Creek is a gently flowing stream typically less than a centimeter deep, but its flow rate is highly variable because meltwater generation from the Canada Glacier is highly sensitive to small variations in temperature and solar radiation (Fountain et al., 1999), such that maximum flows in excess of 500 L/s, comparable to flow volumes at Von Guerard, have been recorded (http://mcm.lternet.edu/content/andersen-creek-stream-gage-measurements). Andersen Creek is one of the two coolest and least thermally variable streams in Taylor Valley, with a median temperature of just 0.5 °C (Wlostowski et al., 2016), and its chemistry is distinctly different from Von Guerard, displaying a mean calculated total dissolved solids (TDS_c) value less than half that for Von Guerard and diminished in solute load by a factor of 1.5–3× for all ionic constituents (Table 2).

Three features particularly important to Andersen Creek deserve comment. First, substantial deposition of eolian material occurs on the Taylor Valley landscape along the west sides of valley glaciers due to föhn winds (Deuerling et al., 2014) that travel from the East Antarctic Ice Sheet toward the Ross Sea. These winds continuously provide new, more reactive material to ice surfaces for mobilization by meltwater. Fortner et al. (2013) have attributed the difference in chemistry between Andersen Creek and its counterpart Canada Stream on the east side of Canada Glacier to the föhn wind loading of salt and crustally derived debris to the supraglacial streams on the west side of the Canada Glacier ablation zone that feed Andersen Creek. Also, Canada Glacier contains many cryoconite melt holes. These are water-filled cylindrical melt features within the surface ice of the ablation zone (Fountain et al., 2004) that contain diverse biotic communities dominated by algae, cyanobacteria, heterotrophic bacteria, protozoa, rotifers, and tardigrades (Porazinska et al., 2004). Cryoconite holes can extend to depth within the glacier, and their biotic communities are thought to directly influence the chemistry of meltwater input to Andersen Creek through the interconnectedness of the glacier's internal hydrologic network (Fortner et al., 2005; Fountain et al., 2008). Finally, a water track located to the west of the Lake Hoare camp noted by Harris et al. (2007) has the potential to interact with Andersen Creek during warm intervals of enhanced melting. Such melting, particularly of the ice-cemented permafrost, will produce water that becomes saline as it dissolves soluble salts accumulated at the permafrost boundary that then are drawn into the active layer through capillary action (Ball et al., 2011). Gooseff et al. (2013) have observed that the moisture content of such subsurface seeps in the Lake Chad/Hoare basin can be up to an order of magnitude higher than that of the adjacent soil and 5–10× more solute-enriched than surface streams.

The Hyporheic Zone

As the primary landscape element across the McMurdo Dry Valley region for interaction between streams and soil, hyporheic zones are water storage areas characterized by flow paths and energy and material exchange processes that operate at multiple spatial and temporal scales (Runkel et al., 1998; Gooseff et al., 2003; Cozzetto et al., 2013). These domains are particularly important hydrochemical elements of Taylor Valley streams because they: (1) exchange water continually as flow travels daily from glacial sources to central valley lakes, (2) are the principal loci of chemical weathering as dilute glacial meltwater percolates through the interstitial space of the wetted alluvial sediment, (3) function across multiple spatial and temporal time scales, and (4) the amount of water contained in well-developed hyporheic zones can be several times greater than annual stream discharge (Nezat et al., 2001; Maurice et al., 2002; Gooseff et al., 2002, 2003; Leslie et al., 2017). As the summer thaw commences and streamflow begins, water moves downward and outward into the highly permeable alluvial soil under and adjacent to stream channels. This creates a wetted area within the shallow active layer that becomes fully saturated at a depth of a few centimeters, with this domain continually expanding downward and laterally as the melt season progresses and flow volumes increase (Conovitz et al., 2006). Across the McMurdo Dry Valley region, stream hyporheic zones are readily recognized as the wetted fringe along stream margins that define the boundary between dry and wet alluvium (Gooseff et al., 2002). Glacial meltwater in a stream continuously interacts with its hyporheic zone to an extent determined by physiographic setting. Conovitz et al. (1998) and Koch et al. (2011) recognized that long streams are more influenced by hyporheic zone storage and exchange than their short counterparts and that a larger proportion of glacial meltwater delivered to small streams directly reaches their outlet lakes without hyporheic zone storage than for long streams.

Hyporheic zones for Taylor Valley streams can range in spatial extent from thin, wetted fringes around smaller streams, as at Andersen Creek (e.g., Fig. 4A), to extensive domains of water storage present along the low-gradient reaches of larger streams that can extend down to the base of the active layer and many meters away from the channel in sections of longer streams, as at Von Guerard (e.g., Fig. 4B). Such expansive hyporheic zones provide the opportunity for large volumes of streamflow to interact with sediment and drive chemical weathering. The dynamic character of hyporheic zones also promotes water-mineral interaction, by expansion and contraction both on a diurnal basis in response to the daily pulse of glacial meltwater as well as over the course of the summer flow season. Additionally, the daily freeze-thaw cycle results in both the precipitation and then dissolution of soluble salts plus the fracturing of mineral grain boundaries to create fresh surfaces that continually increase hyporheic zone chemical reactivity for dissolution, sorption, and ion exchange. For larger streams traversing long sections of alluvial valley fill, a quick-flow, near-stream hyporheic zone is connected to a slow flow lateral hyporheic zone and then to an extended fringe that represents the distal reaches of the wetted zone away from the stream. Flow within a stream's hyporheic zone (denoted by the small arrows with dashed lines in Fig. 4) occurs at multiple spatial and temporal scales (Gooseff et al., 2003). Such flow complexity is a consequence of differences in transmissivity created by the texturally heterogeneous character of the host alluvial soil and can be continuous and rapid, with preferential flow paths of different length established in some parts, but be retarded or discontinuous in others (Cozzetto et al., 2013).

TEMPORAL CONSIDERATIONS

The Inter-annual Perspective

Taylor Valley stream compositions have been analyzed over the two decades of MCM-LTER monitoring. Between 100 and 150 chemical analyses have been obtained for each of the more accessible streams of most consistent flow (e.g., Commonwealth, Lost Seal, Von Guerard, Canada, Andersen Creek, House, and Lawson), whereas 30 or fewer analyses are available for the more inaccessible and, therefore, less frequently visited streams (e.g., Andrews, Vincent, Mason, and Bartlette). Analysis of stream hydrologic data has documented that flow regimes are

TABLE 2. COMPARISON OF TAYLOR VALLEY STREAM CHEMISTRY AND COMPOSITIONAL VARIABILITY

	Short streams											Long streams										
Stream	Length (km)	No. analyses	TDS$_c$ (mg/L)	Cl$^-$ (µM)	SO$_4^{2-}$ (µM)	HCO$_3^-$ (µeq)	H$_4$SiO$_4$ (µM)	Na$^+$ (µM)	K$^+$ (µM)	Ca^{2+} (µM)	Mg^{2+} (µM)	Stream	Length (km)	No. analyses	TDS$_c$ (mg/L)	Cl$^-$ (µM)	SO$_4^{2-}$ (µM)	HCO$_3^-$ (µeq)	H$_4$SiO$_4$ (µM)	Na$^+$ (µM)	K$^+$ (µM)	Ca^{2+} (µM)	Mg^{2+} (µM)
(A) Taylor Valley Stream Chemistry 1993–2014—Average Values																							
Wharton	0.21	72	51	68	21	555	10	62	14	253	21												
Mariah	0.25	51	32	127	14	452	14	192	21	74	18	Bartlette	2.0	21	51	231	38	408	55	148	35	102	139
McKay	0.25	78	40	38	18	431	4	37	8	202	11	McKnight	2.2	69	84	280	34	751	45	525	51	193	72
Andrews	0.38	12	20	59	9	191	13	70	13	69	17	Lost Seal	2.3	119	77	428	63	530	40	368	41	236	86
Bowles	0.42	72	51	96	12	513	62	111	40	209	38	Huey	2.4	67	115	364	130	899	51	388	74	455	92
House	0.46	156	52	108	41	484	6	83	16	250	27	Bohner	2.7	35	129	896	118	771	60	500	74	402	266
Lawson	0.58	126	28	162	40	169	22	159	19	68	37	Priscu	3.2	90	117	567	97	885	41	396	64	403	173
Commonwealth	0.7	108	34	187	28	247	15	182	18	94	38	***Von Guerard***	***4.9***	***112***	***109***	***246***	***51***	***1065***	***78***	***313***	***59***	***415***	***80***
Vincent	0.9	18	55	158	29	509	76	120	32	185	72	Harnish	5.0	69	164	448	80	1500	144	568	101	598	143
Mason	1.0	15	86	210	71	751	102	201	62	340	93	Crescent	5.7	79	147	401	62	1374	124	428	75	596	116
Green	1.2	135	30	73	12	301	22	85	19	114	24	Delta	6.5	91	109	563	84	1129	70	416	61	583	130
Andersen Creek	***1.4***	***112***	***49***	***149***	***77***	***340***	***17***	***133***	***27***	***191***	***37***	Aiken	6.9	99	116	420	54	1027	39	755	76	230	115
Canada	1.4	139	21	65	19	193	22	60	14	65	16												
Mean			**42**	**115**	**30**	**395**	**30**	**115**	**23**	**162**	**35**	**Mean**			**111**	**440**	**74**	**940**	**68**	**437**	**65**	**383**	**128**
(B) Taylor Valley Stream Chemistry 1993–2014—Coefficients of Variation																							
Wharton	0.21	72		125	71	53	152	145	73	47	96												
Mariah	0.25	51		162	107	153	128	155	88	71	76	Bartlette	2.0	21		108	39	62	27	45	33	48	38
McKay	0.25	78		56	38	36	47	94	41	30	40	McKnight	2.2	69		58	44	40	35	45	33	43	50
Andrews	0.38	12		52	48	45	36	42	52	47	44	Lost Seal	2.3	119		149	117	49	43	67	47	103	110
Bowles	0.42	72		76	68	41	31	59	39	39	49	Huey	2.4	67		67	58	31	34	44	31	35	42
House	0.46	156		130	118	26	55	106	50	49	102	Bohner	2.7	35		48	43	37	15	30	23	35	37
Lawson	0.58	126		78	69	45	63	53	255	62	62	Priscu	3.2	90		96	77	25	33	96	40	36	71
Commonwealth	0.7	108		125	105	47	57	68	45	73	96	***Von Guerard***	***4.9***	***112***		***59***	***69***	***29***	***25***	***63***	***29***	***30***	***36***
Vincent	0.9	18		94	29	61	22	39	30	22	68	Harnish	5.0	69		45	51	18	22	28	17	15	22
Mason	1.0	15		43	31	17	46	11	49	20	18	Crescent	5.7	79		48	39	15	14	38	20	15	28
Green	1.2	135		76	55	35	42	53	86	45	51	Delta	6.5	91		59	42	21	24	36	27	35	38
Andersen Creek	***1.4***	***112***		***88***	***107***	***70***	***98***	***76***	***72***	***83***	***86***	Aiken	6.9	99		50	53	34	34	37	29	35	37
Canada	1.4	139		56	30	109	36	44	25	27	33												
Mean				**89**	**67**	**57**	**63**	**73**	**70**	**47**	**63**	**Mean**				**72**	**57**	**33**	**28**	**48**	**30**	**39**	**46**

Note: TDS$_c$—calculated total dissolved solids.

highly flashy, characterized by short and intense peak flow events, and that streamflow is highly variable on inter-annual, seasonal, and daily time scales (Singley et al., 2017). A variety of geochemical studies within Taylor Valley beginning in 1998 have noted spatial trends and linkages in the chemical character of surface waters and discussed influences on dissolved solutes that include landscape position, stream channel morphology, biological processes, and extent of water-sediment interaction as streams move from their glacial source to a central valley lake (e.g., Lyons et al., 1998, 2003; Nezat et al., 2001; Maurice et al., 2002; Gooseff et al., 2002, 2003, 2004; Welch et al., 2010; Stumpf et al., 2012).

Mean solute concentration values and their coefficients of variation based on the nearly 2000 chemical analyses acquired from 1993 to 2014 by the MCM-LTER monitoring program are presented in Table 2 for the 11 long and 13 short Taylor Valley streams examined in this study. Ranges of concentration variation for Cl^-, SO_4^{2-}, HCO_3^-, H_4SiO_4, Na^+, K^+, Mg^{2+}, and Ca^{2+} are displayed in Figure 5. Subsets of these data were evaluated by Lyons et al. (1998) and Welch et al. (2010), who concluded that: (1) streams within Taylor Valley exhibit an extremely wide range of chemical composition; (2) multiple factors related to local geology and landscape position influence stream chemistry; (3) evapoconcentration and/or dissolution of soluble salts is a significant geochemical process, with species derived from marine aerosol transport elevated in streams closer to the coast; and (4) the weathering of silicate minerals occurs within stream channels and floodplains throughout Taylor Valley and across the McMurdo Dry Valley region.

Solute loads of individual Taylor Valley streams are low, with long-term mean TDS_c values ranging from only 20–164 mg/L, averaging 42 mg/L for short streams and 111 mg/L for long streams (Tables 1 and 2, Fig. 5). Alkalinity is the principal anionic component of all stream waters, with bicarbonate (HCO_3^-) the predominant species of alkalinity over the near-neutral pH range of these streams. Ca^{2+} and Na^+ are the main cationic species, with contents of Ca generally elevated over Na in short streams ($Ca_{mean} = 162\ \mu M$ versus $Na_{mean} = 115\ \mu M$), but with the reverse observed for long streams ($Na_{mean} = 437\ \mu M$ versus $Ca_{mean} = 383\ \mu M$). Concentrations of other aqueous constituents are uniformly low, with $SO_4^{2-} < 135\ \mu M$, $Mg^{2+} < 270\ \mu M$, and $K^+ < 105\ \mu M$. Dissolved Si is present in all streams at low levels, with H_4SiO_4 concentrations highest in the long streams in the southeastern sector of Taylor Valley that drain from the Kukri Hills into Lake Fryxell (Fig. 1B) and which have significant flow distances over the alluvial valley floor.

