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1	Review: Impacts of permafrost degradation on inorganic chemistry of surface
2	fresh water
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17	Abstract
18	Recent studies have shown that climate change is impacting the inorganic chemical characteristics of
19	surface fresh water in permafrost areas and affecting aquatic ecosystems. Concentrations of major ions
20	(e.g., Ca ²⁺ , Mg ²⁺ , SO ₄ ²⁻ , NO ₃ ⁻) can increase following permafrost degradation with associated deepening
21	of flow pathways and increased contributions of deep groundwater. In addition, thickening of the active
22	layer and melting of near-surface ground ice can influence inorganic chemical fluxes from permafrost into
23	surface water. Permafrost degradation has also the capability to modify trace element (e.g., Ni, Mn, Al,
24	Hg, Pb) contents in surface water. Although several local and regional modifications of inorganic
25	chemistry of surface fresh water have been attributed to permafrost degradation, a comprehensive review
26	of the observed changes is lacking. The goal of this paper is to distil insight gained across differing
27	permafrost settings through the identification of common patterns in previous studies, at global scale. In

28 this review we focus on three typical permafrost configurations (pervasive permafrost degradation, 29 thermokarst, and thawing rock glaciers) as examples and distinguish impacts on (i) major ions and (ii) 30 trace elements. Consequences of warming climate have caused spatially-distributed progressive 31 increases of major ion and trace element delivery to surface fresh water in both polar and mountain areas 32 following pervasive permafrost degradation. Moreover, localised releases of major ions and trace 33 elements to surface water due to the liberation of soluble materials sequestered in permafrost and ground 34 ice have been found in ice-rich terrains both at high latitude (thermokarst features) and high elevation 35 (rock glaciers). Further release of solutes and related transport to surface fresh water can be expected 36 under warming climatic conditions. However, complex interactions among several factors able to influence 37 the timing and magnitude of the impacts of permafrost degradation on inorganic chemistry of surface fresh 38 water (e.g., permafrost sensitivity to thawing, modes of permafrost degradation, characteristics of 39 watersheds) require further conceptual and mechanistic understanding together with quantitative 40 diagnosis of the involved mechanisms in order to predict future changes with confidence.

41

42 **1. Introduction**

Average atmospheric temperature has increased globally over the last decades and, as a response, the cryosphere is changing (Fountain et al., 2012). Permafrost, a component of the cryosphere, is widespread in the Arctic and Antarctica, and in cold mountains, including densely populated areas of the European Alps and Asian mountain ranges (Gruber, 2012). Permafrost interacts with climate (Walter Anthony et al., 2006; Schuur et al., 2015), hydrology (e.g., Liljedahl et al., 2016; Yang et al., 2017), ecosystems (Jorgenson et al., 2001; Vonk et al., 2015), geophysical processes (e.g., Gruber et al., 2004; Gruber and Haeberli, 2009), and human systems (Nelson et al., 2002; Harris et al., 2009).

Recent reviews have focused on the impacts of permafrost warming and degradation on river biogeochemistry (Frey and McClelland, 2009) and aquatic ecosystems (Vonk et al., 2015) in the Arctic. Notwithstanding, local and regional modifications of water hydrochemistry due to permafrost degradation have been reported from many locations, globally. Given the sparsity of data available, understanding and analysing permafrost degradation impacts on inorganic chemistry of surface fresh water will benefit from identifying common patterns in existing studies. The present review thus aims to distil insight gained
 across differing permafrost environments and configurations globally.

57 Following a brief background section, we distinguish three typical example configurations of permafrost 58 thaw. For those, we review impacts of permafrost degradation on major ions (e.g., Ca^{2+} , Mg^{2+} , SO_4^{2-} , NO_3^{-} 59) and on trace elements (e.g., Ni, Mn, Al, Hg, Pb).

