

Summer–winter transitions in Antarctic ponds: III. Chemical changes

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Abstract: Observations were made of water column chemistry in four Na-Cl dominated ponds on the McMurdo Ice Shelf from the end of January to early April in 2008. During that time the ponds went from ice-free to predominantly frozen, with only a small volume of residual hypoxic, saline liquid trapped at the base of each pond. Changes in the concentrations of inorganic solutes with time distinguished Na, Cl, Mg, K, SO₄, As, U and Mn as ions and trace elements that behave mainly conservatively during freezing, from those which are affected by biological processes (removing HCO₃) and the precipitation of mineral phases such as calcite (removing Ca and more HCO₃). Dissolved Fe, Mo, Cu and Zn also show evidence of precipitation from the water column during freezing; geochemical speciation modelling predicts the formation of stable insoluble mineral phases such as Fe oxides and oxyhydroxides while conditions are oxic, and Fe-, Cu-, Mo- and Zn-sulphide minerals in the presence of H₂S. Consequently, under winter conditions, residual liquid beneath the ice in such ponds is anticipated to be an anoxic Na-Cl brine with the capacity to develop high concentrations of toxic trace elements such as As and U.

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Introduction

Meltwater ponds are widespread in Antarctica and are an important life-supporting component of the Antarctic environment (e.g. Vincent & James 1996, Howard-Williams & Hawes 2007). However, this is an aquatic environment in which physical and chemical conditions show extreme seasonal variations; in summer ponds can be fully melted with relatively dilute water chemistry and high temperatures, while in winter they are predominantly frozen with the only liquid likely to be present as a small volume of cold, highly saline brine, trapped beneath the ice cover. The high salinity develops as dissolved ions are excluded from the ice structure during freezing (Wait *et al.* 2006, 2009, Hawes *et al.* 2010a). Pond waters can exhibit a wide range of intermediate compositions when partially or fully melted, even in the same pond feature if the water column is vertically stratified (e.g. Schmidt *et al.* 1991, Webster *et al.* 1994, Healy *et al.* 2006). Such stratification develops during thawing when dilute, less dense ice melt floats on top of the saline basal brine. If the pond water column remains unmixed by wind, such stratification can persist throughout the summer period.

The extreme chemical and physical conditions associated with the process of freezing play an important role in structuring biological communities (Hawes *et al.* 1999, 2010b). In order to survive, pond biota must be able to tolerate freezing, but also

the complete range of chemical conditions that they are exposed to in the liquid phase over the year. For organisms in deeper parts of ponds, this will include exposure to the more extreme chemical conditions that develop in the basal brines. However, our knowledge of pond water chemistry is largely restricted to the fully melted summer periods and to late spring conditions, when brines at the base of still predominantly frozen ponds have been sampled (Healy *et al.* 2006, Wait *et al.* 2006). The development of brines, however, occurs during autumn and we can expect the most extreme chemistry to occur over winter, periods when access is most difficult.

In 2008 we undertook a time series of observations of ponds on the McMurdo Ice Shelf close to Bratina Island, from January (maximum melt) through to April (substantially frozen). The goal of these observations was to document physical and chemical changes that accompany the pond freezing process and the biological responses, in the belief that extreme autumn and winter conditions will probably play a significant role in dictating the uniquely “Antarctic” characteristics of the biota in these ponds. This is the third in a series of papers describing the findings from this research. The first paper documented water temperatures falling rapidly to freezing, followed by ice formation and subsequent further temperature decreases, a rapid decline in irradiance to near-darkness, and the persistence of increasingly saline liquid water in these ponds for many weeks after ice formation began

(Hawes *et al.* 2010a). The second paper described how microbial communities and biologically active materials, particularly inorganic carbon, dissolved oxygen, sulphide and pH, responded to and interacted with the changing conditions during ice formation (Hawes *et al.* 2010b). In this contribution, the third paper in this series, we describe the behaviour of major ions and trace elements during pond freezing, and identify the key processes controlling the concentrations of dissolved chemicals.

Methods

Study site

Full details of the site and study ponds are given in the first of this series of papers (Hawes *et al.* 2010a). Four small ponds on the McMurdo Ice Shelf close to Bratina Island (78°S, 165.5°E) were selected for the study; Legin, JA, P70 and Bambi ponds; each of similar size and depth, and all ice-free during summer. All ponds were initially fully melted and between 80 cm and 100 cm deep. The ponds were sampled regularly from January–April 2008, during which time ice cover increased at a near-constant rate to reach 80 cm thickness, resulting in an exponential decline in remaining water volume over time (Hawes *et al.* 2010a).

Of the ponds selected, Legin pond (unofficial name) was the only one to be distinctly density stratified at the start of the sampling period (in mid-January). A pocket of warm, highly saline water occurred beneath a much larger, well-mixed volume of more dilute water; a meromictic state reported from many other coastal and inland Antarctic ponds (e.g. Healy *et al.* 2006, Wait *et al.* 2006). The other three ponds (JA, Bambi and P70) were all primarily well mixed, but in each case a very small pool of saline water (< 100 ml) occurred at the extreme base of the pond. These saline pools were too small to be reliably sampled.

As reported in Hawes *et al.* (2010a), partitioning of salts into the remaining liquid phase during ice thickening resulted in a near exponential rise in conductivity as a function of time, during which any trace of salinity stratification disappeared from the three “mixed” ponds, though not from Legin.

Pond sampling

Ponds were sampled repeatedly between 20 January and 7 April 2008, initially from the pond edge using a telescopic pole to reach the centre of the ponds, and later (after 7 February) when the ice cover was thick enough to support weight, through a 50 mm diameter hole through the ice over the deepest part of each pond. Detailed depth profiles of temperature, conductivity, DO and pH were obtained, and are described in the companion papers (Hawes *et al.* 2010a, 2010b). These data are referred to here only when required to interpret changes in inorganic ion or trace element concentrations.

