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Water, heat and solute dynamics of a mud boil, Spitsbergen

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Abstract

Mud boils, a form of non-sorted circles, cover the ground surface in many periglacial landscapes. The vegetation-covered trough acts as an effective buffer to the downward movement of water and chemicals, while the bare center experiences larger fluxes of heat and mass. Since dissolved ions affect the electric conductivity of the soil solution, measurements of the bulk soil electric conductivity offer potential for estimating solute concentration. Since 1998, bulk soil electric conductivity has been measured automatically and hourly using 32 time domain reflectometry probes over an approximately 1 m diameter mud boil close to Ny Ålesund, Spitsbergen. Soil water electric conductivity was calculated from bulk soil electric conductivity using volumetric soil water content and a calibration parameter. The seasonal and spatial behaviour of water, temperature and solute concentration within two profiles of this mud boil were analyzed. Concentrations of estimated soil water electric conductivity were highest during the summer period when the active layer was thawed. Thermodynamic equilibrium modelling of the soil solution during freezing suggests that precipitation of dissolved species leads to the observed decrease in electric conductivity. There is a pronounced vertical solute concentration gradient in both profiles, while there is little evidence for horizontal solute concentration gradients beneath the mudboil.

Keywords: Permafrost; Freezing; Geophysical methods; Electric conductivity; Solute dynamics; Patterned ground

1. Introduction

Analysis of the phenomenology and dynamic processes of patterned ground yields information on past and present climate and environmental conditions (Washburn, 1979; Romanovskii, 1996). The objective of this study is to characterize (seasonally and spatially) the water and solute dynamics of this heterogeneous system using soil solution sampling, high temporal resolution measurements of bulk soil electric conductivity and

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thermodynamic equilibrium modelling of solution chemistry. This, in turn, adds insight to the mechanical dynamic of the mud boil, and to the discussions on the origin and formation of these periglacial features.

Furthermore, these findings contribute directly to the European Science Foundation project on 'Sedimentary Source-to-Sink-fluxes in Cold Environments'. An understanding of climate processes and their control on mass transfer processes, such as subsurface behaviour of solutes in a mudboil, aids in the understanding of mass export of cold drainage baisins.

2. Theories of mud boil formation

Mud boils are symmetric surface features in periglacial environments that have puzzled and fascinated researchers since at least 1900. Early observations and theories of the origin of patterned ground were the beginning of exciting research. Washburn (1956) summarized and discussed postulations of 19 separate mechanisms of formation for non-sorted circles in particular. These ideas are still central in today's discussions of patterned ground formation.

Mud boils (also known as frost boils, frost scars, mud circles and mud hummocks), classified as non-sorted circles, are found in areas where the ground is subject to seasonal freezing and thawing. They are characterized by a bare, usually doming round mineral soil center, surrounded by vegetation. Some of the mechanisms postulated for their formation are: the sorting of soil materials based on grain size; convection cell like cryoturbation; diapir formation or upwellings of lower soil horizons under pressure (Washburn, 1956). A review of the main mechanisms involved in cryoturbations was presented by Van Vliet-Lanoë (1991) based upon field measurements and micromorphological data. She concluded that "differential frost heaving appears to be the main mechanism of cryoturbation" (pp. 123) and that the presence of organics enhances differential frost heaving. Kessler et al. (2001) modelled sorted circle formation (with barren finer grained circle centers surrounded by stones) from two layers distinct in particle size using a purely mechanical model. The freezing front pushed soil to more compressible soil regions, accumulating in soil plugs that reach to the surface. During thawing, consolidation occurred vertically. The circle was maintained at the surface by the circulation of the stone and fine material domains, upward in the circle center and downward at the edges. Walker et al. (2004) presented horizontal soil profiles across a mud boil. Nutrient concentrations (available potassium, phosphor, nitrogen) and water content declined from the margins toward the center, a trend which they attributed to more 'mechanical' activity towards the center of the boil.

2.1. Study site

The Bayelva catchment is located about 3 km from Ny-Ålesund, Spitsbergen (78°55′N, 11°E) in the forefield of the Brøggerbreen glacier (Fig. 1A, B). In this region, continuous permafrost underlies coastal areas to depths of about 100 m and mountainous areas to depths greater than 500 m. The North Atlantic Current warms this area to mean monthly air temperatures around −13 °C in January and 5 °C in July, respectively and provides about 400 mm annual precipitation mostly as snow between September and May. Our study site is located at about 25 m above mean sea level, on top of a small hill covered with unsorted circles (Fig. 1C). It is not clear if the mud boils on this hill are currently being degraded (for example, by gelifluction) or maintained by active cryoturbation. Vegetation encroaching from the sides into the mud boil's center – though the centers are still doming – is an indicator for slow mass displacement and semi-active behaviour. While other patterned ground phenomena (such as sorted circles and stripes) are found in the vicinity of the hill, these mud boils are only present on Leirhaugen hill. The mud boils were or are formed under local conditions favourable for mud boil formation after the last glacial period.

Leirhaugen hill is mainly composed of rock, but partly covered by a mixture of sediments: glacial till, finer glacio-fluvial sediments and clay formed by the last glacial advance (Tolgensbakk, personal communication). The gray color of the sediments suggests that the material was deposited by the Kongsfjorden glacier and not the adjacent Brøggerbreen glacier, which deposits redder material. Marine sedimentation could also have contributed since the hill is located below the marine limit (about 38 m).

3. Methods

We instrumented one of these non-sorted circles (Fig. 1D) in August 1998 to automatically monitor hourly temperature and volumetric liquid water content (θ). Altogether 32 time domain reflectometry (TDR) probes and 32 temperature probes were installed over the 1 × 1 m profile. The position of the TDR probes is shown in Fig. 2. The TDR and temperature data set considered in this study is limited to 1999, the year in which suction lysimeter data were collected. During installation, soil samples were taken for the analysis of physical parameters. The texture and composition of 25

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samples were determined using standard methods. Wet soil was passed through a sieve with 63 µm size to measure sand content. After destruction of organics and limestone, silt and clay were separated by sedimentation

