



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

Elizabeth A. Bagshaw<sup>a,b,\*</sup>, Alexander Beaton<sup>c</sup>, Gemma L. Wadham<sup>b</sup>, Matt Mowlem<sup>c</sup>,  
Jon R. Hawkings<sup>b</sup>, Martyn Tranter<sup>b</sup>

<sup>a</sup> School of Earth and Ocean Sciences, Cardiff University, Cardiff CF10 3AT, UK

<sup>b</sup> Bristol Glaciology Centre, School of Geographical Sciences, University of Bristol, Bristol BS8 1SS, UK

<sup>c</sup> National Oceanography Centre, Southampton SO14 3ZH, UK



### ARTICLE INFO

#### Keywords:

Cryosphere  
Chemical sensors  
Glacial meltwater  
Oxygen  
pH  
Methane  
Nitrate  
Phosphate  
Iron

### 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.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

### Contents

1. Introduction .....	349
2. Dissolved oxygen .....	350
2.1. Optical sensor selection .....	350
2.2. Example deployments .....	350
2.3. Recommendations .....	351
3. pH .....	351
3.1. Potentiometric measurements .....	351
3.2. Spectrophotometric .....	352
3.3. Optodes .....	352
3.4. Recommendations .....	352
4. Methane .....	352
4.1. Available sensors .....	352
4.2. Recommendations .....	353
5. Nitrogen species .....	353
5.1. Potentiometric methods .....	353
5.2. Optical methods .....	353
5.2.1. Direct optical absorption spectroscopy .....	353
5.2.2. Wet chemical colourimetric flow analysers .....	353
5.3. Recommendations .....	354
6. Phosphorus .....	354
6.1. Wet chemical colourimetric flow analysers and recommendations .....	354
7. Iron and manganese .....	354
7.1. Voltammetry and ISE .....	354

\* Corresponding author. Fax: +44 (0)29 2087 4830.

E-mail address: [BagshawE@cardiff.ac.uk](mailto:BagshawE@cardiff.ac.uk) (E.A. Bagshaw).

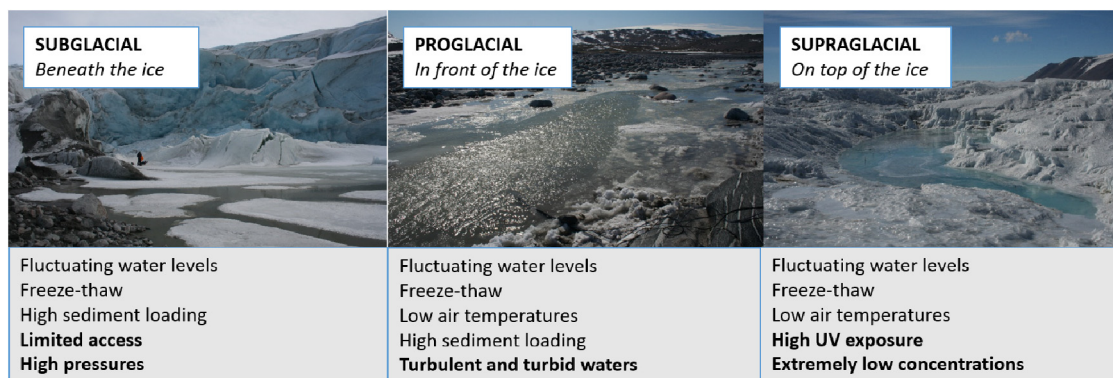
7.2. Wet chemical techniques .....	355
7.3. Recommendations .....	355
8. Conclusions .....	355
Acknowledgements .....	355
References .....	355

## 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<sup>2</sup>), ice caps (masses of glacial land ice <50,000 km<sup>2</sup>) 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<sup>-1</sup>, up to 16 g l<sup>-1</sup> [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 <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	pH
<b>Glacial runoff</b>	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
<b>Icemelt</b>	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 <sub>4</sub>	
<b>Glacial runoff</b>	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
<b>Icemelt</b>	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
<b>Oxygen</b>	1 $\mu\text{M}$	1 $\mu\text{M}$	1–500 $\mu\text{M}$
<b>pH</b>	0.2 pH	0.1 pH	5–11 pH
<b><math>\text{NO}_3^-</math></b>	0.05 $\mu\text{M}$	0.1 $\mu\text{M}$	0.1–100 $\mu\text{M}$
<b><math>\text{PO}_4^{3-}</math></b>	0.05 $\mu\text{M}$	0.1 $\mu\text{M}$	0.1–100 $\mu\text{M}$
<b>Fe</b>	1 nM	0.5 nM	1–5000 nM
<b><math>\text{CH}_4</math></b>	<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 ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ), silica, and indicators of the redox conditions (for example, Fe,  $\text{O}_2$ ,  $\text{CO}_2$ ). In addition, biological markers (such as  $\text{CO}_2$  and  $\text{O}_2$ ) 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), Aanderaa (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].