Water sampling

Chemical variables in the water column in this study are mainly identified as relating to the “top” (just below the ice layer), “mid” (midway between the “top” and “base” sampling depths) or “base” (just above the sediment at the bottom) of the pond. More specifically, the water samples were initially collected from 10, 40 and 80 cm in JA, P70 and Bambi ponds and from 10, 50 and 100 cm depth in Legin. The “top” sample became a sample from just below the ice, when ice thickness exceeded 10 cm. Once the ice was able to be used to access the deepest point, it became obvious that Bambi and Legin were deeper than had been apparent and the Legin was stratified with a mixed layer overlying a salt induced density gradient beginning at a depth of *c.* 120 cm, which remained stable throughout the freezing process (Hawes *et al.* 2010a). To accommodate this, a deeper sample (120 cm depth) became the “base” sample. Thus the regular sampling in Legin targeted the mixed layer only, supplemented with a single profile through the entire water column at the end of the study period.

Water samples were collected using an acid rinsed, 5 mm internal diameter plastic hose inserted to the required depth and connected to a hand-driven peristaltic pump. From March onwards, to reduce freezing of water in the tube, a coil of the tubing was placed in a thermos flask of warm water immediately after exiting the pond ice cover and before it entered the pump. Water samples were pumped into thrice-rinsed HDPE bottles housed in an insulated box containing hot water bottles. Despite these precautions, occasionally ice crystals would begin to form in water samples and these samples were allowed to thaw in the field laboratory before sub-samples were taken for analysis.

Sub-samples were taken for major ion and, at selected depth-time combinations, trace element analysis. Major ion samples were kept refrigerated, but unfiltered and unfrozen for analysis. For dissolved trace elements, waters were filtered through 0.45 µm cellulose filters. One sample was then acidified to pH < 2 using purified 8N HNO₃, while the another sample was filtered, but not acidified, and later used to confirm arsenic (As) concentrations in samples potentially containing H₂S. In such samples, in our experience, the addition of acid can lead to precipitation of As from the solution and an erroneously low As concentration.

Samples for the measurement of dissolved sulphide (as H₂S) were pumped into 50 ml plastic tubes and immediately preserved by the addition of two drops of 1 M zinc acetate solution.

Sample analysis

All chemical analyses, except for dissolved inorganic carbon (DIC) were undertaken after return to New Zealand. Bicarbonate ion (HCO₃⁻) was calculated from DIC, estimated by *in situ* infrared gas analysis (IRGA) (Hawes *et al.* 2010b). It has been assumed that all DIC is in the form of HCO₃⁻ ion, as pond pH remained below the second dissociation constant

Table I. Summary data showing changes in major ion chemistry for the four study ponds; J = 27 January 2008, close to the end of the summer open water period where the water column is mixed and concentrations shown are an average over three depths (top, mid and base), and A = early April 2008 sampling of residual brine under the ice. Major ion concentrations are in mg.l^{-1} and conductivities are in $\mu\text{S.cm}^{-1}$

Pond		Conductivity	Na	K	Ca	Mg	Cl	SO ₄	HCO ₃
Bambi	J	3355	710	26.4	9.00	30.3	875	254	166
	A	17 390	4510	142	2.5	195	4970	1350	2070
JA	J	2430	374	19.6	50.7	77.4	687	91.0	72.1
	A	67 400	14 800	317	377	2330	26 950	3540	2600
P70	J	5980	1060	49.0	46.3	97.8	1790	279	71.2
	A	34 500	8770	254	91.4	967	13 400	2110	409
Legin	J	2995	509	23.1	46.2	78.1	792	235	80.0
	A	39 700	8900	178	434	1020	13 000	5530	478

for carbonic acid, in all but a few samples (see Hawes *et al.* 2010b).

For major ion analysis, samples underwent varying degrees of dilution with ultrapure deionized water to bring them into the analytical range; a procedure that has been validated by Welch *et al.* (1996) for ion chromatography on Antarctic meltwater. Chloride (Cl) and sulphate (SO₄) were analysed using high-pressure ion chromatography (HPIC), with a Dionex AS11, 4 mm diameter column and 10 mM NaOH as eluent. Detection limits were 0.5 mg.l^{-1} for both ions. Sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) analysis was by flame atomic adsorption spectrometry (FAAS), using mixed cation, matrix-matched standards with CsCl added to suppress ionization where the existing Na content was not sufficient for this purpose. The detection limit ranges from 0.1–0.4 mg.l^{-1} for these cations. Field blanks and deionized water blanks had ion concentrations at or below the detection limit. All major ion analyses reported here had ion balances within 10%, and most were within 5%, as a percentage of total ion content. Total sulphide (as H₂S) was determined by the methylene blue method (APHA 1999). Samples were either analysed directly if sulphide concentrations were > 0.05 mg.l^{-1} , or after pre-concentration by settlement and removal of the decant, if concentrations were < 0.05 mg.l^{-1} .

Trace elements were determined using ICP-mass spectrometry, for all except arsenic (As) which suffers from Cl interference by this method. After dilution of the samples for ICP-mass spectrometry, no other interference effects were reported for this method. Detection limits ranged from 0.0004 mg.l^{-1} for uranium (U), to 0.001 mg.l^{-1} for copper (Cu), lead (Pb), manganese (Mn), and molybdenum (Mo), and 0.004 mg.l^{-1} for iron (Fe) and zinc (Zn). Arsenic was determined using hydride generation AAS, with a detection limit of 0.002 mg.l^{-1} . Two field blanks, and two acidified, deionized water blanks were analysed, showing below detectable concentrations of the trace elements analysed here.

Results

Major ions

In late January 2008, near the end of the open water period, the average conductivities in three of the four study ponds

(JA, Bambi and Legin mixed layer) were broadly similar at *c.* 2400–3400 $\mu\text{S.cm}^{-1}$ (Table I). The average conductivity of P70 Pond was significantly higher (5980 $\mu\text{S.cm}^{-1}$). All ponds had relatively high pH (> 9), and were fully oxygenated. All of the study ponds were Na-Cl dominated in January and remained so throughout the autumnal freezing phase. This is the dominant chemistry for Bratina Island ponds.