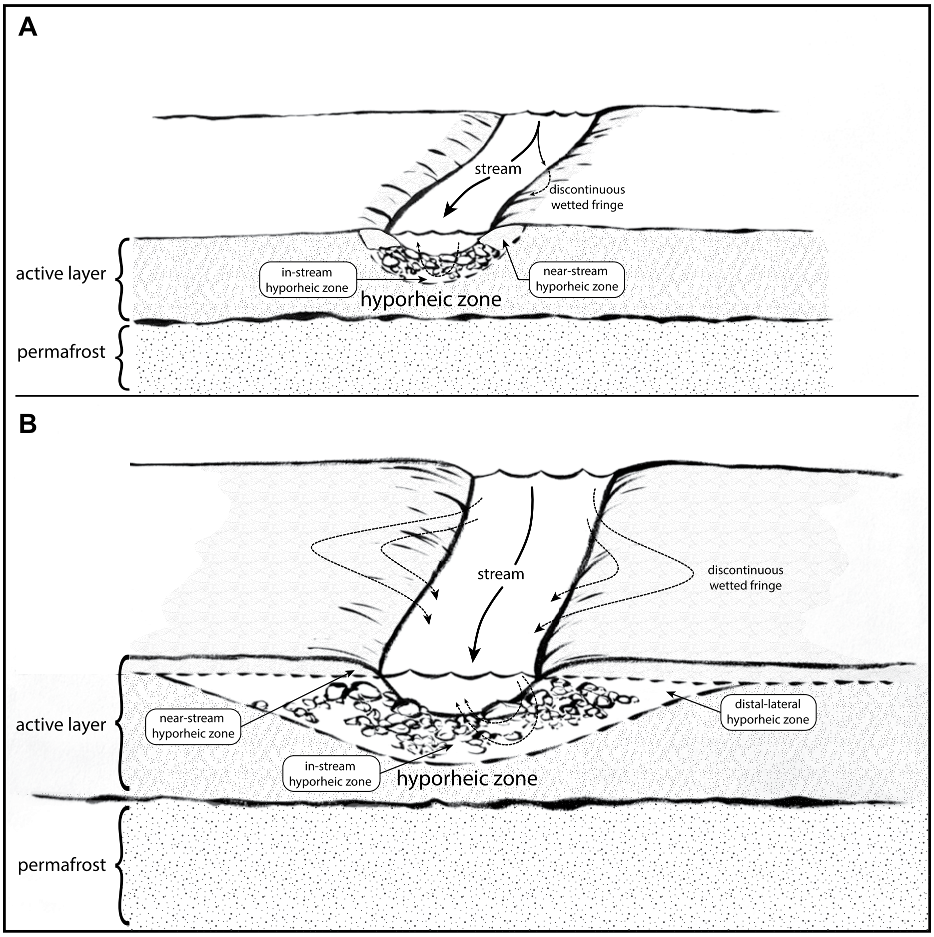

Figure 4. Schematic illustration of the idealized hyporheic zones for seasonally ephemeral (A) short streams and (B) long streams in Taylor Valley. Hyporheic zones develop around each stream channel when flow commences. As the melt season progresses and flow volumes increase, stream water progressively moves downward and outward into the locally heterogeneous alluvial soil column, creating a hyporheic zone around the stream channel, the spatial extent of which varies throughout the summer melt season. Water also gets wicked away from the edge of the hyporheic zone due to capillary suction, creating a wetted fringe of interstitial pore water. Hyporheic zones can range in spatial extent from thin wetted borders around smaller streams, as in the case of Andersen Creek, to extensive domains of water storage that can extend down to the base of the active layer and many meters away from the channel in sections of longer streams as they flow across the more gently sloped alluvial plains of the central valley, as in the case of Von Guerard. The surface water in streams continuously interacts with its hyporheic zone to an extent determined by its physiographic setting. The two examples shown in the figure are idealized end-member situations, and the specific form, structure, and operation of the hyporheic zone around any stream will depend on the interplay of a variety of factors that include landscape position, local physiography and soil texture, time during the glacial melt season, and recent weather.

The four meltwater streams in the western Chad/Hoare basin that flow short distances over rocky beds from their glacial source to outlet lake are the most dilute streams in Taylor Valley (Table 2), having an average TDS_c value of only 48 mg/L. By comparison, streams draining into Lake Fryxell and Lake Bonney carry significantly higher dissolved solid loads and have similar mean TDS_c values of 83 mg/L and 78 mg/L, respectively. Within the Fryxell basin, short streams with rocky beds that drain the Commonwealth and Canada Glaciers of the Asgard Range (Mariah, Andrews, Green, and Canada) also have low mean TDS_c values of <50 mg/L. This contrasts with the higher TDS_c values in excess of 100 mg/L that characterize the longer, higher-order streams on the southeast side of Taylor Valley that drain the glaciers of the

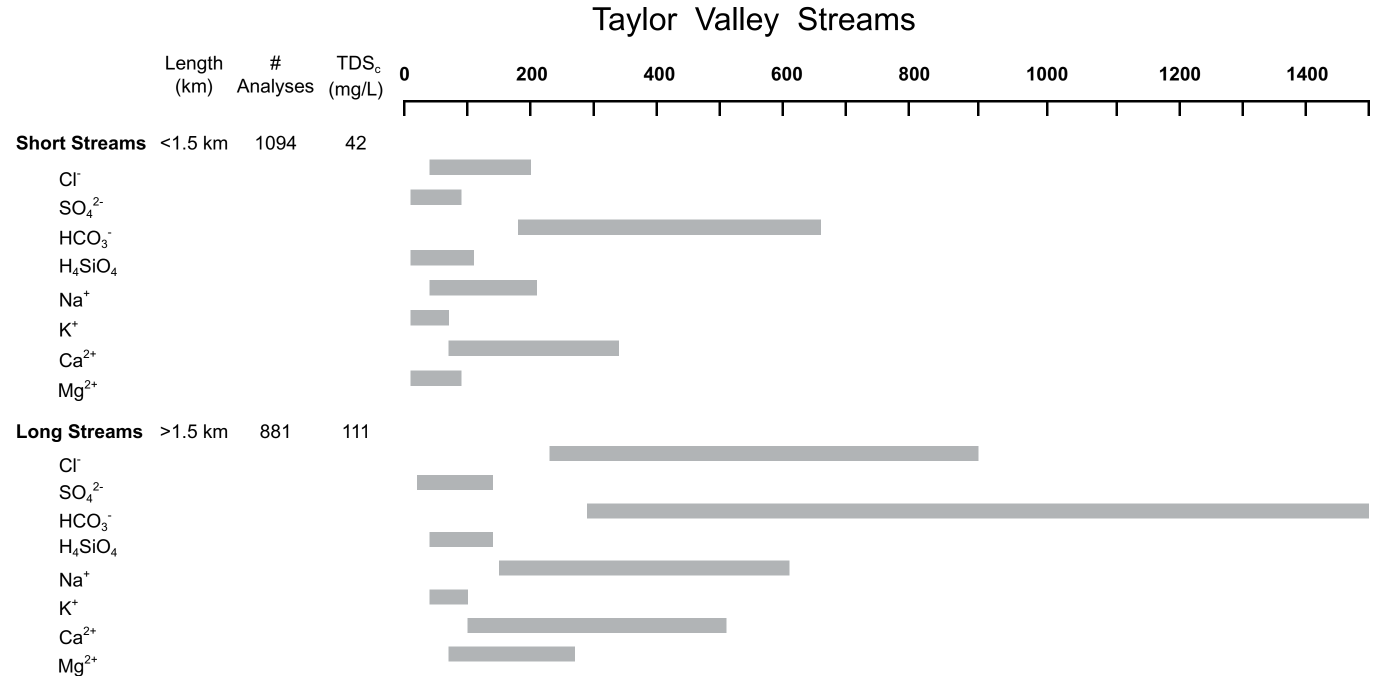

Figure 5. Concentration ranges (µM) for short and long streams in Taylor Valley, Antarctica, over the period of Long-Term Ecological Research monitoring from 1993 to 2014.

Kukri Hills, (e.g., Aiken, Von Guerard, Harnish, Crescent, and Delta) and discharge into Lake Fryxell. These streams contain cyanobacterial mats in some reaches, and a substantial portion of their flow is over low-gradient terrain of unconsolidated alluvium where hyporheic zone development is extensive. Long streams with well-developed hyporheic zones display larger mean dissolved solute loads and exhibit larger ranges of dissolved species concentration but less compositional variability than their shorter counterparts with hyporheic zones of minimal extent.

Although one of the two lengthiest of the short stream class, Andersen Creek is compositionally representative of these 13 streams. Its mean TDS_c value of 49 mg/L falls near the center of the 20–86 mg/L range for this class of streams and is otherwise compositionally reflective of this group (Table 2, Fig. 3). Similarly, Von Guerard, which has a mean TDS_c value of 109 mg/L, more than twice that of Andersen Creek, is representative of the 12 long streams in Taylor Valley (Table 2, Fig. 3).

Stream chemistry across Taylor Valley is diverse and complex, variable both spatially and temporally (Green et al., 1988; Lyons et al., 1998; Welch et al., 2010). By controlling streamflow volumes, seasonal and daily weather patterns also act to modulate McMurdo Dry Valley region stream chemistry on seasonal and diurnal time scales.

Atmospheric transport of aerosols derived from the Ross Sea delivers Cl, SO_4, and Na of marine origin to surface soils across the McMurdo Dry Valley region (Witherow et al., 2006), with more than 30 different soluble salts recognized in dry valley soils (Campbell et al., 1998). There is a strong spatial gradient to this transport inward from the coast (Witherow et al., 2006) that results in glacial ice and meltwater differing in chemical composition across Taylor Valley (Lyons et al., 2003; Fortner et al., 2005). Sulfate salts with isotopic compositions related to seawater sulfate are distributed across the region, whereas the contents of sea salt-derived Cl and Na diminish progressively away from the coast. Calcium is present across the region in pedogenic carbonates (Claridge and Campbell, 1977; Foley et al., 2006), and calcium salts are a constituent in soils associated with all rock types of the region, in contrast with salts of magnesium, which are restricted to soils derived from the weathering of mafic igneous rocks (Keys and Williams, 1981; Campbell et al., 1998). Local winds also deliver terrestrial dust from the valley floors onto surrounding glaciers, recycling some of the salt originally deposited there (Lyons et al., 1998).

Once generated, meltwater streams gain additional solutes from four primary sources during flow and hyporheic zone residence: (1) salts and aerosols of marine origin, (2) soluble salts introduced into the alluvial soils through cryoconcentration and evaporation, (3) secondary carbonates, and (4) silicate minerals. Typically, the most-to-least soluble weathering sequence for minerals is soluble salts of chloride and nitrate, gypsum and other hydrated sulfates, carbonate minerals, mafic to felsic silicate minerals, and quartz (Stallard, 1995). Thus, soluble salts will readily dissolve in wetted soil to elevate concentrations of chloride, sulfate, and sodium as documented by Lyons et al. (2005), Harris et al. (2007), and Levy et al. (2014) in soil seeps and water tracks across Taylor Valley. Initially, as the melt season commences, residual solutes that were excluded from freezing pore water at the end of the previous summer, plus atmospheric salts that accumulated over the winter, are dissolved as soils become wetted and then are flushed by early season meltwater. Streamflow becomes progressively more dilute as the summer melt season progresses, with the timing and magnitude of stream solute loading on daily time scales reflecting both initial meltwater compositions and the extent of streamflow through and water interaction with the glacial, alluvial, and lacustrine deposits on the valley floor.

Lithology is an essential determinant of river chemistry, particularly at the local scale (Drever, 1988) and for low-order streams (Meybeck and Helmer, 1989). X-ray diffraction analysis by Gooseff et al. (2002) documented that the silicate minerals plagioclase, quartz, and muscovite, along with the clay mineral weathering products kaolinite, illite, and smectite, dominate the mineral assemblage of fine-grained alluvium in the hyporheic zone soil at Huey Creek. Maurice et al. (2002) observed direct evidence for silicate mineral weathering via the surficial dissolution of mica within the hyporheic zone of Green Creek. In a site-specific chemical budget study for Von Guerard, Gooseff et al. (2002) measured the downstream enrichment of solutes and estimated that marine aerosol deposition provided 100% of dissolved Cl, 42%–50% of SO_4, 45%–59% of Na, and 0%–2% of K. Transient storage zone modeling highlighted the importance of carbonate and silicate mineral dissolution to stream solute chemistry. Carbonate dissolution was observed to generate >99% of Ca, whereas 50%–58% of SO_4 and 7% of Na was provided from the dissolution of highly soluble sodium sulfate salts. Weathering of primary silicate minerals was the sole source of Si and the predominant contributor of K, with 33%–47% of residual Na remaining after accounting for the marine aerosol and soluble sulfate sources attributed to release during the weathering of sodium silicate minerals.