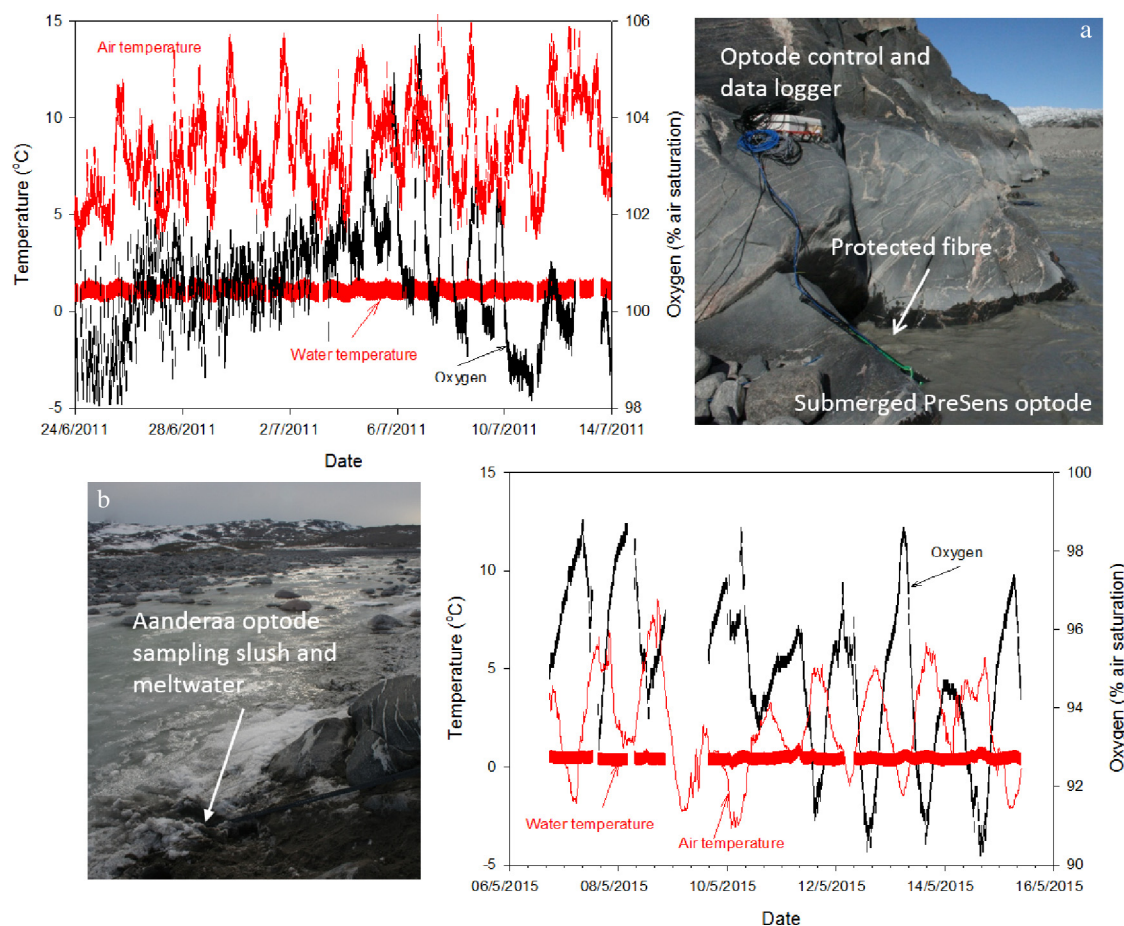
### 2.2. Example deployments

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
<b>Pyro Science: Robust</b>	0.05% at 20% $\text{O}_2$	0.2% at 20% $\text{O}_2$	3 mm
<b>Franatech: D Opto</b>	0.01% at saturation	1% or 0.02 ppm	48 mm
<b>Aanderaa: 3835</b>	0.4%	5% or 1 $\mu\text{M}$	36 mm
<b>PreSens: PSt3</b>	0.05 at 20.9% $\text{O}_2$	0.05%	4 mm
<b>Hach Lange: LDO</b>	0.1%	0.2 ppm	48 mm
<b>Ocean Optics: FOXY</b>	0.3 at 20% $\text{O}_2$	0.02% at 20% $\text{O}_2$	3 mm
<b>Unisense: Microoptode</b>	0.05% at 20% $\text{O}_2$	2% at 20% $\text{O}_2$	430 $\mu\text{m}$



