



# 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.

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## 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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36 thermodynamic equilibrium modelling of solution chem-  
 37 istry. This, in turn, adds insight to the mechanical dynamic  
 38 of the mud boil, and to the discussions on the origin and  
 39 formation of these periglacial features.

40 Furthermore, these findings contribute directly to the  
 41 European Science Foundation project on ‘Sedimentary  
 42 Source-to-Sink-fluxes in Cold Environments’. An un-  
 43 derstanding of climate processes and their control on  
 44 mass transfer processes, such as subsurface behaviour of  
 45 solutes in a mudboil, aids in the understanding of mass  
 46 export of cold drainage basins.

## 47 2. Theories of mud boil formation

48 Mud boils are symmetric surface features in  
 49 periglacial environments that have puzzled and fasci-  
 50 nated researchers since at least 1900. Early observations  
 51 and theories of the origin of patterned ground were the  
 52 beginning of exciting research. Washburn (1956) sum-  
 53 marized and discussed postulations of 19 separate  
 54 mechanisms of formation for non-sorted circles in  
 55 particular. These ideas are still central in today’s discus-  
 56 sions of patterned ground formation.

57 Mud boils (also known as frost boils, frost scars, mud  
 58 circles and mud hummocks), classified as non-sorted  
 59 circles, are found in areas where the ground is subject to  
 60 seasonal freezing and thawing. They are characterized  
 61 by a bare, usually doming round mineral soil center,  
 62 surrounded by vegetation. Some of the mechanisms  
 63 postulated for their formation are: the sorting of soil  
 64 materials based on grain size; convection cell like  
 65 cryoturbation; diapir formation or upwellings of lower  
 66 soil horizons under pressure (Washburn, 1956). A  
 67 review of the main mechanisms involved in cryoturba-  
 68 tions was presented by Van Vliet-Lanoë (1991) based  
 69 upon field measurements and micromorphological data.  
 70 She concluded that “differential frost heaving appears to  
 71 be the main mechanism of cryoturbation” (pp. 123) and  
 72 that the presence of organics enhances differential frost  
 73 heaving. Kessler et al. (2001) modelled sorted circle  
 74 formation (with barren finer grained circle centers  
 75 surrounded by stones) from two layers distinct in par-  
 76 ticle size using a purely mechanical model. The freezing  
 77 front pushed soil to more compressible soil regions,  
 78 accumulating in soil plugs that reach to the surface.  
 79 During thawing, consolidation occurred vertically. The  
 80 circle was maintained at the surface by the circulation of  
 81 the stone and fine material domains, upward in the circle  
 82 center and downward at the edges. Walker et al. (2004)  
 83 presented horizontal soil profiles across a mud boil.  
 84 Nutrient concentrations (available potassium, phosphor,  
 85 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 fore-  
 field 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 dis-  
 placement 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 favour-  
 able 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 communi-  
 cation). 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  
 ( $\theta$ ). 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

134 samples were determined using standard methods. Wet  
 135 soil was passed through a sieve with 63  $\mu\text{m}$  size to  
 136 measure sand content. After destruction of organics and  
 137 limestone, silt and clay were separated by sedimentation

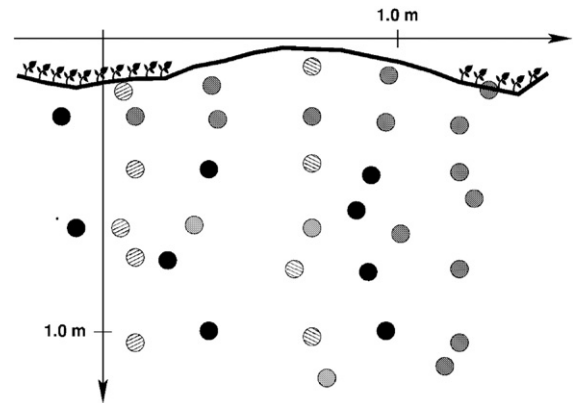
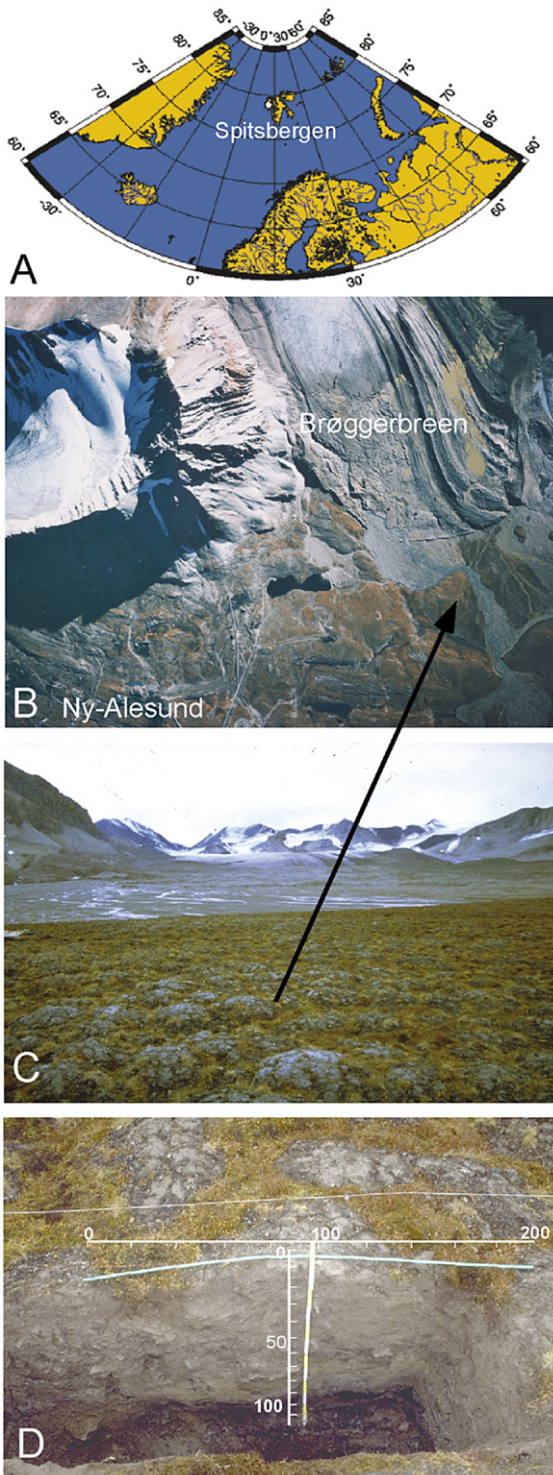


