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Chemical sensors for *in situ* data collection in the cryosphere

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ABSTRACT

Glaciers and ice sheets are recognised as important components of global biogeochemical cycles. Chemical sensors have great potential for *in situ* monitoring in the cryosphere and are available for many analytes of interest, but they are frequently unsuitable for deployment since meltwaters are cold, turbid, experience freeze-thaw cycles and display low ionic strength and concentrations of target analytes. Here, we review *in situ* chemical sensors currently available for measurement of biogeochemically important analytes and assess their suitability for deployment. These include standard parameters such as dissolved oxygen and pH, along with macronutrients (nitrate/nitrite and phosphate), micronutrients (iron and manganese) and biogenic gases (methane). Where no commercial alternatives are available, we discuss sensors currently in development, and their applicability to these extreme environments. The information presented has great relevance for future science in polar environments, and for the ultimate goal of obtaining *in situ* data from extreme, inaccessible subglacial environments.

Contents

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1. Introduction

The Greenland and Antarctic Ice Sheets discharge between 400 and 700 cubic kilometres of glacial meltwater into the ocean each summer, a sum which is likely to increase in coming years [1]. Meltwater from these ice sheets (masses of glacial land ice >50,000 km^2), ice caps (masses of glacial land ice <50,000 km^2) and mountain glaciers (smaller masses of ice constrained by surrounding topography) is a source of bioavailable carbon and both macro- and micro-nutrients to downstream ecosystems [2–4]. This large and increasing annual water flux is likely to have a significant impacts on regional and global biogeochemical cycles [1,5], yet measuring the chemical composition of the meltwater is challenging. Manual sampling is logistically difficult, and hence restricted to the summer season in limited, discrete locations. Sensors offer an attractive solution for gaining *in situ* data from these remote ecosystems, allowing real-time capture of chemical data in the field, and the assessment of analytes which are not sufficiently stable to survive transport back to a laboratory. The use of chemical sensors has the potential to revolutionise monitoring of glacial meltwaters, as has occurred in ocean sciences [6] However, glacial environments challenge many commercially available sensors (Fig. 1), and can significantly impact performance of others. Here we review the suitability of a range of commercial and bespoke sensors for measuring analytes of interest in icy environments.

Source environments for glacial meltwater, or runoff, include ice surfaces (known as ‘supraglacial’), subglacial melt channels (‘subglacial’ - beneath the ice), perennially liquid subglacial lakes (bodies of liquid water beneath ice sheets, maintained in a liquid state by weak geothermal heat fluxes), sub-ice stream meltwaters (large channels draining subglacial meltwater) and subglacial sediment pore waters (saturated sediments beneath the ice). The diversity of aquatic environments on (supraglacial), within (englacial), beneath (subglacial) and adjacent to (proglacial) glaciers and ice sheets means that measuring physical and chemical processes occurring is not straightforward. Glacial meltwaters are characterised by low temperatures (~0.1°C), low ionic strength (~5–100 µS/cm), high sediment concentrations (~1 g l^{-1}, up to 16 g l^{-1} [7]), freeze-thaw cycles and occasionally extreme geochemical conditions, when oversaturated meltwaters first make contact with the atmosphere prior to equilibration [8]. Ice and snow melt are generally dilute (Table 1), but solute is progressively acquired through geochemical interactions with freshly comminuted rock during transit through the glacial drainage system, where weathering reactions are often catalysed by microbial activity [9].

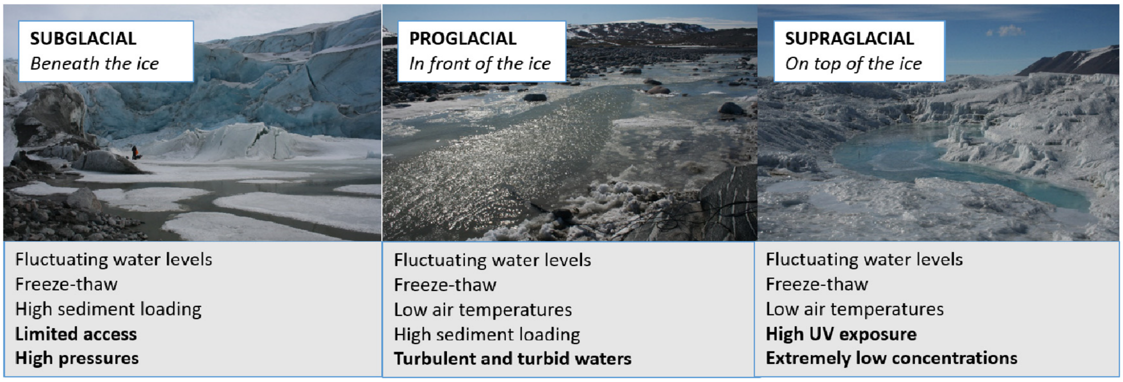

Fig. 1. Descriptions of specific engineering challenges presented by the three primary glacial aquatic environments. *In situ* sensors must be able to cope with such conditions to perform in these extreme natural systems.