60

61 **2.** Permafrost: definition and main characteristics

62 Permafrost is defined as ground (soil and/or rock, including ice and organic material, plus air/gas in 63 unsaturated ground) that remains at or below 0 °C for at least two consecutive years (Muller, 1943). Thus, 64 permafrost is a thermal phenomenon and it can, but does not need to, contain water or ice. Most 65 permafrost areas experience seasonal thaw, during which ground surface temperature rises above 0 °C. 66 The layer of ground that thaws on a seasonal basis is called "active layer" (ACGR, 1988). The depth of 67 permafrost (permafrost base) is determined by the geothermal heat flux, subsurface properties, and the 68 long-term surface temperature. The upper limit of permafrost (permafrost table) is largely controlled by 69 surface temperatures during summer and near-surface ground properties (Williams and Smith, 1989; 70 French, 2007). The difference in depth between the permafrost table and the permafrost base is the 71 permafrost thickness (see Figure 2 in ACGR, 1988, source: https://ipa.arcticportal.org). Permafrost 72 regions are often divided into a continuous permafrost zone, where more than ~90% of the surface area is 73 underlain by permafrost, a discontinuous zone, of which ~10% to ~90% is underlain by permafrost, and a 74 zone of isolated patches of permafrost, where permafrost occurs under less than ~10% of the ground. The 75 discontinuous zone is often divided into extensive discontinuous permafrost (~90% to ~50%) and sporadic 76 discontinuous permafrost (~50% to ~10%, Heginbottom et al., 1995).

The global permafrost region (exposed land surface below which some permafrost can be expected) is estimated to be $22\pm3 \times 10^6$ km², approximately 17% of the global land area (Gruber, 2012). Zhang et al. (1999; 2003) estimated that permafrost could underlie nearly 25% of the exposed land area of the Northern Hemisphere. Despite occupying only 0.36% (49,800 km²) of the Antarctic region, permafrost is estimated to be present beneath all ice-free terrain, except at the lowest elevations of the maritime Antarctic and sub-Antarctic islands (Vieira et al., 2010). Although with increased spatial heterogeneity imposed by topography, permafrost is also widespread in many mountain ranges such as the European
Alps (e.g., Boeckli et al., 2012), the Hindu Kush Himalaya (e.g., Gruber et al., 2017), and the Andes (e.g.,
Brenning, 2005).

86 The aggradation and degradation of permafrost usually occur in association with a change of mean 87 ground temperature due to microclimatic (ground cover) and climatic changes (Williams and Smith, 1989). 88 Permafrost degradation refers to the decrease of volume of a body of permafrost, whereas permafrost 89 thaw or thawing is used to refer to increasing liquid water content and other changes of physical 90 characteristics in response to energy input within a body of rock or soil while still satisfying the definition of 91 permafrost. The term thawed permafrost indicates ground that no longer is permafrost. Global warming 92 over the past several decades is now large enough that regional climate change is emerging above the 93 noise of natural variability (Hansen and Sato, 2016). Despite the small magnitude of warming relative to 94 weather fluctuations, effects of the warming already have notable environmental, social and economic 95 impacts. In this context, the degradation of permafrost is seen as a major challenge in the current 96 discussion of globally rising air temperatures (IPCC, 2013), because of the possible effects on climate 97 (e.g., Harden et al., 2012; Schuur et al., 2015), infrastructure stability (e.g., Nelson et al., 2001; Streletskiy 98 et al., 2012), hydrology (e.g., Liljedahl et al., 2016; Walvoord and Kurylyk, 2016), natural hazards in 99 mountainous areas (e.g., Gruber et al., 2004; Harris et al., 2009), and aquatic biogeochemistry and 100 ecosystems (e.g., Frey and McClelland, 2009; Vonk et al., 2015).

101

102 **3.** Typical configurations of permafrost thaw

We focus on three typical configurations in which permafrost degradation can impact the inorganic chemistry of water bodies. While not exhaustive, these examples currently reflect major interests in this research field:

i) Pervasive permafrost degradation, leading to spatially-distributed modifications in groundwater surface water connectivity and causing volumes of permafrost to thaw and become subject to
 weathering and leaching;

109 ii) thermokarst and associated localised mobilisations of sediments and solutes;

110 iii) rock-glacier thawing and related localised export of solute-rich water.

111 (i) Pervasive permafrost degradation. Permafrost thaw affects hydrology through increasing hydrologic 112 permeability with ice loss in pores (Bense et al., 2009; Kurylyk et al., 2014) and through the release of 113 water stored in frozen material. Permafrost is commonly an aquitard (Woo, 2012; Kane et al., 2013), 114 supporting perched water tables and increasing near-surface soil moisture (Gorbunov, 1978; Ishikawa et 115 al., 2005). Permafrost thaw, through talik growth and higher permeability of partially-frozen material, 116 changes the hydrologic connectivity in a catchment and affects the rates and amounts of flow along 117 differing paths (Hinzman et al., 2005; Rogger et al., 2017), which often produce water with distinct 118 geochemical signatures (Clark et al., 2001).