Fig. 2. Position of TDR probes (grey and hatched circles) installed in the mud boil. Temperature probes are installed adjacent to TDR probes. For the analysis, the left profile under vegetation and the profile underneath the center of the mud are used (hatched circles). In addition, nine suction lysimeters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

in Atterberg cylinders. Soil temperatures were recorded 138  
 using thermistors calibrated at 0 °C with a precision of 139  
 $2.4 \times 10^{-4}$  °C at 0 °C and an absolute error less than 140  
 $\pm 0.02$  °C over the temperature range  $\pm 30$  °C. Volumetric 141  
 liquid water content was calculated from TDR 142  
 measurements with an accuracy of 0.02 to 0.005 and a 143  
 precision better than 0.005. Soil water was sampled in 144  
 1999 using Prenart® suction cups (5 cm long, pore size 145  
 2  $\mu\text{m}$ ; Gravquick, Denmark) cups that were installed in 146  
 1998 at different depths close to TDR probes. Soil water 147  
 was analyzed in the field for pH, electric conductivity 148  
 and alkalinity. The remaining sample water was filtered 149  
 and stored at 4 °C in pre-cleaned HDPE bottles until 150  
 laboratory analysis took place. Cation concentrations 151  
 were analyzed with ICP-OES (Optima 3000 XL, Perkin 152  
 Elemer) and anion concentrations were measured with 153  
 ion chromatograph (Dionex 320). 154

### 3.1. TDR and bulk electric conductivity 155

Data on spatial and temporal distribution of water 156  
 and solutes in frozen and unfrozen soils are essential for 157  
 energy and mass transport models. A fast method to 158  
 measure the volumetric water content *in situ* is TDR. 159

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.

160 TDR has become a reliable and widely used technique  
 161 to measure the water content in frozen and unfrozen  
 162 soils (for example, Topp et al., 1980; Patterson and  
 163 Smith, 1980; Roth et al., 1990). The TDR technique for  
 164 measuring the volumetric water content is based on the  
 165 large disparity in the relative dielectric permittivities of  
 166 water and the other soil constituents. The bulk relative  
 167 dielectric permittivity of the soil determines the velocity  
 168 with which an electromagnetic wave travels through the  
 169 soil, so that measurement of the travel time for a known  
 170 distance allows determination of the material's permit-  
 171 tivity. We use a physically-based dielectric mixing

model to compute the composite dielectric number of a  
 multiphase mixture using the relative dielectric permit-  
 tivities and volume fractions of its constituents (Roth  
 et al., 1990).

TDR can also be used to measure the impedance of the  
 bulk soil  $Z$  ( $\Omega$ ), which is related to the bulk soil electric  
 conductivity as a function of time. The bulk soil electric  
 conductivity is directly 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

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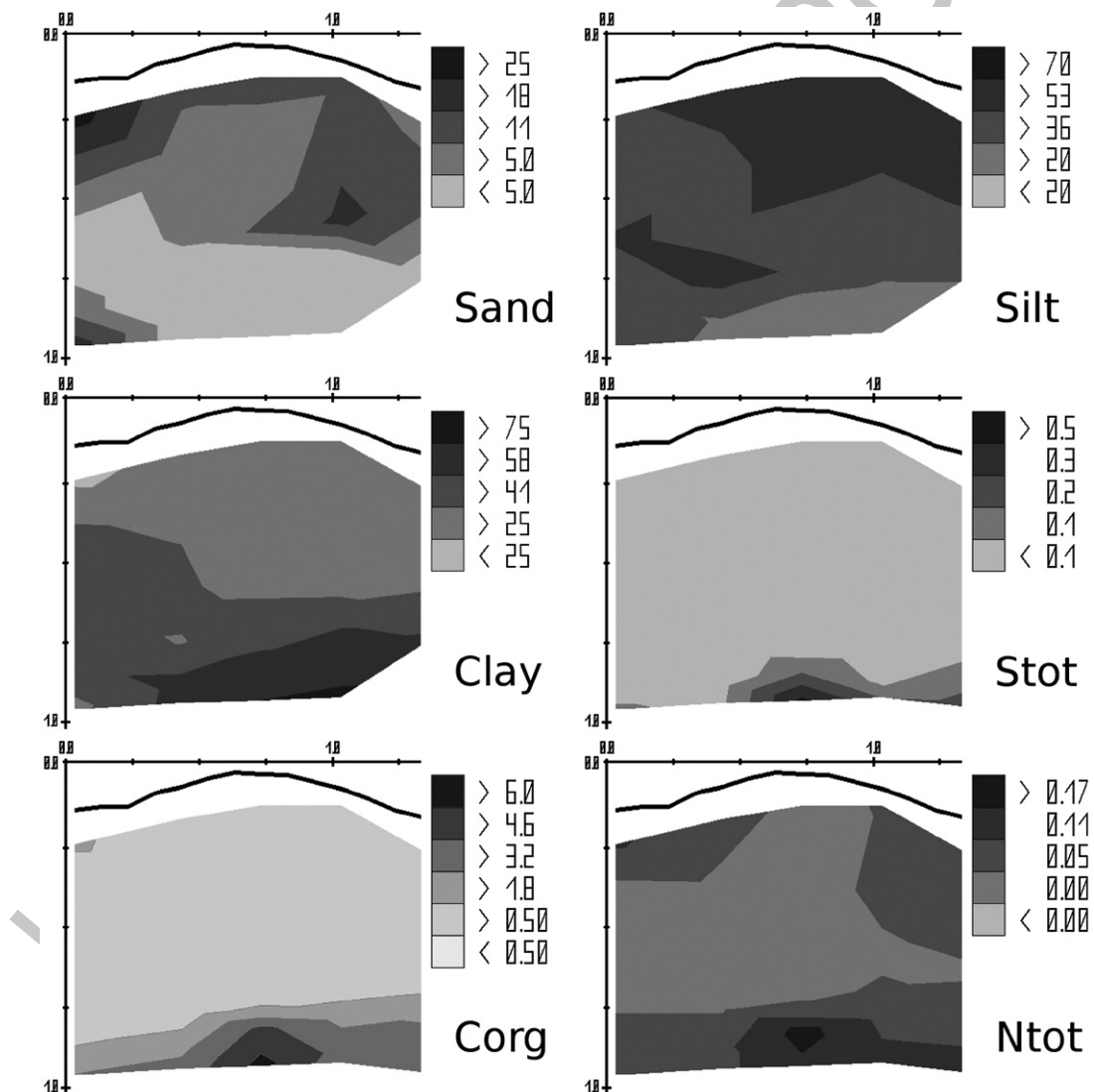


Fig. 3. 2-D distribution of sand, silt, clay and total carbon, nitrogen, sulphur of the mud boil in % weight. Linear interpolation is used between 25 sampling points.