A summary of initial water chemistry in January, compared to residual brine chemistry in April, is given in Table I. Differences in the starting chemistry of the four ponds (e.g. the more concentrated nature of P70, low Ca in Bambi and low SO₄ in JA) is a reflection of differences in pond genesis and history. Previous evaporation, mineral precipitation and inundation events will have influenced the chemical evolution of the pond up to this point. However, for this study, it is the change in each parameter during freezing that is of greater importance. All ions, except Ca in Bambi, show a substantial increase in their concentration in the liquid phase as freezing progresses. The greatest degree of enrichment was shown in JA, where the ions showing the greatest concentration increase were Na, Cl and SO₄. All of these ions showed similar concentration increases (39.3–41.2 times initial concentrations). This consistent enrichment suggests that these ions are the most conservative, i.e. the concentration increases are in direction proportion to the degree of freeze concentration of the fluid, and the ion is neither added to, nor removed from, the melt water by reaction processes. Over all of the study pond data ($n = 73$), Na and Cl showed a stronger linear correlation with conductivity ($r^2 = 0.96$) than did SO₄ ($r^2 = 0.78$). The degree of enrichment shown by Na and Cl can therefore act as a baseline against which the behaviour of other ions during freezing can be assessed. We have chosen Cl enrichment as this baseline, because there have been no reported observations of Cl minerals (such as halite) from Bratina Island.

A simple dimensionless enrichment factor (EF) has been calculated for each ion as:

$$\text{EF}(X) = X_t/X_i, \quad (1)$$

where X_t = concentration of X in the residual liquid under the expanding ice front at time “t” and X_i = concentration

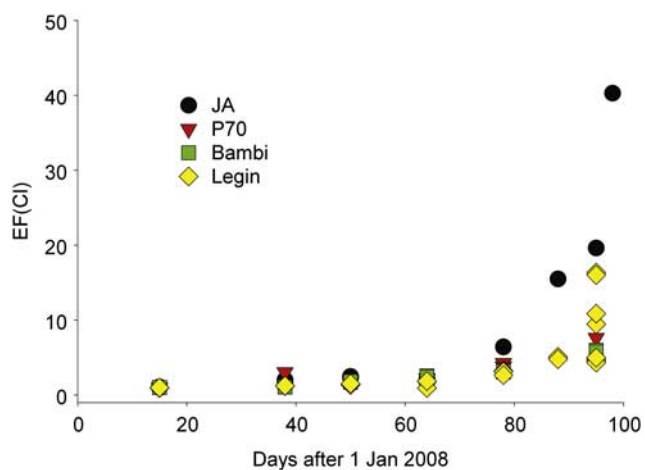


Fig. 1. Changes in the EF(Cl) over time in the four study ponds.

of X in summer open surface water. EF(Cl) provides a measure of the degree of ion enrichment as a result of freeze concentration while deviations of EF of other solutes from EF(Cl) indicate non-conservative processes. EF

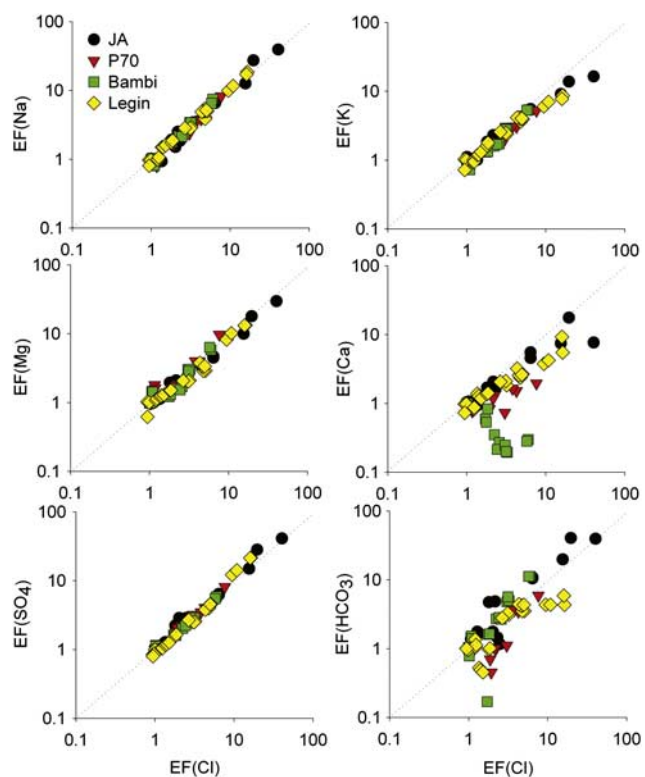


Fig. 2. Enrichment factors for various ions plotted against the EF(Cl) for the four study ponds. The dashed line indicates a 1:1 correlation between these factors, as would be expected of ions behaving as conservatively as Cl. Departures from this line indicate ion loss (below the line) or ion addition (above the line) by processes other than those affecting Cl.

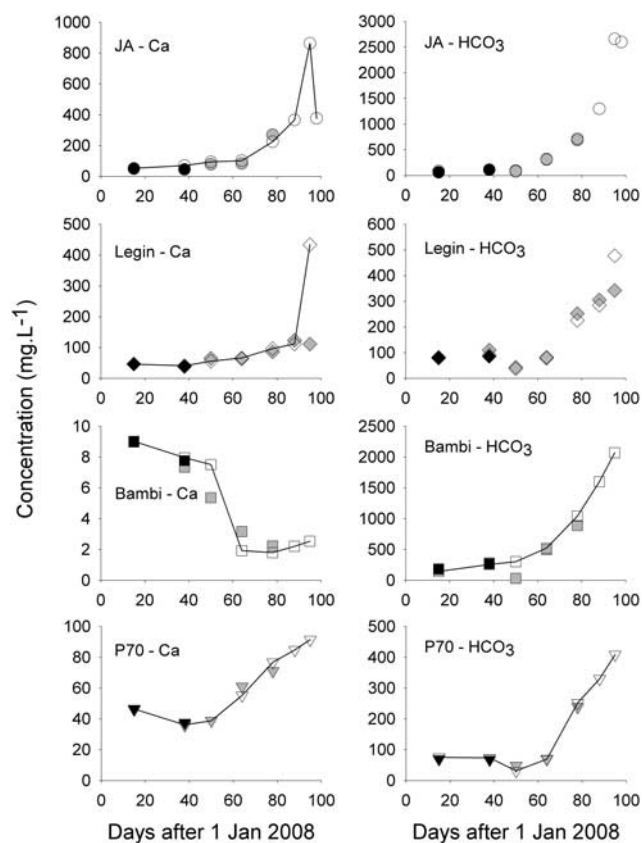


Fig. 3. Concentrations of Ca and HCO_3^- in waters at the top (small black symbols), middle (grey symbols) and base (open symbols) of the water column, as a function of time. The base sample data points are connected by a line to emphasize the overall changes with time in the residual pond waters.

enables comparisons to be made between ponds, because the ratio is normalized to the initial ion concentration in the pond water at the start of freezing, which varies between ponds (Table I).

