

1 Comparison of hydrochemistry and organic compound transport in two non- 2 glaciated High Arctic catchments with a permafrost regime (Bellsund Fjord, 3 Spitsbergen)

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13

14 ABSTRACT

15 An increase in air temperature related to climate change results in the retreat of glaciers, the
16 degradation of permafrost, and the expansion of glacier-free areas in the polar regions. All these
17 processes lead to changes in the Arctic landscape. They influence the hydrochemistry of streams
18 and rivers fed by glaciers and thawing permafrost. In this study, we examine eighty two water
19 samples from two non-glaciated catchments with snow-permafrost regime: the Tyvjobekken
20 Creek and the Reindeer Creek (NW Wedel-Jarlsberg Land, Spitsbergen). We cover
21 hydrometeorological measurements, fluctuations of physicochemical parameters (pH, specific
22 electrolytic conductivity (SEC)), and the presence of selected organic compounds (dissolved
23 organic carbon (DOC), formaldehyde (HCHO), Σ phenols). The obtained levels of DOC (0.061-
24 0.569 mgC L⁻¹) and HCHO (<LOD-0.140 mg L⁻¹) in water samples of these two high Arctic
25 creeks confirm the role of the melting permafrost as a rich source of terrestrial organic carbon
26 and organic pollutants, as well as the impact of rainfall on surface water chemistry. It was found
27 that fluctuations of physicochemical indices (pH, SEC, DOC) were related to changes in mean
28 daily discharge of Reindeer Creek (0.012-0.034 m³ s⁻¹) and Tyvjobekken Creek (0.011-0.015 m³
29 s⁻¹) (r>0.40). The Tyvjobekken Creek catchment, in contrast to Reindeer Creek catchment,
30 turned out to be resistant to rapid changes in meteorological conditions (r <0.10) and surface
31 runoff. The processes of permafrost thawing, calcium carbonate dissolution, and biogeochemical
32 “breathing” of soils proved to be crucial for the development of water chemistry. In conclusion,

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33 the surface water chemistry of the Reindeer Creek was found to result from the mutual influence
34 of hydrometeorological indices and the biogeochemical environment of the catchment.

35

36 **KEYWORDS:** dissolved organic carbon, formaldehyde, surface water, permafrost, Arctic.

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38 **1. Introduction**

39 Glaciers cover approximately 60% of the total land area of Svalbard, with the other 40% of
40 the area in the periglacial environment with permafrost (Humlum et al., 2003). The permafrost
41 thickness in Svalbard is estimated to be around 100 m in major valley floors and up to 400-500
42 m in high mountains (Liestøl, 1976). The published research on the Arctic region confirms that
43 the occurrence, thickness, and thermal state of permafrost depend on many local factors, e.g.:
44 topography, lithology, geothermal heat flow, vegetation cover, distance to ocean, wind, and snow
45 cover (Humlum et al., 2003; Dobiński and Leszkiewicz, 2010; Kasprzak et al., 2016; Sobota et
46 al., 2016). An increase in air temperature over the second half of the 20th century resulted in the
47 widespread permafrost degradation (e.g., Christiansen et al., 2010; Romanovsky et al., 2010;
48 Serreze et al., 2000; Schaefer et al., 2012). Permafrost thawing and an increase in its active layer
49 thickness have also been observed in Svalbard (Isaksen et al., 2003; Christiansen and Humlum,
50 2008), including Calyspostranda in Bellsund (Marsz et al., 2011). Therefore, the consequence of
51 glacier retreat (Serreze et al., 2000; Flink et al., 2015; Rachlewicz et al., 2016) is the appearance
52 of new ice-free land with favourable conditions for the prevalence of permafrost (e.g. Oliva et
53 al., 2016). The new ice-free environment in the polar zones is characterised by highly dynamic
54 geomorphological and ecological processes (Rachlewicz, 2010; Cooper et al., 2011; Oliva et al.,
55 2016).

56 The studies related to the permafrost regions show that hydrological processes are controlled
57 by the thickness of the active layer, total thickness of the underlying permafrost, and the
58 distribution of frozen ground and taliks (e.g. Zhang et al., 2002; White et al., 2007; Cheng and
59 Jin, 2012). The hydrogeological conditions of rivers are determined by the freeze-thaw processes
60 in the active layer (Walvoord and Striegl, 2007; White et al., 2007; Ye et al., 2009; Lyon and
61 Destouni, 2010) therefore permafrost thawing may increase river discharges through enhancing
62 infiltration and supporting deeper groundwater flow paths. The occurrence and thawing of
63 permafrost can also influence catchment geochemistry, changing the seasonal fluxes of nutrients,

64 including carbon and nitrogen (e.g., Carey, 2003; Petrone et al., 2006; Larouche et al., 2015).
65 The role of permafrost in the hydrological and hydrochemical processes has yet to be thoroughly
66 understood, particularly in the context of the coexisting glaciers and permafrost thaw. Few works
67 focus on freshwater chemistry in the periglacial zone of the Arctic (e.g. Polkowska et al., 2011;
68 Ruman et al., 2013; Kozak et al., 2015; Rachlewicz et al., 2016) and these show the dependence
69 of the water chemistry on annual changes in precipitation, snow cover and temperature, long
70 distance air transport of contaminants, local geological conditions, and biota.