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

$$188 \sigma_b^{25} = \frac{K_p}{Z - Z_{\text{cable}}} f_T \quad (1)$$

187 where  $\sigma_b^{25}$  [ $\text{S m}^{-1}$ ] is the soil bulk electric conductivity  
189 corrected to 25 °C,  $K_p$  [ $\text{m}^{-1}$ ] is the geometric cell constant  
190 of the TDR probe,  $Z_{\text{cable}}$  [ $\Omega$ ] accounts for the total  
191 resistance of cables, connectors and cable tester and  $f_T$  [–]  
192 is a temperature factor defined as:

$$193 f_T = 1 + \alpha(T - 25) \quad (2)$$

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

$$202 \sigma_b^{25} = \left( \frac{1}{Z - Z_{\text{cable}}} - B \right) K_p f_T \quad (3)$$

203 where  $B$  is an additional fitting parameter.  $B$ ,  $K_p$  and  
204  $Z_{\text{cable}}$  were determined by non-linear least squares  
205 fitting.

### 206 3.2. Calculation of soil solution electric conductivity $\sigma_w$

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

$$220 \sigma_b = A\theta\sigma_w \quad (4)$$

221 where  $\sigma_w$  [ $\text{S m}^{-1}$ ] is the electric conductivity of the soil  
222 solution,  $\theta$  [–] is the volumetric liquid water content of  
223 the soil and  $A$  [–] is a fitting parameter. For three

different mineral soils the parameter  $A$  varied between 224  
0.7 and 4.8. Best results were obtained with probe 225  
specific calibrations. Furthermore, they suggested that  $A$  226  
did not change from frozen to unfrozen soils and that 227  
this model may be applied to calculate  $\sigma_w$  for frozen 228  
conditions as well. To our knowledge, the only other 229  
model predicting  $\sigma_w$  from TDR-determined  $\sigma_b$  in frozen 230  
soils was introduced by van Loon et al. (1991; also 231  
reviewed in Boike and Roth, 1997). This model has 232  
been applied for the study of solute dynamics in 233  
Swedish field soils (Lundin and Johnsson, 1994) and 234  
in frozen lab columns (Stähli and Stadler, 1997) without 235  
prior calibration to soil solution electric conductivity. As 236  
the model by van Loon et al. (1991) did not predict 237  
solution electric conductivity as well as the regression 238  
model for permafrost soils in Siberia (Boike and Roth, 239  
1997) we did not consider this model further in this 240  
study. 241

## 242 4. Results

Soil composition data from the 25 samples taken 243  
from the profile is presented in Fig. 3. The soil material 244  
generally consists of silty clay with some larger stones. 245  
The silt content decreases from over 50% at the top of 246  
the profile to less than 30% at the bottom, concomitant 247  
with an increase of clay content to over 50% (Fig. 3). 248  
Concentrations of organic carbon, total nitrogen and 249  
total sulphur are highest at the bottom of the profile, 250  
peaking below the mud boil center. Of note are 251  
especially high concentrations of organic carbon (>6% 252

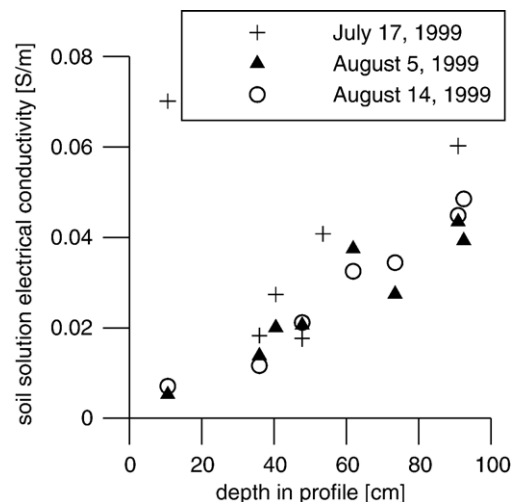


Fig. 4. Soil water electric conductivity obtained from suction lysimeter water at three different times over depth.

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

#### 4.1. Determination of $\sigma_w$

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  $\sigma_w$  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  $\sigma_w$  measured in soil water and the corresponding  $\sigma_w$  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

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

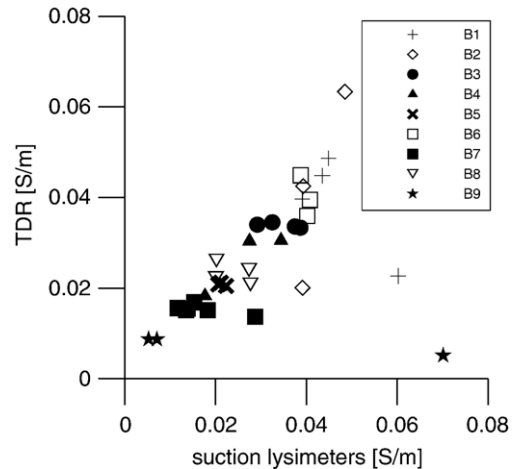


Fig. 5. Soil water electric conductivity obtained from suction lysimeters (names of suction lysimeters in legend) compared to values calculated from bulk electric conductivity (TDR probes) using model (4).

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  $\sigma_w$  and  $\sigma_b$  and  $\theta$  and  $\sigma_b$ . Therefore the qualitative behaviour of  $\sigma_w$  derived from the TDR measurements is expected to be correct even if absolute errors are introduced by disregarding the conductivity of the solid phase.

#### 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  $\sigma_w$  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