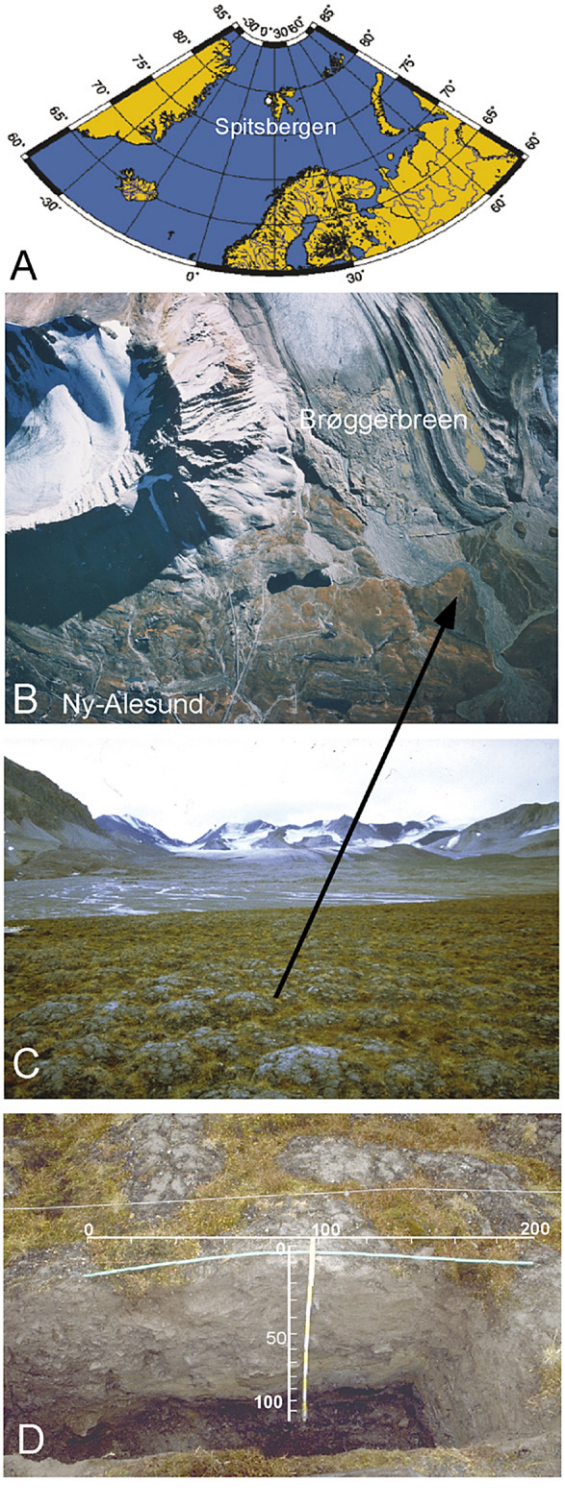

Fig. 1. The location of Spitsbergen (A) and aerial picture (1:15000) of the area around Ny-Ålesund (B). The study site (arrow) is located on Leirhaugen hill close to end moraines of the Brøggerbreen glacier. Parts of the road network of Ny-Ålesund can be seen in the lower left part of the picture. The Bayelva study site (C) is located in a field covered with non-sorted circles. The excavated mud boil is shown in D. The bare soil circle centers range about 1 m in diameter and are surrounded by vegetated borders consisting of a mixture of low vascular plants, mosses and lichens.

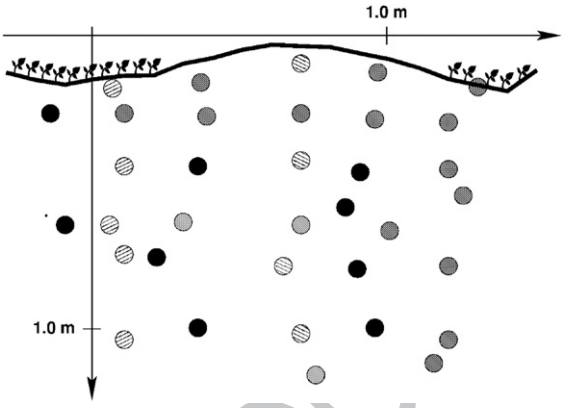

Fig. 2. Position of TDR probes (grey and hatched circles) installed in the mud boil. Temperature probes are installed adjacent to TDR probes. For the analysis, the left profile under vegetation and the profile underneath the center of the mud are used (hatched circles). In addition, nine suction lysimeters (black circles) are installed close to TDR probes (see also Table 1).

in Atterberg cylinders. Soil temperatures were recorded using thermistors calibrated at 0 °C with a precision of 2.4×10^{-4} °C at 0 °C and an absolute error less than ±0.02 °C over the temperature range ±30 °C. Volumetric liquid water content was calculated from TDR measurements with an accuracy of 0.02 to 0.005 and a precision better than 0.005. Soil water was sampled in 1999 using Prenart® suction cups (5 cm long, pore size 2 µm; Gravquick, Denmark) cups that were installed in 1998 at different depths close to TDR probes. Soil water was analyzed in the field for pH, electric conductivity and alkalinity. The remaining sample water was filtered and stored at 4 °C in pre-cleaned HDPE bottles until laboratory analysis took place. Cation concentrations were analyzed with ICP-OES (Optima 3000 XL, Perkin Elemer) and anion concentrations were measured with ion chromatograph (Dionex 320).

3.1. TDR and bulk electric conductivity

Data on spatial and temporal distribution of water and solutes in frozen and unfrozen soils are essential for energy and mass transport models. A fast method to measure the volumetric water content *in situ* is TDR.

TDR has become a reliable and widely used technique to measure the water content in frozen and unfrozen soils (for example, Topp et al., 1980; Patterson and Smith, 1980; Roth et al., 1990). The TDR technique for measuring the volumetric water content is based on the large disparity in the relative dielectric permittivities of water and the other soil constituents. The bulk relative dielectric permittivity of the soil determines the velocity with which an electromagnetic wave travels through the soil, so that measurement of the travel time for a known distance allows determination of the material's permittivity. We use a physically-based dielectric mixing model to compute the composite dielectric number of a multiphase mixture using the relative dielectric permittivities and volume fractions of its constituents (Roth et al., 1990).

TDR can also be used to measure the impedance of the bulk soil Z (Ω), which is related to the bulk soil electric conductivity as a function of time. The bulk soil electric conductivity is in turn related to the concentration of ionic solutes (Reluy, 2004) and hence TDR is suited for *in situ* detection of well-dissociating solutes. The impedance can be determined from the attenuation of an electromagnetic wave traveling along the probe after all multiple

