Editor Dr. Robert Bingham,

Please see below our reply to reviewers. The text of the review is in italics or response is in plain text.

Reviewer 1

General overview

This is an interesting study looking at the temporal variation in the hydrochemistry of a sizeable glacial catchment in SW Greenland. On the downside, there is relatively little data – only four days of coupled relative discharge and chemical composition data, with no absolute discharge data. To be fair, this is clearly a logistically challenging site to work in, with no fixed points to allow reliable continuous data logger monitoring, and even limited robust time series data from such a large catchment is worthwhile. This paper is building on their recent Geology paper 'Chemical weathering under the Greenland Ice Sheet', which examined the bulk chemistry of a series of boreholes waters across the catchment.

We thank the reviewer for their interest in our study. We felt that although the data record presented is relatively short, it is still of interest to the broader community, both in that it presents novel methods for assessing relative discharge and in the unusual features of the record that are observed.

The authors do a commendable job of attempting to maximize the interpretation of the limited data set through the use of time lapse photography. The principal conclusion is that there is a phase shift between relative discharge and solute concentration, perhaps best explained by the expansion of a distributed subglacial hydrologic network into seldom accessed regions during high flow. This conclusion appears intuitively reasonable, although I have some reservations that need to be addressed. My key concern is whether the relative discharge measurements are robust enough given relatively poorly constrained potential variations in water depth and water velocity (see major points below).

Some of the objections in the specific major points section (below) are valid and we have addressed the corresponding uncertainties in the revised version of the manuscript. However, we feel strongly that our photographic record is robust in assessing relative discharge. The reviewer's main objections focus on the relatively few and imprecise velocity measurements. We agree that it would have been wise to assess velocity more frequently. However, the doubling of the width of the active channe over the course of a day is a more important signal than velocity. A well-established property of braided streams in unconsolidated fluvial sediment is that they expand and contract. Without changes in depth or gradient, changes in velocity are not possible. Furthermore, if there were velocity changes that we failed to observe, we would expect the higher flow periods to have higher velocities. This would accentuate the change in relative discharge that we observed, not diminish it.

Major specific points

Lines 159-162 – you base one of your major conclusions on the assumption that the width of the active channel is proportional to discharge. This is based on the assumptions that a) water velocity doesn't change, and b) water depth doesn't change (line 204). I have the following concerns/questions with this approach:

a) You state that your velocity measurements were measured only in the first two days only of the sampling period – from reading the methods, this would appear to be a period when you didn't assess discharge through photography. Since you do not have paired velocity (from surface object movement)-relative discharge measurements (from photography), how can you be sure that your conclusion that velocity does not change during the crucial last 4 day period of study is robust? (line 204; a critical underlying assumption for assuming active channel width is proportional to relative discharge).

Though we did not systematically photograph the stream from a consistent vantage point during the first two days of the study, we did still take plenty of photographs and field notes about the stream's behavior. These qualitative observations support that conclusion that the stream's behavior is consistent between the first two and later four days of the study. I.e. the naled is exposed and covered, and the width of the active channel grows and shrinks similarly over both periods. We have modified both the methods and results to discuss this qualitative similarity between the periods in the text. (Lines 141 and 231)

Particularly as the initial 2 day period was when the naled was completely covered in water hence discharge likely anomalously higher than remainder of study (or bedload sediment depth higher).

The reviewer's impression that the naled was covered for the entire first two days of the study is incorrect. (I do not know what portion of the text gave that impression.)

b) Line 159-162 – you need to give more details of your methods here. How many repeats of surface velocity measurements were made? From results you state 6 total measurements? (this doesn't seem a lot to base your conclusions on over the whole period of study). What were the 'other objects' in the water that you use as velocity indicators? I'd also question the validity of using ice blocks as reliable relative velocity indicators – could they not become snagged by debris in river, or velocity altered by differences in wind direction and speed, position in channel etc? You also need to state that the cross sectional normalized flow rate is likely to be substantially different from the surface velocity, particularly when using non neutrally buoyant objects.

We have now described our method of timing the stream's surface flow in greater detail (line 136).

c) You also state there is no change in depth in the river, although you also state that there is considerable mobility of sediment with collapsing banks, and scouring and deposition of sediment. Surely the assumption of constant river depth (line 204) should be viewed as a guestimate?

We have rewritten the language to better reflect the uncertainty (line 220)

Line 299-301 – given the large uncertainties in relative discharge measurements (see above), I don't think you can make a quantitative statement that the discharge variation is substantially larger than the variation in concentration of dissolved solutes – though fair to say that the likely width of the active channel roughly doubles.

This statement has been removed.

Other specific/technical points Line 8 – would be more correct to state that there are 4 days of continuous relative discharge and hydrochemical data

Text has now been added to clarify that only four of those days had measurements based on repeat photography. During the first two days, we attempted to use velocity and a stage pole. This was unsuccessful for reasons discussed on lines 114-115.

Line 11/12 – don't need to state that element and ions were measured in lab in abstract (plus you also measured suspended sed weights in lab, and

All measurements employed in the study now appear on a single list (without discussion of which are lab and which are field).

Line 17/18 - 1'd omit this sentence from abstract – it is based on the prior season's discharge from a single supraglacial stream. Worth mentioning in main text, but not strong enough for abstract.

The sentence has been removed.

Line 56 – would be worth referencing Wadham et al Global Biogeoch Cycl 'Size Matters' article here

The Wadham et al. citation is appropriate here and has been added.

Line $93 - \text{need to either reference this subjective number of } 500 \, \text{m} 3s-1 \text{ to something}$ (visually, similar to observed discharge at x, which has a discharge of x) or omit.

We have modified the statement to be more qualitative and added referenced the quantitative measurements made in the Watson River.

Line 110 – what kind of bottle, Nalgene PP?, was it cleaned, rinsed with sample etc? how long was pole?

More detail about the bottle, pole, and sample rinsing is now included (Line 169)

Line 120-0.1 um nylon filters seem an odd choice – most studies use 0.2 um or 0.45 um, why were these chosen? What filtration apparatus was used, Nalgene? Were procedural blanks (e.g. using MQ water) carried out, what were these blank values and how did they compare to instrument detection limits?

Our choice to use such fine filters came from concern that colloidal sized particles (from glacial comminution) were able to pass through larger filters. However, we feel that a discussion of this point is beyond the scope of the paper. We now discuss procedural blanks (line 191).

Line 126 – pH is always tough to accurately measure in low conductivity glacial waters. Please give further details – was 2 or 3 point calibration used, how long was pH probe left to stabilize prior to reading? Two decimal points for pH in Table 1 seems v optimistic.

This is now discussed in lines 186.

Line 128 – please state precisions and detection limits here, ditto line 130

Does the reviewer intend for us to list the lower limits of detection for all analyzed elements in the manuscript text? I don't believe this is customary.

Line 130 – what temp were filters dried, and for how long?

This is now in the manuscript (line 192)

Line 176 – typo, should be gauge

Fixed.

Line 176 to 178. What was the comparative weather like during the 6 day main study water sampling? To what depth into ice interior had snow line retreated to during both seasons – the outlet has a large catchment, and snow cover will have a major impact on the timing/magnitude of discharge runoff.

We now discuss the temperature during the study period on lines 166-168. We discuss the comparability of the ablation seasons in lines 150-152. As it turns out, the total progress of ablation was comparable between the two field seasons. The 2012 data are from earlier in the season, but from a year of extraordinary melt.

Line 182 – you start with discharge results. You should ideally be consistent with the order of methods section – perhaps best to start methods with discharge.

We have reordered the methods section to mirror the results section.

Line 200 – you need to put in these calculations, and state assumptions

We added a parenthetical explaining the basic concept (line 216). We feel that the equation sufficiently well known that further elaboration is not necessary.

Line 240 – how were lab TDS calculated: from summing inorganic ions, or by measurement using conductivity/TDS meter?

The text now reads "sum of laboratory measured inorganic ions."

Line 343 – should put relative discharge, not just discharge – also see major points

The word "relative" has been added.

Line 343 – you only measured relative discharge over 6 days, not four

The reference to six days has been removed from the sentence.

Line 344-347 – given many uncertainties in measuring relative discharge, I think this statement is too strong

We have replaced the word "show" with "suggest" to indicate greater uncertainty.

Table 1 – there are too many decimal points – I would have thought one decimal point is sufficient for most (though need to compare to precision of analyses). Also, need to put charges on anions to be consistent with main text. Plus better to have field alkalinity and calculated alkalinity in adjacent columns to aid comparison.

We have dropped the second decimal on everything but the suspended sediment analysis and made the other requested changes.

Figure 2 – these were too small in my printed copy to see properly. Please make photos larger, they are a key component of the study

We have increased the size of the figure and zoomed in most of the images to enlarge the most relevant details.

Figure 3 – Rather than having smoothed lines for min/max discharge, put on hourly points (or as well)

It seemed inappropriate to actually label figure 3a with hourly points from figure 3b, as the two datasets are from different time periods. The smoothed max-min curves are meant to represent the range suggested by the combination of qualitative and quantitative observations discussed in the text. The figure caption has been modified to reflect this.

Reviewer 2 (Bingham):

This paper provides a relatively high-resolution record of hydrochemistry measurements obtained just in front of the subglacial outlet of a western Greenland glacier over 6 days in July 2013. The record is primarily compared with discharge as assessed with time-lapse photography. The authors use these data to infer properties of the subglacial drainage system upstream from the terminus, and suggest that the lack of an inverse relationship between discharge and solute concentrations could be indicative of subglacial water accessing a linked-cavity system during peak discharge and being effective at drawing solutes from these cavities during the falling limb. The paper presents a useful new dataset on subglacial hydrochemistry which was clearly hard won, albeit covers rather a short period (6 days, albeit with 3 hour increments). The use of time-lapse photography to obtain a measure of relative discharge is a neat concept for overcoming the difficulties of measuring stage in such an active environment. So I think that ultimately the authors present some good material here.