Due to thaw and degradation, new hydrological pathways in permafrost are expected to enhance the interaction between mineralised groundwater and surface water, driving transitional permafrost environments from surface-water dominated systems to groundwater-dominated systems (e.g., Frey and McClelland, 2009). Indeed, recent studies have attributed increases in groundwater contributions to base flow of several rivers in permafrost watersheds to permafrost degradation (Walvoord and Striegl, 2007; St. Jacques and Sauchyn, 2009; Kolosov et al., 2016).

125 Most near-surface effects of permafrost thaw stem from increasing Active Layer Thickness (ALT), 126 which has been shown to occur at large scale, across entire landscapes (e.g., Åkerman and Johansson, 127 2008). Recently, Luo et al. (2016) investigated the spatiotemporal characteristics of ALT across the 128 Northern Hemisphere from 1990 to 2015. Significant trends of increasing ALT have been observed at 129 approximately 43 % of the investigated 169 sites analysed. Regionally, increasing ALT have been found in 130 North America (e.g., Oelke et al., 2004; Burn and Zhang, 2009), Asia (e.g., Frauenfeld et al., 2004; Oelke 131 et al., 2004; Wu et al., 2012), Antarctica (e.g., Guglielmin and Cannone, 2012; Guglielmin et al., 2014), 132 and Europe (e.g., Åkerman and Johansson, 2008; Harris et al., 2009), although variation exists due to 133 local conditions.

Increasing ALT can expose newly-thawed soils to near-surface water and increase chemical fluxes from freshly-exposed strata (e.g., Keller et al., 2007; Keller et al., 2010). Furthermore, geochemical constituents previously sequestered within the near-surface permafrost (e.g., Kokelj and Burn, 2005) can be released. Although spatially-distributed modifications in groundwater-surface water connectivity and increasing soil volumes subject to weathering and leaching are distinct processes associated with permafrost degradation, the impacts of these processes on the inorganic chemistry of surface water are not easily discernible. Indeed, both result in diffuse increases of geochemical fluxes into the receiving water bodies and only few studies distinguish the main sources of such fluxes (e.g., Keller et al., 2007, 2010; Lamhonwah et al., 2017).

144 (ii) Thermokarst. Permafrost warming and increasing ALT can cause self-reinforcing thaw of ice-rich 145 ground leading to the development of thermokarst (Jorgenson and Osterkamp, 2005; Rowland et al., 146 2010). The term thermokarst includes a suite of processes and landforms that involve lowering, and often 147 collapsing, of the land surface because of melting excess ground ice. Kokelj and Jorgenson (2013) 148 classified the principal thermokarst types as: a) hillslope processes, including retrogressive thaw slumps, 149 active layer detachment slides, and thermal erosion gullies; b) thaw lake processes, including lake 150 expansion/reduction, drainage, and lake basin evolution; c) wetland processes, including peatland 151 collapse and the development of bogs and fens. Thermokarst can also occur on active rock glaciers 152 (details in (iii) Rock glacier thawing), where increased melting of permafrost ice can cause the formation of 153 small thermokarst lakes (Kääb and Haeberli, 2001). Thermokarst is commonly observed throughout most 154 permafrost regions including Canada (e.g., Watanabe et al., 2011), Alaska (e.g., Andresen and Lougheed, 155 2015), Russia (e.g., Manasypov et al., 2014), Mongolia (e.g., Sharkhuu, 1998), China (e.g., Wu et al., 156 2010), Antarctica (e.g., Gooseff et al., 2016) and the European Alps (e.g., Kääb and Haeberli, 2001).

Thermokarst development has the potential to alter the geochemical signature of surface water because it facilitates mobilisation of sediments and solutes previously sequestered in ground ice (Gooseff et al., 2009), causing localised and strong influences on hydrochemical systems (Malone et al., 2013). The effects of thermokarst are mostly local, but the transport of solutes into downstream aquatic ecosystems can sometimes impact large areas (e.g., Kokelj et al., 2013). Moreover, the formation of new features such as thaw ponds and lakes can modify the hydrochemical characteristics of large areas (e.g., Manasypov et al., 2014).