**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  $800 \text{ m}^3 \text{ s}^{-1}$ ), 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  $+15^\circ\text{C}$ , 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  $\sim 5$  to  $\sim 10$ ) and are frequently at disequilibrium with the atmosphere with respect to  $\text{CO}_2$  (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  $\text{H}^+$ . 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?
<b>pH</b>	Potentiometric (glass electrode)	Various	1–11	No – poor performance at low ionic strength, sensitive to freezing
	Potentiometric (ISFET)	Honeywell, Campbell Scientific	0–14	Yes – <i>although ionic strength impact requires quantification</i>
	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 – <i>limited range</i>
<b>Dissolved oxygen</b>	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 – <i>if sensor head is robust</i>

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<sup>-1</sup> (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  $<10$   $\mu$ S/cm. Preliminary tests by the author (Bagshaw et al., *In Prep.*) suggest that the Durafet is effective at low ionic strength ( $5.45 \times 10^{-5}$  mol dm<sup>-3</sup> NaHCO<sub>3</sub>), but that there is a measurable change in the pH reported by the ISFET in an otherwise constant solution ( $<0.1 \pm 0.05$  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 *in 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 ( $<0.001$  pH) [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 ( $<10$   $\mu$ S/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  $0.3$   $\mu$ g CH<sub>4</sub> h<sup>-1</sup> m<sup>-3</sup> from sediments immediately adjacent to the ice [38], concentrations of  $5.7$  to  $18.4$  nM L<sup>-1</sup> of seawater in a glacial-fed fjord [39], and  $2.7$  to  $83$   $\mu$ M 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<sub>4</sub> 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](http://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 × 600 mm), 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<sub>3</sub><sup>-</sup>) [48], nitrite (NO<sub>2</sub><sup>-</sup>) [49] and

ammonium (NH<sub>4</sub><sup>+</sup>) [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

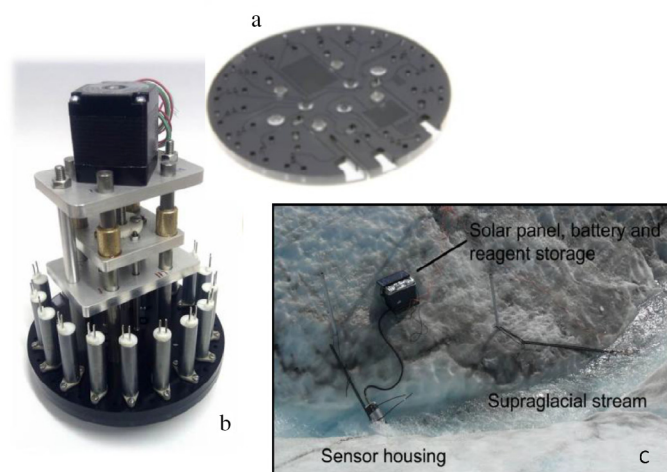
Colourimetric methods utilise the formation and detection of a strongly absorbing dye, whose optical absorption is linearly proportional to the concentration of the target analyte. The concentration-absorption relationship means that measurements can be made at extremely low concentrations by increasing 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
	<i>In Situ</i> UV Spectrophotometer	Satlantic ISUS/SUNA	0.5 µM	No – turbidity too high and concentrations too low
	Wet colourimetric (Greiss assay)	Systea WIZ	0.02 µM	Yes if reagents are anti-freeze and consumption is controlled
		YSI		
Phosphate		Beaton et al. 2012		
	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 poly-methyl 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  $0.45\ \mu\text{m}$  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 as 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 ( $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4$  or  $\text{PO}_4^{3-}$ ). 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  $1^\circ\text{C}$ , although sample processing is limited to two per hour. The detection limit of  $0.075\ \mu\text{M}$  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 ship-board system using the molybdenum blue/ascorbic acid method with detection limit of  $0.8\ \text{nM}$  uses coiled quartz capillaries 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  $\text{LoD} \sim 10\ \text{nM}$ . The packaging is, however, rather large (8 kg,  $860 \times 10\ \text{mm}$ ) 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  $10^{-25}\ \text{M}$  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  $\sim 1\ \mu\text{M}$ , 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 miniaturised 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.