71 There is a need for more studies on the influence of seasonal permafrost degradation on the
72 surface water chemistry, and for hydrochemical characteristics of non-glaciated catchments in
73 Svalbard. According to the literature reviewed, the work in this area is scarce and it was mainly
74 carried out within permafrost areas in Siberia (Frey et al., 2007; Bagard et al., 2011) and North
75 America (O'Donnell and Jones, 2006, Douglas et al., 2013). In order to better understand the
76 sources and transport of organic compounds in the Arctic surface waters, we compare the
77 hydrochemistry of two high Arctic creeks with snow-permafrost regime, located on a marine
78 terrace of Spitsbergen. The comparison of hydrochemistry of both creeks permits: 1) to verify
79 how permafrost degradation influences the chemistry of Arctic surface waters, 2) to identify the
80 factors determining differences in hydrological and chemical parameters of the creeks. The first
81 step was to investigate changes in fluctuations of physicochemical parameters (pH, specific
82 electrolytic conductivity (SEC)), dissolved organic carbon (DOC), and formaldehyde (HCHO) in
83 the surface waters of the two non-glaciated catchments. The second step was to define the effect
84 of hydrometeorological conditions on the chemical features of surface waters and to investigate
85 which other factors (e.g. morphology, lithology) could shape water chemistry in both of the
86 studied creeks. Finally, we provide unique information about the loads and transport of organic
87 compounds in the Tyvjobekken Creek and Reindeer Creek. The results presented in this study
88 could also serve as a reference for future changes and the potential effects of advancing
89 permafrost degradation on water chemistry.

90

91 **2. Study area**

92 This surface water study covers two periglacial catchments with snow-precipitation-
93 permafrost alimentation regime, drained by perennial (periodical in their upper courses) creeks
94 (Tyvjobekken and Reindeer Creek), located in the NW part of the Wedel-Jarlsberg Land, in the

95 Bellsund region of Spitsbergen. The creek valleys have a diverse morphology, from small
96 shallow valleys to gorges. They dissect an area of elevated marine terraces, called
97 Calypsostranda (Fig. 1), which developed as inclined abrasion platforms during glacioisostatic
98 movements in the Younger Pleistocene and Holocene. In Calypsostranda, the terraces develop a
99 system of steps, including the occurrence of berms along the former shorelines, and palaeo-
100 eskers and dead cliffs related to marine abrasion (Landvik et al., 1998).

101 Both catchments are located on the tectonic units of Calypsostranda Graben, filled with clastic
102 Tertiary sediments. To the layer above 120 m depth is formed by metadiamicite, sandstone type
103 rocks, silicite with Tertiary fossils and loose sandstones, as well as hard coal banks, pebbles and
104 plant remains. Below (to 250 m depth) grey and yellow sandstones can be found, with hard coal
105 remains and sandstone pebbles (Harasimiuk and Gajek, 2013).

106 In the Tyvjobekken catchment, glacial and fluvioglacial deposits predominate on the surface,
107 without soil cover. Locally, weakly developed loose and alluvial soils occur, while only rarely
108 brown soils can be found there. The soils in the Reindeer Creek catchment are mainly brown
109 soils (rich in organic matter and humus), with a light granulometric composition allowing for the
110 development of a good drainage system. Also, gley soils occur in the upper part of the
111 catchment, while soils are lacking only in the trough of the creek (Fig.6.2. in Klimowicz et al.,
112 2013).

113

114 *2.1. Hydrological characteristics of the studied catchments*

115 The Tyvjobekken Creek drains the eastern forefield of the Renard glacier, and the slopes of
116 the Bohlinryggen massif, developing a catchment with an area of 1.3 km². Its springs are located
117 in the forefield of the massif. The Tyvjobekken Creek valley extends from WSW to ENE along a
118 section of approximately 1.2 km, with a mean slope inclination of approximately 4.1% (Kociuba
119 2015a). Its upper part is fed by a bifurcated stream and has a character of an extensive, weakly
120 developed catchment occupying an area between the moraine zone of the north-eastern Renard
121 glacier forefield and the eastern Bohlinryggen massif. The middle section has permanent
122 drainage, and is fed by the largest (and nameless) tributary, with a length of 350 m and
123 catchment of 0.1 km². In the middle course, the creek develops a gorge with a depth of up to 25
124 m (Bartoszewski 1998; Bartoszewski et al., 2013) (Fig.1.C.). That section is characterised by a
125 narrow erosion valley developed by the braided system. In this part, the creek is fed by small

126 periodically functioning tributaries with a snow-permafrost regime. The river bed covers the
127 entire valley floor, and is developed by a single-channel river. The small amounts of water and
128 bedload transported by the Tyvjobekken Creek result in periodical lack of surface inflow of the
129 river to the fjord, and contribute to the development of a microlagoon separated from the waters
130 of the fjord with a coastal berm (Harasimiuk and Król 1992, Kociuba and Janicki 2013, Kociuba
131 2015a, 2017a).