Maximum H_4SiO_4 values across Taylor Valley vary between 11 µM and 159 µM for short streams compared to between 73 µM to 201 µM for long streams, alkalinity exceeds chloride content in all streams, and mean bicarbonate values are substantially higher than contents of chloride and sulfate (Table 2). These observations support results from the previous studies cited above that weathering of carbonate and silicate minerals are the dominant processes controlling Taylor Valley stream compositions. The solute budget of waters in contact with carbonate minerals will be dominated by Ca and characterized by high Ca/Mg ratios and high Ca/Si and Mg/Si ratios, whereas waters dissolving silicate minerals should have low molar HCO_3^-/Na, Ca/Na, and Mg/Na ratios (Meybeck, 1986; Gaillardet et al., 1999). Calcite coatings are common on the undersides of rocks and across the lower Taylor Valley (Claridge and Campbell, 1977; Green et al., 1988), and secondary accumulations of carbonate also present as crusts and coatings within the glacial tills, lacustrine deposits, and soils of Taylor Valley, with contents of such carbonate decreasing inland from the coast (Lawrence and Hendy, 1989; Foley et al., 2006). Their dissolution is a source of Ca^{2+} to stream water according to the reaction:

$$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-.$$

Another source of both Na^+ and Ca^{2+} is the weathering and hydrolysis of aluminosilicate minerals within the active layer and at the bedrock–soil cover interface as illustrated by the reactions for chemical weathering of Ca- and Na-feldspar within granitic rocks and sediment:

$$CaAl_2Si_2O_8 + H_2CO_3 + H_2O \\ \rightarrow Al_2Si_2O_5\left(OH\right)_4 + Ca^{2+} + CO_3^{2-}$$

and

$$2NaAlSi_3O_8 + H_2CO_3 + 9H_2O \rightarrow Al_2Si_2O_5(OH) \\ + 4H_4SiO_{4(aq)} + 2Na^+ + 2HCO_3^-$$

and the dissolution of pyroxene in mafic dolerite:

$$\left(Ca_{0.2}Mg_{0.9}, Fe_{0.9}\right)Si_2O_6 + 2.2CO_2 + 5.1H_2O \\ + 0.225O_2 \rightarrow 0.2Ca^{2+} + 0.9Mg^{2+} \\ + 0.45Fe_2O_3 + 2.2HCO_3 + 2H_4SiO_{4(aq)},$$

with Ca^{2+} and some of the HCO_3^- generated having the potential to combine to form $CaCO_3$ (Green et al., 1988; Nezat et al., 2001).

Following Millot et al. (2002) and Dessert et al. (2003), who used cross-plots of river elemental ratios to study the effects of dilution and evaporation, the molar ratio of HCO_3/Na versus Ca/Na for Taylor Valley streams is plotted in Figure 6. The linear array defined by stream long-term average values suggests that two sources of contrasting Ca character dominate the compositional character of Taylor Valley streams. Clustering of most data points within and nearby the field for crystalline rocks, including Andersen Creek and Von Guerard, is a clear indication that silicate mineral dissolution is a significant determinant of stream chemical composition, more so for longer streams than some short streams. The trend of these short stream compositions toward the carbonate field reflects the greater proportional contribution of carbonate dissolution to their composition than for long streams. Displacement of the stream data array slightly below the silicate-carbonate mixing trend in Figure 6 to lower HCO_3/Na ratios implies a minor soluble salt contribution to the chemical budget of both stream types. Also, it was shown in Figure 3 that short streams tend to cluster in a group in the lower left corner of the TDS versus stream length plot and that there is an initial increase of TDS with length that subsequently reaches an ill-defined TDS plateau at around 3 km in length. Together, the compositional relationships shown in Figures 3 and 6 provide insight into the process controls on Taylor Valley stream chemistry and support the idea that transient storage of stream water within the hyporheic zone of longer streams facilitates water-mineral interaction, ionic exchange, the dissolution of carbonate and silicate minerals, and determines the effective upper limit of stream solute loads.

Many but not all streams, particularly in reaches of the longer streams on more gently sloping terrain, contain perennial benthic mats of cyanobacteria that reactivate and grow slowly during periods of summer flow (Vincent and Howard-Williams, 1986; McKnight et al., 1998). Streamflow behavior and biological composition directly reflect channel slope and substrate character, with longer and gentler sloping streams having expansive hyporheic zones that can extend to the base of the active layer and several meters away from a stream margin. The variable extent of aquatic biomass and larger hyporheic zones in longer Taylor Valley streams is an additional control on stream chemistry and reflects a complex interplay between inorganic and organic processes. Long streams like Von Guerard are solute enriched and display less compositional variation than short streams like Andersen Creek (Table 2B). This is a direct manifestation of two complementary processes, the enhanced acidity acquired during passage through cyanobacterial mats during periods of photosynthesis and the prolonged water-mineral interaction, ionic exchange, and mineral dissolution that occurs at multiple spatial and temporal scales within their more extensive hyporheic zones. Hydrological

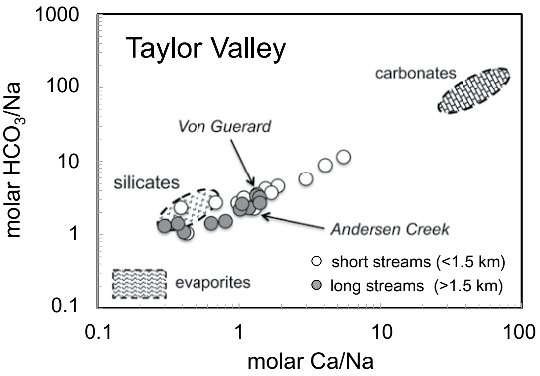

Figure 6. Plot of molar ratios of HCO_3/Na versus Ca/Na for Taylor Valley streams, with the Andersen Creek and Von Guerard streams identified. The global fields from Gaillardet et al. (1999) for rivers draining crystalline silicate rocks, carbonates, and evaporites (i.e., soluble salts in the case of the McMurdo Dry Valley region) are shown for reference.

observations by Wlostowski et al. (2016) and Singley et al. (2017) led to the interpretation that the hyporheic zones around Taylor Valley streams are storage zones that act as chemostatic buffers (Clow and Mast, 2010) to regulate their water chemistry. The compositional plateau in Figure 3 that characterizes long streams compared to their short counterparts supports this view and is consistent with the largely invariant solute concentration-discharge relationships observed by Wlostowski et al. (2018) for seven Taylor Valley streams.

Austral Summer of 2010–2011

For the austral summer of 2010–2011, measurable flow at both stream gages was first recorded on 8 December and continued until 26 January at Andersen Creek and 8 February at Von Guerard. Figure 7 displays stream hydrographs recorded at the Von Guerard and Andersen Creek gaging stations at quarter-hour intervals and their water temperature and electrical conductivity profiles. The hydrographs reflect daily ambient energy fluxes on source glaciers, which display the daily high flow pulse with interspersed episodes of very high flow and no flow intervals that are typical of McMurdo Dry Valley region streams. Across the season, daily flow at Von Guerard varied from 0 L/sec to 487 L/sec while that at Andersen Creek ranged from 0.3 L/sec to 290 L/sec, with the local high flow interval occurring at ~9:30 p.m. for the northwest-facing Von Guerard and some four hours earlier at ~5:30 p.m. for the southwest-facing Andersen Creek (Leslie et al., 2017). At high flow, both Von Guerard and Andersen Creek are dominated by low-solute glacial meltwater, whereas the different compositional influences discussed below can be recognized during low-flow intervals. Daily flow variation was highly variable but fell within the historic ranges of both streams, with a 10–100× maximum daily variation for Von Guerard compared to 5–20× maximum daily variation for Andersen Creek. Discharge from both streams was greatest early in the season, with high daily flows in excess of 200 L/sec occurring repeatedly until the end of December. Such flows were recorded on 19 days at Von Guerard compared with only nine times at Andersen Creek, with higher and more sustained peak flows characterizing the Von Guerard hydrograph (Figs. 7A–7B). A maximum peak flow of 487 L/sec was recorded for Von Guerard on 11 December, compared with a peak flow of only 290 L/sec a day earlier at Andersen Creek. The first diurnal sampling interval occurred within this period of highly variable flow on 9 December at Von Guerard and from 10 to 11 December at Andersen Creek. Discharge diminished at both streams from late December to mid-January, when the second diurnal sampling was undertaken between 31 December and 3 January at Von Guerard and from 3 to 7 January at Andersen Creek. Discharge rose again at both streams during the third week of January and then declined during the remainder of the summer flow season, concluding during the last week in January at Andersen Creek but extending to the end of the first week of February at Von Guerard.

Exposed to solar radiation throughout most of its length as the sun circles above the horizon, Von Guerard's daily high temperatures approached 13 °C. In contrast, temperatures reached only 6 °C at Andersen Creek (Figs. 7C–7D), which is shielded from sunlight for several hours each day because of its course along the western foot of the Canada Glacier. Maximum temperatures at Von Guerard were around 10 °C for most days until the third week of January, after which they declined to 5 °C or below for the remainder of the summer. In contrast, maximum temperatures of 4–6 °C were recorded at Andersen Creek for individual days throughout the summer, although daily high temperatures only exceeded 2.5 °C on 19 days. Although the timing of maximum stream temperature is generally coincident across Taylor Valley (Cozzetto et al., 2006), daily high temperatures occurred between noon to 2:00 p.m. at Andersen Creek but some three hours later between 3:00–5:00 p.m. at Von Guerard. At both streams, times of maximum temperature preceded the daily high flow interval by some 2–4 h. Minimum temperatures at Andersen Creek receded to near the freezing point each night but only approached this point at the Von Guerard stream during cool periods of minimal flow.

Electrical conductivity patterns of the two streams are distinctly different (Figs. 7E–7F), with Von Guerard exhibiting a higher overall dissolved solute load and substantially less day-to-day variation than Andersen Creek. At 106 ± 24 µS/cm with a coefficient of variation of 23%, the average electrical conductivity value for Von Guerard over the summer season was almost five times higher and much less variable than for Andersen Creek at 22 ± 13 µS/cm and a coefficient of variation of 56%. Of note are the different conductivity signal observed at the two streams as the summer flow season commenced and the set of conductivity spikes at Andersen Creek just prior to the midpoint of the flow season.

The low solute load at Andersen Creek during the first three days of seasonal flow (electrical conductivity [EC] = 3–13 µS/cm) falls within the limited range of 3–33 µS/cm recorded throughout the entire summer season, except for the 8-day interval between 31 December to 7 January when the stream was characterized by an interval of elevated and highly variable solute loads that fluctuated sharply up to 82 µS/cm (see discussion below). In contrast, initial flow at Von Guerard

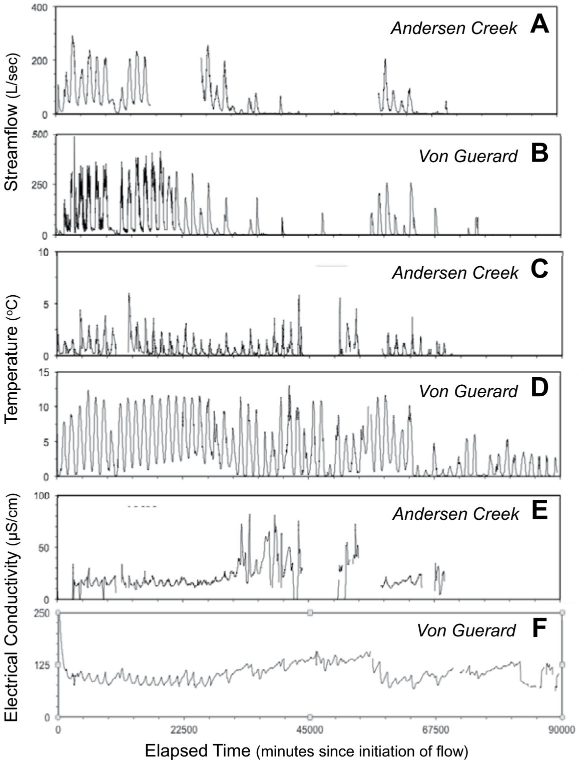

Figure 7. Discharge, water temperature, and specific conductance profiles for Anderson Creek (A, C, E) and Von Guerard (B, D, F) during the austral summer of 2010–2011 (note different ordinate axis scales).

consisted of strongly solute enriched water with an EC of 407 μS/cm that declined to 280 μS/cm during the first day and then reached normal levels around 120 μS/cm by the second day of flow. Thereafter, EC values fluctuated within the narrow range of 62–168 μS/cm, exhibiting an initial period of stable behavior with EC values fluctuating daily around a value of ~80 μS/cm. This was followed by two extended intervals of progressive rise from ~80–150 μS/cm, which then declined sharply back to around 80 μS/cm, the first occurring from 26 December to 15 January and the second from 18 January to 4 February just prior to the conclusion of the 2010–2011 flow season four days later.