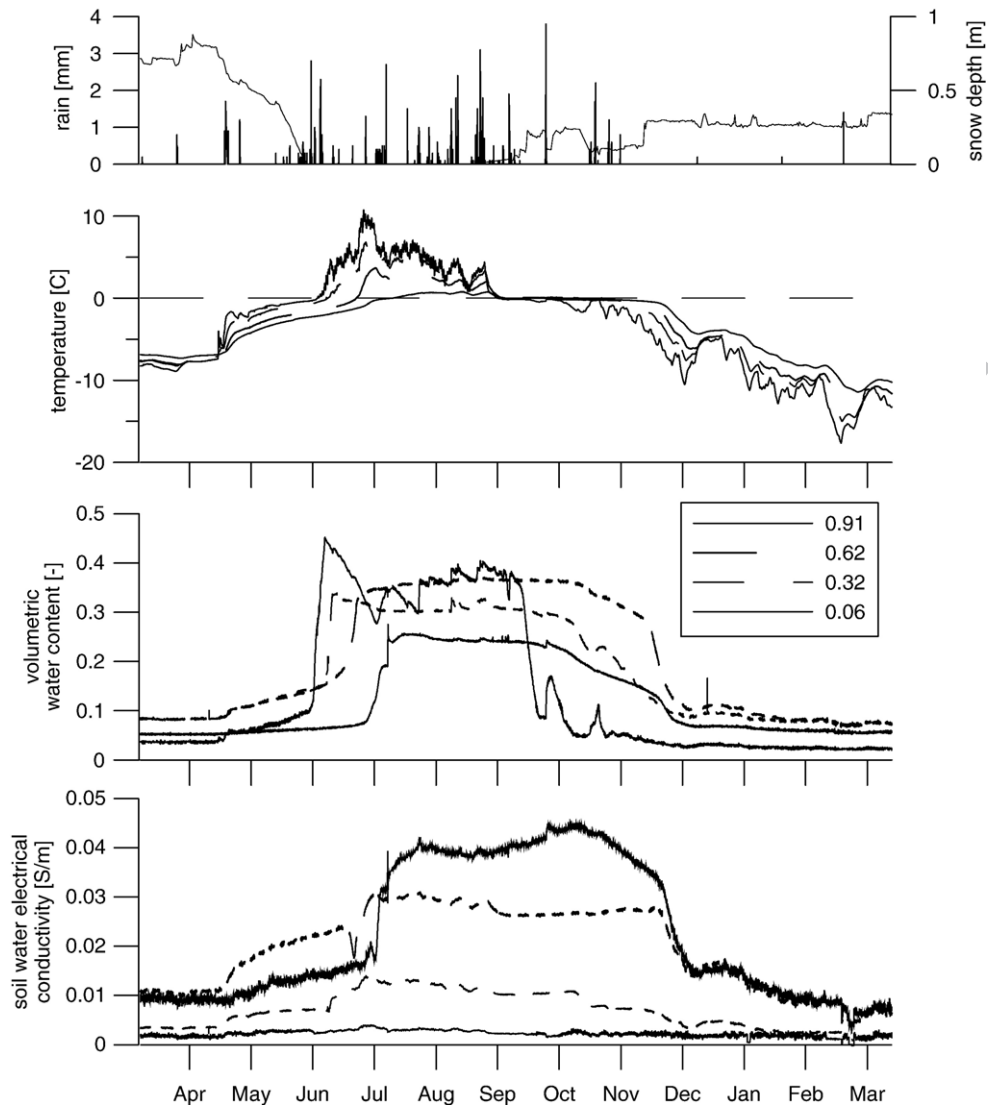


Fig. 6. Rainfall and snow depth, soil temperatures, soil water content and soil water electric conductivity from April 1999 to April 2000 at four depths for a profile underneath the vegetated cover.

319 temperature sensor at 0.91 m depth passes 0 °C around the  
 320 end of July. However, low volumetric water contents  
 321 (~0.25) that remain constant over the summer indicate  
 322 that the soil is not completely thawed. The temperature  
 323 sensor at 1.22 m depth (not shown in diagram) indicates  
 324 that the soil never thaws at this depth. During the summer,  
 325 volumetric water content remains constant at 0.62 m  
 326 depth, indicating the perched water table above the frozen  
 327 ground. Once freezing starts in September, soil tempera-  
 328 tures at all depths drop to below zero and phase change  
 329 from water to ice is initiated (“zero curtain effect”). The  
 330 phase change is completed by mid-November, after which  
 331 the soil profile cools. The volumetric liquid water content  
 332 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  $\sigma_w$  below the  
 organic (except for the probe nearest to the surface at  
 0.06 m) can be summarized as follows: increase of  $\sigma_w$   
 during thawing, highest concentrations during the summer  
 and decrease during fall phase change. However, during  
 the spring thaw, the behaviour of  $\sigma_w$  is different  
 for each soil depth. At intermediate depth (0.32 m),  $\sigma_w$   
 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

347 during thaw at about 15% liquid water content, which  
 348 indicates that dilution of the soil water has occurred,  
 349 probably via downward migration of meltwater with  
 350 lower concentrations of dissolved ionic species. In ad-  
 351 dition, this is the soil depth with the highest  $\sigma_w$  in the  
 352 frozen soil. Since this is the soil depth that remains  
 353 thawed longest in the fall (Boike et al., 2003), migration  
 354 of excluded ions would take place towards this depth.  
 355 This is also suggested by a small increase of  $\theta$  and  $\sigma_w$  in  
 356 December after closure of the zero curtain.

357 Throughout the whole summer  $\sigma_w$  is relatively stable,  
 358 with small increases of  $\sigma_w$  occurring at the three  
 359 intermediate depths simultaneously with an increase of  
 360  $\theta$  after a series of rain events during the latter half of

361 August. However, there is also a peak in  $\sigma_w$  measured 361  
 362 with the deepest probe at the end of July, which is not 362  
 363 connected to a corresponding increase of water content. 363  
 364 Only the surface probe shows an increase in  $\theta$  at this time, 364  
 365 caused by a minor rain event. As the same peak can be 365  
 366 recognized at the deepest probe below the mud boil 366  
 367 center, it is unlikely to be an artefact and either an *in situ* 367  
 368 increase in solute concentration, for example by dissolution 368  
 369 of salts, or lateral inflow must have occurred. 369  
 370 Generally in the thawed organic profile, soil water 370  
 371 conductivity increases with depth and the highest concen- 371  
 372 trations occur at the bottom of the profile (0.91 m). 372

373 In the barren soil below the center of the boil the 373  
 374 fluctuations of temperature, water content (Fig. 7) and  $\sigma_w$  374