(iii) <u>Rock-glacier thawing</u>. Rock glaciers are distinctive and sometimes abundant geomorphological
 features of cold mountain regions (Barsch, 1996). They are slowly-flowing mixtures of rock debris and ice

166 and formed by a continuum of processes from glacial to periglacial (Haeberli et al., 2006). The thawing of 167 ice-rich talus slopes (cf., Gruber and Haeberli, 2009), although not studied in detail, is likely part of the 168 same continuum. Rock glaciers are considered as the visible expression of long term creep of ice-rock 169 mixtures under permafrost conditions (Humlum, 2000; Ikeda and Matsuoka, 2006; Berthling, 2011), and 170 for this reason, they are often used for first-order mapping of permafrost distribution at coarse scales (e.g., 171 Brenning, 2005; Cremonese et al., 2011; Schmid et al., 2015). Compared to glaciers, rock glaciers are 172 believed to react more slowly to rising temperature because of the retardation of heat transfer through 173 thick debris mantles (Barsch, 1996). During the cold season, ice is formed within rock glaciers, their "mass 174 balance", however, is difficult to determine. Emerging observations suggest the thermal and kinematic 175 state of many rock glaciers is changing in concert with climate change (e.g., Roer et al., 2005; Haeberli et 176 al., 2006; Scapozza et al., 2014). Many active (moving) rock glaciers loose some water due to melt during 177 summer. This is because frequently, their tongues extent into microclimatic situations in which the moving 178 ice core undergoes slow degradation. However, at decadal and longer time scales, due to global warming, 179 accelerated melting of the ice within rock glaciers may represent an increasing hydrological contribution to 180 downstream areas (Brenning, 2005). For this reason, active rock glaciers are generally considered to be 181 sources of fresh water (Burger et al., 1999), especially in arid areas, small catchments, and during low 182 flow conditions (e.g., Corte, 1976; Brenning, 2005; Azócar and Brenning, 2010; Millar et al., 2013; 183 Rangecroft et al., 2015). Finally, melting of permafrost ice in active rock glaciers in particular, and also in 184 ice-rich talus (cf., Gruber and Haeberli 2009), is able to increase the porosity of the sediments. In turn, this 185 can increase the storage capacity, causing changes in the discharge pattern (Rogger et al., 2017).

The thaw of rock glaciers due to climate change has the potential to export enriched-solute fluxes and thereby modify the inorganic chemistry of downstream impounded surface waters (e.g., Ilyashuk et al., 2014) and streams (e.g., Thies et al., 2013).

Local and regional modifications of inorganic chemistry of surface fresh water following different configurations of permafrost thaw and degradation have been reported globally and are listed in Tab. 1. The impacts on major ions and trace elements are discussed in the following chapters.

193 **4.** Impacts on major ion content

194 4.1 Pervasive permafrost degradation

195 A strong divergence of inorganic solute concentrations between catchments with differing permafrost 196 extents has been reported, whereby lower concentrations are associated with higher permafrost extent. 197 This has been attributed to permafrost (a) inhibiting the infiltration of surface water into deep mineral soil 198 strata, and (b) confining mineral-rich groundwater in the subpermafrost zone without hydrological 199 connection to surface water (Frey and McClelland, 2009; Woo, 2012; Kane et al., 2013). For example, 200 Frey et al. (2007a) analysed Total Inorganic Solutes (TIS, defined as sum of Ca²⁺, K⁺, Mg²⁺, Na⁺, Si, Cl⁺, 201 SO_4^{2-} and HCO_3^{-}) as a function of latitude in West Siberian streams and rivers in Russia, showing that TIS 202 concentrations were 289 mg L⁻¹ in permafrost-free watersheds compared to 48 mg L⁻¹ on average in 203 watersheds with permafrost (Fig. 1). Other studies highlighted differences in concentrations of major ions, 204 such as HCO₃- (Yukon River basin - Alaska, Striegl et al., 2005; Siberia - Russia, Yukon - Alaska, and 205 Mackenzie - Canada, Tank et al., 2012), Ca²⁺ and Mg²⁺ (Caribou-Poker Creeks Research Watershed -206 Alaska, MacLean et al., 1999), Cl⁻, SO₄²⁻, Ca²⁺, K⁺, Mg²⁺, and Na⁺ (Central Canadian sub-arctic - Canada, 207 Rühland et al., 2003), Na⁺, Ca²⁺, Cl⁻, and SO₄²⁻ (Central Mongolia, Szopińska et al., 2016), SO₄²⁻, Ca²⁺, 208 Mg²⁺, Na⁺, K⁺, and DIC (Dissolved Inorganic Carbon) (western Siberia - Russia, Pokrovsky et al., 2015), 209 among areas with different permafrost distribution. In western Siberia, Pokrovsky et al. (2015) also 210 provided evidence of the importance of plant litter and ground vegetation leaching as element sources 211 comparing K⁺ concentrations as a function of latitude. Indeed, lower solute concentrations were measured 212 in permafrost-bearing zones in spring, during intense plant litter leaching, due to lower biomass and 213 primary productivity of forest-tundra and tundra biomes compared to the productive taiga zone of the 214 western Siberia. Based on their results, Pokrovsky et al. (2015) hypothesised that, assuming a short-term 215 climate warming scenario of hundreds of years, an increase in ALT will be capable to increase the export 216 of major elements from transitional permafrost watersheds.