Mean solute concentrations for Von Guerard and Andersen Creek over the 2010–2011 flow season are presented in Table 3, and daily solute fluctuations are displayed in Figure 8. The Andersen Creek record is complete for the 50 days of 2010–2011 summer flow season because of the permanently occupied station at this site, whereas there are episodic gaps in the Von Guerard record during intervals when the F6 camp was unoccupied. Contents of ionic species for both streams are distinct and fall within the envelope of long-term fluctuation at each stream (Table 3), with individual species concentration-time patterns coherent for each stream. Over the flow season, the mean solute content for Von Guerard is twice that of Andersen Creek, with Von Guerard characteristically elevated over Andersen Creek in all dissolved species except sulfate (Table 3, Fig. 7). Although anion differences are of variable magnitude: 3× for alkalinity, 1.5× for chloride, and 0.8× for sulfate, cation enrichments are essentially constant between 2.2× and 24×. Von Guerard is almost 5× enriched in H_4SiO_4 over Andersen Creek, which is comparable to the long-term average of 4.6× for these two streams. Notably, solute content variations for Von Guerard were significantly smaller than at Andersen Creek ($VG_{cv} = 16–50$ versus $AC_{cv} = 46–77$), a situation that has been maintained over the past quarter century of monitoring ($VG_{cv} = 21–54$ versus $AC_{cv} = 71–100$). The unusual interval of conductivity fluctuation observed at Andersen Creek between 31 December to 7 January (Fig. 7) is clearly illustrated in Figure 8. The synoptic chemistry of both streams was examined at four to five locations in an upstream to downstream sampling twice during the flow season, the first from 10:40 p.m. on 16 December 2010 to 0:04 a.m. on 17 December 2010 at Von Guerard and then from 1:15–3:00 p.m. on 18 December 2010 at Andersen Creek, with the second from 7:15–9:00 p.m. on 16 January 2011 at Andersen Creek and from 5:30–9:30 p.m. on 19 January 2011 at Von Guerard (Table 4). At both times, Von Guerard exhibited a progressive downstream increase in dissolved constituent concentrations, whereas the tendency at Andersen Creek was for a downstream decrease in solute content.

Both Von Guerard and Andersen Creek exhibit stream specific geochemical fingerprints for the 2010–2011 flow season: $HCO_3 > Ca > Na > Cl > H_4SiO_4 > Mg > K > SO_4$ for Von Guerard compared to $HCO_3 > Ca > Cl > Na > SO_4 > Mg > K > H_4SiO_4$ for Andersen Creek (Table 3, Fig. 8). These geochemical patterns also characterize the historical record of each stream (Table 1). The Von Guerard pattern was maintained during both diurnal sampling intervals, whereas the Andersen Creek pattern was only observed during the longer, 4-hourly diurnal monitoring as the hourly diurnal observation recorded a single large diluting flow pulse in which $HCO_3 > Cl > Na > Ca > SO_4 > Mg > K > H_4SiO_4$.

Statistical analysis of the seasonal data set highlights significant elemental behavior (Pearson correlation coefficients of <0.05):

(1) An inverse co-variation of ionic constituents with discharge (1/Q) was observed for both streams that is slightly weaker for each species at Von Guerard than at Andersen Creek. Together, these observations indicate that dilution by glacial meltwater during the daily high flow interval is the primary control on stream chemistry, with the influences of other processes most strongly manifest during baseflow intervals. This observation is consistent with the decrease in dissolved constituents at high flow measured by Fortner et al. (2013) during a 24 h diurnal sampling of Andersen Creek on 22–23 December 2007.

(2) The weakest co-variations are for Cl and SO_4 with alkalinity. Co-variation of Na is stronger for Cl and SO_4 than alkalinity, suggestive of the dissolution of soluble salts, whereas Ca in both streams co-varies strongly with alkalinity compared to Cl or SO_4. Concentrations of H_4SiO_4 co-vary positively with cation concentrations at Andersen Creek but much less so at Von Guerard.

(3) Although H_4SiO_4 enrichment at Von Guerard is almost 5× more than at Andersen Creek, it exhibits a less strong co-variation with flow in both streams than for cation constituents. Although contents varied considerably, H_4SiO_4 concentrations in each stream were higher during the latter part of the summer than earlier in the melt season.

Hyporheic zones develop each year as streamflow is initiated and sediments below and adjacent to stream channels become wetted (Fig. 4). As the interaction of streams with their hyporheic zones has been recognized as an important influence on stream composition (Runkel et al., 1998; Gooseff et al., 2002, 2003, 2004; Cozzetto et al., 2013; Wlostowski et al., 2016; Singley et al., 2017), the chemistry of hyporheic zone waters was examined for both streams. In-stream, near-stream, and distal hyporheic zone waters away from the stream channel were

TABLE 3. COMPARISON OF SOLUTE CONCENTRATIONS AND VARIATIONS FOR VON GUERARD AND ANDERSEN CREEK FOR THE 2010–2011 SUMMER FLOW SEASON WITH THEIR 1993–2014 LONG-TERM AVERAGES

	N	SPC (μS/cm)	Cl^- (μM)	SO_4^{2-} (μM)	HCO_3^- (μeq)	H_4SiO_4 (μM)	Na^+ (μM)	K^+ (μM)	Ca^{2+} (μM)	Mg^{2+} (mM)
Von Guerard										
VG 2010–2011 season	28	31–129	99–533	25–134	520–1248	65–112	146–570	29–88	259–671	42–170
avg		74	166	42	835	86	221	52	367	68
sd		22	82	20	223	14	87	12	108	26
cv		30	50	48	27	16	39	24	29	38
VG long term	112		98–764	21–266	566–2070	31–126	123–1600	27–112	161–712	30–168
avg			246	51	1065	78	313	59	415	80
sd			145	35	306	19	197	17	123	29
cv			59	69	29	25	63	29	30	36
Andersen Creek										
AC 2010–2011 season	48	14–86	46–289	21–144	91–748	5–61	49–212	10–59	49–412	9–72
avg		37	109	56	280	18	98	24	160	28
sd		24	66	32	198	14	45	13	122	19
cv		65	60	57	71	77	46	55	76	69
AC long term	111		23–860	12–433	62–880	2–98	18–544	3–118	53–956	3–190
avg			149	77	340	17	132	27	191	37
sd			131	82	237	17	100	19	158	32
cv			88	107	70	100	76	72	83	86

Notes: N—number of analyses; avg—mean value; sd—standard deviation; cv—coefficient of variation calculated as 100 [avg/sd]; VG—Von Guerard; AC—Andersen Creek.

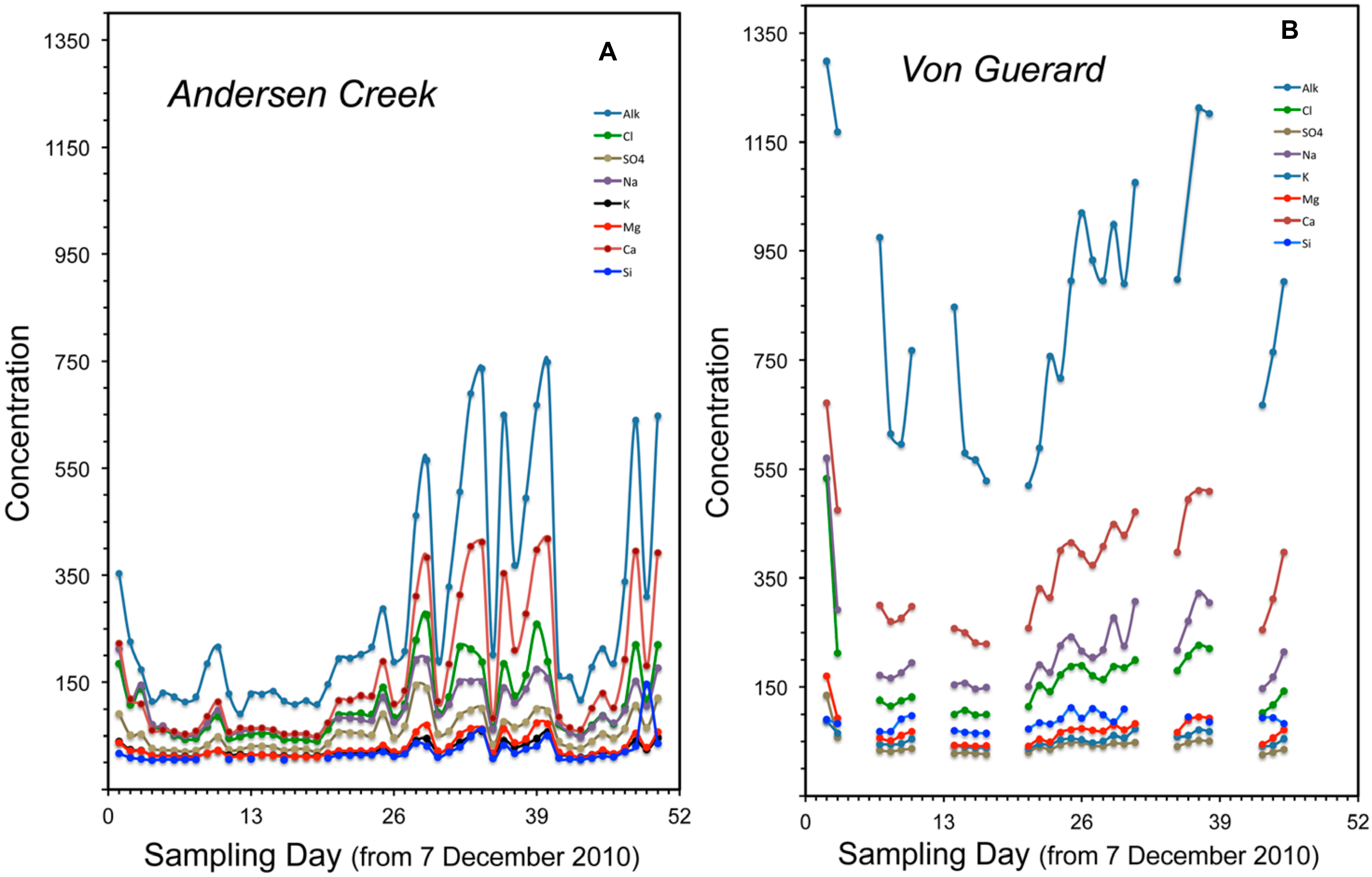

Figure 8. Plot of species concentrations measured over the course of the summer season of 2010–2011 for (A) Andersen Creek sampled at ~4:30 p.m. daily and (B) Von Guerard sampled at ~9:30 p.m. daily. Concentration values are µM for all species except HCO_3^-, which is reported as µeq/L. Gaps in the Von Guerard record are due to intervals when the F6 camp was unoccupied.

sampled at Von Guerard, whereas just in-stream and near-stream hyporheic sampling was possible at Andersen Creek due to the limited areal extent of its lateral hyporheic zone (Table 5). Sampling at Von Guerard began on 9 December 2010 and extended to 19 January 2011, with the in-stream and near-stream hyporheic zones sampled seven times and the distal hyporheic zone sampled twice. Sampling at Andersen Creek commenced on 12 December 2010 and extended to 24 January 2011, and very localized in-stream and near-stream hyporheic zones were sampled seven times (Table 5).

Hyporheic zone waters at both Von Guerard and Andersen Creek display higher TDS_c values and elevated constituent concentrations than their respective streams (Fig. 9). No consistent spatial pattern of concentration variation was observed between the in-stream and near-stream hyporheic zone water at Andersen Creek, whereas hyporheic zone waters at Von Guerard displayed higher solute concentrations at greater distance from the stream channel (Table 5, Fig. 9). When water-saturated at the time of sampling, the distal stream hyporheic zone at Von Guerard had the highest concentration of solutes. This observation is consistent with the longer residence time of pore water in the distal fringes of spatially extensive hyporheic zones, like that at Von Guerard, which provide an extended time for water-sediment interaction and mineral dissolution. Overall, hyporheic zone solute variations at both Von

TABLE 4. UPSTREAM-TO-DOWNSTREAM SAMPLING OF VON GUERARD AND ANDERSEN CREEK DURING THE AUSTRAL SUMMER OF 2010–2011

	Cl^- (µM)	SO_4^{2-} (µM)	Na^+ (µM)	K^+ (µM)	Mg^{2+} (µM)	Ca^{2+} (µM)	HCO_3^- (µeq/L)	H_4SiO_4 (µM)
Von Guerard								
December 2010	nd	28	117	32	37	nd	478	82
	105	30	137	39	44	237	579	87
	109	31	148	43	49	252	638	89
	114	32	160	45	54	265	700	92
January 2011	103	28	126	32	42	227	514	85
	115	31	143	39	43	273	603	70
	117	32	160	43	57	305	728	92
	129	33	185	49	70	348	764	97
Andersen Creek								
December 2010	147	126	172	42	46	204	300	25
	67	38	78	20	17	73	134	10
	56	30	63	15	13	59	126	9
	51	26	61	15	13	59	121	8
	49	25	58	15	12	64	91	8
January 2011	184	134	197	48	54	231	334	29
	96	51	95	22	24	90	149	11
	88	45	82	16	25	83	185	9
	81	41	80	19	21	80	135	10
	75	38	72	19	20	89	163	9

Note: nd—not determined.