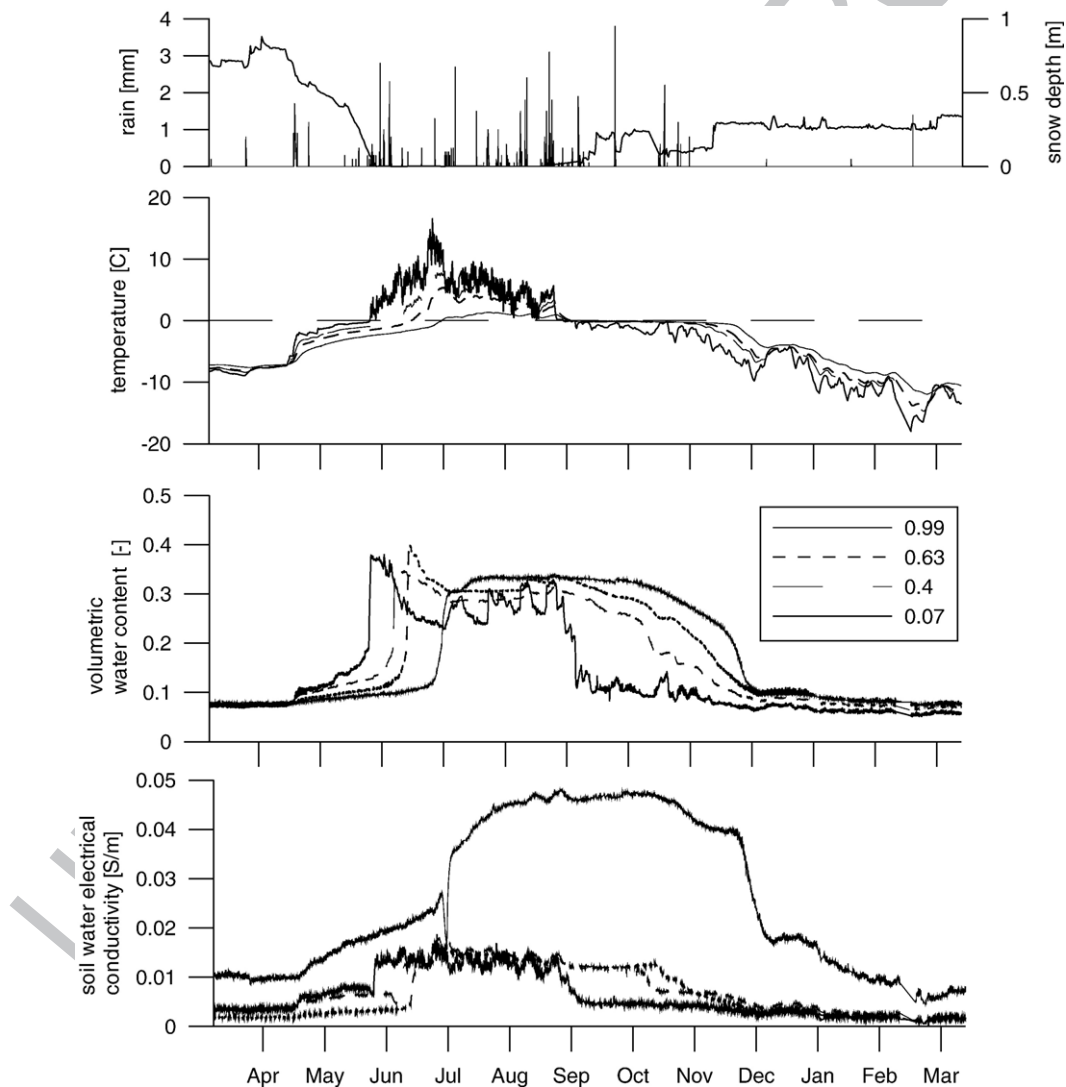
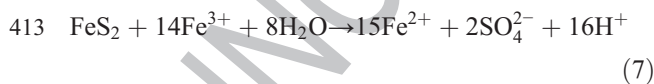


Fig. 7. Rainfall and snow depth, soil temperatures, soil water content and soil water electric conductivity from April 1999 to April 2000 for profile underneath mud.  $A=3.8$  in Eq. (4) was used for TDR probe at 0.07 m under mud.



375 near the surface are generally higher than below the  
 376 vegetation covered trough. Due to the lack of vegetation,  
 377 the profile thaws earlier. In mid-July, the thaw front passes  
 378 the probe at 0.99 m depth. Over the course of the summer,  
 379 the center of the mud boil thaws to greater depth com-  
 380 pared to the vegetated trough. The water content of the  
 381 soil surface layer shows greater fluctuations in response to  
 382 wetting by rainfall and subsequent drying since these  
 383 processes are not buffered by vegetation. The  $\sigma_w$  values  
 384 increase with depth in a fashion similar to the profile  
 385 under the vegetated trough, with highest values of  $\sigma_w$  at  
 386 the bottom of the boil and,  $\sigma_w$  values are generally higher  
 387 at the bottom of the mud profile. Decreases in  $\sigma_w$  from the  
 388 beginning of June (0.07 m) until the middle of July  
 389 (0.99 m) in the mineral profile indicate the dilution of the  
 390 soil solution by downward migration of meltwater. As  
 391 observed for the organic profile, these decreases in soil  
 392 solution electric conductivity are associated with thawing,  
 393 but occur before the liquid water content increases.

394 Soil waters from deep suction lysimeters B1 and B2,  
 395 and from shallower lysimeters B5 and B6, were analyzed  
 396 for cation and anion concentrations. Based on lysim-  
 397 eters B6 and B5 (about 60 cm), the most concentrated  
 398 cations are  $\text{HCO}_3^-$  and  $\text{Mg}^{2+}$  followed by  $\text{Ca}^{2+} >$   
 399  $\text{Si} > \text{SO}_4^{2-} > \text{Cl}^- > \text{K}^+ > \text{NO}_3^-$ . Ionic concentrations at B6,  
 400 beneath the center of the mud boil are generally higher  
 401 than at B5, beneath the vegetated trough, with exception  
 402 of  $\text{NO}_3^-$  and  $\text{Si}_{\text{aq}}$ . The deeper soil solutions (around  
 403 100 cm) are closer to the permafrost table and were  
 404 most concentrated in  $\text{SO}_4^{2-}$ , followed by  $\text{Mg}^{2+} > \text{Ca}^{2+} >$   
 405  $\text{HCO}_3^- > \text{Si}_{\text{aq}} = \text{K}^+ = \text{Cl}^-$ . The first samples collected from  
 406 B2 in July 1999 show very low pHs of 4, higher  $\text{Fe}_{\text{aq}}$   
 407 ( $20\text{--}40 \mu\text{g L}^{-1}$ ) and very high  $\text{Al}_{\text{aq}}$  ( $1\text{--}2 \text{mg L}^{-1}$ )  
 408 concentration compared to later samples. A possible  
 409 inorganic mechanism leading to such a low pH in natural  
 410 water is dissolution of pyrite. Two possible overall redox  
 411 reactions are given below (Langmuir, 1997, pp. 458):



416 This reaction needs electron acceptors that can either  
 417 be provided by oxygen or by an abundance of  $\text{Fe}^{3+}$ .  
 418 Although this reaction would explain both high sulphate  
 419 concentrations and low pH, more details (e.g. redox  
 420 potential) are required to reveal if oxidation and  
 421 dissolution of pyrite is the reason for the low pH values.  
 422 During excavation of this and another soil pit coal  
 423 fragments were found and exploratory excavations for

424 coal are located nearby. The low pH, occurrence of coal  
 425 and enrichment in Fe all support dissolution of pyrite  
 426 as a common cause. The low pH enhances chemical  
 427 weathering and therefore contributes to the overall in-  
 428 crease in solute concentration at depth.