We thank Dr. Bingham for his interest in our data set.

However, in its current form, I did not find the discussion of the data especially insightful or even especially novel. In essence, I feel the authors have to rewrite the discussion for the paper significantly to make a convincing case that the paper is presenting a novel advance. At the moment, because the paper is based on rather limited data, I think that approach has to involve providing a far more comprehensive

grounding of the ideas proposed here against what has, or they might argue has not, been interpreted from elsewhere.

My comments below concern the Discussion section (though some wider referencing and context would also benefit the introduction). I also made some minor comments throughout the paper (not including the Discussion/Conclusions) in the attached supplement.

We have revised the introduction and discussion to better reference the wide range of contexts in which hysteresis between solute flux and discharge is observed, including non-glacial settings. Whereas gradual increases solute flux during waxing flow may been observed in a wide range of contexts, we feel that the observed spikes during waning flow are in fact novel. The only previous study that (to our knowledge) has reported such behavior in a glacial context is the Anderson and others paper cited in the introduction. And in that study, the phenomenon occurred on a multi-day timescale, whereas it occurred on an hourly scale here.

Discussion Given the precariousness of the discharge results (I do have sympathy; I know all about the challenges of getting these data), I'd recommend the discussion explicitly focuses on the hydrochemistry variations, albeit using some of the qualitative discharge observations as context (i.e. I suggest excising Section 5.1). I then think you should partition the discussion into subsections which might broadly be described as (i) synthesise the main finding here, i.e. midsummer lag observed between hydrochemistry and discharge; and propose the conceptual model that water accesses distributed system on falling limb; (ii) compare this model comprehensively with findings/suggested interpretations of subglacial hydrological behaviour from other glacial systems where hydrology and/or hydrochemistry of meltwater have been observed.

We have rewritten the first paragraph of section 5.2 to discuss differences and similarities with other hydrological systems. We felt it was necessary to keep section 5.1 most because the Smith and others paper argued against any diurnal changes in discharge at Isunnguata Sermia, and our study refutes that.

I think the single biggest failing of the paper right now is that it doesn't adequately reference many other relevant studies, and therefore much of the context for justifying the discussion here is missing. For example, I'd say it should be well known from a number of studies of the hydrology of Greenland's outlets (e.g. from the Edinburgh and Bristol groups), and even large polythermal glaciers (Skidmore and Sharp, 1999, Annals of Glaciology) that the larger the catchment, the less likely one is to observe an "alpine-style" inverse relationship between solute concentration and discharge. Similarly, the above groups, and others, have acquired datasets that evince significant subglacial drainage system evolution as the melt season progresses many km upstream of outlet portals (e.g. Bartholomew et al., 2010, Nature Geoscience; 2011, EPSL) — and you'll see in Bingham et al. (2006; Earth Surface Proc. Landforms) evidence that by late July an Arctic subglacial system at similar latitude to your study area can be channelized, but discharge still accesses the distributed (your "linked-cavity") system at times of exceptional melt inputs. If you're going to entitle the paper "gives insight into subglacial conditions" then I think the insight only comes by making a much more comprehensive comparison with other relevant studies.

We now include the papers you suggest in our discussion section.

Finally, since one of the setups of the paper is to assess whether solute/discharge follows a positive/inverse/complex relationship, a comprehensive background for this (albeit pre most Greenland

hydrology studies) is given by G.H. Brown (2002) Glacier meltwater hydrochemistry, Applied Geochemistry, 17, 855-883.

The Brown paper is now cited in the introduction.

Please also note the supplement to this comment: http://www.the-cryosphere-discuss.net/tc-2016-137/tc-2016-137-RC2-supplement.pdf Interactive comment on The Cryosphere Discuss., doi:10.5194/tc-2016-137

Most of the annotations on the PDF have be implemented as requested.

Combined diurnal variations of discharge and hydrochemistry of the Isunnguata Sermia

outlet-of the, Greenland Ice Sheet-give insight on subglacial conditions

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Abstract

In order to examine daily cycles in meltwater routing and storage in the Isunnuguatalsunnguata Sermia outlet of the Greenland Ice Sheet, variationyariations in outlet stream discharge and in major element hydrochemistry were assessed over a six day period in July, 2013. DischargeOver four days, discharge was assessed from hourly photography of the outlet from multiple vantages, including where mid-stream naled ice provided a natural gauge. pH, electrical conductivity, suspended sediment, and alkalinitymajor element and anion chemistry were measured in samples of stream water collected every three hours. Element and ion concentrations were subsequently measured in a laboratory setting.

Photography and stream observations reveal that although river width and stage have only slight diurnal variation, there are large <u>diurnal</u> changes in discharge shown <u>inby</u> the <u>portion doubling in width</u> of <u>what we term</u> the <u>width "active channel"</u>, <u>which is</u> characterized by <u>large</u> standing waves and fast flow. Width of this active channel approximately doubles over a diurnal cycle. Together with changes in flow over the naled, these features allow an observationally based relative record of stream discharge in this unconstrained alluvial setting. Peaks in discharge were offset by 3-7 hours from peak melt of the interior ice surface.

Concentration The concentration of dissolved solutes follows a sinusoidal diurnal cycle, except for large and variable increases in dissolved solutes during the stream's waning flow. Diurnal changes in solute concentration average 31% of the base value. Diurnal solute concentration Solute concentrations vary by ~30% between diurnal minima and maxima. Discharge maxima and minima lag peak and minimum

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streamtemperature and surface melt by 3-7 hours; diurnal solute concentration minima and maxima lag discharge by 3-6 hours.

This phase shift between discharge and solute concentration suggests that during high flow, water is either encountering more rock material or is stored in longer contact with rock material. We suggest that expansion of a distributed subglacial hydrologic network into seldom accessed regions during high flow could account for these phenomena, and for a spike of partial silicate reaction products during waning flow, which itself suggests a pressure threshold-triggered release of stored water.

32 1. Introduction

Dissolved load in glacial outlet streams has long been employed as a metric for assessing waterrock interactions occurring beneath glaciers and ice sheets. Glacierized basins have comparable dissolved
loads to non-glacial rivers, but are enriched in mobile cations and depleted in Si (Anderson et al., 1997).

ChemistryThe chemistry of glacial water typically suggests that observed solute concentrations are
reached due to presence of reactive accessory minerals and fresh mineral surfaces in glacial sediments
(Drever and Hurcomb, 1986). Dissolved load is therefore linked to physical erosion in subglacial
environments (Anderson, 2005). Dissolved load is also indicative of the degree to which atmospheric gases
have been sequestered by chemical processes in the subglacial environment (Hodson et al., 2000).

Diurnal variation of solute concentration is a potential indicator of meltwater routing and storage—Solute concentration is controlled by total water-rock contact during water residence time in the subglacial environment and by (e.g. Brown, 2002). Solute concentration is controlled by total water-rock contact over the water residence time in the subglacial environment and by the reactivity of minerals contacted by the water. In particular, two end member cases are expected: if dilution produces an inverse relationship between discharge and solute concentration, minimal changes in water-rock interaction over

time are suggested, whereas if increased discharge is coupled to increased solute concentration, diurnal changes in the processes of water-rock interaction or storage are suggested.

StudiesSeveral studies of small alpine glaciers have typically found solute concentration and discharge to vary inversely, with rising discharges corresponding to falling concentrations of dissolved solutes (Collins, 1995; Hindshaw et al., 2011; Tranter et al., 1993)(e.g. Collins, 1995; Hindshaw et al., 2011; Tranter et al., 1993); Tranter and Raiswell, 1991). Ions produced by saturation limited reactions, such as calcite dissolution, can show increased load with discharge, but typically with diminished concentration per water volume (Mitchell and Brown, 2007). Elements that are limited by factors such as the rate of sorption/desorption will have constant flux levels and will only be diluted by increased water flow (Mitchell and Brown, 2007). ResultantlyConsequently, correlations between discharge and dissolved load are typically weak (Collins and MacDonald, 2004)(Collins and MacDonald, 2004). These dilution relationships have been attributed to the dominance of conduits, increased water flow will expand the size of thesethe conduits and increase the speed of through-flow but will have a minimal impact on the area of water-bed contact (Nye, 1976; Röthlisberger, 1972).

Studies of larger glacial systems suggest more complex water rock interactions. In Larger glacial systems have more complex water-rock interactions (e.g. Wadham et al., 2010), and have frequently demonstrated more complex hysteresis in the relationship between discharge and solute concentration.

At the outlet of a large glacierized basin in SE Alaska, increases in dissolved load lag spikes in discharge by several days (Anderson et al., 2003). Anderson and others attribute this to storage of water in a distributed system only released during the waning stages of flow. In distributed or linked-cavity flow, increased discharge allows flowing water to spread out across the glacier's bed and thereby increase the area of water-bed contact (Humphrey, 1987; Kamb, 1987). Time series data from the Watson River, near Kangerlussuaq, West Greenland, show out of phase variation in discharge and solute concentration, with

maximum daily solute concentrations occurring as on the rising limb of the discharge is rising and minima occurring as discharge is fallinghydrograph (Yde et al., 2014). However, on the scale of the melt season as a whole, Yde and others find a strong inverse correlation between discharge and solute concentration, which they attribute to conduits carrying a substantially higher portion of the meltwater flow than the distributed subglacial system. Lags between minimum discharge and peak solute concentrations are have also been observed atin karst dominated systems, such as Tsanfleuron Glacier, Swiss Alps, where flux from groundwater is hydrologically important (Zeng et al., 2012) (Zeng et al., 2012). Such lags are also observed in non-glacial streams and have long been understood to result from the mixing of groundwater, soil water, and surface runoff —each having a unique response time to rainfall events (e.g. Evans and Davies, 1998). The existence of a range of distributed and channelized flow mechanisms under larger ice bodies similarly suggests a range of response times to input from surface melt water.