Increasing contributions of highly-mineralised groundwater, and increased contact (time and volume) between soil water and mineral surfaces have been proposed as the main drivers of ion enrichment in surface water of several areas subject to permafrost degradation. A recent investigation performed by Toohey et al. (2016) showed an increase in Ca^{2+} , Mg^{2+} , SO_4^{2-} , and Na^+ in the Yukon River Basin (Alaska)

221 in the period 1982-2014 (Fig. 2), attributing this evidence to altered hydrological flowpaths and increased 222 weathering due to widespread permafrost degradation. Several other studies of Northern-Hemisphere 223 high-latitude streams reported increasing concentrations of ions such as Ca²⁺ and SO₄²⁻ (Noatak National 224 Preserve - Alaska, Stottlemyer, 2001), Ca²⁺ and Mg²⁺ (sub-Arctic - Sweden, Giesler et al., 2014), Ca²⁺, 225 Mg²⁺, K⁺, and Na⁺ (Caribou-Poker Creeks Research Watershed - Alaska, Petrone et al., 2006, 2007), 226 SO₄²⁻, Ca²⁺, Mg²⁺, and alkalinity (Mackenzie basin - Canada, Tank et al., 2016), HCO₃⁻, Cl⁻, SO₄²⁻, Ca²⁺, 227 and Mg²⁺ (Central Siberian Plateau - Russia, Kolosov et al., 2016), following permafrost degradation. 228 Similar findings have been reported for streams and lakes of the Colorado Rocky Mountains (USA) over 229 the last two-three decades, with increasing concentrations of Ca²⁺ and SO₄²⁻ (Baron et al., 2009; Caine, 230 2010; Todd et al., 2012), and Ca²⁺, Mg²⁺, and SO₄²⁻ (Mast et al., 2011).

231 Although increases in major ions concentrations of surface water have been found in several 232 transitional permafrost areas, the causal link with permafrost degradation is not well established. Keller et 233 al. (2007, 2010) and Douglas et al. (2013) proposed the use of Ca/Sr, Ca/Na, Ca/Ba, and ⁸⁷Sr/⁸⁶Sr trends 234 in soils and streams for quantitatively assessing the effects of increasing ALT on mineral fluxes to surface 235 water, where the parent material and soil geochemistry are variable with depth. For instance, geochemical 236 trends point to carbonate concentrations in the ground increasing with depth (higher concentrations in the 237 permafrost than in the active layer), due to decreasing frequency of thaw and hence weathering intensity. 238 Correspondingly, a progressive increase of carbonate weathering signals during the summer season 239 (especially in late summer) was found, associated with increasing thaw depth. New insights on 240 mechanisms and sources of inorganic solutes in surface waters draining permafrost-affected soils can 241 also be gained by using stable isotopes of inorganic solutes such as Ca (Bagard et al., 2013), Mg 242 (Mavromatis et al., 2014, 2016), and Si (Pokrovsky et al., 2013). For example, Pokrovsky et al. (2013) 243 analysed Si isotopic composition of large and small rivers, surface flow, interstitial soil solutions, plant litter 244 and soils in Central Siberia, finding significant variations of the dissolved Si isotopic composition. These 245 variations were linked to 1) the high concentrations of suspended silicate matter during the spring flood, 2) 246 the progressive increase of ALT during summer accompanied by secondary mineral precipitation in 247 surface layers and plant uptake of Si, and 3) the impact of the permafrost-hosted deep underground waters during winter. Under climate change, the resulting permafrost degradation may be the most important factor controlling the Si isotopic composition in the rivers.

Short-time increases in the depth of thaw are also capable to enhance mineral fluxes from permafrost terrain. Increases in major ion concentrations (mainly Ca²⁺, Mg²⁺, Na⁺, SO₄²⁻, and Cl⁻) in surface water have been linked to active-layer thickening following strong thermal perturbations (warm summer conditions) and summer rainfall (Melville Island - Canada, Dugan et al., 2012, Lewis et al., 2012; Lafrenière and Lamoureux, 2013; Roberts et al., 2017) with flushing of solutes stored in near-surface permafrost (Melville Island - Canada, Lamhonwah et al., 2017) as well as to fire disturbance (Central Siberia - Russia, Parham et al., 2013).