132 The Reindeer Creek is the largest tributary of the Scott River, one of the largest proglacial
133 rivers in the study area, flowing directly into the Bellsund Fjord (Kociuba 2017b). This creek
134 also drains an area of approximately 1.3 km², beginning in the eastern part of the massif. The
135 Reindeer Creek valley extends from SW to NE along a section of approximately 1.3 km,
136 reaching a mean slope inclination of approximately 4.2% (Kociuba 2017c). In the northern part
137 of the catchment, the valley is fed by the waters of a perennial stream with origins at the foot of
138 the eastern slope of the moraines of the Scott Glacier. This tributary feeds the main creek
139 approximately 500 m above the mouth of the Reindeer Creek. The upper section of the Reindeer
140 Creek valley includes two spring niches: its own and of its largest tributary. The valleys are
141 weakly developed here, and the outflow is of discontinuous (declining) character. The middle
142 valley section (approximately 50% of the area of the catchment) is morphologically weakly
143 developed catchment (Fig.1.D.), yet with evident incisions of the main stream and tributary. The
144 drainage is permanent in this section, and the main creek is fed by the largest (nameless)
145 tributary of approximately 450 m length. In the lower course of the Reindeer Creek, a gorge
146 occurs with a depth of up to 25 m (Kociuba, 2015b), where the river bed covers the entire valley
147 floor. Below the gorge, the Reindeer Creek flows into the Scott River.

148

149 3. Methodology

150 3.1. *Sampling and hydrometeorological measurements*

151 Eighty two surface water samples were collected in total, each assisted with hydrological and
152 meteorological measurements, during 41 days from 13 July to 22 August 2012. Sampling was
153 conducted in the gorge sections of the both creeks located on the Calypsostranda (Fig.1.B). In the
154 field, the personnel taking samples paid extreme attention to avoid contamination, and wore
155 polyethylene gloves. Sampling containers were rinsed with the sample three times, and then

156 filled without air bubble to prevent the loss of analytes to headspace. The study involved the
157 analysis of blank samples to exclude the impact of the containers.

158 Discharge was measured in gauging sections located in the lower courses of both rivers
159 (Fig.1.B). In the Reindeer Creek, the measurement profile was located 100 m above its mouth to
160 the Scott River, and in Tyvjobekken Creek it was 300 m above the creek's mouth to the
161 Recherche fjord. Water stages in both profiles were recorded 144 times per day with a CTD-
162 Diver meter (Schlumberger Water Services), with a measurement accuracy of ± 0.5 cm. The
163 measurement of flow velocity was performed with a current meter HEGA II and an ultrasonic
164 device OTT ADC, with a range of flow velocity measurements of 0.02 - 3.00 m s⁻¹ and 0.2 - 2.4 m
165 s⁻¹ (and an accuracy of ± 0.25 cm s⁻¹), respectively.

166 For the measurements of wind directions, air temperature (T), and atmospheric precipitation
167 (P), a portable weather station (Campbell Scientific, CR10X Datalogger) and a Hellmann rain
168 gauge were used. Both the precipitation sampler (with 200 cm² of inlet ring surface) and the
169 meteorological station were placed approximately 200 m from the seashore at an altitude of 23 m
170 a.s.l. The automatic meteorological station registered data in 10 minute intervals.

171

172 3.2. *Analytical methods*

173 After collection, the water samples were transported to the laboratory and stored at a
174 temperature of 4°C prior to analysis. The analyses of physical and chemical parameters such as
175 pH and SEC were performed with a microcomputer pH/conductometer CPC-411 by Elmetron,
176 fitted with an EPS-1 electrode and an EC 60 conductivity sensor.

177 The quantitative analyses of organic compounds were conducted immediately after filtering
178 samples through 0.45 µm. Dissolved organic carbon was determined by catalytic combustion
179 (oxidation), with an NDIR detector. Both the Σ phenols and the formaldehyde (HCHO) levels
180 were determined using spectrophotometry techniques (Table 1).

181

182 3.3. *Quality Assurance/ Quality Control (QA/QC)*

183 The determination of various targets of analyte groups involved the application of
184 demineralised water type Mili-Q (Mili-Q® Ultrapure Water Purification Systems, Millipore®
185 production). Various matrix compositions of environmental samples require validation of the
186 analytical procedures applied in the determination of individual components against certified

187 reference materials. Moreover, to ensure high quality of results, all data obtained in the research
188 were subject to strict quality control procedures.

189

190 *3.4. Factors for result analysis*

191 *3.4.1. Discharge and load calculations*

192 The amount of water runoff in the measured profiles of both creeks were determined based
193 on the rating curve (equation 1) (Byczkowski 1999):

194

$$1. \quad Q = ah^b$$

195 where Q is the discharge rate [$\text{m}^3 \text{s}^{-1}$], a and b are the curve parameters, and h is the water stage
196 [cm].

197 The calculation of the chemical compound loads (DOC, Σ phenols, HCHO) from both
198 catchments involved the hydrological-hydrochemical method with the application of the formula
199 (2) after Willson and Bonin (2007) and Buttner (2013).

200

$$2. \quad L = C_i Q_i$$

201 where L is the mean daily load calculated based on concentrations and discharges on the day of sample
202 collection (mg s^{-1}), C_i is the concentration of organic compounds in a sample collected on a given day (mg
203 dm^{-3}) and Q_i is the mean daily discharge ($\text{m}^3 \text{s}^{-1}$).