429 The rapid decrease in  $\sigma_w$  when soils freeze (Figs. 6  
 430 and 7) is counter-intuitive, since an increase in con-  
 431 centration due to the exclusion of ions during freezing is  
 432 expected. A first approach to model the change in solute  
 433 composition and concentration of soil water at sub-  
 434 freezing temperatures can be performed with geochemi-  
 435 cal equilibrium model FREZCHEM62 (Marion and  
 436 Grant, 1994). This program is written to model changes  
 437 in chemistry during stepwise freezing of a water solution  
 438 and considers either continuous contact between solu-  
 439 tion and precipitated phase or fractional removal of  
 440 precipitated phase from solution. It does not incorporate  
 441 soil physical factors like mineral, organic or colloid  
 442 surfaces that most likely contribute to changes in  
 443 water chemistry. However, it allows estimation of the  
 444 chemical development of a solution during freezing.  
 445 Results of the modelling with FREZCHEM of solutions  
 446 B1 and B6 collected at 1 and 0.6 m depth is shown in  
 447 Fig. 8. Liquid water content rapidly decreases below  
 448 subfreezing temperatures and at  $-5 \text{ }^\circ\text{C}$  only 0.006% of  
 449 the total water content present before freezing is still  
 450 unfrozen. During freezing salts of different composition  
 451 precipitate from solution in the sequence:  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  
 452  $\text{MgCO}_3$ ,  $\text{CaMg}(\text{CO}_3)_2$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .  
 453 The precipitation of these salts causes the changes in  
 454 molar elemental ratios displayed in Fig. 8. The most  
 455 striking difference between the soil solution with high  
 456  $\text{SO}_4^{2-}$  concentration (B1, B2) and high  $\text{HCO}_3^-$  concen-  
 457 tration (B6) is in the change of Na/Cl ratios. While in the  
 458 B1 soil solution the Na/Cl ratio constantly increases, it  
 459 decreases in B6 due to the formation of KCl at  $-10 \text{ }^\circ\text{C}$ .  
 460 Compared to TDR measurements, the calculated liquid  
 461 water content based on water chemistry is much lower, a  
 462 difference amounting to up to 9% by volume. An im-  
 463 portant part of liquid water in frozen soils exists as thin  
 464 water films on particle surfaces (Ugolini and Anderson,  
 465 1973), and such water–surface interactions are not  
 466 considered in FREZCHEM. If surface-bound water is  
 467 not in contact with the solute-rich solution excluded  
 468 from the forming ice, then the predicted precipitation of  
 469 salts due to freezing would hold. Measurements of  $\sigma_w$   
 470 depend on a direct current pathway between electrodes  
 471 (in this case, TDR sensor wave guides), so that isolated  
 472 pockets of high concentration will not contribute to the  
 473 measured bulk electric conductivity of the soil. Surface  
 474 bound water, however, contributes to the measurement  
 475 of  $\sigma_b$  (Guy–Chapman double layer theory).

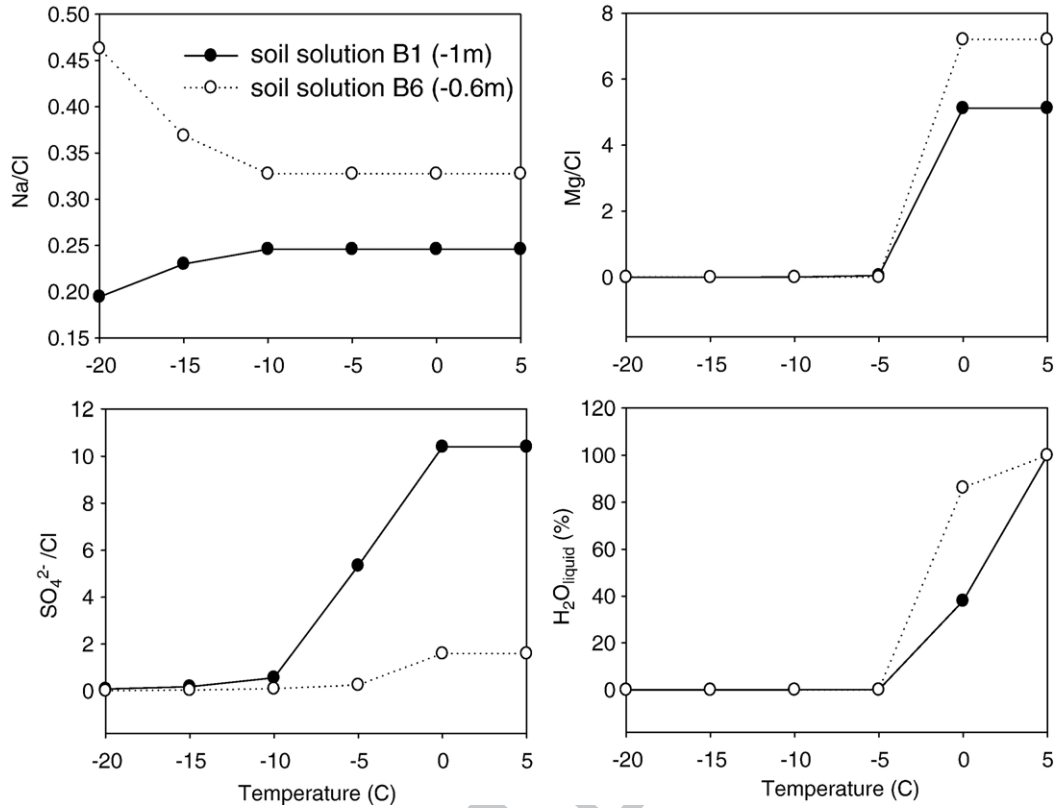


Fig. 8. Molar element ratios and liquid water concentration (%) modelled with FREZCHEM62 between +5 and –20 °C. The soil solutions are taken from suction cups B6 and B1. Changes in element ratios indicate formation of solid salt precipitates that remove specific elements from solution. Liquid water content 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 1‰.