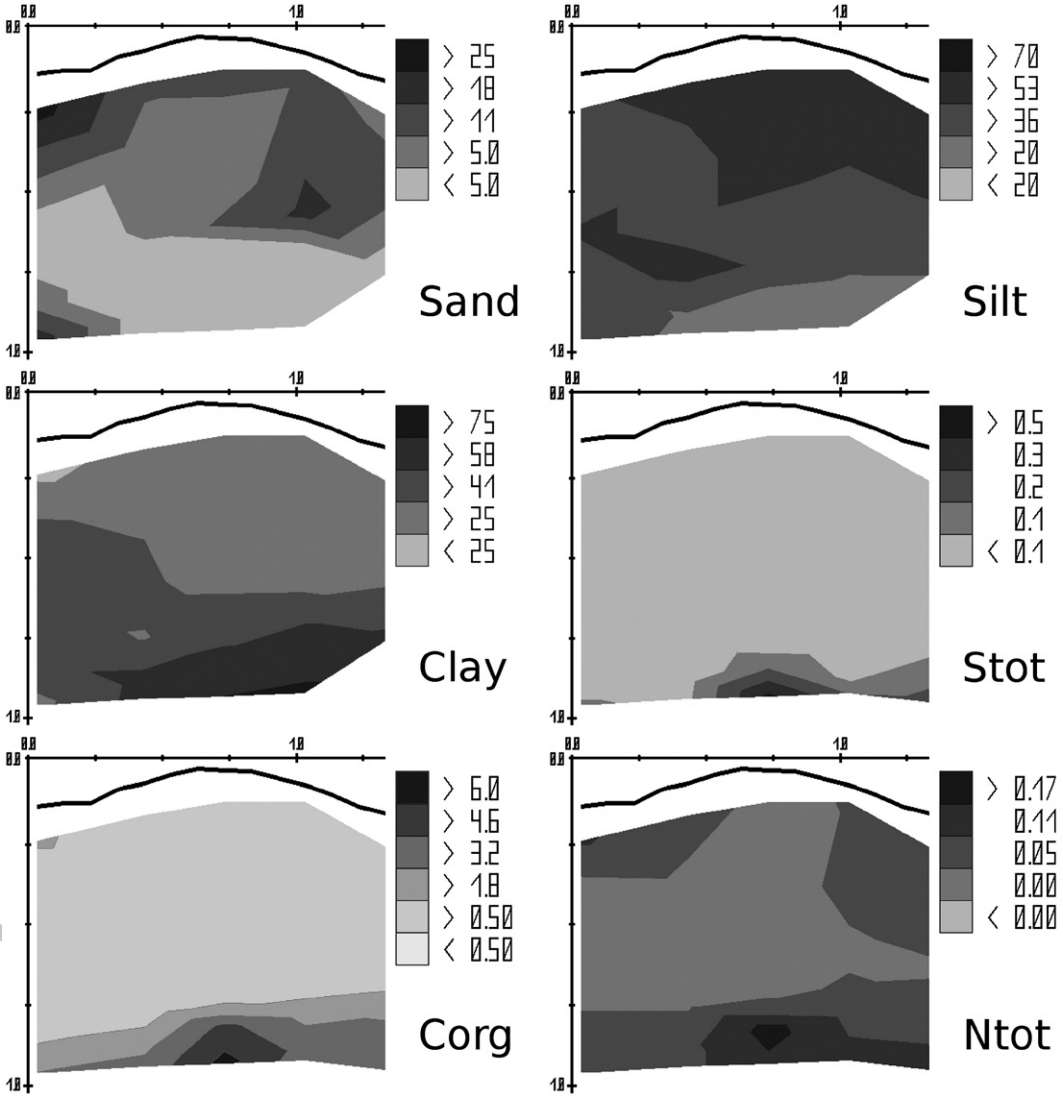

Fig. 3. 2-D distribution of sand, silt, clay and total carbon, nitrogen, sulphur of the mud boil in % weight. Linear interpolation is used between 25 sampling points.

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reflections have ceased and the signal reaches a stable level. Usually it is assumed that the impedance is related to the bulk soil electric conductivity by:

$$\sigma_b^{25} = \frac{K_P}{Z - Z_{cable}} f_T \quad (1)$$

where σ_b^{25} [S m^{-1}] is the soil bulk electric conductivity corrected to 25 °C, K_p [m^{-1}] is the geometric cell constant of the TDR probe, Z_{cable} [Ω] accounts for the total resistance of cables, connectors and cable tester and f_T [−] is a temperature factor defined as:

$$f_T = 1 + \alpha(T - 25) \quad (2)$$

where T [°C] is the soil temperature and $\alpha = 0.019$ °C^{-1} is the temperature coefficient (Heimovaara et al., 1995). We calibrated our TDR probes in a range of solutions with known electric conductivities, following the method of Heimovaara et al. (1995). As there was no longer a linear relation between measured impedance and the inverse of the conductivity for high concentrations, we modified Eq. (2) to:

$$\sigma_b^{25} = \left(\frac{1}{Z - Z_{cable}} - B\right) K_p f_T \quad (3)$$

where B is an additional fitting parameter. B, K_p and Z_{cable} were determined by non-linear least squares fitting.

3.2. Calculation of soil solution electric conductivity σ_w

The relationship between bulk electric conductivity and the electric conductivity of the liquid phase depends on the conductivity of the solid phase and the geometry of the phases, which is related to soil structure and air, ice and water contents. There are several empirical models, partly with some theoretical justification. Boike and Roth (1997) compared the descriptive power of three models for a permafrost site in Siberia by a comparison of the conductivity measured in water extracted from suction cups with the conductivity predicted from TDR measurements. For the coarse textured soils studied they found the best agreement with a simple regression model:

$$\sigma_b = A\theta\sigma_w \quad (4)$$

where σ_w [S m^{-1}] is the electric conductivity of the soil solution, θ [−] is the volumetric liquid water content of the soil and A [−] is a fitting parameter. For three different mineral soils the parameter A varied between 0.7 and 4.8. Best results were obtained with probe specific calibrations. Furthermore, they suggested that A did not change from frozen to unfrozen soils and that this model may be applied to calculate σ_w for frozen conditions as well. To our knowledge, the only other model predicting σ_w from TDR-determined σ_b in frozen soils was introduced by van Loon et al. (1991; also reviewed in Boike and Roth, 1997). This model has been applied for the study of solute dynamics in Swedish field soils (Lundin and Johnsson, 1994) and in frozen lab columns (Ståhli and Stadler, 1997) without prior calibration to soil solution electric conductivity. As the model by van Loon et al. (1991) did not predict solution electric conductivity as well as the regression model for permafrost soils in Siberia (Boike and Roth, 1997) we did not consider this model further in this study.