Seven measurements of dissolved solute chemistry taken from samples collected over the course of 2 days in 2011 at the terminus of Insunnguata Sermia, a major Iand-terminating west Greenland outlet glacier, potentially show a direct relationship between solute concentration and discharge (Graly et al., 2014; Landowski, 2012). In this limited time series, solute concentration appears to peak at midafternoon, while discharge is high, and be minimal in the early morning hours, with total variation of <20%. To further whether a direct relationship exists between discharge and solute concentration exists in the Isunnguata Sermia outlet of the western Greenland Ice Sheet, we returned to the same site for a six day period of the summer of 2013, collecting 8 samples per day for chemical analysis.

92 2. Field site

Water samples were collected from the terminus of the Isunnguata Sermia, a major land-terminating outlet of the western-Greenland Ice Sheet (Figure 1). The outlet glacier Isunnguata Sermia

occupies a deeply cut glacial valley, with surrounding hilltops >400 m above sea level. Deep, glacially-carved trenches continue under the ice sheet for more than 20 km into the interior, withwhere ice depths of greater than reach >1,000 m (Jezek et al., 2013)(Jezek et al., 2013). The Isunnugata Sermia outlet has a catchment that encompasses >2,400 km² of the ablation zone, making it one of the largest regional subglacial drainage basins in Western Greenland (Palmer et al., 2011)(Palmer et al., 2011). RegionalThe regional geology consists of primarily of Paleoproterozoic gneisses and granitoids (van Gool et al., 2002)(van Gool et al., 2002). The Isunnguata Sermia outlet is located 25 km from the town of Kangerlussuaq. It is the next outlet to the north of the Russell Glacier and feeds a separate glacial river system from the Watson River, providing a silicate bedrock substrate for subglacial chemistry.

Water emerges from a single location on the south side of Isunnguata Sermia's terminus front ~30m30 m above sea-level (Figure 1) and traverses a broad, >100 km long sandur to the fjord. Discharge of pressurized subglacial water creates a large upwelling capable of expelling water multiple meters into the air and, although no fully quantitative measurement could be made, peak discharge was estimated to exceed 500 m³s⁻¹-in the hundreds of m³s⁻¹, as is consistent with typical summer discharge in the nearby Watson River (Hasholt et al., 2013). Ice-cored moraines and frozen outwash shape the course of outlet waters. On the sandur, frozen outwash channels the water into a single thread, although the large sediment load creates rapidly changing channel and bed geometry. Near the terminus, the frozen outwash of the sandur is elevated ~2-4 meters above the discharging stream. The main stream is also fed by minor ice surface melt streams. A small stream that runs along the south lateral margin of the glacier joins the main terminal outlet stream just below the primary upwelling site.

This work was performed in the contextas part of several othera wider program of coordinated studies of the Isunnguata Sermia terminus region. Hot water boreholes along a transect from the outlet to 40 km in the interiorupstream have provided data regarding water pressure (Meierbachtol et al., 2013), ice temperature (Harrington et al., 2015), subglacial water chemistry (Graly et al., 2014), and mass balance

between subglacial sediment and rock (Graly et al., 2016). More limited datasets from Isunnguata Sermia's terminal and lateral outlets were reported for the 2010, 2011, and 2012 seasons (Graly et al., 2014). The work reported here is based on samples and data collected over a 6 day period from July 16th to July 21st, 2013.

3. Methods

3.1 Water Sampling

Water sampling began at 8:00 hours local time on July 16th, 2013 and continued in 3 hour increments through 20:00 hours on July 21st, 2013. Samples were collected by lowering a liter bottle attached to a pole into discharging waters within 400 m of the subglacial upwelling. During July 16th and July 17th, samples were collected from the south bank of the outlet stream from the banks at the beginning of the outwash plain (Figure 1). During July 17th, the main course of the river shifted so that location had diminished flow and an emerging bank channeled waters from the lateral side stream to the location. Commencing at 14:00 hours on July 18th, sampling was relocated above the lateral side stream on the banks of the terminal moraine (Figure 1). The sampling location was not subsequently changed. Excepting periods where the emerging bank channeled lateral stream water to the first location, both locations sampled water from the main subglacial outlet and should produce comparable results.

Upon collection, 125 ml of water sample were pumped through 0.1 μm nylon filters, with filtered water and filter papers saved for laboratory analyses. A colorimetric alkalinity test, a conductivity measurement, and a pH measurement were performed on the remaining unfiltered sample. Alkalinity tests were performed with a Hach Model ΛL ΛP alkalinity test kit. Results of field alkalinity tests were only accurate to 25 μM. Alkalinity was therefore also calculated by charge balance from the other measured ions. pH measurements and conductivity measurements were performed with Beckman-Coulter Φ460 multi-parameter meter, pH was measured using a low ionic strength probe.

Subsequent water analyses were performed in the University of Wyoming Aqueous Geochemistry

Lab. Concentrations of Si, Ca, Mg, Na, and K were measured on a Perkin Elmer Elan 6000 inductively

coupled plasma quadrupole mass spectrometer (ICP MS). Concentrations of SQ₄², Cl², NQ₂², and Fl² were

measured on a Dionex ICS 500 ion chromatograph. The filter papers were dried and weighed to assess

suspended load.

3.2 Discharge

Discharge measurements of the outlet were difficult to obtain. There is no exposed bedrock near the stream to act either as an elevation reference or to stabilize the river bed. Obtaining accurate cross profiles of the stream was prohibitively dangerous, with high flows, collapsing banks, and a considerable flux of mobile ice blocks. Attempts to install a stage pole were frustrated by considerable stage variation over time associated with cutting and filling of the riverstream bed and banks. Once the stream opens out from its restriction by remnant glacier ice near the upwelling, stage is poorly correlated with discharge. The stream instead scours sediment during the rising limb and deposits it on the trailing limb of the daily hydrograph. It was decided to assess only relative discharge. This was aided by repeat photography from two fixed locations.

Hourly stream photography began at 10:00 hours on July 18th and continuing through 20:00 hours on July 21st. From one vantage point, the central upwelling of subglacial water was photographed from the south, as it poured out from around the moraine. This vantage captured a ~1—meter—high, mid-channel naled formed from freezing of outlet waters during winter months. The naled was variably covered or exposed as discharge varied and acted as a stream gauge in this respect. This portion of the stream is restricted by frozen sediment and stream height is controlled by discharge.

A second vantage, from a rise above the south bank, captured a ~200m long stretch of the outlet stream. In this portion of the stream, increased discharge caused scour and expansion of the stream's

active channel. Photography allowed assessment of relative active channel width. Large waves and faster velocities are confined to this active channel, allowing fairly unambiguous, though qualitative, determination of which portions of an overhead photograph comprise the active channel. The distance between the upstream end of a persistent, mid-stream point bar and a distinct feature on the south shore was measured on each photograph (Figure 1). The length of the portion of this transect characterized by large waves and flow features was also measured, allowing for the calculation of the percentage fraction of the stream width contained by the active channel. On most of the photographs, the break between the large standing waves and the surrounding quiescent flow was unambiguous. The second vantage also allowed assessment of flow state and Froude number from the presence of features such as standing waves.

During the first two days of the sampling period, stream surface velocity was measured by repeated timing the motion of floating ice and other stream surface features down a 100 m section of the stream-repeatedly running in pace with the movement of the stream surface along a 100 m stretch of the sandur. This was accomplished by observing visually consistent mobile features of the stream, such as lineations within wave forms and small pieces of floating ice. Measurements were taken during morning, afternoon, and evening stages to assess variation in velocity associated with high and low flow. During this earlier period, changes in the width of the active channel and volume of the water pouring over the naled were also observed (though without systematic photography from a consistent vantage).

3.32 Interior Surface Melt

In order to compare variation in terminus discharge to melt in the surface interior, we are also including consider discharge measurements from an interior ice sheet surface stream. The stream was gauged during the summer une of 2012, so the data are not directly comparable to the measurements collected in 2013. However inasmuch as interior melt is primarily controlled by insolation, the stream's

variation likely represents a typical pattern for the timing and scaling of diurnal summer surface melt fluctuations. Coincidentally, the progression of the Greenland Ice Sheet melt season was fairly comparable between June 2012 and July 2013, with ablation rates of 6-10 Gt per day during both periods (Langen et al., 2013). The supraglacial stream was gauged during a period in which bare ice was melting, so water retention in snow did not affect its hydrology.

The surface stream was located at 67.2°N and 49.8°E, ~25 km from the terminal outlet. Stream height was gauged with a calibrated pole drilled into ice. Surface velocity was measured by timing floating ice along a course of known distance. Cross-sectional area was directly measured in the region where the gauge was emplaced and calibrated to gauge height. Transect slope was measured by pole and automatic level. Six measurements of surface velocity used to calculate an average Manning coefficient from the measured slope and hydraulic radius of the stream. Discharge was then calculated from change in gagegauge height. Stage height was measured every half hour or hour for a period from 11:30 6/June 18/12_2012 to 20:00 6/June 21/12_2012. During June 18th, 19th18, 19, and 20th20, sunny weather predominated; June 21th21 had rainy, cooler weather.

3.3 Water Sampling

Water sampling of Isunnguata Sermia's terminal outlet began at 8:00 hours local time on July 16, 2013 and continued in 3 hour increments through 20:00 hours on July 21, 2013. Temperatures in the interior ablation zone measured at PROMICE KAN M weather station stayed at ~0.5 positive degrees per day over July 16-18 and steadily rose to 1.3 positive degrees per day over July 19-21. Samples were collected by lowering a liter Nalgene polypropylene bottle attached to an adjustable-length pole into discharging waters within 400 m of the subglacial upwelling. The bottle was dipped and rinsed in flowing stream water prior to final sample collection. Samples were initially collected from the south bank of the outlet stream, from the banks at the beginning of the outwash plain (Figure 1; Site 1). During July 17, the

main course of the river shifted so that location had diminished flow and an emerging bank channeled waters from the lateral side stream to the location. Commencing at 14:00 hours on July 18, sampling was relocated above the lateral side stream on the banks of the terminal moraine (Figure 1; Site 2). The sampling location was not subsequently changed. Excepting periods where the emerging bank channeled lateral stream water to the first location, both locations sampled water from the main subglacial outlet and should produce comparable results.