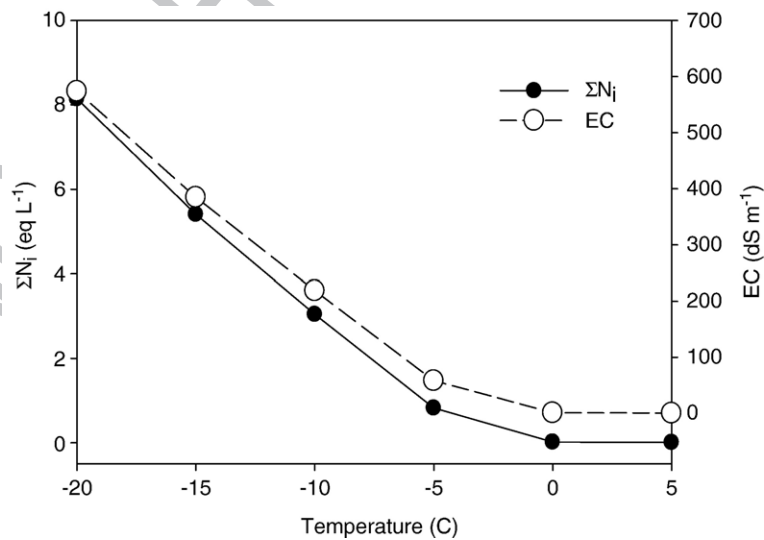


Fig. 9. Calculated total ion concentration in eq L<sup>-1</sup> in remaining solution during freezing. EC is calculated from Eq. (8) using total ion activity (eq/L) ( $\Sigma a_i = \Sigma N_i \gamma_i$ ; where  $\gamma_i$  is the activity coefficient provided by FREZCHEM62) instead of ion concentration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

476 To compare the modelled solution with measured  
 477 conductivity, the electric conductivity is calculated  
 478 following the approach of Reluy et al. (2004) relating  
 479 electric conductivity (EC) to the equivalent concentra-  
 480 tion of ions in solution ( $\sum N$ ). The relation between EC  
 481 and  $\sum N$  is given by:

$$482 \quad EC = 10^{-6} u' F \sum_i N_i \quad (8)$$

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

$$485 \quad u' = \frac{\sum_i N_i u_i}{\sum_i N_i} \quad (9)$$

486 where  $u_i$  is the limiting equivalent ionic mobility of ion  $i$   
 487 [ $\text{mS cm}^2 \text{ mol eq}^{-1} \text{ C}^{-1}$ ]. In our calculation we used values of  $u_i$   
 Q2 488 ~~given in Table 3 in Reluy et al. (2004).~~ Instead of  
 489 normalities,  $N_i$ , we used the activities calculated with  
 490 FREZCHEM for each ion and ion pair. The results of this  
 491 calculation are shown in Fig. 9, indicating that the solution  
 492 electric conductivity increases with increasing solute  
 493 concentration from around  $0.05 \text{ S m}^{-1}$  to  $60 \text{ S m}^{-1}$ .  
 494 The total concentration of ions in the remaining unfrozen  
 495 solution increases by a factor of  $\sim 1000$ , whereas without  
 496 precipitation of salts the concentration would increase by a  
 497 factor of  $\sim 17000$  at the final water content. Modelled  
 498 changes to soil solution, in the absence of mineral–soil  
 499 solution interactions, lead to a predicted increase in soil  
 500 water electric conductivity of three orders of magnitude  
 501 with freezing. The water electric conductivities in the  
 502 thawed soil estimated for the solution analyzed here are of  
 503 the same order of magnitude as those predicted by this  
 504 model (e.g. for a measured solution electric conduc-  
 505 tivity of  $0.038 \text{ S m}^{-1}$ , we predict an electric conductivity  
 506 of  $0.050 \text{ S m}^{-1}$ ).

507 If the contribution of the clay particle surface  
 508 conductivity to  $\sigma_b$  is significant, the isolation of clay  
 509 particles by ice layers could be another reason for the  
 510 reduction of  $\sigma_b$ . In that case  $\sigma_w$  in frozen soil might be  
 511 underestimated by the values calculated from bulk  
 512 electric conductivity measured with the TDR probes.

## 513 5. Discussion

### 514 5.1. Observed changes in soil water electric conductivity 515 with time

516 ~~Changes in estimated soil water electric conductivity~~  
 517 ~~respond~~ to freezing, thawing and summer rainfall

518 events. Using the model of Boike and Roth (1997),  
 519 we show that the largest annual increase and decrease  
 520 are associated with thawing and freezing, respectively,  
 521 of the soil. During thaw, for both soils under the boil and  
 522 the vegetated trough, soil water electric conductivity at  
 523 all depths decreases by up to 30% before the increase  
 524 associated with thawing occurs. The thaw increase  
 525 occurs simultaneously with the increase in liquid water  
 526 content associated with the phase change of ice to water.  
 527 We suggest that the initial decrease in electric  
 528 conductivity indicates that the infiltration and refreezing  
 529 of snow meltwater has diluted the available soil  
 530 solution.

### 531 5.2. Increase in solute concentration with depth

532 Our data show that soil solutes within the mud boil  
 533 are stratified horizontally throughout the year and that  
 534 this stratification, with highest concentrations at the  
 535 bottom of the profile, is dominant over any vertical  
 536 stratification (org. ~~versus~~ mud). Lundin and Johns-  
 537 son (1994) also found that  $\sigma_w$  increased with depth and  
 538 percentage of fines in Swedish agricultural soils.  
 539 Alekseev et al. (2003) and Kokelj and Burn (2003)  
 540 also find the highest concentrations in the soil profile at  
 541 the boundary between seasonally thawed soil and  
 542 permafrost. Alekseev et al. (2003) conclude that  
 543 permafrost landscapes in general accumulate solutes at  
 544 the upper boundary of the permafrost, ~~acting~~ as a  
 545 geochemical barrier.