4. Results

Soil composition data from the 25 samples taken from the profile is presented in Fig. 3. The soil material generally consists of silty clay with some larger stones. The silt content decreases from over 50% at the top of the profile to less than 30% at the bottom, concomitant with an increase of clay content to over 50% (Fig. 3). Concentrations of organic carbon, total nitrogen and total sulphur are highest at the bottom of the profile, peaking below the mud boil center. Of note are especially high concentrations of organic carbon (>6%

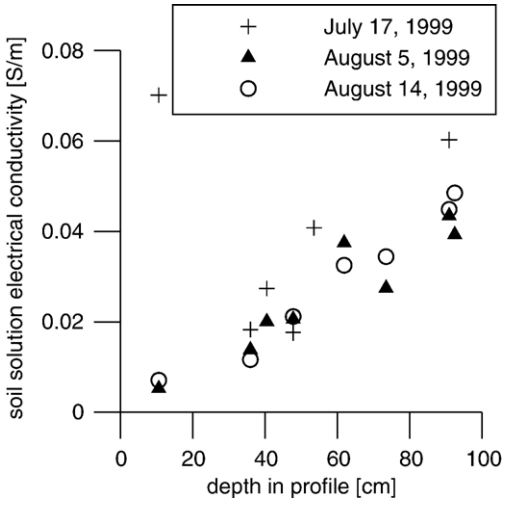

Fig. 4. Soil water electric conductivity obtained from suction lysimeter water at three different times over depth.

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weight) at the bottom of the profile. Nitrogen is also elevated below the vegetated trough of the profile.

4.1. Determination of σw

The bulk electric conductivity of the soil is generally considered to be the sum of the conductive contributions of the liquid phase and the soil matrix surface

$$\sigma_b = \sigma_w + \sigma_s \quad (5)$$

The matrix surface contribution is generally assumed to be low relative to that of the soil solution, and is often neglected (Boike and Roth, 1997). The texture of the soil in this study site is finer and has far more clay than the coarse textured soils studied by Boike and Roth (1997). Since the clay content is high, the conductivity of the solid phase may no longer be negligible and it is not clear if these findings are also valid for this site. To verify this and to calibrate the measurement of σ_w we used the measured electric conductivity of water extracted on three dates (July 17, August 5 and 14, 1999) from suction cups installed at nine positions near the TDR probes (Fig. 4). The electric conductivity of the extracted water increased with increasing profile depth, thus the rise of bulk electric conductivity cannot be attributed solely to the increase in finer soil particles.

Suction lysimeter data were used to calibrate the model (Eq. (4)). The calculated mean A factors for the regression model are given in Table 1. Calculated A values lie within the same range as the ones calculated by Boike and Roth (1997). Fig. 5 shows a comparison of σ_w measured in soil water and the corresponding σ_w calculated from TDR measurements. Altogether we can see a good linear relation with some outliers. The two water samples with high concentrations were collected during the first sampling and have different ion composition, as will be explained later in the Discussion section. A closer examination of the values for individual probes shows a narrow range of conductivities covered by the limited amount of samples taken, so that within the accuracy of the measurements they represent one data point for each probe. This makes verification of the model difficult. However, we assume that there are monotone relations between σ_w and σ_b and θ and σ_b. Therefore the qualitative behaviour of σ_w derived from the TDR measurements is expected to be correct even if absolute errors are introduced by disregarding the conductivity of the solid phase.

Table 1
Mean calculated A factors for the linear regression model

Suction lysimeter	Suction lysimeter location depth [cm]	A factor	No. of water samples	pH
B1	91	1.1	4	Neutral, pH=7.1
B2	93	1.0	3	Acidic, pH=4.1
B3	62	2.4	4	Alkaline, pH=7.8
B4	74	2.8	2	Neutral, pH=7.1
B5	48	4.0	5	Alkaline, pH=7.9
B6	54	1.6	3	Alkaline, pH=8.1
B7	36	4.7	6	Alkaline, pH=7.5
B8	41	3.8	4	Alkaline, pH=8.0
B9	10	4.0	3	Neutral, pH=6.7

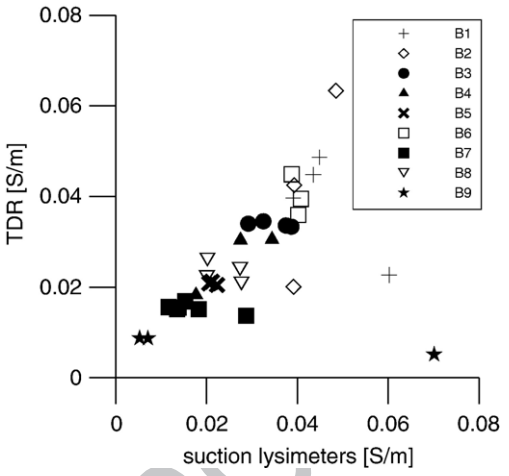

Fig. 5. Soil water electric conductivity obtained from suction lysimeters (names of suction lysimeters in legend) compared to values calculated from bulk electric conductivity (TDR probes) using model (4).

4.2. Temperature, volumetric water content and soil solution electric conductivity dynamics

For the following analysis, we chose two profiles: one located below the vegetated left trough and the other one below the center of the mud boil (Fig. 2).

Fig. 6 shows rainfall and snow depth, soil temperature, soil volumetric water content and σ_w at 4 different depths below the vegetated trough. As expected, the probe closest to the surface (0.06 m) shows higher temperatures and daily temperature fluctuations compared to the lower probes. The temperature signal is attenuated with depth. In May, the snow liquid water content increases considerably, a process also enhanced by rain on snow events (Boike et al., 2003), and infiltration of water rapidly warms the soil at all depths. This is reflected in Fig. 6 by the dramatic increase in the volumetric water content of the soil at successive depths. The liquid water content mirrors most clearly the advance of the thaw front. The phase change ice/water starts during snow ablation and is much enhanced after the snow has ablated. The soil