## Acknowledgements

The work presented in this review is part of the UK Natural Environment Research Council funded DELVE project (NERC grant NE/I008845/1). Fieldwork at Leverett Glacier was enabled by Kangerlussuaq International Science Support centre, HeliGreenland and a team of enthusiastic and helpful field assistants. We extend particular thanks to Jon Telling and Guillaume Lamarche-Gagnon. Two anonymous reviewers suggested valuable improvements to the manuscript.

## References

- [1] J.R. Hawkings, J.L. Wadham, M. Tranter, E. Lawson, A. Sole, T. Cowton, et al., The effect of warming climate on nutrient and solute export from the Greenland Ice Sheet, *Geochim. Perspect. Lett.* 1 (2015) 94–104.
- [2] J. Hawkings, J. Wadham, M. Tranter, R. Raiswell, L. Benning, P.J. Statham, et al., Ice sheets as a significant source of highly reactive nanoparticulate iron to the oceans, *Nat. Commun.* 5 (2014) 3929.
- [3] E. Hood, J. Fellman, R.G.M. Spencer, P.J. Hernes, R. Edwards, D. D'Amore, et al., Glaciers as a source of ancient and labile organic matter to the marine environment, *Nature* 462 (2009) U1044–U1100.
- [4] M.P. Bhatia, E.B. Kujawinski, S.B. Das, C.F. Breier, P.B. Henderson, M.A. Charette, Greenland meltwater as a significant and potentially bioavailable source of iron to the ocean, *Nat. Geosci.* 6 (2013) 274–278.
- [5] J.L. Wadham, R. De'ath, F.M. Monteiro, M. Tranter, A. Ridgwell, R. Raiswell, et al., The potential role of the Antarctic Ice Sheet in global biogeochemical cycles, *Earth Environ. Sci. Trans. Royal Soc. Edinburgh* 104 (2013) 55–67.
- [6] T.S. Moore, K.M. Mullaugh, R.R. Holyoke, A.S. Madison, M. Yucel, G.W. Luther, Marine chemical technology and sensors for marine waters: potentials and limits, *Ann. Rev. Mar. Sci.* 1 (2009) 91–115.
- [7] T. Cowton, P. Nienow, I. Bartholomew, A. Sole, D. Mair, Rapid erosion beneath the Greenland ice sheet, *Geology* 40 (2012) 343–346.
- [8] M. Tranter, J.L. Wadham, Geochemical weathering in glacial and proglacial environments, in: H.D. Holland, K.K. Turekian (Editors), *Treatise on Geochemistry*, Elsevier, Oxford, 2014, pp. 157–173.
- [9] M. Tranter, M.J. Sharp, H.R. Lamb, G.H. Brown, B.P. Hubbard, I.C. Willis, Geochemical weathering at the bed of Haut Glacier d'Arolla, Switzerland – a new model, *Hydrol. Process.* 16 (2002) 959–993.
- [10] M. Skidmore, M. Tranter, S. Tulaczyk, B. Lanoil, Hydrochemistry of ice stream beds – evaporitic or microbial effects?, *Hydrol. Process.* 24 (2010) 517–523.