257 In the McMurdo Dry Valleys (Antarctica) the presence of unusual surface-flow-seep features has been 258 attributed to the potential melting of complex-origin sub-surface ice (e.g., excess ground ice, snow 259 patches, refrozen precipitation that has accumulated in the subsurface, or buried glacier ice) in permafrost 260 (Harris et al., 2007). Seeps showed a different geochemical signature in comparison to glacial meltwater, 261 strongly enriched in solutes (Na⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, SO₄²⁻ and HCO₃⁻). These features associated with 262 water tracks (Levy et al., 2011) might contribute to the desert hydrological cycle exporting solute-263 concentrated fluxes from sub-surface ice to surface water, enhancing the connectivity between the 264 cryosphere and the hydrosphere in the Antarctic polar desert (Levy et al., 2011).

265 Future increases in air temperature, and rain, may enhance the release of major ions from solute-rich 266 layers in near-surface permafrost. Indeed, several studies reported a solute enrichment at the base of the 267 active layer and at the top of permafrost in different permafrost environments due to ion redistribution 268 during thermally-induced moisture migration (Herschel Island - Canada, Kokelj et al., 2002; Northwest 269 Territories - Canada, Kokelj and Burn, 2003, 2005; Lacelle et al., 2014), greater availability of water for 270 chemical aqueous reactions where drainage is inhibited by subjacent permafrost (Yukon Territory -271 Canada, Lacelle et al., 2007; Devon Island - Canada, Lacelle et al., 2008), mineral dissolution reactions 272 taking place in loamy layers slowly flushed by advective flow, with the reaction products transported 273 upward by diffusion to surficial peat layers frequently flushed during summer (Ilulissat - Greenland, Jessen 274 et al., 2014), physical modifications (landslides) of active layer geochemistry (Yamal Peninsula - Russia, Leibman and Streletskaya, 1997), and cryogenic concentration of salts during freezing and humiditydriven salt separation at the soil surface (McMurdo Dry Valleys - Antarctica, Levy et al. 2012).

277 Permafrost degradation can also increase the export of NO₃ from soils to surface water due to deeper 278 pathways that bypass the shallow organic soil horizons where most retention and removal of inorganic 279 nitrogen occurs (Caribou Poker Creeks Research Watershed and Upper Kuparuk River Basin - Alaska, 280 Harms and Jones, 2012). For instance, increased nitrification and decreased nitrate uptake due to 281 enhanced water-inorganic soil and limited water-organic soil contacts have been demonstrated to lead to 282 higher nitrate concentrations in surface water in permafrost environments. Jones et al. (2005) investigated 283 three watersheds underlain by discontinuous permafrost in interior Alaska (Caribou Poker Creeks 284 Research Watershed) over a four-year period. The results showed that deeper flow paths in areas of less 285 extensive permafrost facilitated nitrate export, with the loss of permafrost that could also have released 286 stored nitrogen inaccessible to terrestrial plant uptake, resulting in high nitrification and leaching loss 287 rates. Petrone et al. (2006) followed up on this work and highlighted the sensitivity of nitrate fluxes to 288 changes in active layer thickness, with higher concentrations associated with deeper movements of water 289 into soils. The authors further demonstrated the role of the active layer as source of nitrate during the 290 summer season, especially during summer storms, as also reported by Koch et al. (2013) in the 291 Richardson Catchment (Alaska). Furthermore, McClelland et al. (2007) found a substantial increase in 292 nitrate export from the Upper Kuparuk River (Alaska) between the late 1970s and early 2000s, attributing 293 it to mechanisms potentially linked to warming and permafrost thaw.

294 Conversely, comparison of 96 rivers and streams in western Siberia found no differences in Dissolved 295 Inorganic Nitrogen (DIN) concentrations linked to variations in permafrost extent (Frey et al., 2007b). Frey 296 and McClelland (2009) attributed the difference in findings for western Siberia and Interior Alaska to the 297 greater remineralisation (and subsequent nitrification) of organic nitrogen in the Alaskan watersheds 298 (intermediate permafrost extent), in contrast with a limited remineralisation of organic nitrogen in western 299 Siberia due to limited soil water saturation in peat-dominated terrains and enhanced denitrification due to 300 wet conditions.