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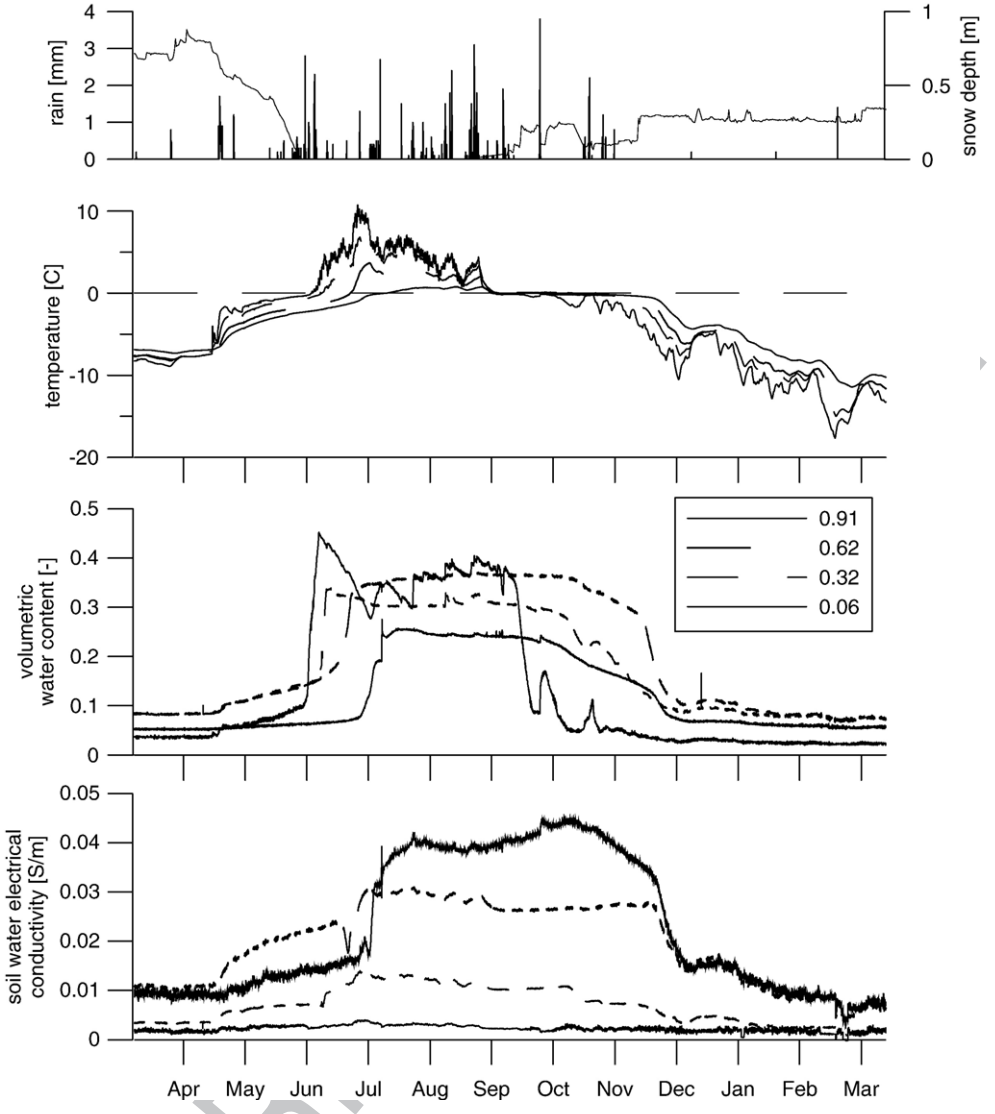

Fig. 6. Rainfall and snow depth, soil temperatures, soil water content and soil water electric conductivity from April 1999 to April 2000 at four depths for a profile underneath the vegetated cover.

temperature sensor at 0.91 m depth passes 0 °C around the end of July. However, low volumetric water contents (~0.25) that remain constant over the summer indicate that the soil is not completely thawed. The temperature sensor at 1.22 m depth (not shown in diagram) indicates that the soil never thaws at this depth. During the summer, volumetric water content remains constant at 0.62 m depth, indicating the perched water table above the frozen ground. Once freezing starts in September, soil temperatures at all depths drop to below zero and phase change from water to ice is initiated ("zero curtain effect"). The phase change is completed by mid-November, after which the soil profile cools. The volumetric liquid water content in these frozen soils during winter ranges between 4 and 9% and is lowest at the surface due to desiccation (vapour migration out of the soil, see Roth and Boike, 2001).

The general seasonal behaviour of σ_w below the organic (except for the probe nearest to the surface at 0.06 m) can be summarized as follows: increase of σ_w during thawing, highest concentrations during the summer and decrease during fall phase change. However, during the spring thaw, the behaviour of σ_w is different for each soil depth. At intermediate depth (0.32 m), σ_w increases during thaw, but continues to increase even after the soil is completely thawed, indicating either transport of solutes to this area or local and continued increases in the concentration of charged solutes. At 0.62 m depth, a pronounced drop in conductivity occurs

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during thaw at about 15% liquid water content, which indicates that dilution of the soil water has occurred, probably via downward migration of meltwater with lower concentrations of dissolved ionic species. In addition, this is the soil depth with the highest σ_w in the frozen soil. Since this is the soil depth that remains thawed longest in the fall (Boike et al., 2003), migration of excluded ions would take place towards this depth. This is also suggested by a small increase of θ and σ_w in December after closure of the zero curtain.

Throughout the whole summer σ_w is relatively stable, with small increases of σ_w occurring at the three intermediate depths simultaneously with an increase of θ after a series of rain events during the latter half of August. However, there is also a peak in σ_w measured with the deepest probe at the end of July, which is not connected to a corresponding increase of water content. Only the surface probe shows an increase in θ at this time, caused by a minor rain event. As the same peak can be recognized at the deepest probe below the mud boil center, it is unlikely to be an artefact and either an *in situ* increase in solute concentration, for example by dissolution of salts, or lateral inflow must have occurred. Generally in the thawed organic profile, soil water conductivity increases with depth and the highest concentrations occur at the bottom of the profile (0.91 m).

In the barren soil below the center of the boil the fluctuations of temperature, water content (Fig. 7) and σ_w