The change in the EF(Cl) with time is shown in Fig. 1. There is a gradual increase in Bambi and P70, reaching a maximum enrichment of only 5–6 fold by the end of the sampling period. However, EF(Cl) in JA increases more rapidly after day 64 (4 March) and in the base of Legin after Day 88 (29 March). These ponds achieved a greater degree of enrichment in these late stages of freezing when any given decrease in the amount of residual fluid corresponded to a significant percentage volume change in increasingly small compartments. For Legin Pond, this “small volume” refers only to the residual mixed layer as, even at the end of the study period, the saline pool below the deep density gradient remained separate.

By plotting the EF for other ions against EF(Cl), departures from conservative behaviour can be more readily identified (Fig. 2). For example, EF(Na), EF(Mg) and EF(SO_4) show a 1:1 correlation with EF(Cl) for all ponds, throughout the entire freezing process. However, EF(Ca), and EF(HCO_3^-)

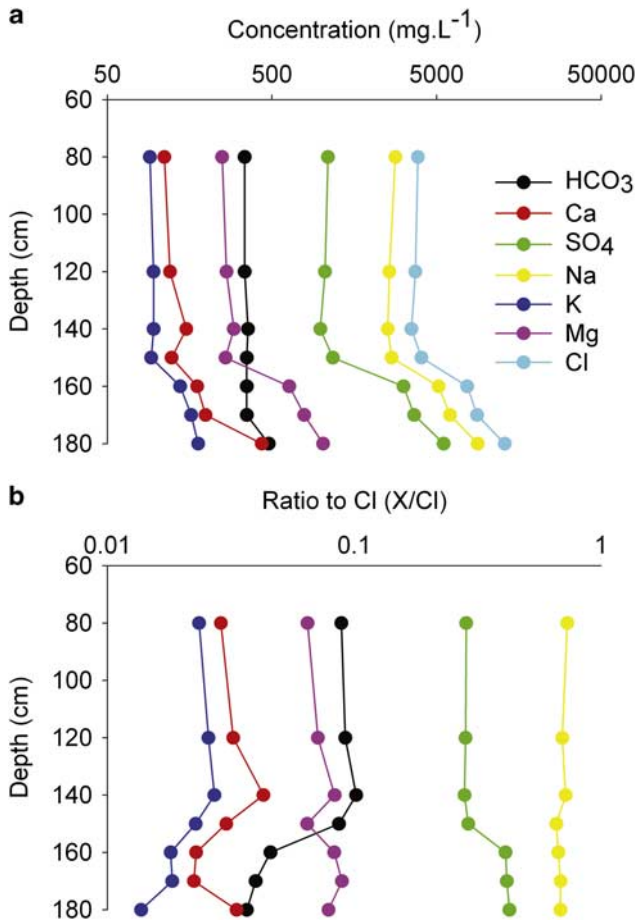


Fig. 4. Legin Pond vertical profiles for **a.** ion concentrations, and **b.** ion:Cl ratios, as sampled on 3 April 2008 when the pond was predominantly frozen.

show major departures from this linear trend, demonstrating a lesser degree of enrichment for Ca and an apparently quite erratic distribution for HCO₃. Enrichment of K also appears to be slightly less than that of Cl towards the end of the sampling period, when the degree of Cl enrichment is > 5 (i.e. in JA and Legin).

On closer examination of the Ca and HCO₃ enrichment factors, it becomes clear that the all of the ponds experience some degree of Ca loss from the water column as freezing progresses (i.e. as EF(Cl) increases), and that this is least pronounced in JA and most pronounced in Bambi. In P70 and Bambi, Ca removal occurs almost from the onset of freezing. In Legin Pond's mixed layer, Ca removal begins somewhat later when EF(Cl) > 2, and in JA Pond not until EF(Cl) > 10. For HCO₃, data often plot above the 1:1 enrichment line for JA and Bambi, particularly in the later part of the freezing process, indicating concentrations are being increased by process(es) other than enrichment by freeze concentration. In P70 and Legin mixed layer there is net removal of HCO₃ relative to Cl, particularly in the early

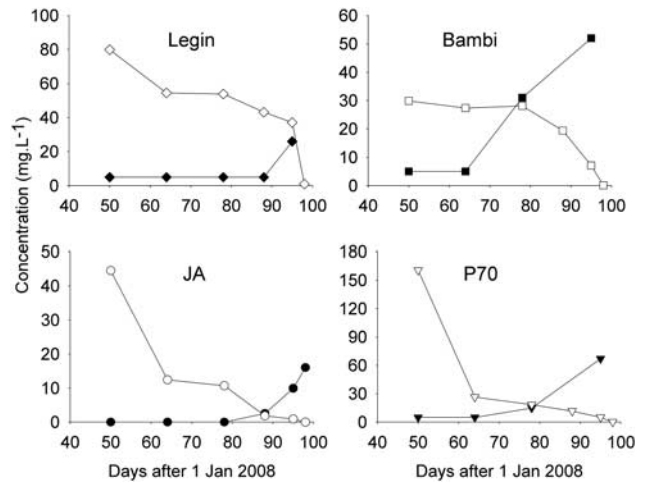


Fig. 5. Concentrations of dissolved oxygen (DO: open symbols) and H₂S (black symbols) at the base of the ponds, from day 50 (7 February 2008) onwards. Concentrations of DO are in mg.L⁻¹ and of H₂S are µg.L⁻¹, except for JA where H₂S is in mg.L⁻¹.

stages of freezing (EF(Cl) < 3), and for Legin this occurs again when EF(Cl) > 5. There is also some evidence for net removal of HCO₃ from Bambi and JA in the earlier freezing phase.