301 Deepening of flow paths can also lead to increasing concentrations of inorganic phosphate and silicate 302 in soil water due to enhanced mineral weathering, which is the primary source of these inorganic nutrients 303 (Frey and McClelland, 2009, Pokrovsky et al., 2015). For instance, Hobbie et al. (1999) demonstrated that 304 permafrost thawing along the MilkyWay stream in northern Alaska contributed 30% of inflowing phosphate 305 into Toolik Lake, causing bottom-up trophic effects. Similarly, increasing concentrations of dissolved 306 silicate with a decrease in permafrost coverage were found in Alaska (MacLean et al., 1999) and in 307 western Siberia (Frey et al., 2007a). However, assuming future climate warming and increasing vegetation 308 density in permafrost-bearing zones, transient uptake of nutrients during summer period may attenuate 309 the expected increase in surface water concentrations linked to progressive involvement of thawed 310 mineral horizons, as hypothesised by Pokrovsky et al. (2015) for Si dynamics in western Siberian rivers 311 (Russia).

312

313 4.2 Thermokarst

314 Thermokarst disturbances in permafrost terrain such as retrogressive thaw slumps, thermal erosion 315 gullies, active-layer detachment slides, and catastrophic thaw of frozen palsa peat bogs have been found 316 to strongly modify major ion concentrations of surface water (mainly SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺, and Cl⁻). The 317 concentrations of solutes released from thermokarst can be several orders of magnitude higher than in 318 background water, due to the liberation of soluble materials sequestered in ground ice. Such instances 319 have been reported globally, but mainly in Arctic areas: Ellesmere Island, Canada (Kokeli and Lewkowicz, 320 1999); Melville Island, Canada (Dugan et al., 2012); Banks Island, Canada (Rudy et al., 2017); Northwest 321 Territories, Canada (Kokelj et al., 2005; Malone et al., 2013); Mackenzie Delta, Canada (Kokelj et al., 322 2009); Peel Plateau and Mackenzie Mountains, Canada (Kokelj et al., 2013); Brooks Range, Alaska 323 (Abbott et al., 2015); western Siberia, Russia (Loiko et al., 2017); and McMurdo Dry Valleys, Antarctica 324 (Gooseff et al., 2016).

Thermokarst can affect surface water chemistry for several decades with the magnitude of effects depending on the proportion of a catchment area influenced by the disturbance (Kokelj et al., 2005) (Fig. 3), although generalisations are difficult since hydrochemical modifications can depend on several factors such as the type of disturbance, its stabilisation rate, the downstream connectivity, and the characteristics of the impacted area (e.g., physical and geochemical characteristics of near-surface permafrost, mineralogical composition of bedrock/sediments). 331 Thermokarst processes can also release Si, and N and P forms into surface water. For example, Si 332 and P were found to be higher in small depressions and permafrost subsidences in actively thawing 333 frozen palsa peat bog areas than in stable palsa peat bog zones in western Siberia, Russia (Loiko et al. 334 2017). Moreover, thermokarst gullies and thaw slumps have been shown to increase N and P form 335 concentrations in water tracks, streams and lakes (Brooks Range - Alaska, Bowden et al., 2008; Harms et 336 al., 2014; McMurdo Dry Valleys - Antarctica, Gooseff et al., 2016). Louiseize et al. (2014) (Melville Island -337 Canada) demonstrated that even small thermokarst occurrences (active-layer detachments) are capable 338 to promote the export of microbially-derived nitrate as result of limited nitrate retention and enhanced 339 nitrification in mineral soils exposed in the scar zones. Abbott et al. (2015) (Brooks Range - Alaska) also 340 suggested that aquatic disturbance of inorganic nitrogen by thermokarst can be long-lived. Conversely, 341 Thompson et al. (2012) (Mackenzie Delta uplands - Canada) found that lakes unaffected by thaw slumps 342 had higher concentrations of the nutrients than slump-affected lakes, despite the high concentrations of 343 inorganic N and P in runoff pools within the slump sites. Within-lake biological uptake, sedimentation and 344 degradation of nutrients were assumed to be the main drivers of this effect.

345

346 **4.3 Rock-glacier thawing**

347 Thies et al. (2007) found strong increases in electrical conductivity (up to 19-fold), SO_4^{2-} (up to 26-fold), 348 Ca²⁺ (up to 13-fold), and Mg²⁺ (up to 68-fold) from 1985 to 2005 in two lakes at the toe of active rock 349 glaciers in the Central Eastern Alps in Europe (Austria and Italy) (Fig. 4). These trends have been 350 attributed to the melting of ice in the rock glaciers and an associated release of solutes, although no direct 351 evidence of the driving processes was provided. A similar evidence was reported in 20 remote high-352 elevation lakes located in Himalaya (Mt. Everest Region, Nepal) over the past two decades. Here, 353 significant enrichments in solutes have been attributed to the retreat of debris-covered glaciers (Salerno et 354 al., 2016) due to the sulphide oxidation processes that occur in subglacial environments, often microbially 355 mediated.