TABLE 5. COMPARISON OF HYPORHERIC ZONE WATER COMPOSITIONS AT VON GUERARD AND ANDERSEN CREEK OVER THE AUSTRAL SUMMER OF 2010–2011

Sample date/time	Cl^- (μM)	SO_4^{2-} (μM)	Na^+ (μM)	K^+ (μM)	Mg^{2+} (μM)	Ca^{2+} (μM)	HCO_3^- (meq)	H_4SiO_4 (μM)	TDS_c (mg/L)
Von Guerard									
In-stream Hyporheic Zone									
12/9/2010 22:30	258	66	352	100	105	517	1156	94	73
12/17/2010 1:00	118	33	176	52	61	276	772	95	83
12/23/2010 21:00	142	41	324	74	64	294	818	115	94
1/1/2011 10:30	169	48	233	84	107	337	955	119	103
1/1/2011 21:30	180	48	260	129	132	338	1049	132	104
1/2/2011 14:00	178	47	304	155	120	314	1054	148	96
1/19/2011 23:20	128	35	402	114	257	164	1012	118	nd
Near-stream Hyporheic Zone									
12/9/2010 22:30	463	133	546	146	332	254	1456	107	155
12/17/2010 1:00	246	56	349	147	197	766	1250	196	140
12/23/2010 21:00	160	55	730	129	260	179	1437	170	134
1/1/2011 10:30	159	45	417	94	308	138	1180	171	108
1/1/2011 21:30	161	50	453	116	243	214	1207	194	114
1/2/2011 14:00	184	52	360	132	232	257	1098	168	108
1/19/2011 23:20	135	39	371	110	251	222	1235	183	112
Distal Hyporheic Zone									
12/9/2010 22:30	701	165	870	140	306	186	1883	162	197
1/19/2011 23:20	330	93	1041	206	530	467	nd	158	84
Andersen Creek									
In-stream Hyporheic Zone									
12/12/2010 23:00	97	44	195	43	42	221	nd	34	nd
12/19/2010 19:30	114	60	310	100	143	368	1016	132	102
12/26/2010 19:00	74	49	211	60	64	322	807	71	79
1/5/2011 15:20	108	67	115	32	36	225	375	33	47
1/7/2011 18:00	214	108	130	72	49	376	553	58	74
1/16/2011 23:30	103	54	113	41	31	217	450	35	50
1/24/2011 17:40	115	65	104	36	35	231	420	26	50
Near-stream Hyporheic Zone									
12/12/2010 23:00	62	26	90	45	26	208	473	29	46
12/19/2010 19:30	83	46	411	127	129	379	1177	179	113
12/26/2010 19:00	112	63	138	76	66	249	nd	120	nd
1/5/2011 17:30	225	122	160	62	57	410	626	35	82
1/7/2011 18:00	219	103	155	nd	56	415	634	50	78
1/16/2011 23:30	87	47	104	100	117	406	997	137	94
1/24/2011 17:40	124	50	152	89	162	505	1261	132	118

Notes: nd—not determined; TDS_c—calculated total dissolved solids.

Guerard and Andersen Creek are independent of stream discharge, with concentrations generally similar at times of high and low flow and across the summer season. Enrichments for individual species at Andersen Creek range between 1.1 and 3.1× for the in-stream hyporheic zone and from 1.2 to 5× for the near-stream hyporheic zone. By comparison, enrichment factors for all species except Ca at Von Guerard vary between 1.1 and 2.0× for the in-stream hyporheic zone, from 1.3 to 3.8× for the near-stream hyporheic zone, and from 1.2 to 2.8× for the distal hyporheic zone. With near constant enrichments between 0.8 and 0.9×, Ca is depleted relative to main channel stream water in all three Von Guerard hyporheic zone domains. On average, waters in the hyporheic zone around Von Guerard are elevated in solute concentrations relative to Andersen Creek. For example, respective mean TDS_c contents of the in-stream and near-stream hyporheic zones at Andersen Creek were 67 mg/L and 88 mg/L compared with 96 mg/L and 124 mg/L at Von Guerard. The same pattern extends to all constituents except Ca, which was depleted in the near-stream hyporheic zone at Von Guerard relative to its abundance in the in-stream hyporheic zone, as was observed for overall stream chemistry (Table 3). Excluding the anomalous situation for Ca in the near-stream hyporheic zone at Von Guerard, hyporheic zone water here exhibited less compositional variation than at Andersen Creek, with coefficients of variation for dissolved constituents for the Von Guerard near-stream and in-stream hyporheic zones ranging from 14%–54% and 10%–53% compared to 26%–69% and 28%–60% at Andersen Creek. For the Andersen Creek hyporheic zone, in-stream waters had higher dissolved constituent concentrations than near-stream waters in mid-December compared to the remainder of the summer season. This contrasts with the hyporheic zone at Von Guerard, where concentrations of near-stream waters over the course of sampling were elevated over in-stream waters but converged to similar levels toward the end of the flow season.

These observations document elevated solute levels within the hyporheic zones around Taylor Valley streams and are in agreement with previous studies. Although hyporheic zones are more chemically enriched than their associated stream waters, they can be small and of limited areal extent in short streams such as Andersen Creek and, therefore, exert only limited influence on stream chemistry (Fortner et al., 2013; Leslie et al., 2017) because less hyporheic volume is available for stream interaction. This contrasts with the situation for larger and longer streams like Von Guerard that are characterized by extensive hyporheic zones that receive and transmit greater volumes of stream water and increase in spatial extent during the course of the summer flow season. Such hyporheic zones not only provide the opportunity for more spatially extensive and longer contact times for water

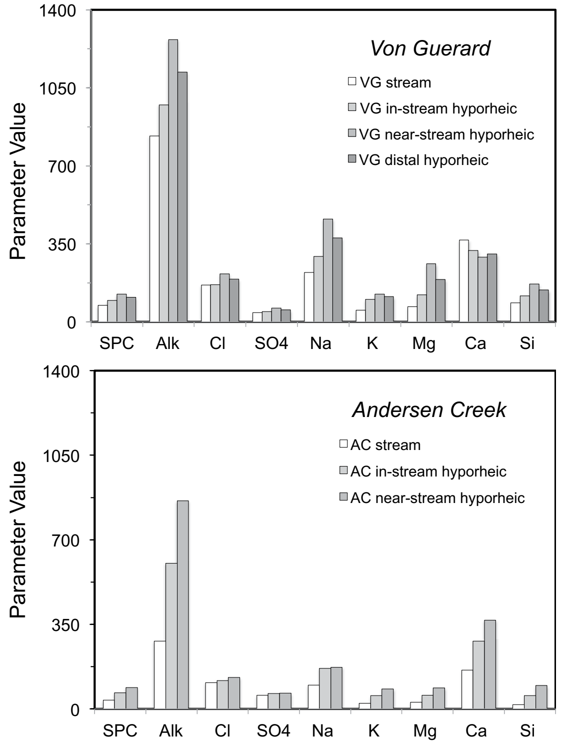

Figure 9. Comparison of hyporheic zone waters at Von Guerard and Andersen Creek during the austral summer of 2010–2011 (electrical conductivity [EC] as μS/cm and chemical species as μM concentration).

with salts, carbonates, and silicate minerals during transient storage at daily to seasonal time scales (Nezat et al., 2001; Gooseff et al., 2002; Cozzetto et al., 2006; Wlostowski et al., 2016; Singley at al., 2017), they can provide a majority of total streamflow during an entire summer season (Leslie et al., 2017) and, therefore, act as the primary control on the chemical budget of these streams.

Diurnal Behavior

Diurnal variations measured at high temporal resolution provide additional insights into process controls on stream composition. Two diurnal sampling studies were undertaken at Von Guerard and Andersen Creek during the summer flow season of 2010–2011. The first was a day-long sampling at hourly intervals at the beginning of the flow season, which was followed by a second 3–4-day sampling at 4-hour intervals during the middle of the flow season. Stream hydrographs with temperature and conductivity profiles for both intervals of diurnal sampling are shown in Figure 10, with solute concentration variations summarized in Table 6.

The initial diurnal sampling at Von Guerard started at 11:00 p.m. on 8 December and continued hourly for one day. Discharge was 30 L/sec at the outset, decreased overnight to a low flow of <5 L/sec during the subsequent afternoon, then rose to 156 L/sec in the early evening before falling back to 89 L/sec and finally rising to the daily high of 175 L/sec just before the conclusion of the sampling interval. Temperature reached a high of nearly 8 °C three hours ahead of the daily peak flow. The dissolved solute load decreased steadily throughout the 24 h period independent of discharge, dropping from an initial EC value of 285 µS/cm to a low of 103 µS/m. During the second diurnal sampling, baseflow at Von Guerard was low and stable around 2 L/sec from 5:00 p.m. on 31 December to 3:20 p.m. on 3 January. High temperatures of 9.6 °C and 10.4 °C on 1 and 2 January preceded daily peak flows of 25 L/sec and 131 L/sec. Electrical conductivity was relatively high and constant during the sampling interval, fluctuating between of 90–127 µS/cm, largely independent of flow. The second diurnal sampling for Von Guerard was undertaken for 4215 min from 5:00 p.m. on 31 December 2010 to 3:20 p.m. on 3 January 2011 at a time of maximum hyporheic zone development. For the second diurnal sampling, four parameters were measured in situ periodically at 5 min intervals at locations in their downstream reaches close to the gages at their respective lake entrances—stream temperature (°C), electrical conductivity (µS/cm), dissolved oxygen (mg/L), and pH.

The first diurnal sampling at Andersen Creek commenced at 11:00 a.m. on 9 December and continued hourly for one day. Discharge during this time was characterized by a single broad, high-flow episode, rising steadily from 10 L/sec at the outset to 167 L/sec 12 h later, and then receding slowly to a volume of 65 L/sec at the conclusion of the monitoring interval. Water temperature was near freezing most of the time, rising only to 1.6 °C during the afternoon of 9 December. Solute loads were extremely low, falling from an initial EC value of around 30 µS/cm to a nearly stable low of ~15 µS/cm for the remainder of the sampling interval. A remarkably stable streamflow was observed at Andersen Creek during the second sampling interval from 5:00 p.m. on 3 January through 2:15 p.m. on 7 January over a total sample time of 5595 min. Discharge was low and sustained at <3 L/sec almost 24 h from the outset, rising to a peak of 67 L/sec at the end of the first day, then falling back to around the same minimal flow and subsequently rising to a maximum of only 9 L/sec at the close of the second day, and

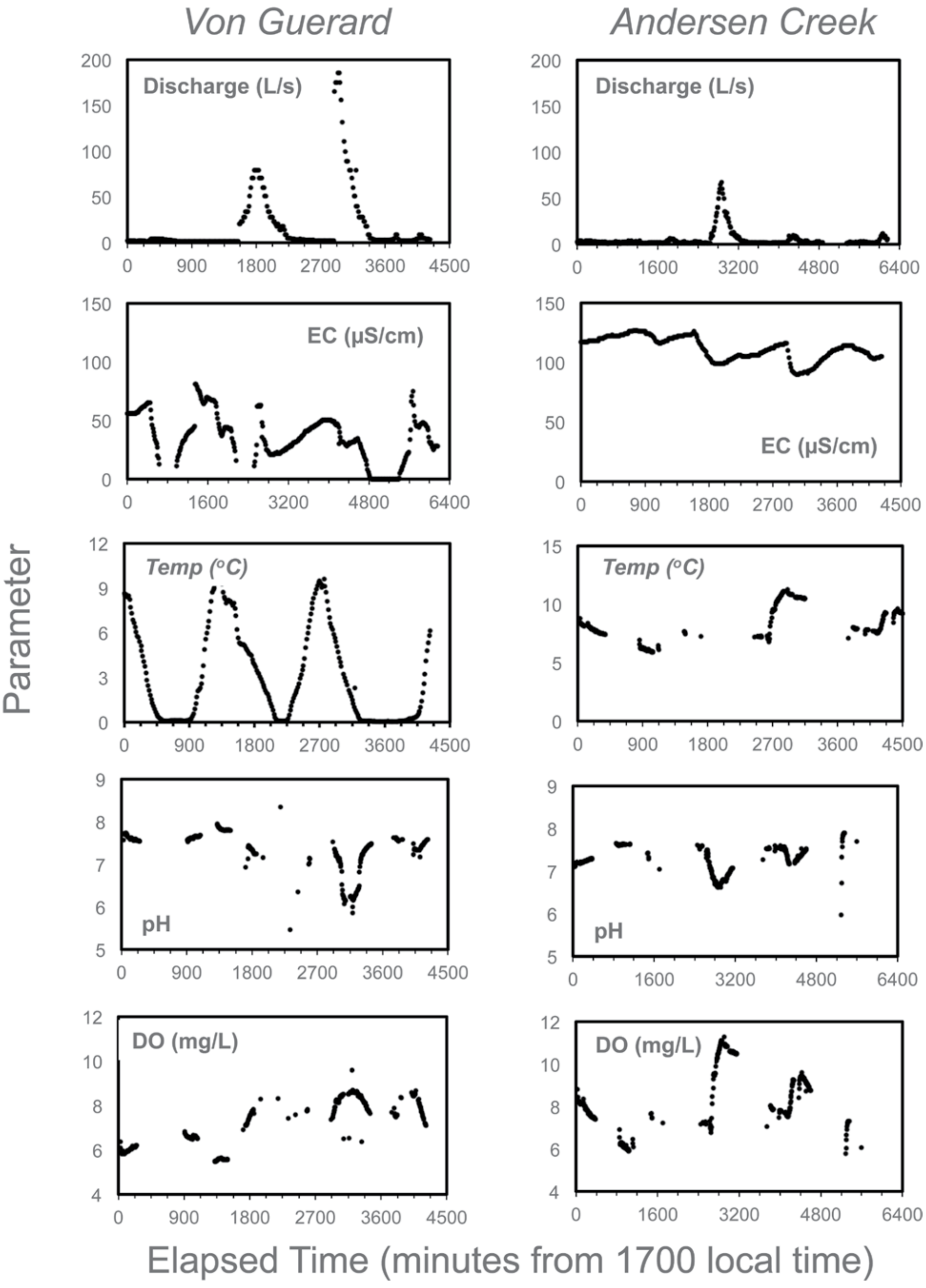

Figure 10. Hydrographs and plots of stream temperature and electrical conductivity during the two diurnal monitoring intervals at Von Guerard and Andersen Creek.