Upon collection, 125 ml of each water sample were pumped through 0.1 μm nylon filters, with filtered water and filter papers saved for laboratory analyses. A colorimetric alkalinity test, a conductivity measurement, and a pH measurement were performed on the remaining unfiltered sample. Alkalinity tests were performed with a Hach Model AL-AP alkalinity test kit. Results of field alkalinity tests were only accurate to 25 μM. Alkalinity was therefore also calculated by charge balance from the other measured ions. pH measurements and conductivity measurements were performed with Beckman-Coulter Φ460 multi-parameter meter. pH was measured using a low ionic strength probe, with a three-point calibration employed daily.

Subsequent water analyses were performed in the University of Wyoming Aqueous Geochemistry

Lab. Concentrations of Si, Ca, Mg, Na, and K were measured on a Perkin Elmer Elan 6000 inductively

coupled plasma quadrupole mass spectrometer (ICP-MS). Concentrations of SO₄²⁻, Cl⁻, NO₃⁻, and Fl⁻ were

measured on a Dionex ICS 500 ion chromatograph. Element and ion analyses were measured together

with procedural blanks, which were consistently measured below the lower limits of detection. The filter

papers were dried overnight at 85° C and weighed to assess suspended load.

4. Results

4.1 Discharge

Over the four days during which repeat photographic observations were made, photographs of the naled show consistent minima at 8:00 hours, with the naled is mostly exposed, and a small volume of water overtopping a portion of the ice body (Figure 2). During the first two days of observationOn July 18 and 19, the naled was completely covered by flowing water from 19:00 to 0:00 hours. On the third dayJuly 20, it was covered from 16:00 hours, and remained covered for the remainder of the study period.

Maximum discharge is harder to determine from observations of the naled alone. Once the naled is completely covered in water, visual interpretation of maximum flow is ambiguous. Some discrimination can be made based on the height of the covered naled feature compared to the surrounding waves and the angle at which the water pours over the naled (greater flows overtop the naled at a lower angle). From these features, maximum stream flow appearsappeared to occur at 21:00 hours on July 18 and 19 and

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Standing waves are observed at all flows (Figure 2), although substantial differences in wave and surface morphology were noted during waxing and waning phases, with rougher water in waning flow and smoother water in waxing flow. The roughness change may represent a change in the sediment load of the river between the erosive waxing stage and the depositional waning stage. The persistence of standing waves implies near critical flow conditions, or a Froude number approximately 1, for the entire study period. Measurements of stream velocity showed surface speeds of 2.86 ± 0.12 m/s (2σ , n=6). Variation in velocity between morning and evening stages was within measurement error. Based on calculations from a Froude number of 1, stream depths of 0.5 - 0.9 m are suggested; these depth estimates were supported by observing ice blocks rolling or bouncing down the flow. The lack of The lack of relationship between stage and discharge and velocity has been noted before in sediment laden glacial rivers (Humphrey and Raymond, 1994).

Field Code Changed

Since neither stream velocity nor depth change with discharge, variations in discharge are accommodated by changes in the width of the active channel. Based on calculations from a Froude number

of 1 (i.e. stream velocity squared is equal to stream depth times acceleration from gravity) and assuming a total velocity within 20% of surface velocity, stream depths of 0.5 - 0.9 m are suggested. These depth estimates were supported by observing ice blocks rolling or bouncing down the flow. The active channel's approximately constant stream velocity and persistent standing waves suggest a fairly constant stream depth. Wide areas of shallow slow water remained present during low flows and the total surface area of the stream remained approximately constant. Pole probing of these shallow areas suggests 10 to 20 cm depths. Because the active channel has an order of magnitude greater discharge per transect meter than the stream's marginal areas and changes in active channel water velocity were not observed, we infer that the cross-sectional area of the active channel is the primary control on discharge. Rising discharge is accommodated by scouring on the margins of the active channel; falling discharge is accommodated by deposition.

Assessment of the active channel width <u>from repeated photography</u> shows substantial differences between morning hours (~5:00-10:00), where 20-30% of the stream is comprised of active channel characteristics, and late afternoon / evening hours (~18:00-0:00) where >40% of the stream is comprised of active channel characteristics. These observations are generally consistent with assessments of the height of water pouring over the naled (Figure 3). <u>Though repeated photography from a consistent vantage was not performed during the first two days of the study, field observations and photographs from that period show similar changes in the active channel width and naled overflow.</u>

4.2 Interior Surface Stream

The calculated Manning coefficient for the interior stream was 0.0117 ± 0.0018 (2σ). Discharge measured in the interior ice surface streamIts discharge varied by as much as an order of magnitude during the course of diurnal cycles, with low values as small as 0.3 m³s⁻¹ and high values greater than 3.5 m³s⁻¹ (Figure 3). Minimum stage heights consistently occurred around 4:00 hours. Maximum stage heights

consistently occurred at 14:00 or 15:00 hours. These data contrast with our observations of water pouring over the naled. The naled minimum occurred approximately 4 hours later than minimum of surface melt. The naled maximum occurred approximately 6 hours later than maximum surface melt. This delay is representative of the integration of the travel time delays from the entire glacier catchment.

291 4.3 Water Analyses

Sampled The sampled waters arewere generally chemically dilute, with 292±50 micromoles per liter dissolved solutes (Table 1). Ca iswas the dominant cation, followed by Na, K, and Mg (Figure 4). Mg abundances arewere an order of magnitude lower than the other major cations. Dissolved Si occursoccurred at comparable abundance to Na. Standard deviations of the mass spectrometer measurements were <1% of the measured value. Bicarbonate (measured as alkalinity) iswas the dominant anion. SO₄²⁻ and Cl⁻ are detected in all samples, but occur at an order of magnitude lower concentration. Trace amounts of NO₃⁻ and Fl⁻ were detected in some samples, at values an order of magnitude below SO₄²⁻ and Cl⁻ concentrations (Figure 4). On average, field alkalinity measurements exceedexceeded the alkalinity estimates from charge balance by 25 ± 14 μM (2σ). Some over-measurement in the field titration is expected, as the value is recorded at the level where the color tracer disappears (and therefore is a maximum compared to previous drop). Charge imbalance may also result from absorption of H⁺ particles to suspended sediment in unfiltered water. Field electrical conductivity measurements showshowed similar results to the sum of laboratory analyses measured inorganic ions (p<0.0001) (Figure 4). Suspended sediment concentration does did not show a consistent correlation or anti-correlation with dissolved load (Figure 4).

Relative<u>The relative</u> abundances of cation species <u>isare</u> comparable to measurements taken at the Isunnguata Sermia terminus in the summer of 2011 (Graly et al., 2014)(Graly et al., 2014). The SO₄²·/alkalinity ratios are diminished compared to those measured in 2011, but are comparable to those found

in samples collected in 2010 and 2012. The concentrations of suspended sediment are similar to those observed at nearby Leverett Glacier during the summer of 2010 (Cowton et al., 2012).

Field Code Changed

When normalized to average concentration, the magnitude and timing of cation and silica concentration variation iswere highly consistent between species over time (Figure 5). Covariation of all cation and Si species is statistically significant with p<0.05. Covariations of K-Mg, K-Si, and Na-Si have p-values ranging from 0.01 to 0.05; all others are <0.0001. All cations and silica concentrations followfollowed a diurnal pattern, with higher concentrations present during morning and early afternoon hours and significantly lower concentrations present during later afternoon and evening hours. In several of the studied cycles, large changes in total concentration arewere limited to the 20:00 and 23:00 hours samples, which are substantially lower than the other samples collected throughout the day.

There are two major deviations from the diurnal pattern. The 11:00, 14:00, 17:00, and 20:00 samples from July 17th have17 had substantially lower solute concentrations than would be otherwise suggested by diurnal fluctuations observed elsewhere in the record. This corresponds with the period during which an emerging bank partially separated site 1 from the main channel allowing a surface-fed side stream to substantially dilute the water.

At 2:00 on July 20th 20, there iswas a >60% spike in total concentration of all cations. Similar, but smaller magnitude spikes arewere also present induring the 2:00 samples other four measured periods of July 19th and 21st and the July 16th 23:00 samples waning flow. The most clearly expressed largest of these spikes (July 20th and 21st) are substantially more expressed in Na and K concentrations than in Ca, Mg, or Si- (Figure 5). During the July 21st final measured overnight spike, the spike inelevated concentrations of Mg and Si appears to proceed the spike inpreceded those of Ca, Na, and K in that it appears during the previous sampling by a 3-hour measuring period. Large The large variability in the magnitude of these spikes suggests that the 3-hour sampling schedule was insufficiently frequent to characterize them entirely.

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Anions generally follow similar patterns, but with greater variability (Figure 4). In particular, Cladoes not co-vary with other ions toward the end of the record. The; the 2:00 spike on July 18th coincides with a drop in SO₄-concentration; the spike on the 20th 20 coincides with a drop in Claconcentration. SO₄SO₄²⁻ concentrations generally only increased very minimally increase during the waning flow spikes, and in one case declined. During the final spike, SO₄²⁻ rises during the 11:00 period, together with Mg and Si.