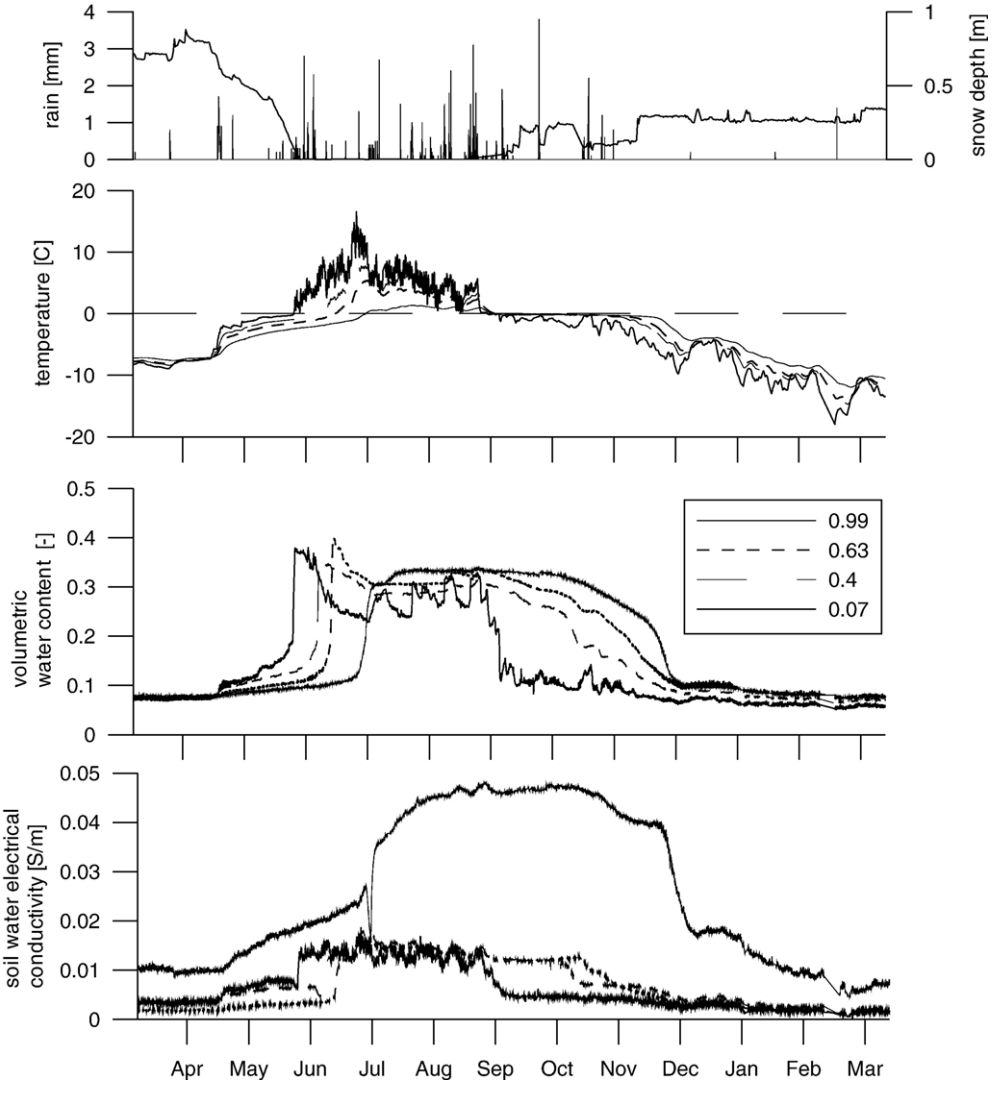

Fig. 7. Rainfall and snow depth, soil temperatures, soil water content and soil water electric conductivity from April 1999 to April 2000 for profile underneath mud. $A=3.8$ in Eq. (4) was used for TDR probe at 0.07 m under mud.

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near the surface are generally higher than below the vegetation covered trough. Due to the lack of vegetation, the profile thaws earlier. In mid-July, the thaw front passes the probe at 0.99 m depth. Over the course of the summer, the center of the mud boil thaws to greater depth compared to the vegetated trough. The water content of the soil surface layer shows greater fluctuations in response to wetting by rainfall and subsequent drying since these processes are not buffered by vegetation. The σ_w values increase with depth in a fashion similar to the profile under the vegetated trough, with highest values of σ_w at the bottom of the boil and, σ_w values are generally higher at the bottom of the mud profile. Decreases in σ_w from the beginning of June (0.07 m) until the middle of July (0.99 m) in the mineral profile indicate the dilution of the soil solution by downward migration of meltwater. As observed for the organic profile, these decreases in soil solution electric conductivity are associated with thawing, but occur before the liquid water content increases.

Soil waters from deep suction lysimeters B1 and B2, and from shallower lysimeters B5 and B6, were analyzed for cation and anion concentrations. Based on lysimeters B6 and B5 (about 60 cm), the most concentrated species are HCO_3^- and Mg^{2+} followed by $Ca^{2+} > Si > SO_4^{-2} > Cl^- > K^+ > NO_3^-$. Ionic concentrations at B6, beneath the center of the mud boil are generally higher than at B5, beneath the vegetated trough, with exception of NO_3^- and Si_{aq}. The deeper soil solutions (around 100 cm) are closer to the permafrost table and were most concentrated in SO_4^{2-}, followed by $Mg^{2+} > Ca^{2+} > HCO_3^- > Si_{aq} = K^+ = Cl^-$. The first samples collected from B2 in July 1999 show very low pHs of 4, higher Fe_{aq} (20–40 μg L^{-1}) and very high Al_{aq} (1–2 mg L^{-1}) concentration compared to later samples. A possible inorganic mechanism leading to such a low pH in natural water is dissolution of pyrite. Two possible overall redox reactions are given below (Langmuir, 1997, pp. 458):

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (6)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (7)$$

This reaction needs electron acceptors that can either be provided by oxygen or by an abundance of Fe^{3+}. Although this reaction would explain both high sulphate concentrations and low pH, more details (e.g. redox potential) are required to reveal if oxidation and dissolution of pyrite is the reason for the low pH values. During excavation of this and another soil pit coal fragments were found and exploratory excavations for coal are located nearby. The low pH, occurrence of coal and enrichment in Fe all support dissolution of pyrite as a common cause. The low pH enhances chemical weathering and therefore contributes to the overall increase in solute concentration at depth.

The rapid decrease in σ_w when soils freeze (Figs. 6 and 7) is counter-intuitive, since an increase in concentration due to the exclusion of ions during freezing is expected. A first approach to model the change in solute composition and concentration of soil water at subfreezing temperatures can be performed with geochemical equilibrium model FREZCHEM62 (Marion and Grant, 1994). This program is written to model changes in chemistry during stepwise freezing of a water solution and considers either continuous contact between solution and precipitated phase or fractional removal of precipitated phase from solution. It does not incorporate soil physical factors like mineral, organic or colloid surfaces that most likely contribute to changes in water chemistry. However, it allows estimation of the chemical development of a solution during freezing. Results of the modelling with FREZCHEM of solutions B1 and B6 collected at 1 and 0.6 m depth is shown in Fig. 8. Liquid water content rapidly decreases below subfreezing temperatures and at −5 °C only 0.006% of the total water content present before freezing is still unfrozen. During freezing salts of different composition precipitate from solution in the sequence: $CaSO_4 \cdot 2H_2O$, $MgCO_3$, $CaMg(CO_3)_2$, K_2SO_4, and $Na_2SO_4 \cdot 10H_2O$. The precipitation of these salts causes the changes in molar elemental ratios displayed in Fig. 8. The most striking difference between the soil solution with high SO_4^{2-} concentration (B1, B2) and high HCO_3^- concentration (B6) is in the change of Na/Cl ratios. While in the B1 soil solution the Na/Cl ratio constantly increases, it decreases in B6 due to the formation of KCl at −10 °C. Compared to TDR measurements, the calculated liquid water content based on water chemistry is much lower, a difference amounting to up to 9% by volume. An important part of liquid water in frozen soils exists as thin water films on particle surfaces (Ugolini and Anderson, 1973), and such water–surface interactions are not considered in FREZCHEM. If surface-bound water is not in contact with the solute-rich solution excluded from the forming ice, then the predicted precipitation of salts due to freezing would hold. Measurements of σ_w depend on a direct current pathway between electrodes (in this case, TDR sensor wave guides), so that isolated pockets of high concentration will not contribute to the measured bulk electric conductivity of the soil. Surface bound water, however, contributes to the measurement of σ_b (Guy–Chapman double layer theory).