204

205 *3.4.2. Statistical methods*

206 The Student's t-test and Pearson's correlation coefficients were computed with the software
207 package STATISTICA 6.1 (StatSoft Inc., Tulsa, OK, USA). The significance of differences in
208 the mean of the tested variables (Q , SEC, pH, DOC) between compared creeks was determined
209 by the Student's t-test for 2 independent trials. The calculation of the Pearson's correlation

210 coefficients (r) allows for the detection of pairwise relationships between the meteorological
211 conditions (T, P), mean daily water discharge (Q) and pH, SEC, DOC and HCHO determined in
212 the investigated water samples. Statistical significance of Student's t-test and correlation
213 coefficients was defined at a $p < 0.05$.

214

215 **4. Results**

216 *4.1. Meteorological conditions*

217 Meteorological conditions in summer season 2012 in comparison to previous multiannual
218 observations (Mędrek et al., 2014, Franczak et al., 2016), was characterised by lower mean air
219 temperature (4.6°C), lower total precipitation (26.4 mm), and lower mean wind velocity (3.6
220 m/s).

221 The prevailing wind directions presented in Fig. 2.A. are also described in detail in Lehmann
222 et al. (2016), and only a brief comparison with the wind conditions in August 2012 (Fig.2.B) will
223 be provided here. Fig. 2.B. shows considerable intensification of winds from WNW and NW
224 (17% and 19%, respectively) in comparison to wind conditions in July presented in the Fig.2.A.
225 In August, we observed the fading of wind coming from the direction of ENE (16% to 2%) and
226 E (10% to 2%), whereas these were among the prevailing wind directions in July. Instead, winds
227 coming from SSE, S, SSW, SW, and W started to prevail (7%, 9%, 11%, 7%, and 7%,
228 respectively). The contributions of the winds coming from the remaining directions (N, NNE,
229 NE, ENE, E, ESE, SE, WSW, NNW) in August ranged between 2% and 4%. During the field
230 sampling in July and August (Fig.2.C), both of the studied catchments were under the influence
231 of the same air masses predominantly coming from WNW and NW (14% and 17%,
232 respectively). Other wind directions, with higher contributions in Fig.2.C., include ENE, E, S,
233 and SSW (8%, 6%, 7%, and 8%, respectively). The Tyvjobekken Creek and Reindeer Creek
234 were hardly ever under the influence of winds coming from N, NNE, NE, ESE, SE, SSE, SW,
235 WSW, W, or NNW (2-5%).

236

237 *4.2. Hydrochemistry characteristics*

238 Table 2 presents the values of measured hydrological and physicochemical parameters as
239 well as concentration levels of chemical compounds determined in the water samples collected in
240 both catchments.

241 The frequency distribution of hydrological and physicochemical parameters and organic
242 compound concentrations is shown in Fig. 3. In all samples, the concentrations of phenols were
243 <LOD, hence they are not included in the figure.

244 The discharges measured in the two creeks differ from each other significantly. Throughout
245 the measurement period in July and August, discharge values in the Tyvjobekken Creek did not
246 exceed 0.016 m s^{-1} , while in the Reindeer Creek 63% of measurements were above that value
247 (Fig. 3). Moreover, the fluctuation of water discharges in the Reindeer Creek was almost 6 times
248 greater than in Tyvjobekken. Marked differences also occurred between creeks in the determined
249 values of water pH. In the Tyvjobekken Creek, pH of water samples in 90% varied between 8.00
250 and 8.20, while for water samples from the Reindeer Creek, such values were recorded only in
251 12% of the measured samples. In water samples collected from the Reindeer Creek catchment,
252 values between 7.60-7.80 pH and 7.80-8.00 pH were predominant (27% and 54% of measured
253 samples, respectively) (Fig.3).

254 Specific electrolytic conductivity values $<260 \mu\text{S cm}^{-1}$ in the water collected from
255 Tyvjobekken and Reindeer Creeks were detected rarely (20% and 27%, respectively) (Fig. 3).
256 Values of SEC varying from $260 \mu\text{S cm}^{-1}$ to $290 \mu\text{S cm}^{-1}$ as well as $290 \mu\text{S cm}^{-1}$ to $320 \mu\text{S cm}^{-1}$
257 are characteristic of the Tyvjobekken Creek (44% and 29% of results, respectively). In water
258 samples collected from the Reindeer Creek, SEC ranging from 260 to $290 \mu\text{S cm}^{-1}$ were much
259 less frequent (only 7% of results). Characteristic values of SEC for this creek ranged from 290 to
260 $320 \mu\text{S cm}^{-1}$, or exceeded $320 \mu\text{S cm}^{-1}$ (41% and 32%, respectively).