Table 1
Typical range of concentrations of major ions and nutrients in glacial meltwaters. Values are minimum and maximum reported from Haut Glacier d’Arolla, Switzerland; John Evans Glacier, Canada; Robertson Glacier, Canada [9,10];, Leverett Glacier, Greenland [2,11]; Lower Wright Glacier, Antarctica; N Glacier, Greenland [5] and Russell Glacier, Greenland [12]. *ND* indicates no data, and * below detection limits

Major ions		Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	pH
Glacial runoff	*Min µM*	0.1	0.4	3	20	1	10	20	50	6.5
	Max µM	50	10	150	50	20	50	240	400	8.5
Icemelt	*Min µM*	0.1	0.1	0.1	2.5	1	5	2.5	5	5.5
	Max µM	20	0.4	2.5	15	3	10	20	20	8.5

Nutrients		Si	Fe(III)	DOC	DIN	DON	DIP	DOP	CH_4
Glacial runoff	*Min µM*	6	0.01	4	0.1	0.6	0.01	0.04	2.7
	Max µM	600	10	400	20	60	1.0	4.0	83
Icemelt	*Min µM*	0.1	*	0.1	0.01	0.01	*	*	*ND*
	Max µM	2	0.015	0.5	0.05	0.04			

Table 2
Key analytes that can provide information about biogeochemical processes in the cryosphere, for which chemical sensors are available, and the range, resolution and limit of detection (LoD) required for measurement in glacial meltwaters (Table 1). LoD is determined by the equivalent laboratory method

Analyte	Required LoD (limit of detection) or precision	Optimal resolution	Optimal range
Oxygen	1 µM	1 µM	1–500 µM
pH	0.2 pH	0.1pH	5–11 pH
NO_3^-	0.05 µM	0.1 µM	0.1–100 µM
PO_4^{3-}	0.05 µM	0.1 µM	0.1–100 µM
Fe	1 nM	0.5 nM	1–5000 nM
CH_4	<5 nM	1 nM	1–1000 nM

Geochemical characteristics of ice, snow melt and runoff can provide information about the poorly accessible subglacial environment, where there is a diverse and chemosynthetically active microbial population [13]. The presence of methanogenic archaea in subglacial sediments [14] means that there is potential for the degradation of organic carbon to methane beneath glaciers and ice sheets, and subsequent release to the atmosphere in the event of ice sheet retreat [15]. Table 1 shows the typical composition of icemelt and runoff from example Alpine, Arctic and Antarctic glaciers. The primary geochemical parameters of interest in glacial meltwaters are those resulting from chemical weathering reactions, namely major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, NO_3^-), silica, and indicators of the redox conditions (for example, Fe, O_2, CO_2). In addition, biological markers (such as CO_2 and O_2) can show the presence and function of microbial life, and the release of macro- (C, N, P) and micro-nutrients (Fe, Mn) can impact downstream ecosystems.

Chemical sensors are available for a number of these parameters, but the necessary range and limit of detection is frequently insufficient for glacial meltwaters. Table 2 shows the required lower limit of detection and/or precision, resolution and range for a selection of key analytes for which sensors are available (although not necessarily at the desired range and resolution), and which can provide valuable information about solute acquisition and export in the cryosphere. We review the available options below.

2. Dissolved oxygen

Oxygen is traditionally determined via Winkler titration. Titration is, however, impractical in the field (particularly at sub-zero temperatures), and prolonged sample storage can introduce measurement errors even when samples are chemically fixed [16]. Development of the potentiometric Clark electrode [17], revolutionised *in situ* measurement by allowing direct estimation of oxygen concentrations in surface waters. However, the electrode must be fully immersed and requires constant stirring because oxygen is consumed at the sensing head. The flow dependence can be up to 25 % of the recorded concentration [16]. Stirring sensitivity may be reduced by using a microsensor, where the active area of the electrode (and therefore consumption of analyte) is very small [18]. However, fragile microsensors can be unsuitable for extremely turbid meltwater flows or systems which experience repeated freeze-thaw cycles.

More recently, optical methods have been used to measure dissolved oxygen (DO). Optodes were developed in the early 1990s [19] and are now commercially available (a review can be found in [20]). Typically, the exposed end of an optical fibre or optical window is coated with an immobilised indicator compound, which is photoluminescent and sensitive to the measured parameter [21]. A ruthenium complex is commonly used for the determination of DO where luminescence lifetime is progressively quenched by increasing oxygen concentration. Optodes are advantageous for use in environmental monitoring because they: a) consume no oxygen, b) are relatively robust, c) measure oxygen in both the gas and liquid phase, and d) require no stirring.

2.1. *Optical sensor selection*

The size of the sensing element and the longevity of the sensing film are the primary considerations for choosing an optical sensor for oxygen. There are several manufacturers to choose from, including PreSens (Germany), Franatech (Germany), Pyroscience (Germany), Unisense (Denmark), Aandera (Norway), Hach Lange (Germany) and Ocean Optics (USA). The sensing film is liable to decay over time; typically each manufacturer can specify a maximum lifetime. For example, assessment of PreSens probes [16] showed that they are stable for at least 100k measurements, after which photobleaching degraded the sensing film. Reducing the duration or intensity of illumination can extend the life of each sensor. Table 3 lists the characteristics of a number of available optodes.