- [11] E.C. Lawson, J.L. Wadham, M. Tranter, M. Stibal, G.P. Lis, C.E.H. Butler, et al., Greenland Ice Sheet exports labile organic carbon to the Arctic oceans, *Biogeosciences* 11 (2014) 4015–4028.
- [12] M. Diesner, E.L.J.E. Broensen, K.A. Cameron, G.M. King, A. Achberger, K. Choquette, et al., Molecular and biogeochemical evidence for methane cycling beneath the western margin of the Greenland Ice Sheet, *ISME J.* 8 (2014) 2305–2316, doi:10.1038/ismej.2014.59.
- [13] B.C. Christner, J.C. Prisco, A.M. Achberger, C. Barbante, S.P. Carter, K. Christianson, et al., A microbial ecosystem beneath the West Antarctic ice sheet, *Nature* 512 (2014) 310–313.
- [14] M. Stibal, J.L. Wadham, G.P. Lis, J. Telling, R.D. Pancost, A. Dubnick, et al., Methanogenic potential of Arctic and Antarctic subglacial environments with contrasting organic carbon sources, *Global Change Biol.* 18 (2012) 3332–3345.
- [15] J.L. Wadham, S. Arndt, S. Tulaczyk, M. Stibal, M. Tranter, J. Telling, et al., Potential methane reservoirs beneath Antarctica, *Nature* 488 (2012) 633–637.
- [16] E.A. Bagshaw, J.L. Wadham, M. Mowlem, M. Tranter, J. Eveness, A.G. Fountain, et al., Determination of dissolved oxygen in the cryosphere: a comprehensive laboratory and field evaluation of fiber optic sensors, *Environ. Sci. Technol.* 45 (2011) 700–705.
- [17] L.C. Clark, C.F. Wolf, D. Granger, Z. Taylor, Continuous recording of blood oxygen tensions by polarography, *J. Appl. Physiol.* 6 (1953) 189–193.
- [18] N.P. Revsbech, An oxygen microsensor with a guard cathode, *Limnol. Oceanogr.* 34 (1989).
- [19] I. Klimant, V. Meyer, M. Kuhl, Fiberoptic oxygen microsensors: a new tool in aquatic biology, *Limnol. Oceanogr.* 40 (1995) 1159–1165.
- [20] O.S. Wolfbeis, Fiber-optic chemical sensors and biosensors, *Anal. Chem.* 80 (2008) 4269–4283.
- [21] K.R. Rogers, E.J. Poziomek, Fiber optic sensors for environmental monitoring, *Chemosphere* 33 (1996) 1151–1174.
- [22] M. Martini, B. Butman, M.J. Mickelson, Long-term performance of Aanderaa optodes and sea-bird SBE-43 dissolved-oxygen sensors bottom mounted at 32 m in Massachusetts Bay, *J. Atmospher. Oceanic Technol.* 24 (2007) 1924–1935.
- [23] A. Kortzinger, J. Schimanski, U. Send, High quality oxygen measurements from profiling floats: a promising new technique, *J. Atmospher. Oceanic Technol.* 22 (2005) 302–308.
- [24] A. Tengberg, J. Hovdenes, H.J. Andersson, O. Brocandel, R. Diaz, D. Hebert, et al., Evaluation of a lifetime-based optode to measure oxygen in aquatic systems, *Limnology Oceanography Meth.* 4 (2006) 7–17.