261 The values of DOC presented in Table 2, differ significantly between the two streams. Both
262 the lowest and the highest values of DOC in the Tyvjobekken Creek are almost twice lower than
263 those determined for the Reindeer Creek. Almost half (44%) of the measured values of DOC in
264 the Tyvjobekken Creek water samples showed concentration $<150 \text{ mg C L}^{-1}$, while in the
265 Reindeer Creek, the concentration of DOC within that range was determined only in 5% of
266 surface water samples (Fig. 3). In surface water samples from the Tyvjobekken Creek,
267 concentrations of DOC within the range of $0.150\text{-}0.200 \text{ mg C L}^{-1}$ (39% of measurements)
268 prevailed, while ranges of higher concentration such as $0.200\text{-}0.250 \text{ mg C L}^{-1}$, $0.250\text{-}0.300 \text{ mg C L}^{-1}$,
269 and $>0.300 \text{ mg C L}^{-1}$ occurred less frequently (in 10%, 5%, and 2% of the measured
270 samples, respectively). For surface water samples from the Reindeer Creek, the dominant values
271 of DOC concentration were recorded in the range of $0.190\text{-}0.230 \text{ mg C L}^{-1}$ (54% of measured

272 samples), while the concentration ranges of 0.150-0.190 mg C L⁻¹ and 0.230-0.270 were
273 determined less frequently (17% and 12%, respectively). Values of DOC exceeding the
274 concentration of 0.270 mg C L⁻¹ were recorded in 14% of the measured samples. As shown in
275 Table 2 during 41 days of the measurement period, DOC load considerably differed in the
276 Tyvjobekken Creek and Reindeer Creek. Mean daily loads of DOC in the Reindeer Creek (4.97
277 mg C s⁻¹) are more than twice as high as in the Tyvjobekken Creek (2.03 mg C s⁻¹).

278 Formaldehyde, a pollutant with potential carcinogenic and mutagenic properties, was
279 transported by the waters of both creeks. Even though DOC concentrations determined in the
280 Reindeer Creek were often higher than those recorded in the Tyvjobekken Creek, the occurrence
281 of HCHO in this creek was rather rare (Fig. 3). Although HCHO occurred less often in the
282 Reindeer Creek, the value of its maximum concentration was twice as high as that determined in
283 the Tyvjobekken Creek (Table 2). In 90% of surface water samples collected from the
284 Tyvjobekken Creek, HCHO showed values >LOD, while in the Reindeer Creek, HCHO was
285 determined in only 24% of water samples. In the Tyvjobekken Creek, HCHO was recorded
286 predominantly in the concentration range of 0.02-0.06 mg L⁻¹ (78%), while in the Reindeer
287 Creek this range corresponded to less than 15% of all samples. However, values above 0.06 mg
288 L⁻¹ in both of the creeks occurred similarly in around 10% of the examined samples. In the
289 surface waters of the Tyvjobekken Creek, HCHO occurred almost four times more often than in
290 the Reindeer Creek. The mean loads of HCHO in the studied creeks were 0.539 mg s⁻¹
291 (Tyvjobekken Creek, 37 days) and 1.39 mg s⁻¹ (Reindeer Creek, 10 days).

292

293

294 4.3. *Fluctuations of water discharge*

295 Based on the conducted hydrometeorological measurements, the fluctuation of water
296 discharge in both creeks on the background of changing meteorological conditions is presented.
297 In the Fig.4., two variables are shown with a possible influence on the fluctuation of water
298 discharge: mean air temperature and rainfall.

299 In the Tyvjobekken Creek, a systematic decrease in discharges occurred since the beginning
300 of the measurement period, from the maximum value of 0.015 m³ s⁻¹ on 13th July to a minimum
301 of 0.011 m³ s⁻¹ on 7th August. The mean discharge in the entire study period of 2012 amounted to
302 0.013 m³ s⁻¹, which corresponds to a total runoff of 46 000 m³ and a runoff layer of 35 mm. The



303 discharge of the Reindeer Creek, however, was characterised by a marked variability. At the
304 beginning of the ablation season, two maximum values of discharge were recorded amounting to
305 $0.034 \text{ m}^3 \cdot \text{s}^{-1}$. The mean discharge in the Reindeer Creek amounted to $0.021 \text{ m}^3 \cdot \text{s}^{-1}$. The value
306 corresponds to the total runoff of $73\,000 \text{ m}^3$ and a runoff layer of 56 mm (Fig.4).

307 Daily air temperature fluctuations and precipitation events presented in Fig. 4. show no
308 influence on discharge in the Tyvjobekken Creek, whereas rapid increases in discharge are
309 observed in the Reindeer Creek in response to precipitation events.

310

311 *4.4. Temporal variations in hydrochemistry*

312 Fig. 5. A.-F. presents the temporal and spatial distribution of the pH, SEC, DOC, and HCHO
313 concentration on the background of the water discharge in the both creeks.

314 As presented in Fig. 5.A.B., on the first days of the research (13th-21st July), in both of the
315 studied catchments, marked increases in pH and SEC were observed. In the Tyvjobekken Creek,
316 pH increased over only three days from 7.40 to 7.94. In the Reindeer Creek during the same
317 time, pH increased rapidly from 7.26 to almost 7.79. During the rest of the summer season, pH
318 values in the Tyvjobekken Creek were stable, and oscillated between 8.00 and 8.20 pH
319 independently of the occurrence of precipitation events or temperature changes. pH values in the
320 Reindeer Creek during the rest of the summer season were much more variable, from 7.67 to
321 8.09. On 22nd July, the only case of water pH decrease in response to the occurrence of a heavy
322 rainfall event (11.4 mm) was recorded (Fig. 5.B).