The means by which the sensing film is immobilised and secured on the fibre tip or optical window influences the suitability of the sensor for low temperature applications, since freeze-thaw cycling can mechanically detach sensing films [16]. The sensor head design is also of primary concern: larger sensors are generally more robust, but can be impractical in environments with low water volumes. The Aanderaa Optode series, which have 36–40 mm diameter heads (Table 3), are routinely used in oceanographic observations because of their long-term stability, low sensitivity to fouling and ability to operate at high pressures [22–24]. They are also insensitive to freezing, and the large and robust sensor head is also well suited to proglacial meltwaters (Fig. 2b). For deployments in limited volumes of meltwater, for example, supraglacial melt pools, a smaller sensor head is desirable [25].

2.2. *Example deployments*

PreSens Fibox sensors have been deployed into supraglacial meltwater features (cryoconite holes) in Antarctica, where they revealed previously unseen and extreme fluctuations in oxygen concentration associated with freeze-thaw cycling and biological activity [25]. Long term datasets have also been collected from runoff in south

Table 3
Characteristics of a range of oxygen optodes available to market

Supplier/Model	Resolution	Accuracy	Sensor head diameter
Pyro Science: Robust	0.05% at 20% O_2	0.2% at 20% O_2	3 mm
Franatech: D Opto	0.01% at saturation	1% or 0.02 ppm	48 mm
Aanderaa: 3835	0.4%	5% or 1 µM	36 mm
PreSens: PSt3	0.05 at 20.9% O_2	0.05%	4 mm
Hach Lange: LDO	0.1%	0.2 ppm	48 mm
Ocean Optics: FOXY	0.3 at 20% O_2	0.02% at 20% O_2	3 mm
Unisense: Microoptode	0.05% at 20% O_2	2% at 20% O_2	430 µm