Changes in ion concentrations with time, at various depths in the pond water column, are shown in Fig. 3 for the non-conservative ions Ca and HCO₃. With the exception of the final sampling of Legin (discussed below), there is little or no vertical stratification developing in Ca or HCO₃ concentrations in the ponds as freezing progresses. This was also observed for the other major ions (data not shown). The HCO₃ concentrations decrease temporarily midway through the freezing phase (40–60 days on Fig. 3), but increases again thereafter. This is particularly obvious in Legin and P70, but does occur to some extent also in Bambi and JA. The Ca concentrations in P70, Legin and JA show a broadly similar trend with time. However, in Bambi Ca concentrations are relatively low initially, and decrease further with freezing, showing a particularly rapid decrease between 40–60 days (mid phase). There is only a slight increase at the final sampling date, though concentrations increase markedly in the base of the pond.

The final sampling of Legin Pond in April did show that the deep vertical stratification had remained, with increased concentrations of all ions in the lower 15 cm of the water column (Fig. 4a). However, only some of the ions showed enrichment or depletion relative to chloride ion (Fig. 4b); the basal waters were relatively depleted in HCO₃ (and slightly in K), and enriched in SO₄ ion.

Dissolved oxygen and H₂S concentrations are shown in (Fig. 5), because of the important role these variables play in the solubility of trace elements. The onset of oxygen

Table II. Dissolved trace element concentrations in the four study ponds; F = 7 February 2008, at the end of the summer open water period, and A = 4–7 April 2008 when the pond was predominantly frozen and residual brine was retrieved from under the ice.

Pond		Fe mg.l ⁻¹	Mn mg.l ⁻¹	As mg.l ⁻¹	Mo µg.l ⁻¹	U µg.l ⁻¹	Cu mg.l ⁻¹	Pb mg.l ⁻¹	Zn mg.l ⁻¹
Bambi	F	0.09	0.004	0.011	0.50	0.61	0.003	< 0.001	< 0.004
	A	0.02	0.028	0.049	0.62	3.6	0.011	< 0.001	< 0.004
JA	F	0.16	0.008	0.002	0.50	0.58	0.003	< 0.001	0.017
	A	0.69	4.60	0.110	2.8	14.0	0.007	< 0.001	< 0.004
Legin	F	< 0.004	0.006	0.002	2.2	1.5	0.002	< 0.001	< 0.004
	A	0.07	1.20	0.022	2.7	4.0	0.005	< 0.001	0.025
P70	F	0.01	< 0.001	0.007	1.3	0.61	0.001	< 0.001	< 0.004
	A	0.03	0.18	0.030	6.7	1.8	0.005	< 0.001	< 0.004

depleted conditions occurred later than expected, signalled by decreasing DO concentrations around day 80 (mid-March) in Legin, JA and Bambi, and perhaps 20–30 days earlier in P70. Dissolved oxygen was present in the water column until the very last sampling in early April, when conditions became truly anoxic for the first time. The first appearance of measurable H₂S in the base of the ponds was in Bambi and P70 (18 March), followed by JA (29 March) and finally Legin (4 April). In all cases, DO concentrations were still detectable at the time H₂S appeared as a result of sulphate reduction, at the base of the water column.

Trace elements

Fewer samples were collected and analysed for trace elements than for major ions, due to logistics and the need to minimize the volume sampled at each time point and not compromise the volume of water remaining. Only 27 filtered water samples were analysed for the dissolved trace elements; Fe, Mn, Cu, Pb, Zn, Mo, As and U. Of these elements, Pb was consistently below detectable levels (0.001 mg.l⁻¹) in the waters and these data are not further discussed. Similarly Zn concentrations were below detection (0.004 mg.l⁻¹) in > 60% of the samples. Further, two anomalously high Zn concentrations (> 0.1 mg.l⁻¹) raised concerns of onsite contamination during sampling or sample filtration, despite the evidence of the clean field blanks. This is not unexpected given the arduous field conditions under which sample filtration was undertaken and the prevalence of Zn in many sunscreens and other anthropogenic materials. These two data points have also been omitted from further consideration here. All other trace element data appear reliable and are summarized in Table II.

The highest trace element concentrations were for Mn, particularly in the late stage residual brine where concentrations up to 4.6 mg.l⁻¹ were measured (at the base of JA). The average over all ponds, for all sampling events and depths, was 0.47 mg.l⁻¹. The next most abundant trace elements were Fe and As, with maxima (also in JA) of 0.73 mg.l⁻¹ (average 0.13 mg.l⁻¹) and 0.11 mg.l⁻¹ (average 0.017 mg.l⁻¹) respectively. Cu, Mo and U are present at considerably lower concentrations; with maxima of 0.011 mg.l⁻¹ for Cu in the base of Bambi (average over all ponds = 0.005 mg.l⁻¹), 0.014 mg.l⁻¹ for U in the base of JA (average = 0.002 mg.l⁻¹) and 0.0067 mg.l⁻¹ for Mo in the base of P70 (average = 0.0024 mg.l⁻¹).