TABLE 6. COMPARISON OF STREAM CHEMISTRY FOR VON GUERARD AND ANDERSEN CREEK OVER THE TWO INTERVALS OF DIURNAL MONITORING WITH THE AUSTRAL SUMMER OF 2010-2011 AND THE TWO-DECADE PERIOD OF MCM-LTER MONITORING

	1st Diurnal				2nd Diurnal				2010–2011 Seasonal				Long Term			
Species	N	Avg	Stdev	CV	N	Avg	Stdev	CV	N	Avg	Stdev	CV	N	Avg	Stdev	CV
	12/16/2010–12/17/2010				12/31/2010–1/3/2011				12/8/2010–1/20/2011				1994–2013			
Von Guerard	24				14				63				111			
Cl^- (μM)		110	4	4		174	17	10		174	18	11		246	145	59
SO_4^{2-} (μM)		30	2	6		44	4	9		44	4	10		59	17	29
HCO_3^- (meq)		599	94	16		914	94	10		925	89	10		1065	306	29
H_4SiO_4 (μM)		87	4	5		98	9	9		85	19	22		78	19	25
Na^+ (μM)		141	18	13		219	29	13		214	28	13		313	197	63
K^+ (μM)		40	6	15		52	6	12		51	6	12		59	17	29
Ca^{2+} (μM))		251	14	6		390	37	10		381	36	10		415	123	30
Mg^{2+} (μM)		46	7	16		72	7	10		72	8	11		78	28	36
	12/16/2010–12/17/2010				1/3/2011–1/7/2011				12/7/2010–11/25/2011				1994–2013			
Andersen Creek	24				10				82				112			
Cl^- (μM)		74	42	56		209	72	34		112	77	69		139	131	88
SO_4^{2-} (μM)		49	44	89		107	33	31		54	39	73		77	82	107
HCO_3^- (meq)		154	83	54		425	136	32		253	192	76		340	264	70
H_4SiO_4 (μM)		12	7	61		23	8	32		16	20	122		17	17	100
Na^+ (μM)		86	49	56		156	39	25		98	47	48		132	100	76
K^+ (μM)		22	10	54		37	36	10		23	13	60		27	19	72
Ca^{2+} (μM))		92	63	68		284	100	35		149	126	85		191	158	83
Mg^{2+} (μM)		20	14	71		50	18	36		27	21	79		38	32	86

Notes: MCM-LTER—McMurdo-Long-Term Ecological Research project; N—number analyses; Avg—mean value; Stdev—standard deviation; CV—coefficient of variation.

afterwards continuing at <3 L/sec until the conclusion of the monitoring interval. Daily high temperatures between 3 °C and 5 °C occurred shortly after midday during the three days of sampling. Electrical conductivity values over the sampling interval were highly variable, fluctuating strongly from just above 1–81 μS/cm, and largely independent of discharge.

Distinctly different solute concentrations and diurnal patterns of variation were observed for the two streams during the diurnal sampling intervals (Table 6, Fig. 10). Andersen Creek exhibited lower ionic concentrations and more compositional variability than Von Guerard, with coefficients of variation for its dissolved constituents ranging from 10%–36% for the former compared with only 9%–12% for the latter. Von Guerard concentration variations during this time were comparable to those recorded for this stream over the entire summer season, whereas those at Andersen Creek were somewhat above the seasonal average. While conductivity ranges for the two streams were similar over the course of the summer season, varying from 14 μS/cm to 105 μS/cm for Andersen Creek compared with 31–129 μS/cm for Von Guerard, the latter is characteristically enriched by 1.8–3.1× for all dissolved species, except for sulfate, which is equivalent for the two streams, and H_4SiO_4, which averaged 5.5× greater at Von Guerard. Solute concentrations at Andersen Creek were higher and displayed more compositional variability during the second diurnal sampling interval. It is during this time of elevated TDS_c values of 70–100 mg/L on 4–5 January, when TDS values were a factor of 3–5× higher than during the first diurnal sampling interval, that the influence of a local subsurface seepage on Andersen Creek stream composition is inferred. Leslie et al. (2017) observed that this high-TDS Andersen Creek water also was enriched in D and ^{18}O compared to Andersen Creek flow at other times of the 2010–2011 summer season and had a strongly negative d-excess value between −8.9‰ to −6.5‰, a feature which characterizes a seep within the active layer that has been subject to near-surface evaporation (Harris et al., 2007). Von Guerard exhibited much less overall compositional variation than Andersen Creek over the full flow season. Variations in ionic species concentration fall in a modest range from 21%–38% for Von Guerard compared to those at Andersen Creek, where observed concentration variations were 69%–76% for anions and 48%–85% for cations. Significantly, variation in dissolved Si was lower than for ionic species at Von Guerard (12%), but it was higher at Andersen Creek (122%).

Total dissolved solid loads for both Von Guerard and Andersen Creek during both 4-day sampling intervals are comparable to those at other streams across the McMurdo Dry Valley region during the austral summer of 2010–2011 and fall within the historic ranges documented for Taylor Valley streams. In a study of meltwater sources from the Canada Glacier that did not determine alkalinity, Fortner et al. (2005) observed that meltwater in the proglacial Andersen Creek during the 2000–2001 summer season contained slightly higher solute loads than supraglacial streams in the western sector of Canada Glacier, with respective geochemical fingerprints of $Ca >> SO_4 \sim Cl > Na > Mg$ for Andersen Creek, $Ca >> Cl > Na > SO_4 > Mg$ for supraglacial streams, and $Ca >> Cl >> SO_4$ for cryoconite hole waters. This observation readily explains some of the differences in stream chemistry and compositional variability observed at Von Guerard and Andersen Creek. The extensive hyporheic zone present in the middle and lower reaches of Von Guerard, which is a domain of biogeochemical activity such as denitrification (Gooseff et al., 2003) and water-sediment interaction through ion exchange and mineral dissolution (Maurice et al., 2002; Gooseff et al., 2002, 2004; McKnight et al., 2004), act to affect the overall solute content and enrich stream water in dissolved Si to produce its geochemical fingerprint of $HCO_3 > Ca > Na > Cl > H_4SiO_4 > Mg > K > SO_4$. In contrast, flow in Andersen Creek is dominated by supraglacial stream water with a contribution from cryoconite hole waters enriched in chloride and sulfate from the dissolution of eolian dust and salt deposited on the surface of the Canada Glacier that are strongly depleted in silica. As noted above, Leslie et al. (2017) explained the unusual chemistry observed at Andersen Creek during the second diurnal sampling interval on 4–5 January as a consequence of influence from a local subsurface seep, as evidenced by elevated TDS_c values ranging between 70 mg/L and 100 mg/L and a more evaporative stable isotope signature. Further evidence of this seepage influence is noted in Table 6, where the parameter concentrations for the second diurnal sampling are up to a factor of three higher than for both the first interval of diurnal sampling during the 2010–2011 season and the long-term average. Despite this anomaly, the chemistry of Andersen Creek, with its minimal hyporheic zone, more closely reflects the composition and high variability of its glacial source waters and, therefore, exhibits the long-term geochemical fingerprint $HCO_3 > Ca > Cl > Na > SO_4 > Mg > K > H_4SiO_4$, which is based toward chloride and sulfate and can even elevate these species over Ca^{2+} during high-flow intervals such that $HCO_3 > Cl > Na > Ca > SO_4 > Mg > K > H_4SiO_4$. The influence of subsurface saline seeps and water tracks is intermittent, influencing stream geochemistry only during warmer intervals of the austral summer when soil temperatures are the highest, and certainly varies in extent and influence from one year to another.

Respective measurements of EC, T, DO, and pH during the second interval of diurnal monitoring were: EC = 90–127 µS/cm, T = 0.6–10.6 °C, DO = 5.5–9.6 mg/L (86%–99% saturation), and pH = 5.6–8.3 for Von Guerard compared with EC = 1–81 µS/cm, T = –0.7–2.9 °C, DO = 5.8–11.3 mg/L (67%–99% saturation), and pH = 6.0–7.9 for Andersen Creek. Both streams exhibit well-defined diurnal cycles for all four parameters, with episodes of stream baseflow characterized by greatest dissolved solute contents, elevated temperature, high pH values, and low concentrations of dissolved oxygen. Solute contents at both streams, as reflected by electrical conductivity, decrease on the rising limb of the daily meltwater pulse, with highest conductivity values recorded during intervals of lowest flow. Andersen Creek is characterized by strongly fluctuating solute loading and different daily response patterns over the four days of 4-hourly monitoring, whereas solute fluctuation was more subdued and modulated at Von Guerard. Both streams are characterized by low, near-freezing temperatures in the early morning. At Andersen Creek, temperature reached a daily maximum of just below 3 °C at midday and throughout the daily cycle was largely uncorrelated with discharge, whereas the Von Guerard stream reached its high temperature of around 10 °C in the mid–late afternoon during the lowest flow interval of the daily cycle that immediately preceded the daily high flow pulse, when it decreased sharply. Cozzetto et al. (2013) demonstrated that cooler streams have less infiltration and hyporheic zone mixing than warmer streams, so its higher temperature regime may also enhance silicate weathering at Von Guerard. As expected, times of highest dissolved oxygen content correspond to episodes of enhanced glacial melting, when streams are well oxygenated because of high, turbulent flow. Variations in pH are more strongly correlated with dissolved oxygen at Andersen Creek than at Von Guerard.

FURTHER CONSIDERATIONS

Three aspects of our stream chemistry study deserve further consideration—hyporheic zone influence on stream chemistry, the solute-discharge relationship, and stream meltwater sources. These are discussed in the paragraphs that follow.

A weekly sampling was undertaken over the course of the 7-week 2010–2011 flow season to investigate the compositional relationships between the Von Guerard and Andersen Creek streams and their hyporheic zones. As noted above, the two most abundant cations in Taylor Valley streams are derived predominantly from different sources, Ca from the dissolution of carbonates and Na from the dissolution of soluble salts. To remove the influences of dilution and evaporation, the ratios of Ca/Cl to Na/Cl are plotted for Von Guerard and Andersen Creek along with their hyporheic zone waters in Figure 11. Because of the well-developed and wide hyporheic zone in the lower reaches of Von Guerard, hyporheic zone sampling was possible under the stream, immediately adjacent to the stream, and in its distal margins away from the stream, whereas the minimal hyporheic zone around Andersen Creek only permitted in-stream and near-stream sampling of its hyporheic zone. Snow was sampled at both sites, and the supraglacial streams that provide flow to Andersen Creek from Canada Glacier were also sampled.

Over the course of the 2010–2011 flow season, stream water at Von Guerard defines a strongly linear array from beginning compositions of Ca/Cl ~1.2 and Na/Cl ~1.1 to a final composition of Ca/Cl ~2.8 and Na/Cl ~1.5 (Fig. 11A). Early season stream water is characterized by elevated contents of Na, Ca, and Cl around 500 µM. Whereas Ca contents are relatively stable throughout the flow season, concentrations of both Na and Cl decrease from December into January, with Cl more strongly depleted than Na. As seen in Figure 11, stream water compositions at Von Guerard can be explained in terms of three-component mixing between an end member having Na/Cl close to unity (evaporite), an end member having elevated Ca/Cl (carbonate), and a strongly Na-enriched end member (soluble salt). The evaporite component dominates the chemical signature of early January snow at the F6 camp, streamflow in early December, and the near-stream and distal hyporheic zone waters sampled on 9 December at the beginning of the flow season, a feature attributed to the dissolution of halite deposited within streambed soil at the end of the previous summer flow cycle. As the flow season developed over the next fortnight and the hyporheic zone at Von Guerard expanded progressively outwards, the chemistry of the near-stream sampling site first reflects a carbonate influence on 17 December and then is dominated by a soluble salt signature on 23 December. Later in the flow season, waters are less influenced by the soluble salt component, as dissolution increasingly removes it from the active zone soils adjacent to the Von Guerard stream. Andersen Creek contrasts with the systematic behavior of Von Guerard. Here, its proglacial stream water is compositionally

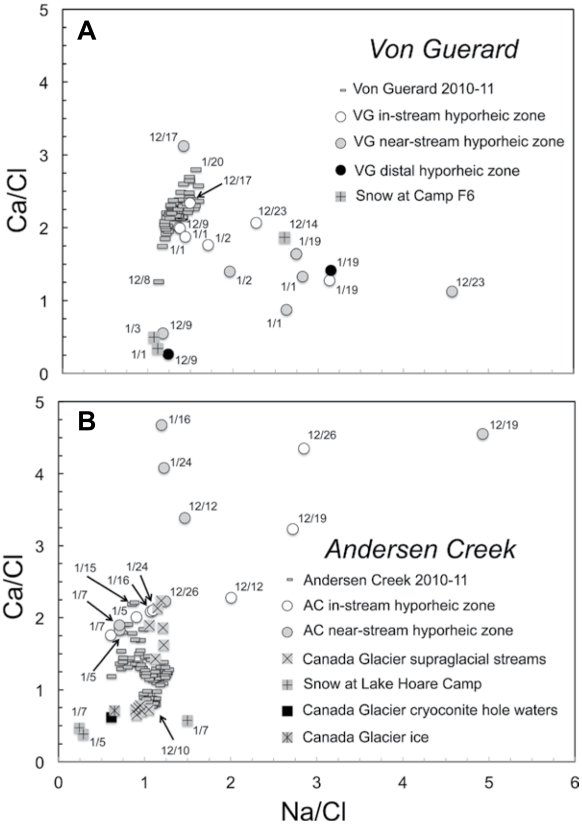

Figure 11. Plot of molar ratios Ca/Cl versus Na/Cl for waters at (A) Von Guerard (VG) and (B) Andersen Creek (AC) sampled in December 2010 and January 2011, with dates denoted for selected samples. Average values for Canada Glacier ice and cryconite hole water are from Bagshaw et al. (2013).