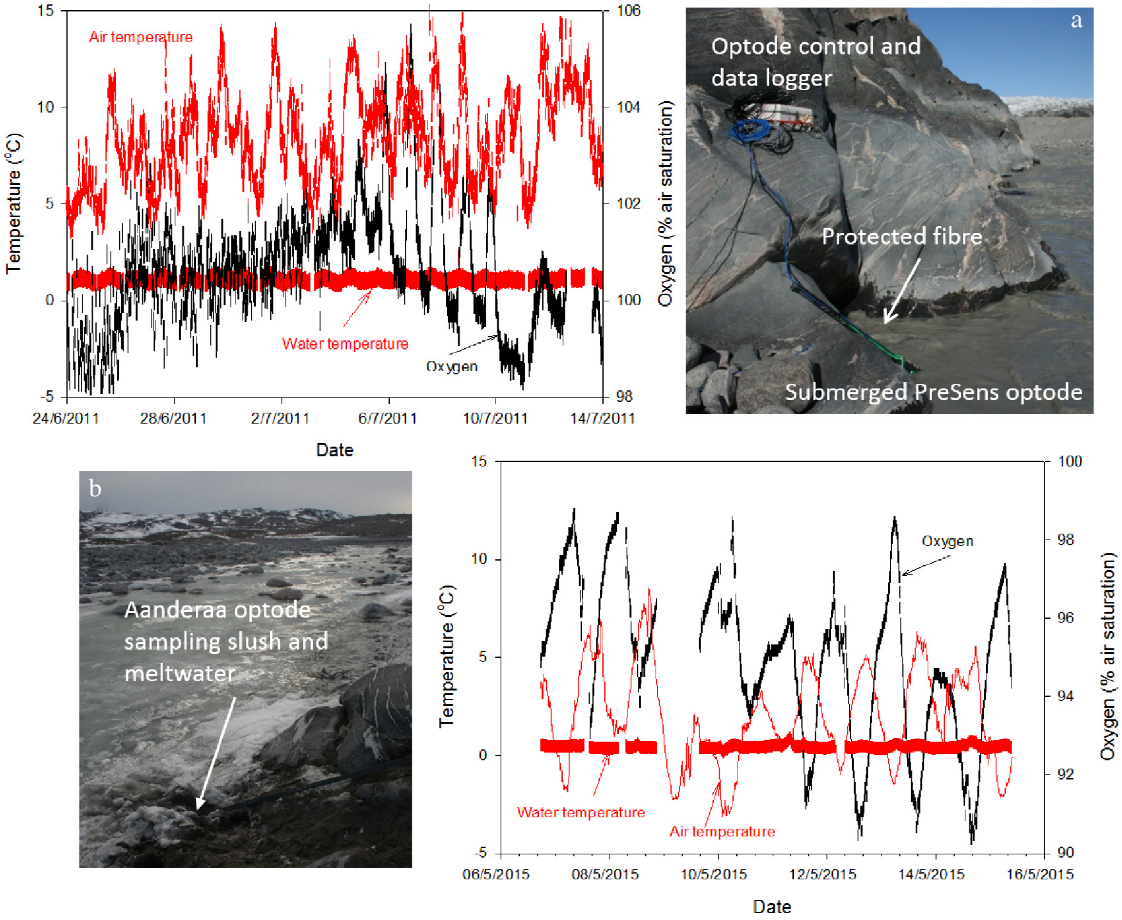

Fig. 2. Dissolved oxygen records from proglacial meltwaters in Greenland at Leverett Glacier, using (a) a PreSens Fibox 3 and (b) an Aanderaa 3585. Air and water temperatures were lower during the earlier Aanderaa deployment (early May vs late June). The smaller, more fragile PreSens probe was protected from the turbid waters by a length of hose pipe, whereas the larger Aandera sensor head was more robust. Sensor drift was minimal (<3%) over the both deployments.

Greenland, at Leverett Glacier (PreSens Fibox and Aanderaa 3585, Fig. 2) and Kiattuut Sermia (Aanderaa 3585). The river draining the Leverett Glacier has extremely high discharge in the peak melt season (up to 800 m^3 s^{-1}), so the PreSens sensor was protected from moving obstacles in the flow by a length of hosepipe (Fig. 2a). The sensors operated continuously in water temperatures just above freezing, with air temperatures ranging from −3 to +15°C, and revealed diurnal fluctuations caused by daily melt cycles.

2.3. Recommendations

Optical sensors are a relatively mature technology which have a number of advantages over Clark-type sensors for monitoring of glacial meltwaters, since they are not impacted by stirring, do not consume oxygen and remain stable for relatively long periods. Care must be taken when selecting the sensor head to ensure that the size is appropriate for the environment in question and that the sensing foil can survive repeated freeze-thaw cycles. For long-term deployments, the ability to control the length of time that the sensing film is illuminated can extend longevity.

3. pH

pH is a bulk indicator of the chemical status of aquatic environments, which can provide information about systems through which the water has travelled prior to sampling, and its potential for further chemical weathering. It also provides an indicator of biological activity, yet it remains challenging to measure reliably in the field. Glacial waters range from acidic snowmelt to alkaline meltwaters (pH ~5 to ~10) and are frequently at disequilibrium with the atmosphere with respect to CO_2 (for example, subglacial meltwaters). Low ionic strength can be a significant problem for pH measurement because of the low potential supply of electrons to the measuring electrode [26]. Similarly, varying flow rates can cause streaming effects at the electrode surface. There are three primary approaches to measuring pH in natural waters: potentiometric, spectrophotometric and fluorescent (Table 4).

3.1. Potentiometric measurements

Glass electrodes are commonly used for determination of pH. However, they are susceptible to high drift and typically perform poorly at very low ionic strength, resulting in errors of >0.01 pH [27]. An alternative potentiometric method is based on an ion selective field effect transistor (ISFET). A FET uses an electrical field to control the shape and hence conductivity of a channel of charge carrier in a semiconductor. In a pH sensitive ISFET, for example, Honeywell Durafet and Sentron by Campbell Scientific, the gate electrode is provided by the solution, and is separated from the channel by a barrier that is sensitive to H^+. The pH is obtained by measurement of the voltage between a reference electrode and the sensing layer [27]. The choice of reference electrode can have a significant impact on measurement accuracy [28]. The Honeywell Durafet II/III and Campbell Scientific Sentron probes both use a silver wire in AgCl

Table 4
A summary of available techniques and their suitability for measuring pH and DO in glacial meltwaters

Analyte	Technique	Example suppliers	Range	Suitable for deployment in glacial melt water?
pH				
	Potentiometric (glass electrode)	Various	1–11	No – poor performance at low ionic strength, sensitive to freezing
	Potentiometric (ISFET)	Honeywell, Campbell Scientific	0–14	Yes – *although ionic strength impact requires quantification*
	Spectro-photometric	Sunburst Sensors (SAMI-pH)	7–9	No – too complex, and sensitive to freeze-thaw
	Fluorescent (immobilised dye)	PreSens, Ocean Optics	5–9	Some – *limited range*
Dissolved oxygen				
	Potentiometric (Clark electrode)	Various	0–1.5 mM	No – requires constant flow rate
	Fluorescent (optode)	Various, see Table 3	0–1.4 mM (optimal range 0–0.7 mM)	Yes - *if sensor head is robust*

and KCl saturated gel which comes into contact with the test solution through a liquid junction. Martz et al. [27] add an external chloride ion selective reference electrode to the Durafet, forming the 'Seafet' sensor (Satlantic, USA) specifically for seawater applications.