A similar approach to that used for the interpretation of major ion data can be used with the trace element data. The calculation of enrichment factors (where EF(TE) = TE_v/TE_c) allows for direct comparison with the enrichment of a conservative ion such as Cl (Fig. 6). Note that values below detection (< DL) have been taken to be 0.5 DL for the purposes of enrichment factor calculation. A strong positive correlation is shown with EF(Cl) for EF(As) ($r^2 = 0.90$),

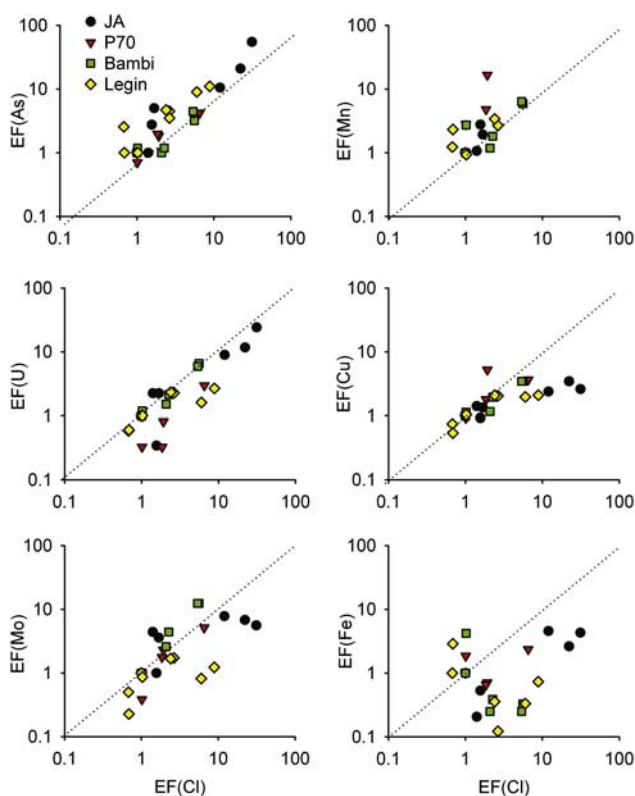


Fig. 6. Enrichment factors for dissolved trace elements, plotted against EF(Cl). As for Fig. 2, the dashed line indicates a 1:1 correlation between these factors.

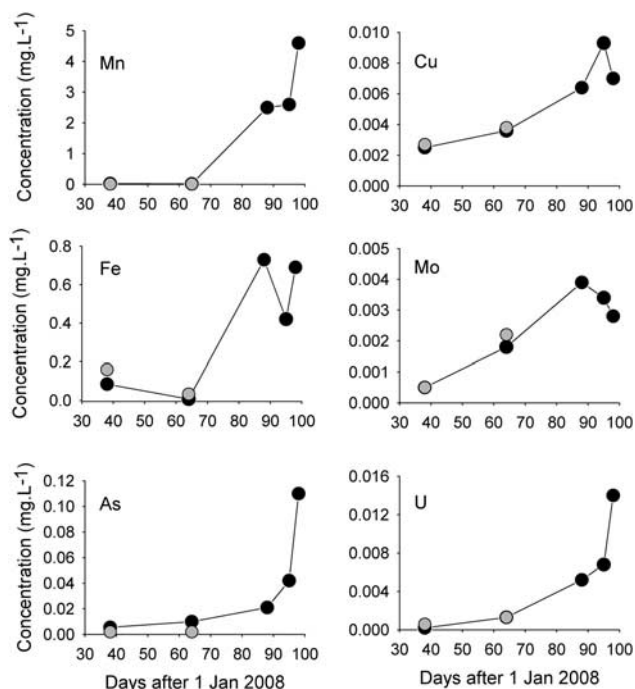


Fig. 7. The concentrations of trace elements in waters at the top or middle (grey symbol) and base of the water column (open symbol), as a function of time in JA Pond. The base sample data points are connected by a line to emphasize the overall changes with time in the residual basal pond waters.

EF(Mn) ($r^2 = 0.81$) and EF(U) ($r^2 = 0.90$), indicating predominantly conservative behaviour. There is greater deviation from the 1:1 correlation line for these elements than noted for major ions, but this may reflect the greater degree of error inherent in the analysis of saline brines for low levels of trace elements. Mn enrichment factors in the late stage residual brines ($EF(Cl) > 5$) plot consistently above the 1:1 line, suggesting an additional source of Mn to these brines, augmenting the freeze concentration process.

The EF(Cu) and EF(Mo) do not have a strong linear correlation with EF(Cl), but it appears there may be two groups of data that could be considered here: EFs in the earlier stages of freezing ($EF(Cl) < 3$) show a stronger correlation than those in more concentrated brines ($EF(Cl) > 5$, in Legin and JA) which show little further enrichment with increasing brine concentration. The relationship between EF(Fe) and EF(Cl), suggests significant removal of Fe from the water during freezing, in all ponds. For Zn, $> 60\%$ of the data points were $< DL$ Zn (0.004 mg.l^{-1}) and so the lack of correlation between EF(Zn) and EF(Cl) (not shown) was not a useful indication of chemical processes.

Changes in trace element concentrations with time support the evidence from the enrichment factors. The trace elements which demonstrated the most conservative behaviour (Mn, As and U), increased significantly in the

final stages of freezing of all ponds as had been observed for Cl. Copper and Mo demonstrated a more gradual increase, and to a lesser degree, reflecting their less conservative behaviour at high Cl enrichment. All ponds show similar trends with time for these trace elements, which are shown for JA Pond in Fig. 7, except for Fe which increased in the final stages of freezing in JA (Fig. 7) and P70, but decreased in Bambi and Legin. There appeared to be little evidence of vertical stratification of trace element concentrations in the ponds during the early stages of freezing. There is unfortunately no data for the upper layers of residual pond water in the later stages of freezing.

Discussion

Chemicals enriched in the pond water during freezing

All of the study ponds have relatively high dissolved salt contents even during maximum melt. They would best be described as “brackish”, and P70 is the most saline with a conductivity approximately twice that of the other ponds. All ponds have a Na-Cl dominated chemistry in midsummer and throughout the freezing process. During the freezing phase, ions are (imperfectly) excluded from the expanding ice structure and become concentrated in the residual meltwater beneath the ice (cf. Wait *et al.* 2006, 2009).

Some ions behave conservatively during freezing; they are excluded from the ice and accumulate in residual meltwaters but undergo no chemical, biological or physical process of removal from solution thereafter, nor are concentrations augmented by release of ions from mineral or biotic phases. In this study of Bratina Island ponds, Cl, Na, K, Mg, SO_4 and the trace elements As, U and Mn behaved predominantly conservatively. Thus, during the final stages of freezing the residual meltwaters are enriched in these elements. The degree of enrichment of conservative ions ranges from 5.7 fold (Bambi) to 39.2 fold (JA), depending on the final ratio of pond ice:residual water. Hawes *et al.* (2010b) noted that the residual volume of JA was less than 5% of the starting volume, while for Bambi almost 20% of the original volume of pond water remained unfrozen. Ion and trace element enrichment is therefore potentially greatest in JA Pond. This led to high concentrations of the toxic trace element As ($110 \mu\text{g.l}^{-1}$) in the JA Pond basal brine for example.