323 Fig. 5.C.D. shows a rapid increase in SEC values on 21st July in both of the creeks. In the
324 Tyvjobekken Creek, an increase in SEC of almost $50 \mu\text{S cm}^{-1}$ occurred from $196 \mu\text{S cm}^{-1}$ to 245
325 $\mu\text{S cm}^{-1}$, while in the Reindeer Creek, an increase in SEC of approximately $100 \mu\text{S cm}^{-1}$ was
326 observed, from $205 \mu\text{S cm}^{-1}$ to $297 \mu\text{S cm}^{-1}$. On 21st July, an event of heavy rain began which
327 lasted until 23rd July. During that time, 15.5 mm of precipitation fell. SEC values in both of the
328 creeks increased gradually until the end of the measurement period. A gradual increase in SEC
329 accompanied by a slow decrease in water discharge (Fig. 5.C.D) indicates high importance of
330 water discharge for SEC values in surface waters. However, on 21st July, no rapid changes in the
331 water discharge of the Tyvjobekken Creek or the Reindeer Creek were observed that could
332 explain the sudden increase in SEC values in surface waters on that day.

333 The transport of organic compounds in each of the creeks was different (Fig. 5.E.F).
334 Dissolved organic carbon levels in the Reindeer Creek were almost twice as high as in the
335 Tyvjobekken, where the presence of organic carbon in surface waters included HCHO occurring
336 almost every day. A decrease in the water discharge was accompanied by an increase in DOC
337 levels (Fig. 5.E). However, in the Reindeer Creek, throughout the measurement period, DOC
338 levels oscillated around 0.200 mgC L^{-1} . From 21st to 23rd July, as well as on days when
339 precipitation events occurred and water discharge increased, also an increase in DOC
340 concentration was observed (Fig. 5.F). In the beginning of August (from 6th to 10th August), the
341 presence of HCHO was recorded, simultaneous with a precipitation event and the lowest levels
342 of water discharge across the whole measurement period. In the following days, when water
343 discharge in the Reindeer Creek increased, an increase in DOC concentration was also observed.
344 HCHO occurred in the waters of the Reindeer Creek more often when water discharge was
345 below 0.100 m s^{-1} .

346

347 4.5. Correlation analysis

348 The degree of correlation between the obtained data and hydrological and meteorological
349 parameters was interpreted as follows: +/- ($r > 0.50$) - no justification for rejecting the significant
350 correlation hypothesis; +/- ($r = 0.30 - 0.50$) - suspected correlation; +/- ($r < 0.30$) - no correlation
351 (Stanisz 1998). The correlation matrix of the analysed indices (Table 3.A.B) showed significant
352 negative correlations between Q (discharge) and pH and SEC in both creeks, as well as the DOC
353 concentration (only in the Tyvjobekken Creek), while a strong positive correlation was found
354 between Q and DOC in the Reindeer Creek. Meteorological variables showed a moderate
355 positive correlation between temperature (T) and precipitation (P) ($r = 0.38$); T also showed a
356 weak positive correlation with Q in the Reindeer Creek ($r = 0.24$) and HCHO concentration in the
357 Tyvjobekken Creek ($r = 0.21$). A moderate positive correlation was recorded between pH and
358 SEC in both the Tyvjobekken and the Reindeer Creek ($r = 0.51$ and $r = 0.40$, respectively). A
359 significant negative correlation occurred between SEC and DOC in the Reindeer Creek ($r = -0.34$)
360 while a weak positive correlation occurred between these variables in the Tyvjobekken Creek
361 ($r = 0.20$). In conclusion, no significant correlations were observed between meteorological
362 parameters: P (precipitation), T (temperature), and Q (discharge) as well as with other analysed
363 physical-chemical indices.



364 **5. Discussion**

365 *5.1. Morphological factors of the catchment affecting water hydrochemistry*

366 The thickness of the permafrost active layer on Calypsostranda in the catchment areas of the
367 Tyvjobekken Creek and Reindeer Creek in 2012 was at the same level (>202cm) (Repelewska-
368 Pękalowa et al., 2013). According to AMAP report (2012), permafrost affecting water storage
369 and stream runoff responds very slowly to rapidly changing climate conditions. That explains
370 very small oscillation of water discharge in the Tyvjobekken catchment, characterised by almost
371 no response to changes in meteorological conditions. Conversely, the considerable variations of
372 water discharge in the Reindeer Creek were caused mainly by intensive surface runoff of rain
373 water.

374 Both studied creeks are fed in summer by thawing permafrost waters, precipitation, and snow
375 cover (mainly during spring) (Bartoszewski et al., 2013). Water discharges presented in this
376 paper concerning both of the creeks differ significantly despite their similar alimentation regime,
377 catchment area and mean inclination. The discharge in the Tyvjobekken Creek is regular and half
378 of the level found in the Reindeer Creek. It responds neither to mean air temperature changes ($r=$
379 0.07) nor occurrence of precipitation ($r=0.07$). Meanwhile, water discharge in the Reindeer
380 Creek responds to changes in temperature, and temporally increases with each precipitation
381 event. Although the effect of rainfall on the hydrological conditions of the Reindeer Creek is not
382 confirmed by the correlation matrix results presented in Table 3 ($r= 0.07$), it cannot be excluded,
383 considering even 50% errors related to rainfall collection in Svalbard, caused by: high wind
384 speed, open tundra and non-representative locations for precipitation stations (Killingtveit et
385 al.,2004). Throughout the measurement period, both catchments were under the influence of the
386 same meteorological conditions. The dissimilarity of the hydrology between the studied creeks
387 results from morphological differences of their catchments and differentiation of their soil
388 formation. Shape of the Tyvjobekken catchment is irregular with a poorly developed network of
389 watercourses in its upper part. Moreover, the catchment is rich in numerous small tundra lakes
390 which impede surface runoff. Additionally, the scarcity of soil cover, poor vegetation in this part
391 of Calypsostranda, and the dry surfaces of marine terraces favour the evaporation of water which
392 reaches this catchment through rainfall (Klimowicz et al., 2013; Repelewska-Pękalowa et al.,
393 2013). Changes in water discharge in the Tyvjobekken Creek during the 1987 hydrological year