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Excluding these anomalies the spikes that occur during waning flow, the highest concentration of dissolved solids occurs at 11:00 on July 16th, 19th, 20th 16, 19, 20, and 21st 21 (Figure 5). On July 17th 17 and 18th 18, the 11:00 sample was likely diluted by the side stream (which was a significant component of flow to site 1 during that period). Concentration minima are reached at 23:00 hours on July 17th 17 through 20th 20. On July 16th 16, the minima minimum occurs in the 20:00 sample. The size of the diurnal variation varies from maximum solute concentration ranged between 22% to 49% of larger than the lowest value minimum concentration, with an average daily rangeyalue of 31 ± 9%.

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5. Discussion

5.1 Discharge and Outlet Stream Observations

Observations from oblique photography suggest large diurnal changes in discharge. Width The width of the active channel, with deeper faster water, approximately doubles in the course of the day (Figure 3b). An approximate doubling of discharge is also suggested by observations of the midstream naled. The naled is of comparable scale to the depth of the stream (both order of 1 meter). Its exposure during low flow and burial during high flow suggests a change in stage comparable to its height. At the naled site, increased width of active channel flow is restricted by ice. Increases in flow height at the naled location are therefore approximately equivalent to increases in active channel width downstream.

During high flows, diurnal increases in discharge of up to 50% of base value are observed in the Watson River at Kangerlussuaq, where a bridge over a narrow gorge has allowed for the construction of a reliable gauge (Hasholt et al., 2013)(Hasholt et al., 2013). As the Watson River is 20-30 km from its glacial outlet sources and integrates several independent glacial outlet streams, these diurnal cycles are likely muted compared to their expression at the ice margin. Larger diurnal changes are therefore expected directly at glacier outlet termini. Contrastingly, Smith and others . Contrastingly, Smith and others (2015)(2015) found minimal diurnal variation in discharge at Isunnguata Sermia terminus. However, as Smith and others estimated discharge based solely on the surface area of the outlet stream water, their analysis missed the variation in the width of the active channel and height of its flow over static features that we present. Based on our limited observational record, it appears that changes in discharge at the Isunnguata Sermia terminus are similar or larger in magnitude to those recorded at the Watson River.

5.2 Diurnal Changes in Solute Flux

The critical observation is that variability in the dissolved solute concentrations cannot be explained by dilution alone. First, the scale of discharge variation is substantially larger than variation in concentration of dissolved solutes. Approximate width of the main channel doubles during diurnal cycles, while concentrations of dissolved solutes only change by an average of 21 40% (Figure 5). Secondly, maximum and minimum solute concentrations are offset from minimum and maximum discharge. Such lags imply periods where solute concentration is increasing even as discharge rises and periods where solute concentration is falling even as discharge falls.

Periods of in-phase changes between discharge and solute concentration suggest that increased water flow is either stimulating increased water rock interaction or allowing for release of stored water (that has developed higher solute concentrations over longer residence times). While the single upwelling structure of the terminus of Isunnguata Sermia implies local channelized flow, observations of water

water residence time regions under high flow conditions.

Sudden The lag between relative discharge minima and maximum solute concentrations is similar to other glacial and non-glacial systems where waters of differing response times are merged into a single stream. Similar lags are observed when groundwater, soil water, and surface flow mix into a stream after a rainfall event (Evans and Davies, 1998). Substantial lags between discharge and solute flux are also observed where glacial melt mixes with groundwater in a karstic system (Zeng et al., 2012) and in the mixing of marginal melt streams with a subglacial pool in a polythermic setting (Skidmore and Sharp, 1999). Even in a small alpine system, observable chemical differences between the leading and lagging limbs of the discharge hydrograph have been attributed to mixing of englacial and subglacial waters (Tranter and Raiswell, 1991).

In the context of the Greenland Ice Sheet, periods of in-phase change between discharge and solute concentration are best explained by the flushing of a linked-cavity or other distributed hydrological system as hydraulic pressure rises. Seasonal changes in ice velocity in this sector of the Greenland ice sheet have been linked to a combination of distributed and channelized subglacial flow (Bartholomew et al., 2011). Dye-tracing of the hydrological connections between moulins and glacial outlets has also indicated a mixture of subglacial flow regimes (Chandler et al., 2013). Though the single upwelling structure of the terminus of Isunnguata Sermia implies locally channelized flow, observations of water pressures at interior sites (Meierbachtol et al., 2013) and hydrologic theory for low ice surface slopes (Werder et al., 2013) both suggest that much of the catchment interior has a distributed flow system.

<u>The sudden</u> increases in solute concentration during waning flow suggest that discharge from subglacial regions with a-high concentrations of dissolved solutes is triggered when a

threshold is reached. Multiple triggeringTo our knowledge, the release of stored water during waning flow has only been previously documented on a multiday scale (Anderson et al., 2003), whereas here it occurred as part of the diurnal melt cycle. For slow-moving, distributed subglacial water to be both flushed by rising hydraulic pressures and released from storage by falling hydraulic pressures, multiple subglacial flow paths or mechanisms are plausible must be operating simultaneously.

The contrast in solute chemistry between the long-wavelength increases in solute concentration (in which, all major chemical constituents respond comparably) and the waning flow spikes (in which Na, K, and alkalinity dominate) suggests differing subglacial environments and mechanisms. Na- and K-dominated waters likely form in settings where water-rock interactions occur only over a limited time, such that cation exchange occurs on fresh feldspar and mica surfaces, but complete silicate dissolution and clay precipitation does not occur (Blum and Stillings, 1995; Graly et al., 2014). The lack of constituents derived reactive accessory minerals such as pyrite (i.e. SO_4^{2-}) implies the waters were reacting with sediment that has been depleted of accessory minerals. Such accessory mineral depletion can occur if sediment residence time in the subglacial system is sufficiently long (Graly et al., 2014). Sampling of sediment beneath ice boreholes has shown the greatest chemical depletion in portions of the ice sheet most influenced by distributed flow (Graly et al., 2016).

This variation in water chemistry suggests that the spike of chemical solutes comes from water that has temporarily entered regions of distributed flow as a part of a diurnal cycle. Modeling of subglacial water pressures suggests that near the ice sheet margin, water flows from conduits to the distributed cavity system at high conduit water pressures and back to conduits at low pressures (Meierbachtol et al., 2013) (Meierbachtol et al., 2013). Solute The spikes in solute concentration spikes result from the crossing of a pressure threshold allowing that allows water stored during high flow to suddenly enter the glacial outlet system.

Solute concentration spikes might also be explained by creep closure of linked cavities that opened during high flow and expulsion of remaining solute-concentrated water. Anderson and others (2003) proposed a similar creep closure mechanism to explain increases in solute concentration during waning flow that occurred on a multiday scale in a mountain glacier setting. Following the Glenn-Nye relation, the rate of creep closure of ice scales to approximately the third power of effective pressure (Cuffey and Paterson, 2010). Differences in timing of these effects between ice sheets and mountain glaciers can therefore be explained by differences in ice thickness.

Relative dominance of Na and K in these spikes is consistent with water rock interactions occurring only over a limited time, such that cation exchange occurred on fresh feldspar and mica surfaces but complete silicate dissolution and clay precipitation did not (Blum and Stillings, 1995; Graly et al., 2014). Contrastingly, constituents associated with weathering of reactive accessory minerals such as pyrite and calcite (especially SO₄) are minimally expressed. This implies that the spikes' composition reflects waters that have rapidly passed through reactive sediment that is depleted of accessory minerals. Such accessory mineral depletion can occur if sediment residence time in the subglacial system is sufficiently long (Graly et al., 2014). Sampling of sediment beneath ice boreholes has shown the greatest chemical depletion in portions of the ice sheet most likely to be influenced by distributed flow (Graly et al., 2016). This suggests that the spike of chemical solutes comes from water that has temporarily entered regions of distributed flow as a part of a diurnal cycle.

6. Conclusions

A semi-quantitative <u>relative</u> discharge record can be constructed through hourly photographic monitoring of the static and dynamic features of a large, sediment laden glacial outlet stream. These assessments <u>showsuggest</u> large diurnal changes in discharge over the <u>six day</u> study period at the Isunnguata Sermia outlet of the Greenland Ice Sheet (c.f. Smith et al., 2015). Simultaneously collected

chemical measurements show substantially smaller fluctuation in dissolved load; thus this Greenland outlet glacier does not show the discharge-driven dilution of solute concentration that is common in smaller ice masses. Periods where dissolved solute concentration concentrations increase and decrease along with discharge, and abrupt and variable increases in solute concentration during waning flow imply that significant contributions to the solute load is made by changes to the routing and storage of meltwater in the subglacial system over the course of the day. In particular, these results indicate considerable diurnal exchange of water diurnally between the conduit and linked cavity drainage systems, as well as implying threshold pressure conditions for these exchanges.

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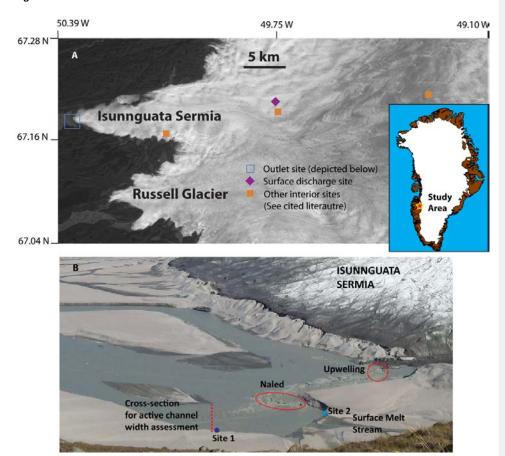
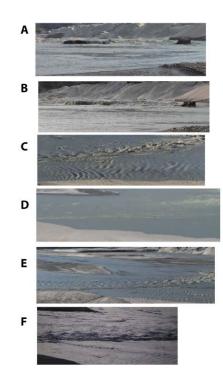


Figure 1. A) Location of the study area-on satellite imagery provided by polar geospatial datacenter. B) Overhead photograph of the study area (taken 7/22/13) with important July 2013 on an overlooking ridge, 400 m above and 900 m away from the stream. Important sampling and observational features are labeled. Samples were collected at site 1 from 10:00 hrs on 7/16/13 through 11:00 hours on 7/18/13. Samples were collected at site 2 from 14:00 hrs on 7/18/13 through 20:00 hrs on 7/22/13. Beginning at 10:00 hrs on 7/18/13, hourly photographs on the labeled naled and ~100 m cross-section were taken.