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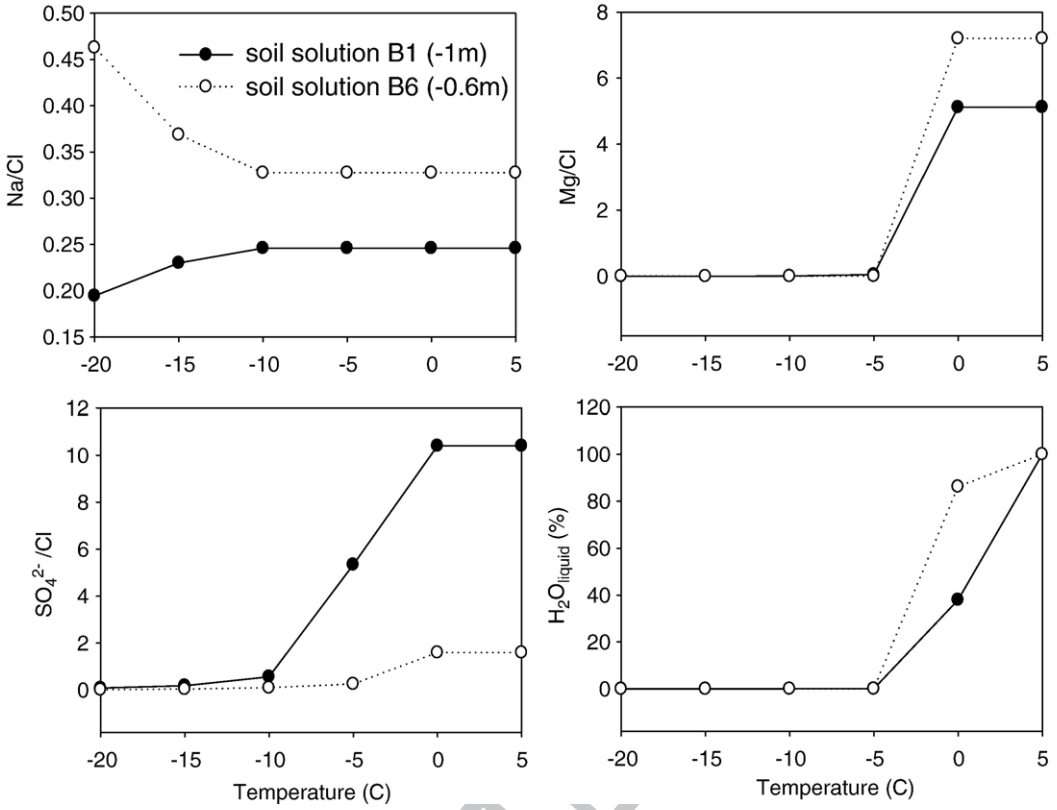

Fig. 8. Molar element ratios and liquid water concentration (%) modelled with FREZCHEM62 between +5 and −20 °C. The soil solutions are taken from suction cups B6 and B1. Changes in element ratios indicate formation of solid salt precipitates that remove specific elements from solution. Liquid water content refers to percent of liquid water of total amount of water that was present before freezing. At −20 °C liquid water content is less than a per mille.

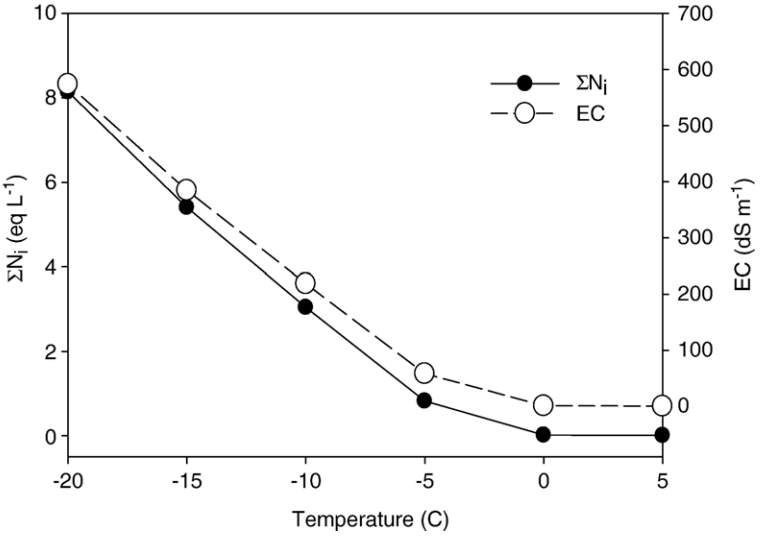

Fig. 9. Calculated total ion concentration in eq L^{-1} in remaining solution during freezing. EC is calculated from Eq. (8) using total ion activity (eq/L) ($\sum a_i = \sum N_i \gamma_i$ where γ_i is the activity coefficient provided by FREZCHEM62) instead of ion concentration N_i.

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To compare the modelled solution with measured conductivity, the electric conductivity is calculated following the approach of Reluy et al. (2004) relating electric conductivity (EC) to the equivalent concentration of ions in solution ($\sum N$). The relation between EC and $\sum N$ is given by:

$$EC = 10^{-6} u' F \sum_i N_i \quad (8)$$

where F is Faraday's constant ($Cmol^{-1}$), and u' is the concentration-weighted mean equivalent mobility:

$$u' = \frac{\sum_i N_i u_i}{\sum_i N_i} \quad (9)$$

where u_i is the limiting equivalent ionic mobility of ion i [mS cm^2 mol eq^{-1} C[illegible] calculation we used values of u_i ~~given in Table 3 in~~ Reluy et al. (2004). Instead of normalities, N_i, we used the activities calculated with FREZCHEM for each ion and ion pair. The results of this calculation are shown in Fig. 9, indicating that the solution electric conductivity increases with increasing solute concentration from around 0.05 S m^{-1} to 60 S m^{-1}. The total concentration of ions in the remaining unfrozen solution increases by a factor of ~1000, whereas without precipitation of salts the concentration would increase by a factor of ~17000 at the final water content. Modelled changes to soil solution, in the absence of mineral–soil solution interactions, lead to a predicted increase in soil water electric conductivity of three orders of magnitude with freezing. The water electric conductivities in the thawed soil estimated for the solution analyzed here are of the same order of magnitude as those predicted by this model (e.g. for a measured solution electric conductivity of 0.038 S m^{-1}, we predict an electric conductivity of 0.050 S m^{-1}).