The ISFETs are subject to reduced drift and noise compared to glass electrodes, as a result of lower impedance [27]. Application of the Honeywell Durafet ISFET and Satlantic Seafet to seawater measurements (both in the laboratory and *in situ*) showed negligible drift (<0.005 pH) over weeks to months, and short-term precision of 0.0005 pH over several hours [28]. Stirring effects are also greatly reduced: initial estimates show a maximum sensitivity of 0.03 pH at 0.02–0.2 m s^{-1} (Bagshaw, unpublished data). The response is based on surface reactions rather than diffusion limited changes to the bulk of the surface insulator. The ISFET is sensitive to temperature, but since the response is linear this poses little problem as long as temperature is simultaneously measured [28,29].

Ionic strength remains an issue for pH sensor measurements. The Honeywell Durafet ISFET is not recommended for high purity waters <10 µS/cm. Preliminary tests by the author (Bagshaw et al., *In Prep.)* suggest that the Durafet is effective at low ionic strength (5.45×10^{-5} mol dm^{-3} $NaHCO_3$), but that there is a measurable change in the pH reported by the ISFET in an otherwise constant solution (<0.1 ± 0.05 pH). This must be quantified before very high accuracy measurements of glacial waters.

3.2. Spectrophotometric

Spectrophotometric determination of pH uses an acid/base indicator dye [27]. The major advantage of the method is that it is not subject to drift, and can produce extremely precise measurements (to 0.0004 pH [30]). For glacial applications, meta Cresol Purple (pK = 8.32) is an appropriate indicator, similar to surface seawaters although it must be characterised for temperature and ionic strength dependence prior to use, and potentially be purified [31]. The method can be performed to a high accuracy (0.001 is technically feasible), though in practice accuracy is constrained by the certified TRIS buffer (supplied by A. Dickson) to 0.004 [32,33]. Additionally, continuous i*n situ* monitoring requires a fairly complex pump system with significant operation times [28]. Whilst there are numerous successful examples of the methodology in oceanographic applications (e.g. Robert Byrne's laboratory including SOAS-pH, SAMI-pH [34], among others), the complexity of the measuring system has restricted use in glacial waters. Miniaturised microfluidic methods are in development for oceanic applications [27], but the technique is immature.

3.3. Optodes

Optodes can also be used to measure pH using immobilised indicator dyes. Typically a pH-sensitive indicator dye embedded in a sensing film, either on a spot (PreSens, Ocean Optics) or probe (Ocean Optics) is illuminated by an LED light source and the luminescent or spectrophotometric optical response recorded. The technique offers high precision (<0.001pH) [35], simplicity and requires no additional calibration, although the indicator selected will have a limited range and measurement quality deteriorates at the range extremes (Ocean Optics 5–9, PreSens 5.5–8.5). An additional problem is optical interference, which may be significant in turbid glacial meltwaters if not managed (e.g. with an opaque layer over the foil, which slows the time response [36]). Response time is likely to decrease at low temperatures, bleaching of the sensing film also occurs with time (similar to DO, Section 2.1), and some films are sensitive to ionic strength (e.g. PreSens).

3.4. Recommendations

There is, as yet, no satisfactory method for continuous, long-term determination of pH in glacial meltwaters. The ISFET and optode-based methods offer the most promising solutions, provided that the response to ionic strength can be adequately quantified, and that the indicator used in optical sensing films covers the entire range of pH anticipated. ISFET sensors have the advantage of long periods of stability with minimal drift, demonstrated by prolonged deployments of Seafet sensors in oceanic environments [37]. Further work is required to quantify the response to ionic strength at very low concentrations (<10 µS/cm). Microfluidic solutions which simplify the spectrophotometric method have the potential to enable high-accuracy measurement of pH (eg [33].) but they are generally more complex than is necessary for the required resolution of glacial meltwater studies (Table 2) and likely sensitive to freeze-thaw.

4. Methane

Dissolved methane in glacial meltwaters is an indicator of methane production (either biologically or thermogenically) in the subglacial environment [15]. There have been few measurements in meltwaters to date. Limited studies from the margins of the Greenland Ice Sheet demonstrate the potential for fluxes of up to 0.3 µg CH_4 h^{-1} m^{-3} from sediments immediately adjacent to the ice [38], concentrations of 5.7 to 18.4 nM L^{-1} of seawater in a glacial-fed fjord [39], and 2.7 to 83 µM in meltwaters issuing directly from the subglacial portal of Russell Glacier [12] (Table 1).

4.1. Available sensors

An excellent review of methane sensors for marine applications is available [40]. We apply their assessment to glacial meltwaters, additionally reviewing recent advances. Sensing solutions are based on one of three methods: oxidation of methane using bacteria in a biosensor [41]; diffusion through a gas-permeable membrane followed by detection via semi-conductor (METS sensor [42],); or equilibration of dissolved methane into a gas headspace before analysis using infrared absorbance spectroscopy. Biosensors are unsuited to low temperature operations, and the METS sensor exhibits significant temperature and flow sensitivity [40]. Optical techniques show potential for a reliable sensor; for example, a new sensor using cryptophane as a methane capture molecule which modulates the refractive index of the indicator layer has been demonstrated in the Baltic sea with a detection limit of 3–7 nM [43], but it remains commercially unavailable. Raman spectroscopic methods are also in development [44], but the instability of surface-enhanced Raman scattering effects at low concentrations is problematic. *In situ* mass spectrometry has excellent LoD [45] but is hampered by poor portability as a result of large payload and high power consumption. This makes the technique largely unsuited to glaciological applications.