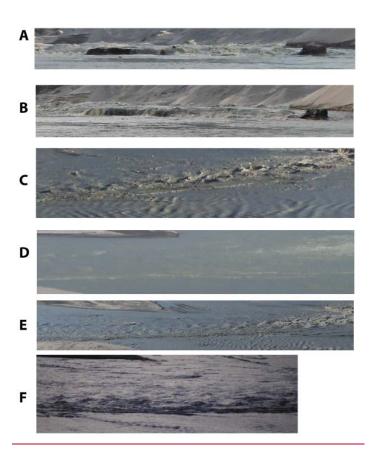


Figure 2. Photographs of typical flow patterns in the Isunnguata Sermia outlet. A) Midstream naled exposed at during low flow (8:00). B) Midstream naled covered during high flow (21:00). C-F show images of flow captures from the overhead vantage during low (8:00), waxing (14:00), high (21:00) and waning (0:00) stages. Waxing and waning stages show different wave morphology but maintain standing wave features.

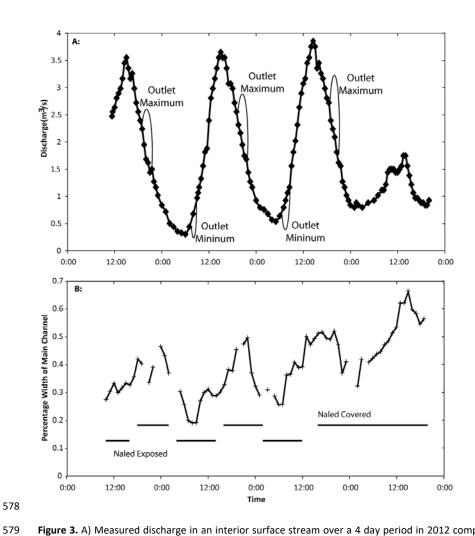
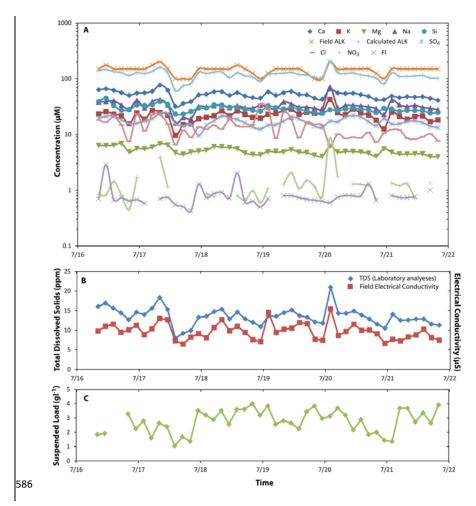


Figure 3. A) Measured discharge in an interior surface stream over a 4 day period in 2012 compared to time ranges of maximum and minimum discharge as suggested by <u>qualitative observation of</u> flow volumes over midstream naled ice in the outlet of Isunnguata Sermia during the study period. B) Assessment of percentage of distance between a point bar and the shore that is characterized by large waves suggestive of deep, fast flow. Periods of time where the midstream naled is exposed and covered are included for comparison.



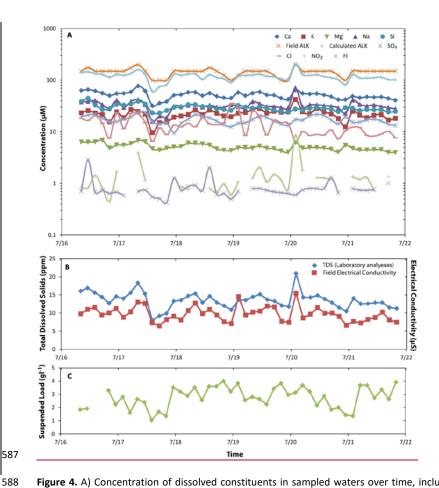


Figure 4. A) Concentration of dissolved constituents in sampled waters over time, including laboratory measurements of cations and Si by ICP-MS, anions by ion chromatography, and field measurements of alkalinity (ALK). Alkalinity as calculated by charge balance is also depicted. B) Total dissolved solids from the sum of the laboratory measurements and charge balance alkalinity (HCO₃) compared to field conductivity measurements. Co-variation is statistically significant (p<0.0001). C) Dry weight of suspended sediment on filters.

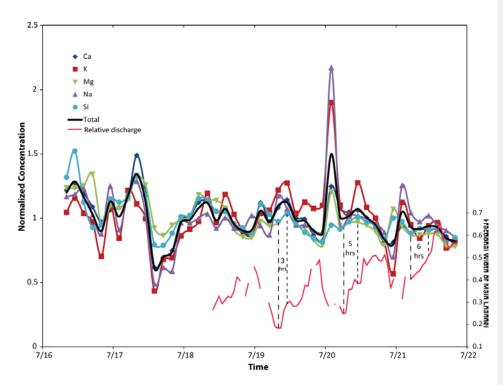


Figure 5. Concentration of dissolved cations and Si normalized to average concentration. Discharge from relative active channel width is shown for comparison. Lags between active channel width channel minima and solute concentration maxima are illustrated with dashed lines.

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Table 1. Field and laboratory measurements (results in micro-molarity unless otherwise noted)