In some cases the concentrations in the final residual brine exceed those that might be expected from the simple process of enrichment during freeze concentration. For example, HCO_3 concentrations were augmented in JA and Bambi, and Mn showed concentrations higher than expected in the final stages of freezing in all ponds except Bambi. In such cases, another source of the ion or element must be sought. An evaluation of the effects of ion addition from other pond compartments, such as mineral salts, pond sediments or relic brines from previous freezing

episodes, requires accurate quantification of the ion load available in each such compartment. This was not undertaken as a part of this study, but the potential for mineral salt precipitation (and therefore for re-dissolution when conditions change at a future time) is assessed below using geochemical modelling.

The increase in H₂S concentrations in the residual water, with progressive freezing, owes little to freeze concentrations processes, but is instead a response to decreasing redox conditions (Fig. 5). The reduction of sulphate and other sulphur oxyanions to H₂S or bisulphide ion is a common phenomenon in anoxic aquatic environments, facilitated by sulphur-reducing bacteria. However, the co-existence of H₂S and O₂ observed in these ponds is highly unusual in low temperature natural systems, where the oxidation of sulphide by dissolved oxygen is both thermodynamically favoured and facilitated by sulphur-oxidizing bacteria. Wait *et al.* (2009) observed a similar phenomenon; the perseverance of H₂S in the base of other Bratina Island ponds throughout summer, again in the presence of dissolved oxygen. Possible explanations offered by Wait *et al.* (2009) include a dominance of sulphur-reducing bacteria, or an absence or reduced activity of sulphur-oxidizing bacteria, allowing kinetic obstacles that exist in the oxidation reaction pathway to prevent or slow H₂S oxidation. It is possible that the activity of sulphur-oxidizing bacteria could be inhibited by the cold temperatures (e.g. -2°C at the base of Legin pond in late March, Hawes *et al.* 2010a).

Chemicals removed during freezing

Other ions do not show the same degree of enrichment as chloride because they are removed from the water column during the freezing process. For example, Ca and to a lesser extent K removal occurs at all stages of freezing. Ca removal was most pronounced in Bambi, even though initial concentrations were already almost an order of magnitude lower than in the other ponds. HCO₃ showed a more complex removal process in Legin and P70 with freezing, with initial depletion followed by enrichment, then further depletion (Fig. 3). For the trace elements, Fe showed evidence of mid-stage (early March) removal in all ponds, followed by a resurgence of Fe concentrations in late stage residual brines in JA and P70, and to a lesser degree in Legin, but not at all in Bambi. Cu and Mo appear to be removed in the later stages of freezing (late March) in JA, and to a lesser degree in Legin, although conservative behaviour had been demonstrated up to that point.

The situation was more complex in Legin Pond than in the other study ponds. Legin contained a relic brine layer from previous winter freezes (cf. Wait *et al.* 2006, Hawes *et al.* 2010b). This basal brine appeared enriched in SO₄ and depleted in K and HCO₃ relative to Cl (Fig. 4), when compared to the overlying water column. While depletion in K and HCO₃ is consistent with the pattern seen

Table III. Mineral salts predicted to form (+) in residual meltwaters in the study ponds. “-” indicates salts that will dissolve if present. Fe-O, Fe-S, Mn-O and Cu-S indicate that various minerals in the group designated as Fe oxides/oxyhydroxides, Fe sulphides, Mn oxides/oxyhydroxides and Cu sulphides respectively are predicted to form.

Pond	Date	CaCO ₃	Fe-O	Fe-S	Mn-O	MnCO ₃	Cu-S	ZnS	UO ₂
JA	7 Feb	+	+	-	+	-	-	-	-
	4 Mar	+	+	-	+	-	-	-	-
	28 Mar	+	-	+	-	+	+	+	+
	4 Apr	+	-	+	-	+	+	+	+
	7 Apr	+	-	+	-	+	+	+	+
P70	7 Feb	+	+	-	+	-	-	-	-
	4 Mar	+	+	-	+ *	-	-	-	-
	4 Apr	+	-	+	-	+	+	+	+
Bambi	7 Feb	+	+	-	+	-	-	-	-
	4 Mar	+	+	-	+	-	-	-	-
	4 Apr	+	-	+	-	-	+	+	+
Legin	7 Feb	+	+	-	+	-	-	-	-
	4 Mar	+	+	-	+	-	-	-	-
	28 Mar	+	+	-	+	-	-	-	-
	4 Apr	+	-	+	-	+	+	+	+

*excluding MnO₂

developing in the Legin Pond mixed layer during freezing in this study, the enrichment of SO₄ is not. The evolution of this relic brine in Legin may have been a multi-year process, with previous introduction of SO₄ by a mechanism such as the dissolution of previously precipitated CaSO₄ (gypsum) salts, for example.

Processes removing ions during the freezing process may be abiotic, biotic, or a combination thereof. Abiotic processes include the precipitation of minerals and adsorption of chemicals onto sediment surfaces, both of which can be affected by variables such as pH and redox conditions, which can be under biotic control. Microbial uptake and transformation can also directly affect ion concentrations; for example, HCO₃ is particularly labile through a wide range of microbial processes, and reversible transformations between H₂S and SO₄ are also biologically mediated.