546 In addition to this depth stratification, we observe a  
 547 slight increase in soil electric conductivity beneath the  
 548 center of the mud boil. Depressions, as in our case the  
 549 bowl-shaped region beneath the mud boil, have even  
 550 higher concentrations of solutes. These subtle variations  
 551 in concentration might be the initiator of irregularities in  
 552 the permafrost table due to the depression of the freezing  
 553 point and thus, the precursor of certain patterned  
 554 ground, such as these non-sorted circles. Once a bowl-  
 555 shaped depression of the permafrost table exists, cell-  
 556 like circulation pattern within the active layer can be  
 557 initiated (i.e. the equilibrium model after Mackay,  
 558 1980). However, Fig. 8 shows that the depression of  
 559 the freezing point by solute exclusion from a freezing  
 560 solution with the chemistry of extracted soil water is  
 561 only sufficient to maintain less than 0.1 mL of water in  
 562 the liquid state per liter of soil solution below  $-10 \text{ }^\circ\text{C}$ ,  
 563 implying that the effect of solute exclusion on the  
 564 permafrost table depth are minimal compared to those of  
 565 differences in surface cover and overlying soil thermal  
 566 properties. ~~Therefore it seems plausible that differential~~  
 567 ~~frost heave is responsible~~ for the formation of the mud

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  $\sigma_w$  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) 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 carbons combined 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 attaching, 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

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

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## 683 References

- 684 Alekseev, A., Alekseeva, T., Ostroumov, V., Siegert, C., Gradusov, B.,  
685 2003. Mineral transformation in permafrost-affected soils, North  
686 Kolya Lowland, Russia. *Soil Sci. Soc. Am. J.* 67 (2), 596–605.
- 687 Boike, J., Roth, K., 1997. Time domain reflectometry as a field method  
688 for measuring water content and soil water electrical conductivity  
689 at a continuous permafrost site. *Permafr. Periglac. Process.* 8 (4),  
690 359–370.
- 691 Boike, J., Roth, K., Ippisch, O., 2003. Seasonal snow cover on frozen  
692 ground: energy balance calculations of a permafrost site near Ny-  
693 Ålesund, Spitsbergen. *Geophys. Res.* 108 (D2), 8163. doi:10.1029/  
694 2001JD000939.
- 695 Heimovaara, T.J., Focke, A.G., Bouten, W., Verstraten, J.M., 1995.  
696 Assessing temporal variations in soil water composition with time  
697 domain reflectometry. *Soil Sci. Soc. Am. J.* 59, 689–698.
- 698 Isaksen, K., Holmlund, P., Sollid, J.L., Harris, C., 2001. Three deep  
699 alpine permafrost boreholes in Svalbard and Scandinavia. *Permafr.*  
700 *Periglac. Process.* 12, 13–25.
- 701 Kessler, M.A., Murray, A.B., Werner, B.T., Hallet, B., 2001. A model  
702 for sorted circles as self-organized patterns. *J. Geophys. Res.* 106  
703 (B7), 13,287–13,306.
- 704 Kokelj, S.V., Burn, C.R., 2003. Ground ice and soluble cations in near-  
705 surface permafrost, Inuvik, Northwest Territories, Canada. *Permafr.*  
706 *Periglac. Process.* 14, 275–289.
- 707 Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice-  
708 Hall, Upper Saddle River, New Jersey. 600 pp.
- 709 Lundin, L.-C., Johnsson, H., 1994. Ion dynamics of a freezing soil  
710 monitored in-situ by time domain reflectometry. *Water Resour.*  
711 *Res.* 30 (12), 3471–3478.
- Mackay, J.R., 1980. The origin of hummocks, western Arctic coast. 712  
*Can. J. Earth Sci.* 17 (8), 966–1006. 713
- Marion, G.M., Grant, S.A., 1994. FREZCHEM: A chemical- 714  
thermodynamic model for aqueous solutions at subzero tempera- 715  
tures. Hanover, NH, Cold Regions Research and Engineering 716  
Laboratory, U.S. Army Corps of Engineers. 717
- Ostroumov, V., Hoover, R., Ostroumova, N., Van Vliet-Lanoë, B., 718  
Siegert, C., Sorokovikov, V., 2001. Redistribution of soluble com- 719  
ponents during ice segregation in freezing ground. *Cold Reg. Sci.* 720  
*Technol.* 32, 175–182. 721
- Patterson, D.E., Smith, M.W., 1980. The use of time domain 722  
reflectometry for the measurement of unfrozen water content in 723  
frozen soils. *Cold Reg. Sci. Technol.* 3, 205–210. 724
- Reluy, F.V., de Bécares, J.M., Hernández, R.D., Díaz, J.S., 2004. 725  
Development of an equation to relate electric conductivity to soil 726  
and water salinity in a Mediterranean agricultural environment. 727  
*Aust. J. Soil Res.* 42, 381–388. 728
- Romanovskii, N.N., 1996. Periglacial processes as geoindicators in 729  
the cryolithozone. In: Berger, A.R., Jans, W.J. (Eds.), *Geoin dica-* 730  
*tors: Assessing Rapid Environmental Changes in Earth Systems.* 731  
Rotterdam, Balkema. 47–68 pp. 732
- Roth, K., Boike, J., 2001. Quantifying the thermal dynamics of a 733  
permafrost site near Ny-Ålesund, Svalbard. *Water Resour. Res.* 37 734  
(12), 2901–2914. doi:10.1029/2000WR000163. 735
- Roth, K., Schulin, R., Flüher, H., Attinger, W., 1990. Calibration of time 736  
domain reflectometry for water content measurement using a com- 737  
posite dielectric approach. *Water Resour. Res.* 26 (10), 2267–2273. 738
- Stähli, M., Stadler, D., 1997. Measurement of water and solute 739  
dynamics in freezing soil columns with time domain reflectometry. 740  
*J. Hydrol.* 195, 352–369. 741
- Topp, G.C., Davis, J.L., Annan, A.P., 1980. Electromagnetic 742  
determination of soil water content: measurements in coaxial 743  
transmission lines. *Water Resour. Res.* 3 (16), 574–582. 744
- Ugolini, F.C., Anderson, D.M., 1973. Ionic migration and weathering 745  
in frozen Antarctic soil. *Soil Sci.* 115, 461–470. 746
- van Loon, W.K.P., Perfect, P.H., Groenevelt, P.H., Kay, B.D., 1991. 747  
Application of dispersion theory to time domain reflectometry in 748  
soils. *Transp. Porous Media* 6, 391–406. 749
- Van Vliet-Lanoë, B., 1991. Differential frost heave, load casting and 750  
convection: converging mechanism; a discussion of the origin of 751  
cryoturbations. *Permafr. Periglac. Process.* 2, 123–139. 752
- Walker, D.A., Epstein, H.E., Gould, W.A., Kelley, A.M., Kade, A.N., 753  
Knudson, J.A., Krantz, W.B., Michaelson, G., Peterson, R.A., Ping, 754  
C.-L., Reynolds, M.K., Romanovsky, V.E., Shur, Y., 2004. Frost- 755  
boil ecosystems: complex interactions between landforms, soils, 756  
vegetation and climate. *Permafr. Periglac. Process.* 15, 171–188. 757
- Washburn, A.L., 1956. Classification of patterned ground and review 758  
of suggested origins. *Bull. Geol. Soc. Am.* 67, 823–866. 759
- Washburn, A., 1979. *Geocryology — a survey of periglacial processes* 760  
*and environments*. Edward Arnold, London. 406 pp. 761