- [25] E.A. Bagshaw, M. Tranter, J.L. Wadham, A.G. Fountain, M. Mowlem, High-resolution monitoring reveals dissolved oxygen dynamics in an Antarctic cryoconite hole, *Hydrol. Process.* 25 (2011) 2868–2877.
- [26] R.G. Bates, Determination of pH: Theory and Practice, Wiley, 1973.
- [27] V.M.C. Rerolle, C.F.A. Floquet, M.C. Mowlem, R. Bellerby, D.P. Connelly, E.P. Achterberg, Seawater-pH measurements for ocean-acidification observations, *Trends Analyt. Chem.* 40 (2012) 146–157.
- [28] T.R. Martz, J.G. Connery, K.S. Johnson, Testing the Honeywell Durafet (R) for seawater pH applications, *Limnology Oceanography Meth.* 8 (2010) 172–184.
- [29] P. Bergveld, Thirty years of ISFETOLOGY – What happened in the past 30 years and what may happen in the next 30 years, *Sens. Actuators B Chem.* 88 (2003) 1–20.
- [30] R.A. Easley, R.H. Byrne, Spectrophotometric calibration of pH electrodes in seawater using purified m-cresol purple, *Environ. Sci. Technol.* 46 (2012) 5018–5024.
- [31] X.W. Liu, M.C. Patsavas, R.H. Byrne, Purification and characterization of meta-cresol purple for spectrophotometric seawater pH measurements, *Environ. Sci. Technol.* 45 (2011) 4862–4868.
- [32] T.A. DelValls, A.G. Dickson, The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol ('tris') in synthetic sea water, *Deep-Sea Res. Part I Oceanographic Res. Papers* 45 (1998) 1541–1554.
- [33] V.M. Rerolle, C.F. Floquet, A.J. Harris, M.C. Mowlem, R.R. Bellerby, E.P. Achterberg, Development of a colorimetric microfluidic pH sensor for autonomous seawater measurements, *Anal. Chim. Acta* 786 (2013) 124–131.
- [34] M.P. Seidel, M.D. DeGrandpre, A.G. Dickson, A sensor for in situ indicator-based measurements of seawater pH, *Mar. Chem.* 109 (2008) 18–28.
- [35] M. Larsen, S.M. Borisov, B. Grunwald, I. Klimant, R.N. Glud, A simple and inexpensive high resolution color radiometric planar optode imaging approach: application to oxygen and pH sensing, *Limnology Oceanography Meth.* 9 (2011) 348–360.
- [36] G. Liebsch, I. Klimant, C. Krause, O.S. Wolfbeis, Fluorescent imaging of pH with optical sensors using time domain dual lifetime referencing, *Anal. Chem.* 73 (2001) 4354–4363.
- [37] P.J. Bresnahan Jr., T.R. Martz, Y. Takeshita, K.S. Johnson, M. LaShomb, Best practices for autonomous measurement of seawater pH with the Honeywell Durafet, *Meth. Oceanography* 9 (2014) 44–60.
- [38] T.G. Barcena, J.C. Yde, K.W. Finster, Methane flux and high-affinity methanotrophic diversity along the chronosequence of a receding glacier in Greenland, *Annal. Glaciol.* 51 (2010) 23–31.
- [39] O. Crabeck, B. Delille, D.N. Thomas, N.X. Geilfus, S. Rysgaard, J.L. Tison, CO<sub>2</sub> and CH<sub>4</sub> in sea ice from a subarctic fjord, *Biogeochem. Discuss* 11 (2014) 4047–4083.
- [40] C. Boulart, D.P. Connelly, M.C. Mowlem, Sensors and technologies for in situ dissolved methane measurements and their evaluation using Technology Readiness Levels, *Trends Analyt. Chem.* 29 (2010) 186–195.
- [41] L.R. Damgaard, L.P. Nielsen, N.P. Revsbech, Methane microprofiles in a sewage biofilm determined with a microscale biosensor, *Water Res.* 35 (2001) 1379–1386.
- [42] T. Fukasawa, S. Hozumi, M. Morita, T. Oketani, M. Masson, IEEE, Dissolved methane sensor for methane leakage monitoring in methane hydrate production, *Oceans* 2006 1–4 (2006) 449–454.
- [43] C. Boulart, R. Prien, V. Chavagnac, J.P. Dutasta, Sensing dissolved methane in aquatic environments: an experiment in the central baltic sea using surface plasmon resonance, *Environ. Sci. Technol.* 47 (2013) 8582–8590.
- [44] K.C. Hester, R.M. Dunk, S.N. White, P.G. Brewer, E.T. Peltzer, E.D. Sloan, Gas hydrate measurements at Hydrate Ridge using Raman spectroscopy, *Geochim. Cosmochim. Acta* 71 (2007) 2947–2959.
- [45] N.G. Davey, E.T. Krogh, C.G. Gill, Membrane-introduction mass spectrometry (MIMS), *Trends Analyt. Chem.* 30 (2011) 1477–1485.
- [46] M. Schmidt, P. Linke, D. Esser, Recent development in IR sensor technology for monitoring subsea methane discharge, *Mar. Technol. Soc. J.* 47 (2013) 27–36.