The Contros Hydro C sensor uses infrared absorption spectroscopy to measure CH_4 in the gas phase and has been successfully tested in several oceanographic deployments [46,47], and was tested for the subglacial Lake Whillans access probe (www.wissard.org). A high sensitivity version that uses a laser diode is now available, with a range 0–40,000 µatm and LoD <1 µatm. Preliminary tests demonstrate good resolution (signal to noise ratio of 5 at 0.06 µM). A subsea deployment via a remotely operated vehicle (ROV) measured concentrations of 50 nM with little difficulty [46]. There were a number of issues with hysteresis reported in this deployment, where sensor response time was increased after measuring high concentrations [46], possibly as a result of time lags due to diffusion through the membrane [43]. The size of the sensor package is also potentially prohibitive (25 kg, 130 × 600mm), but its successful deployment via ROV suggests that this is not insurmountable.

4.2. Recommendations

For assessment of methane extracted into the gas phase, the most promising techniques are in situ mass spectrometry and infrared absorption spectroscopy The most promising technique is based on non-dispersive infrared sensing, a simple spectroscopic method for gas analysis which does not consume methane [40,46], utilised by the Contros HydroC.

5. Nitrogen species

Nitrate, nitrite and ammonium are exported in glacial runoff [1]. *In situ* measurement of dissolved N species is possible via potentiometric methods, those which utilise biosensing, optical techniques, or traditional wet chemical analyses (Table 5).

5.1. Potentiometric methods

Potentiometric Ion Selective Electrodes (ISE) exist for almost all ionic species: for example, nitrate (NO_3^-) [48], nitrite (NO_2^-) [49] and ammonium (NH_4^+) [50]. Of particular note is a nitrate-ISE deployed in the River Taw (Devon, UK) [51] for two months without the need for calibration. However, the LoD (0.5 µM) is insufficient for many glacial analyses (Table 2). Biosensors have a more promising LoD (Unisense, Denmark = 0.2 µM), and utilise biological recognition to convert the target chemical analyte into a form that is more easily detected. However, the microbial activity on which the sensors depend reduces significantly at low temperatures, resulting in a minimum operating temperature of 10°C.

5.2. Optical methods

5.2.1. Direct optical absorption spectroscopy

Direct optical absorption sensors are reagent-free devices that detect chemical species by measuring optical absorption over a range of wavelengths in either the water or gas phase. Nitrate and nitrite absorb light in the ultraviolet (UV) electromagnetic spectrum, which is utilised by spectrophotometric analyses [52]. An In Situ UV Spectrophotometer (ISUS) is commercially available through Satlantic Inc. (Canada), alongside the newer 'SUNA' version more suited to turbid waters [53]. The ISUS has been successfully deployed in marine [54] and freshwater environments [55], including spring snowmelt [56] and Arctic oceans [57] However, the precision (±0.5 µM) and accuracy (±2 µM) are insufficient for measuring the very low concentrations present in glacial melt.

5.2.2. Wet chemical colourimetric flow analysers

Colourimetric methods utilise the formation and detection of a strongly absorbing dye, whose optical absorption is linearly proportional to the concentration of the target analyte. The concentration-absorption relationship means that measurements can be made at extremely low concentrations by increasing the optical path length. Several miniaturised submersible flow analysers have been developed (e.g [58,59].), and some are now available commercially (e.g. Systea WIZ, YSI 9600). The analysers are usually deployed with on-board standard solutions, which allow the system to be calibrated *in situ* as often as required and facilitates very high accuracy measurements. However, the method requires reagents, and their consumption limits operating time and temperature.

The application of microfluidics (lab-on-chip technology) to in situ colorimetric nutrient analysis can reduce reagent and power consumption, as well as sensor package size, enabling long-term deployment in remote locations [60]. Beaton et al. [56] describe a microfluidic wet chemical analyser for nitrate/nitrite for natural waters based on the Greiss assay and cadmium reduction, with LoD of 0.025 µM for nitrate and 0.02 µM for nitrite. The system consists of a polymer microfluidic chip, to which are attached a syringe pump, solenoid valves and a custom electronics package for logging and control (Fig. 3). All reagents, including standards and blanks

Table 5
A summary of available techniques and their suitability for measuring nitrate and phosphate in glacial meltwaters