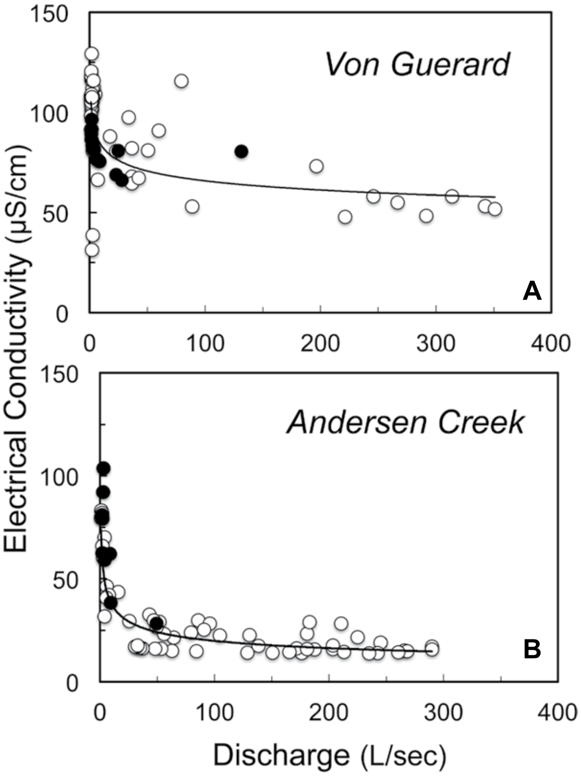

Figure 12. Plots of electrical conductivity (µS/cm) versus discharge (L/sec) for (A) Von Guerard (VG) and (B) Andersen Creek (AC) over the austral summer season of 2010–2011 (open symbols) and during the second diurnal sampling interval (filled symbols).

comparable to supraglacial streams generated on the Canada Glacier. Glacial ice, cryoconite hole waters, and two of three fresh snow samples from the Lake Hoare camp are compositionally similar and plot to the left of the stream water array with Ca/Cl and Na/Cl ratios <0.7. Fortner et al. (2005) observed that dissolved calcium increases in Canada Glacier meltwater during its evolution from snow and ice to supraglacial water due to calcite dissolution, so such an evolution would produce the least compositionally evolved Andersen Creek stream water. As at Von Guerard, Ca/Cl ratios increase over the course of the flow season but are accompanied by slightly decreasing Na/Cl ratios, which suggests the increasing influence of carbonate dissolution. No spatial or temporal consistency is observed between in-stream and near-stream hyporheic zone waters at Andersen Creek. About half the hyporheic zone waters sampled here overlap the upper portion of the stream water array, with other samples showing elevated Ca/Cl and Na/Cl ratios scattered across the diagram. This compositional diversity may be explained by the dissolution of binary salts in localized areas of dry soil under and around the stream that are not normally wetted but become so at times of highest streamflow.

Conductivity measurements for the 2010–2011 flow season are plotted as a function of stream discharge in Figure 12, where a similar conductivity-discharge relationship is observed for both streams that records the dilution of solute loads during the daily high flow pulse from glacial melting. However, the individual EC-Q relationships shown in the figure suggest different controls on stream geochemistry at Von Guerard and Andersen Creek during their daily flow cycles. Although both streams reach somewhat similar elevated daily maximum dissolved loads (EC_{max} for AC = 104 µS/cm versus EC_{max} for VGS = 131 µS/cm), their daily minima are distinctly different, with that of Von Guerard being more than double that of Andersen Creek (EC_{min} for AC = 14 µS/cm EC_{min} for VGS ~50 µS/cm). It is notable that minimum EC values are higher for Von Guerard than Andersen Creek and that conductivity co-varies strongly with flow volume at Andersen Creek but much less so at Von Guerard.

Andersen Creek displays a power law conductivity-discharge behavior (Fig. 12B) over the 2010–2011 flow season, with lowest flows exhibiting the highest solute contents and vice versa. As stream discharge diminishes and flow returns to its low condition as inputs from supraglacial streams and the daily melting of glacial ice diminish, high-conductivity water from cryoconite holes sourced from the internal hydrologic network of the Canada Glacier dominates the solute budget (Fortner et al., 2005, 2013) and is unaffected by secondary processes and unmodified during its short distance of surface channel travel. The exception to this typical behavior occurred during the second diurnal sampling interval, when Andersen Creek stream chemistry was influenced by an adjacent intermittent subsurface seep. The contributions from waters having resided in, and interacted with, the trapped sediment and biological ecosystem present within cryoconite holes on the surface of the Canada Glacier are temporally and compositionally variable. Isolated cryoconite holes contain compositionally distinct waters that typically are an order of magnitude more solute rich than the surrounding glacial ice (Bagshaw et al., 2007). These features can exist for up to a decade and create a near-surface hydrologic system tens of centimeters below the ice surface. Fountain et al. (2004) observed that some half of cryoconite holes on the Canada Glacier were isolated and the other half were connected to the near-surface hydrologic system. Separate holes have been observed to exhibit independent cycles of water storage and release to the larger internal glacier hydrologic network. This signal is diluted at times of higher flow, when water derived from melting glacial ice—with EC values <20 µS/cm (Lyons et al., 2013) —comprises the bulk of the flow. The small solute fluctuations observed for higher discharges are attributed to differential partitioning of the contributions from supraglacial stream, glacial ice melt, and cryoconite hole sources into Andersen Creek as well as their compositional variability over time.

Similar concentration-discharge behavior is observed at Von Guerard (Fig. 12A) but with much more variability. Here, as streamflow diminishes toward its daily minimum, water equilibrated in the higher temperature portions of the hyporheic zone contributes return flow into the stream channel, which raises water temperature to around 10 °C ahead of the daily high discharge meltwater pulse. The relative compositional consistency of solute contents at Von Guerard over the entirety of a summer flow season reflects compositional modulation by its extensive mid-reach hyporheic zone, where water in transient storage introduced during times of high streamflow volumes has an extended opportunity for water-sediment interaction and pore water exchange before a portion returns to the main stream channel during the daily low-flow interval. Hyporheic zone waters have been determined to have varying residence times depending on the streamflow regime (Gooseff et al., 2003; Koch et al., 2011). Our observations support the idea of a two-part hyporheic zone for larger Taylor Valley streams. As illustrated in Figure 4, a well-connected and thermally regulated hyporheic zone is present around large stream channels that holds water in transient storage and exchanges water with the main stream on multiple temporal and spatial scales (Runkel et al., 1998; Gooseff et al., 2002; Cozzetto et al., 2013; Gooseff, 2010; Wlostowski et al., 2016). The highly interactive near-stream hyporheic envelope experiences rapid stream water exchange on a flow equivalent time scale as water travels from glacier source to lake inflow. This dynamic interface is connected to a more distant hyporheic domain that extends to the distal reaches of the wetted zone away from the stream, with the latter characterized by longer flow paths and slower exchange. The higher minimum electrical conductivity value for Von Guerard is interpreted to reflect a steady input of such distal hyporheic zone water to the main-stream channel. Contributions of this solute-rich water, produced during extensive fluid-sediment interaction (Gooseff et al., 2002, 2003, 2017b; McKnight et al., 2004), are greatest during low-flow intervals when it buffers the dissolved solute load of Von Guerard to higher ion concentration levels than are observed at Andersen Creek, where glacial meltwater dominates streamflow. However, the more variable conductivity-discharge behavior observed at Von Guerard over the course of the entire flow season is a reflection of the complex dynamics of hydrologic and hydraulic processes influencing hyporheic zone behavior of the longer Taylor Valley streams (Wlostowski et al., 2016; Singley et al., 2017).

In a study that examined hyporheic exchange processes for selected Taylor Valley streams, using high-frequency electrical conductivity-discharge relationships, Singley et al. (2017) concluded that the effect of seasonally variable discharge and hyporheic exchange on EC-Q relationships differs for long and short streams because of buffering by the greater storage volumes of longer streams. Examination of diurnal concentration-flow patterns of Von Guerard and Andersen Creek (Fig. 13) supports this observation. Electrical conductivity is plotted as function of discharge at Andersen Creek and Von Guerard for two consecutive days during our diurnal monitoring, with each stream exhibiting a distinct concentration-discharge dynamic. Electrical conductivity at Andersen Creek varied from 11 μS/cm to 63 μS/cm on 4 January over flows of 0.9–67 L/sec compared with the slightly larger range of 11–81 μS/cm on 5 January over flows of only 0.7–7 L/sec. In comparison, EC values at Von Guerard ranged from 99 μS/cm to 127 μS/cm on 1 January for flows of 1–79 L/sec and then 90–116 μS/cm on 2 January for flows of 1.9–186 L/sec. The two hysteresis loops for Von Guerard (Figs. 13A–13B) are characterized by short, intense times of flushing and anti-diluting but extended intervals of diluting and concentrating. This systematic behavior directly records compositional control on Von Guerard solute loading during the point in the summer flow season when its hyporheic zone is well developed and of greatest extent. At that time, the storage of a large volume of water in the Von Guerard hyporheic zone acts to buffer its solute concentration within narrow limits. In contrast, the compressed and non-systematic hysteresis loops for Andersen Creek (Figs. 13C–13D) throughout the two diurnal cycles highlight the fact that this simple proglacial stream receives flow from compositionally diverse sources that can vary chemically on short time scales. This behavior reflects mixing in variable proportions of different types of Canada Glacier water, i.e., that from supraglacial streams atop the glacier, meltwater from the glacier walls, and internally derived meltwater including that from cryoconite holes as well as input from a nearby saline subsurface seep during this specific episode of warm temperature in early January 2011.

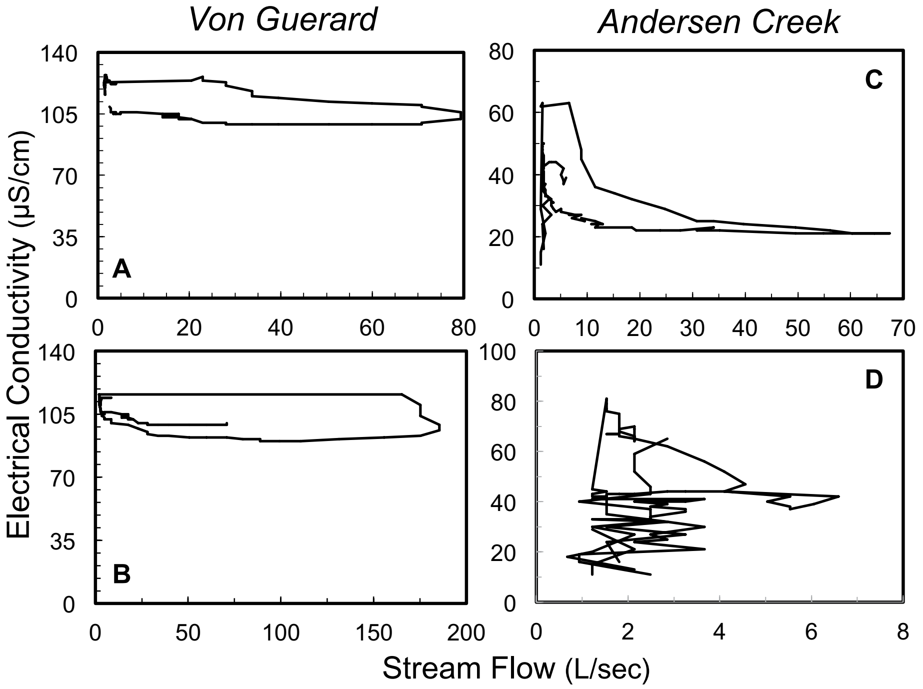

Figure 13. Plots of electrical conductivity (μS/cm) versus discharge (L/sec) for (A, B) Von Guerard on 1 and 2 January 2011 and for (C, D) Andersen Creek on 4 and 5 January 2011.

Minimum solute concentrations for Andersen Creek of 62 μM for HCO_3^- and 53 μM for Ca^{2+} are elevated compared to both Canada Glacier ice and meltwater ($HCO_3^- = 43$ μM and $Ca^{2+} = 18$ μM; Lyons et al., 2003) and supraglacial streams ($HCO_3^- = 49$ μM and $Ca^{2+} = 34$ μM; Fortner et al., 2005), an observation best explained by a flow contribution from cryoconite holes. Cryoconite holes cover ~4–6% of glacial surfaces across Taylor Valley, are connected to the internal glacier hydrologic flow network, and are estimated to contribute >13% of glacial runoff (Fountain et al., 2004, 2008). Cryoconite holes collect aerosol debris and biological material while exposed to the atmosphere before their ice lids form, and these spaces subsequently become habitats for a range of microbial life. As a consequence, the photosynthesis and biogeochemical processes in cryoconite holes will result in extreme geochemical conditions that strongly alter the chemistry of trapped water (Bagshaw et al., 2007). For example, of the ionic species of interest to this study, mean μM concentrations of $Cl^- = 91$, $SO_4^{2-} = 51$, $HCO_3^- = 202$, Na^+, = 57, $K^+ = 16$, $Ca^{2+} = 202$, and $Mg^{2+} = 5$ were measured by Bagshaw et al. (2013) in waters from cryoconite holes on the Canada Glacier. This solute enrichment was explained as a product of surface dissolution of minerals contained within cryoconite hole sediments. Cl-normalized depletions calculated for cryoconite hole waters compared to those from Canada Glacier ice were 0.45× for Mg, 0.94× for Na, and 1.03× for K, respectively, but there were strongly elevated levels of 1.49× for SO_4, 1.69× for HCO_3, and 3.55× for Ca. In contrast, Von Guerard chemistry is affected during low flow by both the benthic algal mat community present in its middle reaches and return flow of hyporheic zone water. As flow in Von Guerard diminishes toward its daily minimum, water equilibrated in the higher temperature portions of the hyporheic zone contributes return flow

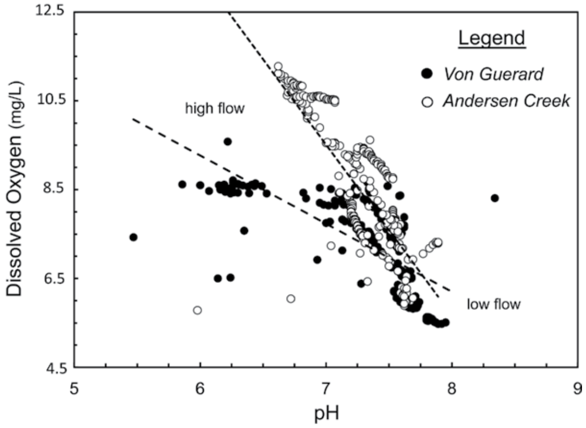

Figure 14. Plot of dissolved oxygen (mg/L) versus pH for Von Guerard from 0:05 p.m. on 31 December 2010–3:20 p.m. on 3 January 2011 and for Andersen Creek from 5:00 p.m. on 3 January to 2:15 p.m. on 7 January 2011.

into the stream channel and raises stream water temperature ahead of the daily high discharge meltwater pulse. The relative compositional consistency of Von Guerard on a daily basis over the course of a summer flow season (Tables 3 and 6) thus reflects regulation by its hyporheic zone, where water is introduced into transient storage during times of high streamflow and then has an extended opportunity for water-sediment interaction and pore water exchange at multiple spatial and temporal scales before returning to the main stream channel during the daily low-flow interval.