- [47] P. Fietzek, S. Kramer, D. Esser, IEEE, Deployments of the HydroC (TM) (CO<sub>2</sub>/CH<sub>4</sub>) on stationary and mobile platforms – Merging trends in the field of platform and sensor development, 2011.
- [48] D. Debeer, J.P.R. Sweerts, Measurement of nitrate gradients with an ion-selective microelectrode, *Anal. Chim. Acta* 219 (1989) 351–356.
- [49] D. De Beer, A. Schramm, C.M. Santegeods, M. Kuhl, A nitrite microsensor for profiling environmental biofilms, *Appl. Environ. Microbiol.* 63 (1997) 973–977.
- [50] D. Debeer, J.C. Vandenheuvel, Response of ammonium-selective microelectrodes based on the neutral carrier nonactin, *Talanta* 35 (1988) 728–730.
- [51] T. Le Goff, J. Braven, L. Ebdon, D. Scholefield, Automatic continuous river monitoring of nitrate using a novel ion-selective electrode, *J. Environ. Monit.* 5 (2003) 353–358.
- [52] M.S. Finch, D.J. Hydes, C.H. Clayson, B. Weigl, J. Dakin, P. Gwilliam, A low power ultra violet spectrophotometer for measurement of nitrate in seawater: introduction, calibration and initial sea trials, *Anal. Chim. Acta* 377 (1998) 167–177.
- [53] K.S. Johnson, L.J. Coletti, In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean, *Deep-Sea Res. Part I Oceanographic Res. Papers* 49 (2002) 1291–1305.
- [54] K.S. Johnson, L.J. Coletti, H.W. Jannasch, C.M. Sakamoto, D.D. Swift, S.C. Riser, Long-term nitrate measurements in the ocean using the in situ ultraviolet spectrophotometer: sensor integration into the APEX profiling float, *J. Atmospher. Oceanic Technol.* 30 (2013) 1854–1866.
- [55] R.C. Sandford, A. Exenberger, P.J. Worsfold, Nitrogen cycling in natural waters using in situ, reagentless UV spectrophotometry with simultaneous determination of nitrate and nitrite, *Environ. Sci. Technol.* 41 (2007) 8420–8425.
- [56] B.A. Pellerin, J.F. Saraceno, J.B. Shanley, S.D. Sebestyen, G.R. Aiken, W.M. Wollheim, et al., Taking the pulse of snowmelt: in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream, *Biogeochemistry* 108 (2012) 183–198.
- [57] A. Randelhoff, A. Sundfjord, M. Reigstad, Seasonal variability and fluxes of nitrate in the surface waters over the Arctic shelf slope, *Geophys. Res. Lett.* 42 (2015) 3442–3449.
- [58] P. Gardolinski, A.R.J. David, P.J. Worsfold, Miniature flow injection analyser for laboratory, shipboard and in situ monitoring of nitrate in estuarine and coastal waters, *Talanta* 58 (2002) 1015–1027.
- [59] N. Le Bris, P.M. Sarraadin, D. Birot, A.M. Alayse-Danet, A new chemical analyzer for in situ measurement of nitrate and total sulfide over hydrothermal vent biological communities, *Mar. Chem.* 72 (2000) 1–15.
- [60] A.D. Beaton, C.L. Cardwell, R.S. Thomas, V.J. Sieben, F.E. Legiret, E.M. Waugh, et al., Lab-on-Chip Measurement of Nitrate and Nitrite for In Situ Analysis of Natural Waters, *Environ. Sci. Technol.* 46 (2012) 9548–9556.
- [61] A. Beaton, M. Mowlem, J. Wadham, Miniaturised 'lab-on-a-chip' nitrate analyser applied to high resolution in situ analysis of glacial meltwater, *AGU Fall Meeting Abstr.* 1 (2013) 1521.
- [62] J. Hawkings, J. Wadham, M. Tranter, J. Telling, E. Bagshaw, A. Beaton, et al., The Greenland Ice Sheet as a hot spot of phosphorus weathering and export in the Arctic, *Glob. Biogeochem. Cycle* (2016) doi:10.1002/2015 GB005237. Epub ahead of print.
- [63] Z.Q. Zhang, N. Jaffrezic-Renault, F. Bessueille, D. Leonard, S.Q. Xia, X.J. Wang, et al., Development of a conductometric phosphate biosensor based on tri-layer maltose phosphorylase composite films, *Anal. Chim. Acta* 615 (2008) 73–79.
- [64] M.J. Cohen, M.J. Kurz, J.B. Heffernan, J.B. Martin, R.L. Douglass, C.R. Foster, et al., Diel phosphorus variation and the stoichiometry of ecosystem metabolism in a large spring-fed river, *Ecol. Monogr.* 83 (2013) 155–176.
- [65] A. Hodson, P. Murnford, D. Lister, Suspended sediment and phosphorus in proglacial rivers: bioavailability and potential impacts upon the P status of ice-marginal receiving waters, *Hydrol. Process.* 18 (2004) 2409–2422.