If the contribution of the clay particle surface conductivity to σ_b is significant, the isolation of clay particles by ice layers could be another reason for the reduction of σ_b. In that case σ_w in frozen soil might be underestimated by the values calculated from bulk electric conductivity measured with the TDR probes.

5. Discussion

5.1. Observed changes in soil water electric conductivity with time

~~Changes in estimated soil water electric conductivity respond~~ to freezing, thawing and summer rainfall events. Using the model of Boike and Roth (1997), we show that the largest annual increase and decrease are associated with thawing and freezing, respectively, of the soil. During thaw, for both soils under the boil and the vegetated trough, soil water electric conductivity at all depths decreases by up to 30% before the increase associated with thawing occurs. The thaw increase occurs simultaneously with the increase in liquid water content associated with the phase change of ice to water. We suggest that the initial decrease in electric conductivity indicates that the infiltration and refreezing of snow meltwater has diluted the available soil solution.

5.2. Increase in solute concentration with depth

Our data show that soil solutes within the mud boil are stratified horizontally throughout the year and that this stratification, with highest concentrations at the bottom of the profile, is dominant over any vertical stratification (org[illegible] versus mud). Lundin and Johnsson (1994) also found that σ_w increased with depth and percentage of fines in Swedish agricultural soils. Alekseev et al. (2003) and Kokelj and Burn (2003) also find the highest concentrations in the soil profile at the boundary between seasonally thawed soil and permafrost. Alekseev et al. (2003) conclude that permafrost landscapes in general accumulate solutes at the upper boundary of the permafrost, ~~acting~~ as a geochemical barrier.

In addition to this depth stratification, we observe a slight increase in soil electric conductivity beneath the center of the mud boil. Depressions, as in our case the bowl-shaped region beneath the mud boil, have even higher concentrations of solutes. These subtle variations in concentration might be the initiator of irregularities in the permafrost table due to the depression of the freezing point and thus, the precursor of certain patterned ground, such as these non-sorted circles. Once a bowl-shaped depression of the permafrost table exists, cell-like circulation pattern within the active layer can be initiated (i.e. the equilibrium model after Mackay, 1980). However, Fig. 8 shows that the depression of the freezing point by solute exclusion from a freezing solution with the chemistry of extracted soil water is only sufficient to maintain less than 0.1 mL of water in the liquid state per liter of soil solution below −10 °C, implying that the effect of solute exclusion on the permafrost table depth are minimal compared to those of differences in surface cover and overlying soil thermal properties. ~~Therefore it seems plausible that differential frost heave is responsible~~ for the formation of the mud

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boils as also stated by Van Vliet-Lanoë (1991). Walker et al. (2004, pp. 178) postulated that frost boils typical of coastal areas pump solutes to the surface as a result of relatively high evaporation rates and that the salts thus deposited inhibit vegetation growth. In contrast to these findings, our data suggest that net accumulation of solutes occurs at the base of the active layer, with little difference between mud boil and adjacent vegetated regions. In both profiles, the highest values of σ_w occur at depth, whereas the lowest values are found in the upper coarser horizon.

The increase with depth probably results from one or both of two general processes. First, seasonal freezing may lead to a cumulative downward migration of solutes as a result of solute exclusion from the freezing soil water. This downward migration is ultimately limited by the presence of the permafrost table, which provides a natural boundary to downward percolation. Secondly, the fraction of finer material increases with depth at this site providing a higher surface area susceptible for chemical weathering.

5.3. Comparison to thermodynamically modelled freezing

The high temporal resolution of soil water electric conductivity data derived from TDR measurements permits qualitative identification of processes such as dilution (melting of pure ice) and concentration in frozen soil during snow ablation and migration in the thawed soil. These are in congruence with the observed hydrologic and thermal dynamic. However, the absolute concentration values during the frozen period are much lower than expected if exclusion of solutes from the freezing soil solution occurs, despite the fact that thermodynamically modelled freezing indicates that several salts precipitate from soil solution during freezing. The time difference between the increase in water content and soil water electric conductivity during thawing might indicate kinetic delay of re-dissolution of these salt crystals. Furthermore, some of precipitates, like carbonates and Ca-sulfates, may not re-dissolve completely. The higher amount of particulate inorganic carbon found at depth of mud boil may be a direct result of precipitation of fine carbonates combined with mechanical movement of fines to bottom of mud boil. The contribution of solute movement is unlikely since it would be against the concentration gradient.

The calculation of electric conductivity from salt concentration and salt composition strongly depends on ion mobility. However, values used for u_i have been determined for temperate solutions. Subfreezing temperatures and changes in the viscosity of water may decrease ion mobility and electric conductivity. Further experimental investigations are needed to determine mobilities of single ions and ion pairs at temperature below 0 °C. Furthermore, water bound to clay particle and ice surfaces may have lower solute concentrations than regions containing solutes excluded from freezing pore water, leading to lower overall measured salt concentration per unit volume of soil. Ostroumov et al. (2001) found that liquid drops on the surface of the forming ice were probably responsible for solute transport in frozen deposits close to the freezing front. The implication is that excluded solutes are restricted to small, unconnected domains within the soil that would not contribute to measured bulk soil electric conductivity.

5.4. Implications for cryoturbation

Walker et al. (2004) hypothesize that particles and dissolved organic material are carried downward at the margins of frost boils by soil movement and leaching, whereas organics accumulate in the thawed of the frost boil. At the center of the mud boil, upward migration of organics occurs. The high concentrations (>6%) of organic carbon in our mud boil (Fig. 2) support their hypothesis. The differences in thermal and hydrologic regime, thaw depth, and total nitrogen, organic carbon and total sulfur concentrations between mud and vegetated trough profiles create a physically different environment. This, in turn, affects the vegetation and possibly governs the mechanical forces that create the mud boils. Cryoturbation is the most effective process in moving organics and (weathered) minerals upwards from the bottom of the active layer, thus counteracting the downward fluxes. Cryoturbation is likely to change with a changing climate. On Svalbard, mean annual ground surface temperature currently increases at a rate of ~0.4 °C per decade (Isaksen et al., 2001).

6. Conclusion

The influence of mud boils on solute migration is small compared to the influence of the seasonal freeze–thaw cycle in the presence of permafrost. The soil solution electric conductivity increases with depth beneath a mud boil, irrespective of lateral position, but seasonal changes in conductivity between frozen and thawed soil are up to 5 times greater. TDR-determined bulk electric conductivity is a useful tool, since it permits high temporal resolution measurement of changes in soil electric conductivity, and thus a means of investigating solute dynamics. The deviation between TDR determined and thermodynamically modelled changes in soil solution chemistry

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identifies two future research goals: (i) a new model accounting for changes in phase geometry during freezing and (ii) including the effects of soil surface physics in thermodynamic models of freezing.

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