Analyte	Technique	Supplier/Author	LoD	Suitable for glacial melt?
Nitrate/nitrite				
	Potentiometric Ion selective electrode	Various	0.5 µM	No – concentrations too low
	Biological reactor	Unisense	0.2 µM	No – temperatures too low
	In Situ UV Spectrophotometer	Satlantic ISUS/SUNA	0.5 µM	No – turbidity too high and concentrations too low
	Wet colourimetric (Greiss assay)	Systea WIZ YSI Beaton et al. 2012	0.02 µM	Yes *if reagents are anti-freeze and consumption is controlled*
Phosphate				
	Potentiometric Ion selective electrode	Various	10 µM	No – concentrations too low
	Biological reactor	Zhang et al. 2008	1 µM	No – temperatures too low
	Wet colourimetric (molybdenum blue)	Wetlabs Cycle	0.075 µM	No – concentrations too low
	Wet colourimetric (molybdenum blue)	Legiret et al. 2013	0.8 nM	Not presently *although future developments in antifreeze and microfluidics likely*

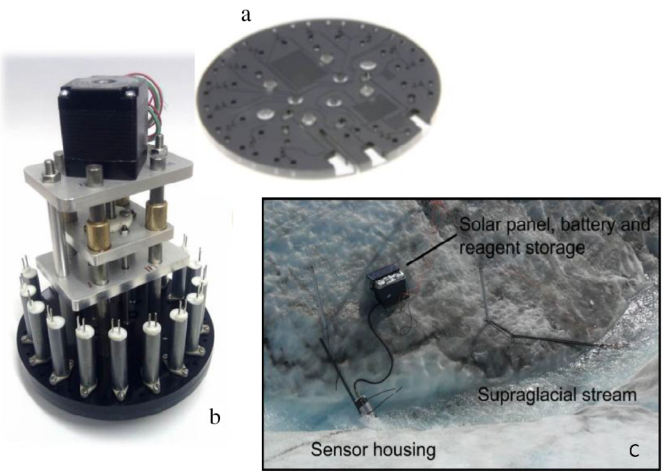

Fig. 3. Lab-on-chip sensor for nitrate analysis, incorporating a milled tinted polymethyl methacrylate (PMMA) chip (a) system assembled with pump and valves for fluid handling (b), and deployed in a supraglacial stream on the Greenland Ice Sheet (c).

(deionised water) are stored in flexible bags above the sensor package. Samples to be measured are passed through a 0.45 µm inline filter before entering the analyser. A 26 day test deployment in a tidal estuary demonstrated excellent stability and performance similar to conventional lab-based analysers, and the analyser has been deployed in a proglacial meltwater stream [61].

5.3. Recommendations

Miniaturised wet chemical analysers (e.g. using lab-on-chip) present the most promising solution for measuring nitrate in glacial meltwaters, as no other technology provides the low limit of detection or stability required for measuring nitrate in low concentration glacial meltwaters. A primary issue with deploying these sensors in cold environments is the possibility of liquid reagents and calibration standards freezing. Low temperatures also slow down reaction kinetics and diffusive mixing, resulting in slower response times or lower sensitivity. Incorporation of antifreeze into the reagents allows use in cold climates [61]. Further tests are required to fully prove the system's resilience to extreme cold conditions (such a spring/autumn melt periods in the polar regions, where air temperatures may be well below zero but meltwaters flow), but sensors such as these represent the most realistic solution for *in situ* monitoring of nitrate/nitrite in meltwaters at present.

6. Phosphorus

Phosphorous is another essential element for life which is exported in glacial meltwaters [62]. In its dissolved inorganic form it exists as phosphate (HPO_4^{2-}, H_2PO_4 or PO_4^{3-}). Dissolved phosphate and organic phosphorus levels in glacial meltwaters are low [1,62]. Phosphate has the tendency to adsorb onto the surface of suspended particles, meaning that highly turbid proglacial waters may be exporting important amounts of sediment bound phosphorous to downstream ecosystems. This is not measured as dissolved P and must be detected using sediment extractions. Protocols for the detection of phosphate and nitrate are similar, in that potentiometric, biosensing, optical, or traditional wet chemical analyses may be used. The primary problem for glacial waters is the requirement for low LoD (Table 2). Cobalt ISEs are unsuitable candidates for this reason, and available biosensors [63] perform poorly at low temperatures.

6.1. Wet chemical colourimetric flow analysers and recommendations

Wet chemical colorimetric methods are the best candidate for dissolved P measurement in glacial meltwaters. The WetLabs Cycle sensor is a promising option for long-term (>3 months) deployment in natural waters (eg [64].). The sensor utilises microfluidics and operates at temperatures as low as 1°C, although sample processing is limited to two per hour. The detection limit of 0.075 µM may be insufficient for many glacial waters [65]. Alternative methods based on microfluidic lab-on-chip colorimetric analyses have been developed [66], but are currently commercially unavailable. A shipboard system using the molybdemnum blue/ascorbic acid method with detection limit of 0.8 nM uses coiled quartz capilliaries to increase optical path length in the measurement cell, increasing sensitivity [67]. The technique was successfully demonstrated during a 4 week sub-Tropical sea cruise, with concentrations of 10–90 nM. Reagent freezing remains a potential problem, although this may be addressed by the addition of antifreeze to reagents (see section 5.2). Further development of the technique is required before it is suitable for deployment in glacial environments, but this remains the most promising candidate.