| | | | Eletrical | Suspended | Field | | | | | | | | | | Calculated |
|---------|-----------------|------|--------------|---------------------|-------|-------|-------|------|-------|-------|--------|-------|--------|--------|------------|
| Sample | Time | pН | Conductivity | | | Ca | K | Mg | Na | Si | FI | CI | NO_3 | SO_4 | Alkalinity |
| | | | (µS) | (gl ⁻¹) | (μM) | | | | | | | | | | |
| GL13-1 | 7/16/2013 8:10 | 8.59 | 9.74 | 1.84 | 150 | 63.11 | 23.24 | 6.36 | 38.12 | 38.67 | 0.70 | 18.24 | 0.85 | 19.67 | 141.17 |
| GL13-2 | 7/16/2013 11:00 | 8.82 | 10.98 | 1.92 | 175 | 65.99 | 25.72 | 6.33 | 38.77 | 44.68 | 2.86 | 16.65 | 0.82 | 21.16 | 146.46 |
| GL13-3 | 7/16/2013 14:00 | 8.70 | 11.54 | NA | 150 | 61.88 | 23.10 | 6.43 | 40.20 | 32.96 | 0.67 | 20.58 | 1.43 | 21.68 | 133.87 |
| GL13-4 | 7/16/2013 17:00 | 8.70 | 9.44 | NA | 150 | 56.32 | 21.61 | 6.89 | 33.53 | 27.25 | 0.73 | 14.71 | 0.81 | 18.27 | 128.76 |
| GL13-5 | 7/16/2013 20:00 | 8.65 | 10.04 | 3.28 | 150 | 50.31 | 15.65 | 4.87 | 28.65 | 27.84 | 0.64 | 7.53 | 0.45 | 15.63 | 114.79 |
| GL13-6 | 7/16/2013 23:00 | 8.75 | 11.22 | 2.24 | 150 | 55.07 | 24.32 | 5.60 | 40.89 | 33.75 | 0.68 | 23.38 | 1.69 | 15.88 | 129.06 |
| GL13-7 | 7/17/2013 2:00 | 8.73 | 8.82 | 2.80 | 150 | 55.96 | 18.77 | 5.52 | 29.67 | 32.96 | 0.58 | 11.53 | < 0.45 | 17.62 | 124.03 |
| GL13-8 | 7/17/2013 5:00 | 8.84 | 10.32 | 1.60 | 175 | 59.65 | 27.05 | 5.94 | 38.90 | 34.34 | < 0.43 | 22.57 | < 0.45 | 19.35 | 135.86 |
| GL13-9 | 7/17/2013 8:00 | 8.90 | 13 | 2.64 | 200 | 77.11 | 24.73 | 6.83 | 42.06 | 38.95 | 0.70 | 22.27 | 3.91 | 23.84 | 160.13 |
| GL13-10 | 7/17/2013 11:00 | 8.51 | 12.66 | 2.40 | 150 | 61.76 | 22.14 | 6.46 | 33.64 | 34.54 | 0.74 | 15.23 | 1.16 | 23.85 | 127.40 |
| GL13-11 | 7/17/2013 14:00 | 8.01 | 7.28 | 1.04 | 100 | 31.93 | 9.62 | 4.74 | 15.96 | 23.29 | 0.55 | 6.56 | < 0.45 | 15.56 | 60.69 |
| GL13-13 | 7/17/2013 17:00 | 8.32 | 6.46 | 1.68 | 100 | 35.97 | 15.07 | 4.44 | 20.12 | 23.15 | 0.51 | 11.90 | < 0.45 | 14.14 | 75.32 |
| GL13-14 | 7/17/2013 20:00 | 8.62 | 8.2 | 1.36 | 100 | 38.71 | 15.41 | 4.85 | 19.19 | 25.86 | 0.43 | 8.85 | < 0.45 | 14.99 | 82.45 |
| GL13-15 | 7/17/2013 23:00 | 8.80 | 9.1 | 3.52 | 150 | 51.23 | 19.17 | 5.06 | 31.51 | 29.70 | 1.27 | 13.49 | < 0.45 | 9.54 | 129.42 |
| GL13-16 | 7/18/2013 2:00 | 8.71 | 8.04 | 3.20 | 150 | 52.52 | 20.33 | 5.21 | 31.44 | 29.94 | 0.74 | 12.48 | 0.87 | 14.55 | 124.02 |
| GL13-17 | 7/18/2013 5:00 | 8.53 | 10.66 | 2.88 | 150 | 58.17 | 21.66 | 6.06 | 32.69 | 33.77 | 0.87 | 14.59 | 0.76 | 17.66 | 131.26 |
| GL13-18 | 7/18/2013 8:00 | 8.90 | 12.7 | 3.52 | 150 | 58.34 | 26.52 | 5.85 | 33.74 | 33.52 | 0.92 | 12.56 | < 0.45 | 21.50 | 132.18 |
| GL13-19 | 7/18/2013 11:00 | 8.48 | 9.82 | 2.56 | 150 | 50.27 | 21.52 | 5.84 | 30.12 | 30.90 | 0.73 | 18.38 | < 0.45 | 19.98 | 104.80 |
| GL13-20 | 7/18/2013 14:00 | 8.53 | 10.98 | 3.60 | 175 | 56.00 | 26.34 | 5.53 | 32.80 | 30.84 | 2.03 | 14.21 | 0.80 | 18.63 | 127.88 |
| GL13-21 | 7/18/2013 17:00 | 8.66 | 9.42 | 3.60 | 150 | 48.92 | 22.88 | 4.68 | 30.15 | 28.08 | 0.61 | 13.82 | 0.66 | 16.16 | 112.80 |
| GL13-22 | 7/18/2013 20:00 | 8.61 | 7.56 | 4.00 | 125 | 45.92 | 20.21 | 4.39 | 29.79 | 27.19 | 0.64 | 14.99 | 0.98 | 13.68 | 106.64 |
| GL13-23 | 7/18/2013 23:00 | 8.60 | 7.06 | 3.20 | 100 | 44.93 | 19.53 | 4.35 | 33.33 | 26.04 | 0.50 | 34.89 | 0.60 | 12.51 | 90.43 |
| GL13-24 | 7/19/2013 2:00 | 8.68 | 14.54 | 3.84 | 125 | 58.06 | 23.07 | 5.00 | 30.77 | 32.56 | 0.71 | 29.45 | 1.08 | 14.63 | 119.46 |
| GL13-25 | 7/19/2013 5:00 | 8.27 | 9.42 | 2.56 | 150 | 50.26 | 23.64 | 4.83 | 28.40 | 30.22 | < 0.43 | 8.51 | < 0.45 | 14.96 | 123.76 |
| GL13-26 | 7/19/2013 8:00 | 8.58 | 10.24 | 2.80 | 150 | 56.08 | 27.09 | 4.95 | 38.39 | 28.60 | 0.79 | 24.85 | 1.27 | 17.39 | 125.83 |
| GL13-27 | 7/19/2013 11:00 | 8.70 | 10.5 | 2.64 | 150 | 59.22 | 28.32 | 5.32 | 35.07 | 30.39 | 0.80 | 18.63 | 2.05 | 20.54 | 129.90 |
| GL13-28 | 7/19/2013 14:00 | 8.46 | 11.92 | 2.24 | 150 | 52.04 | 23.07 | 4.82 | 30.99 | 28.33 | 0.74 | 8.69 | 1.07 | 19.07 | 119.13 |
| GL13-29 | 7/19/2013 17:00 | 8.35 | 11.66 | 3.44 | 125 | 51.33 | 25.01 | 4.73 | 30.98 | 26.10 | 0.69 | 16.41 | 1.50 | 16.31 | 116.88 |
| GL13-30 | 7/19/2013 20:00 | 8.58 | 7.68 | 3.84 | 100 | 44.99 | 23.94 | 4.26 | 29.57 | 24.76 | 0.66 | 15.06 | 1.17 | 14.15 | 106.81 |
| GL13-31 | 7/19/2013 23:00 | 8.58 | 7.42 | 2.96 | 100 | 42.73 | 24.46 | 4.05 | 29.26 | 23.92 | 0.64 | 14.57 | 0.77 | 13.32 | 104.67 |
| GL13-32 | 7/20/2013 2:00 | 8.53 | 15.46 | 3.12 | 200 | 64.60 | 42.27 | 6.17 | 70.99 | 27.76 | 0.60 | 6.56 | 8.54 | 17.23 | 204.64 |
| GL13-33 | 7/20/2013 5:00 | 8.03 | 8.62 | 3.68 | 150 | 55.74 | 24.52 | 4.85 | 30.50 | 26.84 | 0.75 | 10.08 | 1.78 | 16.88 | 129.83 |
| GL13-34 | 7/20/2013 8:00 | 8.37 | 9.66 | 3.20 | 150 | 54.24 | 22.61 | 4.97 | 33.37 | 28.51 | 0.81 | 8.52 | < 0.45 | 20.50 | 124.06 |
| GL13-35 | 7/20/2013 11:00 | 8.30 | 11.48 | 2.16 | 150 | 54.99 | 28.39 | 4.97 | 33.30 | 29.61 | 0.79 | 8.94 | 1.29 | 21.77 | 127.04 |
| GL13-36 | 7/20/2013 14:00 | 8.39 | 9.94 | 2.88 | 150 | 51.93 | 24.12 | 4.84 | 32.49 | 28.51 | 0.79 | 8.71 | 1.28 | 20.74 | 117.89 |
| GL13-37 | 7/20/2013 17:00 | 8.48 | 10.02 | 1.84 | 150 | 48.16 | 22.25 | 4.60 | 31.28 | 27.60 | 1.29 | 10.85 | 1.19 | 16.96 | 111.80 |
| GL13-38 | 7/20/2013 20:00 | 8.69 | 9.06 | 2.00 | 125 | 42.10 | 18.12 | 4.06 | 29.09 | 24.59 | 0.66 | 7.35 | < 0.45 | 14.37 | 102.76 |
| GL13-39 | 7/20/2013 23:00 | 8.12 | 6.62 | 1.44 | 100 | 42.13 | 12.60 | 5.49 | 22.80 | 29.38 | < 0.43 | 10.54 | < 0.45 | 19.25 | 81.60 |
| GL13-40 | 7/21/2013 2:00 | 8.80 | 7.68 | 1.36 | 150 | 48.73 | 24.96 | 4.80 | 40.99 | 28.59 | 0.80 | 12.31 | 1.35 | 15.40 | 127.78 |
| GL13-41 | 7/21/2013 5:00 | 8.20 | 7.22 | 3.68 | 150 | 45.80 | 21.11 | 4.45 | 34.07 | 25.88 | 0.74 | 12.08 | 1.20 | 15.56 | 110.55 |
| GL13-42 | 7/21/2013 8:00 | 8.70 | 8.24 | 3.68 | 150 | 47.55 | 18.79 | 4.46 | 31.80 | 26.99 | 0.74 | 8.58 | 1.30 | 17.01 | 109.97 |
| GL13-43 | 7/21/2013 11:00 | 8.42 | 8.76 | 2.72 | 150 | 46.89 | 20.93 | 4.51 | 33.33 | 26.81 | 0.76 | 8.28 | 0.72 | 17.63 | 112.03 |
| GL13-44 | 7/21/2013 14:00 | 8.12 | 10.24 | 3.36 | 150 | 47.52 | 21.48 | 4.49 | 30.72 | 26.82 | < 0.43 | 9.04 | < 0.45 | 16.26 | 114.65 |
| GL13-45 | 7/21/2013 17:00 | 8.32 | 8.08 | 2.64 | 150 | 44.42 | 17.05 | 4.03 | 29.55 | 24.22 | 1.01 | 10.22 | 1.36 | 14.10 | 102.73 |
| GL13-46 | 7/21/2013 20:00 | 8.62 | 7.44 | 3.92 | 150 | 40.93 | 18.31 | 4.00 | 27.84 | 24.85 | < 0.43 | 7.66 | < 0.45 | 13.31 | 101.73 |