394 were described by Bartoszewski et al. (2013). In comparison to their description, in 2012 the
395 studied water discharges and chemical composition in the Tyvjobekken Creek were particularly
396 related to the thawing of permafrost. Shape of the Reindeer Creek valley is close to a trough. It is
397 wider in the upper part of the catchment, and due to the domination of brown soils has a well-
398 developed network of watercourses which provide water also from the Scott Glacier terminal
399 moraine where gley soils dominate. These factors favour easier surface runoff from the entire
400 area of the catchment, and result in higher water discharge in the creek. According to
401 Repelewska-Pękalowa et al. (2013), in the area of the Reindeer Creek catchment, zones of active
402 solifluction and periodically wet terraces predominate, favouring accumulation of water and its
403 easier release in response to rainfall events. This suggests that the hydrochemistry of the
404 Reindeer Creek waters was determined by rainfall, thawing of permafrost, and melting of the
405 snow cover from the area of the glacier terminal moraine.

406

407 *5.2. Hydrochemistry and loads of organic compounds*

408 The pH values in the Tyvjobekken Creek and Reindeer Creek correlate negatively with
409 water discharge. A similar effect is even more striking for SEC values. This correlation between
410 the hydrology of non-glaciated streams and the chemistry of their waters was also pointed out by
411 Chmiel et al. (2013). Repelewska-Pękalowa and Magierski (1989) found that changes in SEC
412 values of non-glaciated streams are related to an additional load of waters coming from thawing
413 of permafrost and the cryochemical effect. This explains the fluctuations of SEC in the
414 Tyvjobekken Creek and the results of the matrix correlation analysis showing a negative
415 correlation with water discharge. More varied fluctuations of pH and SEC values in the Reindeer
416 Creek during the summer season of 2012 are most likely related to an increase in the contribution
417 of water coming from other sources than permafrost thawing (e.g. rainfall, snow cover).
418 According to Kozak et al. (2015) and Lehmann et al. (2016), the pH of rain in Svalbard ranges
419 from 4.43 to 7.93 pH, and could possibly affect the pH of surface water. One of the main factors
420 determining the chemistry of surface waters in Svalbard is rock-water interaction such as
421 dissolution of calcium carbonate (Stutter and Billet, 2003; Dragon and Mariciniak, 2010; Chmiel
422 et al., 2013) which is responsible for the alkaline character of the surface waters. Less alkaline
423 character of the Reindeer Creek in comparison to the Tyvjobekken Creek may be explained by
424 the vulnerability of this catchment to rainfall and the domination of brown soils which are a

425 source of humic acids. A noticeable moderate positive correlation between pH and SEC, found in
426 both the Tyvjobekken Creek and Reindeer Creek is related to the biogeochemical factor. The
427 aforementioned process of calcium carbonate dissolution increases water pH and SEC values,
428 and may be understood as the chemical factor here. According to Chmiel et al. (2013), the
429 alkaline character and the higher concentration of ions in water in the non-glaciated areas of
430 Svalbard, such as the Tyvjobekken Creek and Reindeer Creek, is also determined by a biotic
431 factor (“breathing” of biogeochemicals in soils).

432 The occurrence of organic pollutants in the Arctic may be a consequence of their long range
433 atmospheric transport (LRTAP) from industrialised and urbanised areas of Eurasia (Hallanger et
434 al., 2011; Kozak et al., 2013). Xu et al. (2016) point to South and East Asia as the main sources
435 of black carbon (BC) and organic carbon (OC) in the world. Studies of Ruman et al. (2014) and
436 Kozak et al. (2015) prove that wet precipitation is a source of organic compounds (TOC, HCHO,
437 Σ phenols) in Svalbard in each season of the year. However, according to AMAP (2012),
438 terrestrial permafrost is also a rich source of carbon. Chmiel et al. (2013) suggest that high values
439 of organic compounds in peat bogs surrounding the Reindeer Creek correspond with high levels
440 of nitrogen and phosphorus indicating their local biological source (bird colonies and reindeer
441 herds in the vicinity of the creek).

442 According to Weishaar et al. (2003), a vast amount of organic matter in water samples has
443 the form of DOC. Arctic surface water can transport large amounts of organic compounds from
444 the terrestrial environment to neighbouring seas and fjords (Büttner and Tittel, 2013; Dittmar and
445 Kattner, 2003). The DOC determined in the surface waters of Tyvjobekken corresponds
446 negatively with Q, while the DOC determined in the Reindeer Creek has a strong positive
447 correlation with Q. A negative influence of Q on DOC in Tyvjobekken is particularly noticeable
448 in July (13th-25th July). Higher water discharge during that time could be related to melting of the
449 snow cover or to a more intense thawing of permafrost. Both of these process result in an
450 additional load of fresh water, and a dissolution of organic compounds flushed out from the soil.
451 Based on the correlation matrix analysis, DOC determined in water samples from the
452 Tyvjobekken Creek, as well as pH and SEC, was related to the biogeochemical processes
453 occurring in soils.