7. Iron and manganese

Dissolved iron in glacial meltwaters is derived from rock-water contact with iron-bearing minerals in the subglacial environment, such as iron sulphides [2]. Its export can influence the productivity of downstream environments [4]. Manganese(II) can be used as a tracer for anoxia in subglacial environments, since it persists in reduced form for longer than iron(II). Dissolved iron exists in natural waters in two oxidation states: iron(II) and iron(III). Iron(II) is more soluble but is only stable in anoxic conditions, being oxidised to iron(III) in oxic waters. Iron is present in aquatic environments in a broad spectrum of size fractions that range from truly dissolved to colloids and oxyhydroxide nanoparticles. A small number of studies report measurements of total dissolved iron concentrations in glacial meltwaters [2,4,68–72], typically using inductively coupled mass spectrometry (ICP-MS) or graphite furnace atomic absorption spectrophotometry on manually collected samples. Due to the difficulties associated with sampling and analysis in the field no studies have measured the dissolved speciation of Fe (Fe(II) and Fe(III)), and manganese concentrations are yet to be reported. Contamination during sample collection and transfer/storage is of particular concern with trace element analysis, which makes *in situ* measurement particularly desirable.

7.1. Voltammetry and ISE

In situ voltammetry provides a potential option for studying reduced forms of Fe and Mn in glacial meltwaters. A voltammetric *in situ* profiling (VIP) system [73] is available from Idronaut (Italy) and is capable of measuring Mn(II) and Fe(II) in freshwater or seawater at LoD ~10 nM. The packaging is, however, rather large (8 kg, 860 × 10 mm) since it is designed for ship-board deployment. Alternatively, Fe-sensitive ISEs have been developed which claim to measure ultra-low concentrations of Fe(III), down to 10^{-25} M in saline citrate and salicylate buffers [74]. However, the ability of such technologies to measure these concentrations has been disputed [75], since the ISE technique is typically limited to ~1 µM, likely in excess of typical glacial melt concentrations.

7.2. Wet chemical techniques

Performance of field colorimetric techniques for Fe(III), Fe(II) and Mn is now comparable to laboratory analyses, using either shipboard flow injection analysis (60 nM Fe(II) [76],) or miniaturised wet chemical techniques (20 nM Fe(III) and Mn [77], 27 nM Fe(II) and 28 nM Mn [78], 25 nM Mn(II) [79]). The small packaging of miniature sensors enables portability and deployment on autonomous vehicles. Use of longer pathlengths and microfluidic chips formed of tinted plastic can improve LoD [80]. Chemiluminescence techniques, which measure the production of light by a chemical reaction, further improve LoD since they do not require a radiation source and hence have significantly improved signal to noise ratios [81]. Reactions are typically manipulated and measured using flow injection analysis, and pre-concentration using various resins can extend LoD down to pM concentrations [82]. The technique has been successfully deployed on numerous shipboard surveys, including in iron limited regions of the Southern Ocean [83], and recent application of the technique in a Greenlandic fjord has measured concentrations of dissolved (<0.2 µm) Fe in meltwaters. This study, which includes a preconcentration step, revealed concentrations of Fe of 200 nM in meltwater entering the fjord, 38 nM in glacier ice, and 80 nM in meltwaters adjacent to the glacier [72].

7.3. Recommendations

Although voltammetry and ISEs present relatively simple solutions for iron determination, it is unlikely that a consistently low LoD is possible in the near future. Wet chemical techniques present the most promising solution, particularly with the addition of antifreeze reagents, although none are presently available commercially. A defined filtration system which excludes contaminants and distinguishes between truly dissolved, colloidal/nanoparticulate and sediment bound phases is also required to fully assess the importance of glacial meltwaters to downstream ecosystems [1].

8. Conclusions

Continuous, high-resolution monitoring of biogeochemical parameters in glacial meltwaters can reveal hitherto unseen processes and help to determine the impact of ice melt on biogeochemical cycles. Monitoring key chemical parameters using *in situ* sensors can reveal weathering processes and biological activity in otherwise inaccessible environments. In particular, sensors offer an attractive solution for gaining *in situ* data from deep, remote ecosystems such as Antarctic subglacial lakes. This is important for gathering data on less stable analytes (e.g. Fe(II)), and for de-risking the deployment of probes which rely upon sample collection and return. The availability of *in situ* chemical sensors for natural waters has typically been driven by marine applications. Some marine sensors are directly applicable to remote glacial environments, but others require adaptation and additional development to extend detection limits and enable operation at low temperatures. More mature examples of these technologies, for example, DO optodes, have successfully been deployed for extended periods at multiple locations in the cryosphere. Others are in early stages of field or laboratory testing to determine their response to low ionic strength, low concentration, low temperature meltwaters, which experience freeze-thaw cycles. Development priorities should focus on enabling these *in situ* measurements of a wide range of chemical parameters, particularly in the era of exploration of subglacial aquatic environments. Such chemical diagnostics will enhance scientific understanding of some of the most extreme and dynamic habitats on Earth.

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