- [66] F.E. Legiret, V.J. Sieben, E.M.S. Woodward, S. Bey, M.C. Mowlem, D.P. Connelly, et al., A high performance microfluidic analyser for phosphate measurements in marine waters using the vanadomolybdate method, *Talanta* 116 (2013) 382–387.
- [67] M.D. Patey, M.J.A. Rijkenberg, P.J. Statham, M.C. Stinchcombe, E.P. Achterberg, M. Mowlem, Determination of nitrate and phosphate in seawater at nanomolar concentrations, *Trends Analyt. Chem.* 27 (2008) 169–182.
- [68] J. Mickuki, C. Foreman, B. Sattler, W.B. Lyons, J. Priscu, Geomicrobiology of blood falls: an iron-rich saline discharge at the terminus of the Taylor Glacier, *Aquatic Geochem.* 10 (2004) 199–220.
- [69] A. Mitchell, G.H. Brown, R. Fuge, Minor and trace element export from a glacierized Alpine headwater catchment (Haut Glacier d'Arolla, Switzerland), *Hydrol. Process.* 15 (2001) 3499–3524.
- [70] A. Hodson, T. Heaton, H. Langford, K. Newsham, Chemical weathering and solute export by meltwater in a maritime Antarctic glacier basin, *Biogeochemistry* 98 (2010) 9–27.
- [71] P.J. Statham, M. Skidmore, M. Tranter, Inputs of glacially derived dissolved and colloidal iron to the coastal ocean and implications for primary productivity, *Glob. Biogeochem. Cycle* 22 (2008).
- [72] M.J. Hopwood, D.P. Connelly, K.E. Arendt, T. Juul-Pedersen, M. Stinchcombe, L. Meire, et al., Seasonal changes in Fe along a glaciated Greenlandic fjord, *Front. Earth Sci.* 4 (2016).
- [73] M.L. Tercier-Waeber, M. Taillefert, Remote in situ voltammetric techniques to characterize the biogeochemical cycling of trace metals in aquatic systems, *J. Environ. Monit.* 10 (2008) 30–54.
- [74] R. De Marco, D.J. Mackey, Calibration of a chalcogenide glass membrane ion-selective electrode for the determination of free Fe<sup>3+</sup> in seawater I. Measurements in UV photooxidised seawater, *Mar. Chem.* 68 (2000) 283–294.
- [75] C.M.G. van den Berg, Comments on "Calibration of a chalcogenide glass membrane ion-selective electrode for the determination of free Fe<sup>3+</sup> in seawater: I. Measurements in UV photooxidised seawater" by De Marco and Mackey (*Marine Chemistry* 68 (2000) 283–294), *Mar. Chem.* 71 (2000) 331–332.
- [76] P.M. Sarraadin, N. Le Bris, C. Le Gall, P. Rodier, Fe analysis by the ferrozine method: adaptation to FIA towards in situ analysis in hydrothermal environment, *Talanta* 66 (2005) 1131–1138.
- [77] D. Meyer, R.D. Prien, O. Dellwig, D.P. Connelly, D.E. Schulz-Bull, In situ determination of iron(II) in the anoxic zone of the central Baltic Sea using ferene as spectrophotometric reagent, *Mar. Chem.* 130 (2012) 21–27.
- [78] A. Milani, P.J. Statham, M.C. Mowlem, D.P. Connelly, Development and application of a microfluidic in-situ analyzer for dissolved Fe and Mn in natural waters, *Talanta* 136 (2015) 15–22.
- [79] P.J. Statham, D.P. Connelly, C.R. German, T. Brand, J.O. Overnell, E. Bulukin, et al., Spatially complex distribution of dissolved manganese in a fjord as revealed by high-resolution in situ sensing using the autonomous underwater vehicle Autosub, *Environ. Sci. Technol.* 39 (2005) 9440–9445.
- [80] C.F.A. Floquet, V.J. Sieben, A. Milani, E.P. Joly, I.R.G. Ogilvie, H. Morgan, et al., Nanomolar detection with high sensitivity microfluidic absorption cells manufactured in tinted PMMA for chemical analysis, *Talanta* 84 (2011) 235–239.
- [81] P.J. Worsfold, R. Clough, M.C. Lohan, P. Monbet, P.S. Ellis, C.R. Quetel, et al., Flow injection analysis as a tool for enhancing oceanographic nutrient measurements—A review, *Anal. Chim. Acta* 803 (2013) 15–40.

- [82] A.R. Bowie, E.P. Achterberg, S. Ussher, P.J. Worsfold, Design of an automated flow injection-chemiluminescence instrument incorporating a miniature photomultiplier tube for monitoring picomolar concentrations of iron in seawater, *J. Autom. Meth. Manage. Chem.* (2005) 37–43 DOI.
- [83] P.N. Sedwick, C.M. Marsay, B.M. Sohst, A.M. Aguilar-Islas, M.C. Lohan, M.C. Long, et al., Early season depletion of dissolved iron in the Ross Sea polynya: implications for iron dynamics on the Antarctic continental shelf, *J. Geophys. Res. Oceans* 116 (2011).