Geochemical modelling of mineral precipitation

The geochemical speciation modelling programme PHREEQC v2.17.4137 (updated February 2010; initial documentation by Parkhurst & Appelo 1999) was used to identify possible mineral precipitation reactions which may remove ions or trace elements from the residual pond waters, assuming conditions of thermodynamic equilibrium. Input data included the major ion and trace elements concentrations determined in this study, as well as pH and temperature for these ponds as described in Hawes *et al.* (2010a, 2010b). In the model, redox conditions must be specified as these will affect the behaviour, and these were calculated from SO₄/H₂S equilibria. If, as noted previously, there is a kinetic obstacle preventing the thermodynamically-favoured oxidation reaction of H₂S and O₂ to form SO₄⁻²,

then this may influence the redox conditions calculated in the model. However, the only feasible alternative was to control redox conditions using DO, and this would cause the model to convert all H₂S to sulphate, and the presence of H₂S is an important factor in the formation of insoluble sulphide minerals. The PHREEQCi programme used the WATEQ4F database. A summary of modelling data, listing the mineral phases predicted to form, or dissolve, in selected representative ponds meltwaters, is shown in Table III.

Notably there appears to be no mineral phase that would remove minor amounts of K from the water column at the latest stages of freezing in Legin and JA ponds. There are no non-silicate K mineral phases other than jarosite (a K-bearing iron sulphate) included in the WATEQ4F database, as all K minerals forming at low temperature are highly soluble. Thus a removal mechanism for K remains uncertain, but could involve interaction with clay surfaces, by cation exchange, for example.

Ca and HCO₃

All pond waters, at all stages of freezing are saturated with respect to calcite, which explains the ongoing removal of Ca throughout the freezing process. This is particularly evident in ponds with a low initial Ca concentration such as Bambi Pond. Dolomite (CaMgCO₃) is also predicted to form, but rarely does so from natural waters at low temperatures, and the lack of Mg removal suggests the precipitation of dolomite is not significantly affecting Ca concentrations.

The initial removal of HCO₃ from ponds where the concentrations of Ca were high enough to form enough calcite, and therefore to significantly reduce HCO₃ concentrations (i.e. all except Bambi) may also be partially explained by this process. However, HCO₃ is also significantly affected by biological processes, and by speciation changes (and the formation of carbonate ion) if the pH is raised above ~ 10.5. Hawes *et al.* (2010b) argued that ongoing photosynthesis during the early phase of ice formation was responsible for depletion of HCO₃, as it was accompanied by an increase in dissolved oxygen. Therefore calcite precipitation and photosynthesis may be acting together to reduce HCO₃ concentrations at an early stage of freezing. Such process may also be the cause of HCO₃ depletion in the relic brine in Legin pond.

In Legin, P70 and JA ponds, HCO₃ concentration increase significantly after day 60. Ca shows a similar increasing trend in all ponds except Bambi. As all waters remain saturated with respect to calcite, to more-or-less the same degree, calcite formation or dissolution cannot provide an explanation for changes in Ca and HCO₃ concentrations during these later stages of freezing. Biological processes are the most probable agency of change. Whereas photosynthesis can be a net sink for HCO₃ up to day ~ 50, after the reverse process (respiration) may become an important source. During the later part of freezing, biotic enrichment of HCO₃ will be

working against precipitation; more than compensating for the effects of calcite precipitation in Bambi and JA, but not in Legin and P70.

Fe and Mn

Prior to the appearance of measurable H₂S and the onset of anoxic conditions (see Hawes *et al.* 2010b), meltwater in all of the study ponds are oxic and oversaturated with respect to low temperature Fe- and Mn-oxide and -oxyhydroxide phases, such as ferrihydrite (Fe(OH)₃) and manganite (MnOOH). This is a likely explanation for the removal of Fe during the early stages of freezing (Fig. 6), but does not appear to have influenced Mn concentrations to a significant degree.

As DO decreases and H₂S increases, (mid March for Bambi and P70, late March for JA and early April for Legin) these phases are no longer stable and dissolve. This may explain the increase in Mn concentrations seen late in the freezing process, augmenting Mn enrichment by freeze concentration processes (Fig. 6). In the anoxic late stage fluids the only Mn phase predicted to form is MnCO₃ (rhodocrosite), and then only in some of the ponds. This is a relatively soluble phase allowing high concentrations of dissolved Mn to persist. However, Fe forms stable sulphide minerals in the presence of H₂S, such as amorphous FeS, and FeS₂ (pyrite). This would significantly limit the degree of enrichment of Fe due to freeze concentration process, at the onset of anoxic conditions.

Other trace elements

Cu-, U- or Zn-bearing mineral phases are not predicted to form during the early oxic, stages of freezing. It is, however, probable that dissolved Cu and Zn concentrations are controlled by adsorption onto Fe- and/or possibly Mn oxyhydroxide solid phases suspended in the water column; a process reported to be an important control on trace element mobility in oxic Antarctic meltwater (e.g. Green *et al.* 1993, Webster *et al.* 1997, Webster-Brown & Webster 2007). Controls on U and Mo concentrations in such environments have not previously been studied, though both elements do form oxyanions that will adsorb to Fe-oxide surfaces under low pH conditions (e.g. Dzombak & Morel 1990). However, the alkaline pH of the pond waters in this environment will not favour such adsorption, so the ions are likely to remain predominantly dissolved and behave conservatively while conditions are oxic.

At the onset of anoxic conditions, or in this case the first appearance of H₂S, the solubility of trace elements capable of forming stable insoluble sulphides will be significantly reduced. Cu sulphides (such as chalcocite; Cu₂S, covellite; CuS and chalcopyrite; CuFeS₂) are predicted to form. Sphalerite (ZnS) is also predicted to form, even at Zn concentrations as low as 0.002 mg.l⁻¹ (0.5x DL). Unfortunately there is no thermodynamic data for Mo complexes in the WATEQ4F database, nor in the other databases available to

the PHREEQCi model. However, Mo does form an insoluble sulphide phase for which solubility data are available and could be added into the PHREEQCi model, confirming that MoS will control Mo concentrations when H₂S is present in the latter stages of freezing.

In summary, in the final stages of freezing, residual liquid beneath the ice in the study ponds was anoxic Na-Cl brine, which had evolved through the freeze concentration of all major ions, accompanied by the removal of Ca and HCO₃ as calcite. Trace element concentrations were also enriched by freeze concentration, leading to high concentrations of Mn, As and U in the basal brines. The enrichment of Fe, Zn, Cu and Mo was, however, limited by the precipitation of sulphide minerals when H₂S was formed during the last stages of freezing.

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