454 Dissolved organic carbon in the Reindeer Creek catchment was positively correlated with Q.
455 The highest concentration of DOC (0.569 mg C L⁻¹) was a result of the occurrence of a heavy

456 rain event (21st-23rd July). The Reindeer Creek catchment is rich in wet tundra, and both plant
457 vegetation and the activity of reindeer in that area is important. It has a direct effect on the high
458 levels of DOC in the creek water. Moreover, easy surface runoff also favours flushing of organic
459 pollutants which reach the catchment through wet and dry deposition. Dissolved organic carbon
460 indices correspond negatively with geochemical conditions of the environment. This suggests the
461 importance of the activity of reindeer herds and surface runoff as the main factors determining
462 the level of DOC in the Reindeer Creek.

463 Taking into consideration that plant vegetation, the activity of reindeer herds, and the
464 intensity of surface runoff are poorer in the Tyvjobekken catchment than in the Reindeer Creek
465 catchment, the DOC level in the Tyvjobekken Creek results particularly from biogeochemical
466 processes in the soil, and less from surface runoff or wet and dry deposition, while the origin of
467 the DOC in the Reindeer Creek is much more complex.

468 Studies of Ruman et al. (2014) confirm the presence of HCHO and phenols in precipitation
469 water collected during all four seasons of the year in Svalbard (reporting levels of 0.025-0.150
470 mg L⁻¹ and 0.025-0.075 mg L⁻¹, respectively). This suggests constant inflow of these
471 contaminants to the Arctic. However, no phenols were determined in the surface water samples
472 from either of the two sampled creeks. The correlation matrix results do not point to the
473 influence of any variables mentioned herein on the occurrence of HCHO in both creeks. A small
474 amount of rain has no effect on the hydrochemistry of the Tyvjobekken Creek, and has little
475 impact on Q and pH in the Reindeer Creek. Therefore, HCHO determined in the waters of the
476 Tyvjobekken Creek is most certainly related to the thawing of permafrost and biogeochemical
477 processes occurring in soils (F2). The occasional occurrence of HCHO in the Reindeer Creek is
478 related to the dilution of HCHO from thawing permafrost by the water coming from surface
479 runoff or rainfall. HCHO determined in the Tyvjobekken Creek may be identified as being of
480 local origin. HCHO occurs in the Reindeer Creek particularly when the discharge is lower (26th
481 July to 17th August), and when rainfall occurs (7th-10th August). Considering the natural sources
482 of HCHO and the increased plant vegetation and reindeer herds activity in the Reindeer Creek
483 catchment, it cannot be excluded that HCHO present in its water origin from natural sources as
484 well as from LRTAP.

485 The transport of organic compounds from the Tyvjobekken Creek catchment is more difficult
486 than in the case of the Reindeer Creek due to the morphological aspects of the area (see section

487 5.1). However, next to morphological aspects favouring surface runoff, higher loads of organic
488 compounds in the surface waters of the Reindeer Creek are also largely determined by the soil
489 type, vegetation cover in the area of the catchment, and the related activity of animals. Presented
490 results show that even low levels of chemical compounds determined in the Tyvjobekken and
491 Reindeer Creek could correspond to relatively high levels of loads of such substances due to the
492 discharge of the creeks. The calculated loads of chemical compounds show what amounts of
493 pollutants may actually reach Arctic fjords as a result of permafrost thawing.

494

495 **6. Conclusions**

496 Hydrometeorological research showed that 4.6°C of mean air temperature was enough to
497 have influence on permafrost degradation in Calypsostranda and the provision of melt waters to
498 feed both creeks during all summer season in year 2012. Based on the conducted chemical
499 analyses, we were able to conclude that thawing permafrost is a source of dissolved organic
500 carbon, including formaldehyde, which was clearly visible in water of the Tyvjobekken Creek. A
501 further rise in air temperature in the Arctic may result in an intensification of permafrost
502 degradation which would lead to changes in surface water discharge, and release higher loads of
503 HCHO, which due to its carcinogenic and mutagenic properties may negatively impact the Arctic
504 environment.

505 The correlation matrix analysis confirms an important role of rock-water interaction in
506 shaping the chemistry of High Arctic surface waters. The presented study proves also that the
507 influence of permafrost degradation and rainfall on surface water hydrochemistry in a non-
508 glaciated Arctic catchment, depends significantly on the morphology of catchments as well as
509 the types of soils covering them. The predominance of brown soil in the Reindeer Creek
510 catchment resulted in a better developed water drainage, a lush plant cover and a more intense
511 activity of reindeers in this area in comparison to Tyvjobekken catchment. These factors
512 combined directly affect the differences in hydrochemistry of the creeks.

513 In conclusion, next to atmospheric deposition and rock-water interaction, the crucial
514 influence on surface water hydrochemistry of a non-glaciated Arctic catchment in Svalbard, is
515 also exerted by: the rate of permafrost degradation, the geomorphology of the catchment, the
516 dominating types of soils, the presence of vegetation and animal activity.

517

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529

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