Times of high flow at both Andersen Creek and Von Guerard are dominated by solute-depleted glacial meltwater that has had little opportunity for water-streambed interaction and is well oxygenated because of its turbulent flow. As illustrated in Figure 14, there is a well-expressed negative co-variation of pH with DO for both streams, such that times of high DO are characterized by low pH and vice versa. For Andersen Creek, this effect is interpreted to reflect control by the biological processes within the cryoconite holes of the Canada Glacier. Photosynthesis by the diverse community of photoautotrophs within cryoconite holes consumes dissolved inorganic carbon and can be written as $H_2CO_3 \Leftrightarrow CH_2O + O_2$), which generates CO_2-depleted waters of elevated DO and leads to an increase in pH as carbonate equilibria respond to the change (Weber and Stumm, 1963). The alkaline water produced is then transmitted through the internal glacial drainage network that generates the proglacial stream but is degassed during this flow. This effect is most pronounced during intervals of baseflow, when the supraglacial streams that feed the internal hydrological network of the Canada Glacier are in a frozen state so that the proportional contribution of cryoconite hole water to the flow budget of the stream is maximized. The situation is more complex for Von Guerard because of its algal mat community and extensive hyporheic zone. Times of high pH at Von Guerard reflect photosynthesis by the benthic algal mats present in the middle reaches of the stream. Benthic mat photosynthesis will consume bicarbonate and generate oxygen, thus elevating pH and DO, the signature of which will be greatest during intervals of stream baseflow. Also, at times of high pH, particulate organic matter produced through biological activity at Von Guerard is introduced into the near-stream hyporheic zone (Ball et al., 2011; Cullis et al., 2014). This impact on stream chemistry is most significant during low-flow episodes, which is the same time that solute-enriched hyporheic zone waters are being returned to the main Von Guerard streamflow from transient storage. This water has a higher pH than is observed at Andersen Creek due to additional alkalinity generated by both acid neutralization reactions resulting in dissolution of carbonate and/or silicate minerals and the oxidation of organic material during its hyporheic zone residence.

SUMMARY AND CONCLUSIONS

The geochemistry of ephemeral streams that develop each year in the polar desert of Taylor Valley of Antarctica was presented through an analysis and discussion of their elemental composition at inter-annual, annual, and diurnal time scales. Solute loads of individual Taylor Valley streams are low, with long-term average TDS_c values ranging from only 20–164 µM, but they are important as chemical weathering over the flowpath of water is the only mechanism available to transport and disperse solutes, and more importantly nutrients, to the aquatic ecosystems of the McMurdo Dry Valley region (Deuerling et al., 2014).

Stream chemistry across Taylor Valley is spatially diverse, with stream geochemical character reflecting a complex interplay of multiple factors that vary among individual streams and include landscape position, proximity to source glaciers, interaction with seeps and water tracks, extent of hyporheic zone development, and biological loading. For example, streams closer to the coast in the Fryxell basin receive greater inputs of sea salt and marine aerosols than those in the Hoare and Bonney watersheds. Short streams adjacent to their source glaciers more directly reflect the chemical composition of their glacial meltwater sources than longer streams that have a greater opportunity for interaction with their more extensive hyporheic zones. High-gradient streams or stream reaches that are localized in the same place from year to year will have removed soluble salts from the streambed and adjacent hyporheic zone sediments to a greater extent than low gradient streams and reaches whose course changes from year to year. Streams with well-developed hyporheic zones provide a greater opportunity for transient storage and water-sediment interaction at multiple spatial and temporal scales than short streams with minimal hyporheic zones; and where seeps and water tracks intersect streams, their influence will be greater on small streams than on large streams.

The four short meltwater streams in the western Chad/Hoare basin that flow short distances over rocky beds from their glacial source to outlet lake are the most dilute streams in Taylor Valley, having an average TDS_c value of only 48 mg/L. In comparison, streams draining into Lake Fryxell and Lake Bonney carry significantly higher dissolved solid loads and have similar mean TDS_c values of 83 mg/L and 78 mg/L, respectively. Four components dominate the solute budgets of Taylor Valley streams—HCO_3^-, Cl^-, Ca^{2+}, and Na^+. Across Taylor Valley, streams are characterized by their consistent anionic geochemical fingerprint of $HCO_3 > Cl > SO_4$ but are divided in cation composition between 14 streams with $Ca > Na > Mg > K$ and 10 streams with $Na > Ca > Mg > K$. Proportions of HCO_3^- are greatest in short streams, and contents of Ca^{2+} are elevated over Na^+ in short streams, indicating that carbonate dissolution makes an important contribution to the chemical budget of short streams. The reverse can be the case for some long streams, where the leaching of soluble salts from sediments of the alluvial valley floor cover can be locally significant. Concentrations of other ionic constituents, SO_4^{2-}, Mg^{2-}, and K^+, are generally low in both short and long streams. Dissolved Si is present in all streams, attesting to silicate mineral weathering across the Taylor Valley landscape, with H_4SiO_4 concentrations highest in the long streams of the southeastern sector of Taylor Valley that drain from the Kukri Hills into Lake Fryxell and have significant flow distances through established hyporheic zones on the alluvial valley floor. Long streams with well-developed hyporheic zones display larger mean dissolved solute loads and exhibit larger ranges of dissolved species concentration but less compositional variability than their shorter counterparts with hyporheic zones of minimal extent. The transient storage of stream water within the hyporheic zone of longer streams, along with the diurnal flushing of its water-saturated sediment, facilitates water-mineral interaction and ionic exchange, the mineral dissolution that determines the effective upper limit of Taylor Valley stream solute loads.

Andersen Creek is a first-order glacial meltwater stream that flows in a narrow rocky channel for 1.4 km along the west side of the Canada Glacier to Lake Hoare and is representative of the group of 13 short streams that flow <1.5 km from source to gage. By contrast, the 4.9-km-long Von Guerard is a complex stream network that has a well-developed hyporheic zone and supports an abundant algal mat community in its middle-to-lower reaches and is representative of the group of 11 long streams 2–7 km in length. Inter-elemental concentration variations among ionic species are highly correlated for both streams but less so for Von Guerard than Andersen Creek. There is an inverse co-variation of ionic constituents with discharge for both streams that is slightly weaker for each species at Von Guerard than for Andersen Creek. These observations indicate that dilution during the daily high flow interval is the primary control on stream chemistry, with the influences of other processes most strongly manifest during baseflow episodes.

This work shows that hyporheic zone dynamics influence the stream water chemistry at both Von Guerard and Andersen Creek throughout the flow season, with stream water hyporheic zone interaction acting an intrinsic control on the hydrochemistry of Taylor Valley streams that occurs across a continuum of extent and duration that depends on individual stream physical setting. Hyporheic zone waters at both the Von Guerard and Andersen Creek display higher TDS_c values and elevated constituent concentrations than their respective streams. Hyporheic zone waters at Von Guerard exhibited less compositional variation than at Andersen Creek. No consistent spatial pattern of concentration variation was observed between the in-stream and near-stream hyporheic zones at Andersen Creek, whereas Von Guerard hyporheic zone waters displayed higher solute concentrations at greater distance from the stream channel. Although hyporheic zones are more chemically enriched than their associated stream waters, they are small and of limited areal extent at short streams like Andersen Creek and, therefore, exert only limited influence on overall stream composition. However, the limited hyporheic zone development around small streams can lead these streams to be more readily affected by occasional interaction with subsurface seeps. For larger, longer, and warmer streams like Von Guerard, where water infiltration in adjacent stream sediment is greater and produces extensive hyporheic zones that are highly dynamic and expand and contract in spatial extent over the course of a summer flow season, the opportunity is provided for longer contact times of water with soluble salts, carbonates, and silicate minerals during transient soil zone storage at daily to annual time scales. For these streams, return flow from hyporheic zone storage can provide the overall majority of stream water during an entire summer season and act as a determinant of the overall annual hydrochemical budget of larger streams and, therefore, as the ultimate control on the composition of meltwater to the central valley lakes.

Diurnal variations measured at high temporal resolution provide insight into process controls on stream chemistry in the McMurdo Dry Valley region. Two diurnal sampling studies were undertaken at Von Guerard and Andersen Creek during the summer flow season of 2010–2011, the first a day-long sampling at hourly intervals at the beginning of the flow season followed by a second 3–4 day sampling conducted at 4-hourly intervals in the middle of the flow season. Solute loads of Von Guerard and Andersen Creek during the 4-day sampling interval are comparable to those of other streams across the McMurdo Dry Valley region during the austral summer of 2010–2011 and fall within the historic ranges documented for Taylor Valley streams, but distinctly different solute concentrations and diurnal patterns of variation were observed at the two streams. Andersen Creek exhibited lower ionic concentrations and more compositional variability than Von Guerard, with concentration variations for Von Guerard comparable to those recorded for this stream over the entire summer season whereas those at Andersen Creek were somewhat above the seasonal average. The differences observed in stream chemistry and species variation of the two streams is explained in terms of influences from a local subsurface seep and Canada Glacier cryoconite hole water to baseflow at Andersen Creek, whereas return flow from transient hyporheic zone storage regulates baseflow solute composition at Von Guerard. At high flow, compositions at both streams are dominated by low solute meltwater from their glacial source. For Andersen Creek, streamflow throughout the diurnal cycle directly reflects mixing in variable proportions of input water from an intersecting subsurface seep plus that from different types of Canada Glacier meltwater, i.e., that derived from supraglacial streams, bulk ice melting, and cryoconite holes. Once in Andersen Creek, this proglacial water is largely unmodified during subsequent channel flow to Lake Hoare except during local episodes of high temperature when it may be influenced by localized saline seepage produced by the melting of subsurface permafrost. In contrast, Von Guerard chemistry is affected during baseflow both by the biological activity of the benthic algal mat community present in its middle reaches and return flow from water in transient storage within its extensive and structurally complex hyporheic zone. As flow in Von Guerard diminishes toward its daily minimum, water equilibrated in the higher temperature portions of the hyporheic zone contributes return flow to the stream channel and raises stream water temperature ahead of the daily high discharge meltwater pulse. The progressive downstream increase in dissolved constituent concentrations observed for the middle to lower reaches of Von Guerard twice during the flow season reflects the return of solute-enriched hyporheic zone water to the main stream channel along its flow path, whereas the tendency at Andersen Creek for a downstream decrease in solute loading along its course is a consequence of the continuous addition of meltwater from the adjacent Canada Glacier. The relative compositional consistency of Von Guerard chemistry over the summer flow season reflects chemostatic regulation, where water in transient storage introduced during times of high streamflow has an extended opportunity for water-sediment interaction, silicate mineral dissolution, and pore water exchange at multiple spatial and temporal scales before returning to the main stream channel during the daily low-flow interval.

A final consequence of this work is the new insight gained regarding the compositional evolution of McMurdo Dry Valley region stream chemistry over the course of an austral summer flow season. As illustrated in Figure 8, the first streamflow of the melt season acquires high solute loads as aerosol and particulate deposition onto the soil surface over the previous dry interval are leached and highly soluble salts deposited within the active zone at the end of previous flow season are dissolved. At Von Guerard, the highest solute loadings of the entire 2010–2011 flow season were recorded at this time. After this short interval, streams become deficient in solutes through the next phase of the season, when flow volumes increase in response to progressively larger amounts of daily glacial meltwater production. Hyporheic zones are established around streams during this time, and at larger streams they continually expand throughout the flow season, driving increasing solute loads as soluble constituents are dissolved from newly wetted soil, as observed at Von Guerard. Subsurface seeps and water tracks become active during the height of the summer melt season as the active zone is warmed to depth. These features can intersect with stream hyporheic zones and impact their chemistry, as inferred at Andersen Creek, where solute loadings observed during a 10-day period in early January at the height of summer exceeded those at the beginning of the flow season. Finally, when flow volumes decrease as the summer melt season ends, stream waters again become solute-enriched. These waters are trapped in the pore space of wetted soil, which becomes even more solute-enriched through evaporation and daily freeze-thaw cycling that is increasingly dominated by freezing. This, together with the end-of-season freeze up of the active zone, leads to the widespread precipitation of soluble salts within the wetted soil around streams, water tracks, and subsurface seeps, conditioning the McMurdo Dry Valley region soil system for next year's summer melt season.

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