| Sample | Time | рН | Eletrical Conductivity (µS) | Suspended Sediment (gl ⁻¹) | Field Alkalinity | Calculated Alkalinity | Ca | к | Mg | Na | Si | FÍ | CI. | NO ₃ ²⁻ | SO ₄ - |
|--------------------|-----------------|-----|-----------------------------------|--|---------------------|--------------------------|------|------|-----|------|------|-------|------|-------------------------------|-------------------|
| GL13-1 | 7/16/2013 8:10 | 8.6 | 9.7 | 1.84 | 150 | 141.2 | 63.1 | 23.2 | 6.4 | 38.1 | 38.7 | 0.7 | 18.2 | 0.8 | 19.7 |
| GL13-2 | 7/16/2013 11:00 | 8.8 | 11.0 | 1.92 | 175 | 146.5 | 66.0 | 25.7 | 6.3 | 38.8 | 44.7 | 2.9 | 16.6 | 0.8 | 21.2 |
| GL13-3 | 7/16/2013 14:00 | 8.7 | 11.5 | NA | 150 | 133.9 | 61.9 | 23.1 | 6.4 | 40.2 | 33.0 | 0.7 | 20.6 | 1.4 | 21.7 |
| GL13-4 | 7/16/2013 17:00 | 8.7 | 9.4 | NA | 150 | 128.8 | 56.3 | 21.6 | 6.9 | 33.5 | 27.2 | 0.7 | 14.7 | 0.8 | 18.3 |
| GL13-5 | 7/16/2013 20:00 | 8.7 | 10.0 | 3.28 | 150 | 114.8 | 50.3 | 15.6 | 4.9 | 28.6 | 27.8 | 0.6 | 7.5 | 0.5 | 15.6 |
| GL13-6 | 7/16/2013 23:00 | 8.7 | 11.2 | 2.24 | 150 | 129.1 | 55.1 | 24.3 | 5.6 | 40.9 | 33.8 | 0.7 | 23.4 | 1.7 | 15.9 |
| GL13-7 | 7/17/2013 2:00 | 8.7 | 8.8 | 2.80 | 150 | 124.0 | 56.0 | 18.8 | 5.5 | 29.7 | 33.0 | 0.6 | 11.5 | < 0.5 | 17.6 |
| GL13-8 | 7/17/2013 5:00 | 8.8 | 10.3 | 1.60 | 175 | 135.9 | 59.7 | 27.1 | 6.0 | 38.9 | 34.3 | < 0.4 | 22.6 | < 0.5 | 19.6 |
| GL13-9 | 7/17/2013 8:00 | 8.9 | 13.0 | 2.64 | 200 | 160.1 | 77.1 | 24.7 | 6.8 | 42.1 | 39.0 | 0.7 | 22.3 | 3.9 | 23.8 |
| GL13-10 | 7/17/2013 11:00 | 8.5 | 12.7 | 2.40 | 150 | 127.4 | 61.8 | 22.1 | 6.5 | 33.6 | 34.5 | 0.7 | 15.2 | 1.2 | 23.9 |
| GL13-11 | 7/17/2013 14:00 | 8.0 | 7.3 | 1.04 | 100 | 60.7 | 31.9 | 9.6 | 4.7 | 16.0 | 23.3 | 0.6 | 6.6 | <0.5 | 15.6 |
| GL13-13 | 7/17/2013 17:00 | 8.3 | 6.4 | 1.68 | 100 | 75.3 | 36.0 | 15.1 | 4.4 | 20.1 | 23.2 | 0.5 | 11.9 | <0.5 | 14.1 |
| GL13-14 | 7/17/2013 20:00 | 8.6 | 8.2 | 1.36 | 100 | 82.5 | 38.7 | 15.4 | 4.8 | 19.2 | 25.9 | 0.4 | 8.9 | < 0.5 | 15.0 |
| GL13-15 | 7/17/2013 23:00 | 8.8 | 9.1 | 3.52 | 150 | 129.4 | 51.2 | 19.2 | 5.1 | 31.5 | 29.7 | 1.3 | 13.5 | <0.5 | 9.5 |
| GL13-16 | 7/18/2013 2:00 | 8.7 | 8.0 | 3.20 | 150 | 124.0 | 52.5 | 20.3 | 5.2 | 31.4 | 29.9 | 0.7 | 12.5 | 0.9 | 14.6 |
| GL13-17 | 7/18/2013 5:00 | 8.5 | 10.7 | 2.88 | 150 | 131.3 | 58.2 | 21.7 | 6.1 | 32.7 | 33.8 | 0.9 | 14.6 | 0.8 | 17.7 |
| GL13-18 | 7/18/2013 8:00 | 8.9 | 12.7 | 3.52 | 150 | 132.9 | 58.3 | 26.5 | 5.8 | 33.7 | 33.5 | 0.9 | 12.6 | <0.5 | 21.5 |
| GL13-19 | 7/18/2013 11:00 | 8.5 | 9.8 | 2.56 | 150 | 104.8 | 50.3 | 21.5 | 5.8 | 30.1 | 30.9 | 0.7 | 18.4 | <0.5 | 20.0 |
| GL13-20 | 7/18/2013 14:00 | 8.5 | 11.0 | 3.60 | 175 | 127.9 | 56.0 | 26.3 | 5.5 | 32.8 | 30.8 | 2.0 | 14.2 | 0.8 | 18.6 |
| GL13-21 | 7/18/2013 17:00 | 8.7 | 9.4 | 3.60 | 150 | 112.8 | 48.9 | 22.9 | 4.7 | 30.1 | 28.1 | 0.6 | 13.8 | 0.7 | 16.2 |
| GL13-22 | 7/18/2013 20:00 | 8.6 | 7.6 | 4.00 | 125 | 106.6 | 45.9 | 20.2 | 4.4 | 29.8 | 27.2 | 0.6 | 15.0 | 1.0 | 13.7 |
| GL13-23 | 7/18/2013 23:00 | 8.6 | 7.1 | 3.20 | 100 | 90.4 | 44.9 | 19.5 | 4.4 | 33.3 | 26.0 | 0.5 | 34.9 | 0.6 | 12.5 |
| GL13-23 | 7/19/2013 2:00 | 8.7 | 14.5 | 3.84 | 125 | 119.5 | 58.1 | 23.1 | 5.0 | 30.8 | 32.6 | 0.7 | 29.5 | 1.1 | 14.6 |
| GL13-25 | 7/19/2013 5:00 | 8.3 | 9.4 | 2.56 | 150 | 123.8 | 50.3 | 23.6 | 4.8 | 28.4 | 30.2 | <0.4 | 8.5 | <0.5 | 15.0 |
| GL13-26 | 7/19/2013 8:00 | 8.6 | 10.2 | 2.80 | 150 | 125.8 | 56.1 | 27.1 | 4.9 | 38.4 | 28.6 | 0.8 | 24.9 | 1.3 | 17.4 |
| GL13-27 | 7/19/2013 11:00 | 8.7 | 10.5 | 2.64 | 150 | 129.9 | 59.2 | 28.3 | 5.3 | 35.1 | 30.4 | 0.8 | 18.6 | 2.1 | 20.5 |
| GL13-28 | 7/19/2013 14:00 | 8.5 | 11.9 | 2.24 | 150 | 119.1 | 52.0 | 23.1 | 4.8 | 31.0 | 28.3 | 0.7 | 8.7 | 1.1 | 19.1 |
| GL13-29 | 7/19/2013 17:00 | 8.4 | 11.7 | 3.44 | 125 | 116.9 | 51.3 | 25.0 | 4.7 | 31.0 | 26.1 | 0.7 | 16.4 | 1.5 | 16.3 |
| GL13-20 | 7/19/2013 17:00 | 8.6 | 7.6 | 3.84 | 100 | 106.8 | 45.0 | 23.9 | 4.3 | 29.6 | 24.8 | 0.7 | 15.1 | 1.2 | 14.2 |
| GL13-30 | 7/19/2013 23:00 | 8.6 | 7.4 | 2.96 | 100 | 104.7 | 42.7 | 24.5 | 4.1 | 29.3 | 23.9 | 0.6 | 14.6 | 0.8 | 13.3 |
| GL13-32 | 7/20/2013 2:00 | 8.5 | 15.5 | 3.12 | 200 | 204.6 | 64.6 | 42.3 | 6.2 | 71.0 | 27.8 | 0.6 | 6.6 | 8.5 | 17.2 |
| GL13-32 | 7/20/2013 5:00 | 8.0 | 8.6 | 3.68 | 150 | 129.8 | 55.7 | 24.5 | 4.9 | 30.5 | 26.8 | 0.7 | 10.1 | 1.8 | 16.9 |
| GL13-33 | 7/20/2013 8:00 | 8.4 | 9.7 | 3.20 | 150 | 124.1 | 54.2 | 22.6 | 5.0 | 33.4 | 28.5 | 0.8 | 8.5 | <0.5 | 20.5 |
| GL13-34 | 7/20/2013 11:00 | 8.3 | 11.5 | 2.16 | 150 | 127.0 | 55.0 | 28.4 | 5.0 | 33.3 | 29.6 | 0.8 | 8.9 | 1.3 | 21.8 |
| GL13-35 | 7/20/2013 11:00 | 8.4 | 9.9 | 2.88 | 150 | 117.9 | 51.9 | 24.1 | 4.8 | 32.5 | 28.5 | 0.8 | 8.7 | 1.3 | 20.7 |
| GL13-30 GL13-37 | 7/20/2013 17:00 | 8.5 | 10.0 | 1.84 | 150 | 111.8 | 48.2 | 22.3 | 4.6 | 31.3 | 27.6 | 1.3 | 10.8 | 1.2 | 17.0 |
| GL13-37 | 7/20/2013 17:00 | 8.7 | 9.1 | 2.00 | 125 | 102.8 | 42.1 | 18.1 | 4.1 | 29.1 | 24.6 | 0.7 | 7.4 | <0.5 | 14.4 |
| GL13-38 GL13-39 | 7/20/2013 20:00 | 8.1 | 6.6 | 1.44 | 100 | 81.6 | 42.1 | 12.6 | 5.5 | 22.8 | 29.4 | <0.4 | 10.5 | <0.5 | 19.6 |
| GL13-39 GL13-40 | 7/21/2013 2:00 | 8.8 | 7.7 | 1.36 | 150 | 127.8 | 48.7 | 25.0 | 4.8 | 41.0 | 28.6 | 0.8 | 12.3 | 1.4 | 15.4 |
| GL13-40 GL13-41 | 7/21/2013 2:00 | 8.2 | 7.7 | 3.68 | 150 | 110.6 | 45.8 | 21.1 | 4.5 | 34.1 | 25.9 | 0.8 | 12.1 | 1.4 | 15.4 |
| GL13-41 | 7/21/2013 5:00 | 8.7 | 8.2 | 3.68 | 150 | 110.0 | 47.5 | 18.8 | 4.5 | 31.8 | 27.0 | 0.7 | 8.6 | 1.3 | 17.0 |
| GL13-42 | 7/21/2013 11:00 | 8.4 | 8.8 | 2.72 | 150 | 112.0 | 46.9 | 20.9 | 4.5 | 33.3 | 26.8 | 0.7 | 8.3 | 0.7 | 17.6 |
| GL13-43 | 7/21/2013 11:00 | 8.4 | 10.2 | 3.36 | 150 | 114.6 | 47.5 | 20.9 | 4.5 | 30.7 | 26.8 | <0.4 | 9.0 | <0.5 | 16.2 |
| GL13-44 | 7/21/2013 17:00 | 8.3 | 8.1 | 2.64 | 150 | 102.7 | 44.4 | 17.1 | 4.0 | 29.6 | 24.2 | 1.0 | 10.2 | 1.4 | 14.1 |
| GL13-45 | 7/21/2013 17:00 | 8.6 | 7.4 | 3.92 | 150 | 102.7 | 40.9 | 18.3 | 4.0 | 27.8 | 24.2 | <0.4 | 7.7 | < 0.5 | 13.3 |