Increased geochemical fluxes from thawing permafrost and ice melt in rock glaciers have been also found to influence the seasonal hydrochemistry of small streams in the Austrian Alps (Krainer and Mostler, 2002; Berger et al., 2004; Krainer et al., 2007), although no specific analyses on major ions were 359 conducted and instead, conductivity measurements were used as proxy. Williams et al. (2006) in 2003 360 filled this gap, reporting strong seasonal increases for SO₄²⁻ (60-fold), Mg²⁺ (30-fold) and Ca²⁺ (20-fold) in 361 the outflow of rock glacier RG5 in the Colorado Front Range (Rocky Mountains - USA) compared to 362 nearby streams and lakes during the low-flow season. Longer-term measurements from 1998 to 2002 363 showed the same pattern of elevated concentrations of these solutes in the fall. The elevated 364 concentrations of major ions in rock glacier outflows and downstream lakes are consistent with the results 365 of a precursor study performed by Giardino et al. (1992), who noted that water exiting rock glaciers in the 366 San Juan Mountains of Colorado (USA) acquired a significant dissolved load during movement through 367 the rock glaciers. Specific hydrochemical characteristics in rock glacier meltwaters were found also in the 368 hyperarid Agua Negra river basin - Andes of Argentina (meltwaters enriched in SO₄²⁻, HCO₃⁻ and Ca²⁺, 369 Lecomte et al., 2008) and in Central Eastern Alps - Austria (meltwaters enriched in SO₄²⁻, Ca²⁺ and Mg²⁺, 370 Thies et al., 2013).

371 During the last decades, the increasing solute concentrations in lakes with rock glaciers in their 372 catchments were attributed to the enhanced melting of ice due to atmospheric warming (Thies et al., 373 2007). Williams et al. (2006) further supported this hypothesis, assuming this process may occur 374 seasonally, with a flushing of mineralised water at the end of summer when the 0 °C isotherm proceeds 375 towards the ice under conditions of degrading permafrost. Williams et al. (2006) reported the highest ion 376 concentrations in rock glacier outflows during particularly dry years. In this case, there would be more 377 internal melt than in wetter years, with a higher proportion of mineralised groundwater. The authors also 378 hypothesised that long-lasting snow cover might be able to reduce solute export by delaying subsurface 379 melt and by dilution of solute-rich water with snowmelt. Not only snowmelt, but also rain has been 380 reported to lower solute contents in rock glacier outflows (Krainer et al., 2007) through dilution effects. 381 Conversely, Thies et al. (2007) hypothesised that solute fluxes from rock glaciers intensify after periods of 382 intense rainfall during summer and fall, as these might enhance water percolation through rock glaciers 383 and thus cause the flushing of geochemical products. In summary, three hypotheses exist: (a) Warm 384 periods cause increased subsurface melt, which releases solutes. (b) Dry periods reduce the input of 385 meteoric water and thus reduce the dilution of rock-glacier outflow. (c) The percolation of meteoric water 386 through the rock glacier exports solutes. Considerable uncertainty exists about the processes, and their 387 interactions, driving the export of solutes from internal ice in rock glaciers.

388 Recent research attributed increased NO₃⁻ concentrations in surface water melt in permafrost and rock 389 glaciers (Rocky Mountains - USA, Baron et al., 2009). Williams et al. (2007) found that nitrate 390 concentrations in the outflow of a rock glacier were higher than all other analysed surface waters of the 391 same area in the Colorado Front Range, Rocky Mountains (USA), from 1998 to 2004 (Fig. 5). Fegel et al. 392 (2016) provides addition support that elevated biogeochemical and microbial characteristics of rock 393 glaciers in the Cascade Mountains, Rocky Mountains, and Sierra Nevada (USA) result in elevated nitrate 394 content in surface water. Further, microbial communities adapted to the extreme environment of the 395 interior of rock glaciers have been indicated as potential sources of the elevated nitrate in the rock glacier 396 outflows (Williams et al. 2007). The observed increase in surface-water nitrate concentration may also be 397 a result of melt water flushing microbially-active sediments (Barnes et al., 2014) and/or active microbial 398 populations in sediment pockets within talus fields in the Rocky Mountains (USA) (Ley et al., 2004).

399

400 5. Impacts on trace elements

401

Pervasive permafrost degradation 5.1

402 Although several studies dealt with the analysis of trace element concentrations in surface fresh water 403 in cold areas, especially in the boreal and sub-Arctic regions (e.g., Rember and Trefry, 2004; Voss et al., 404 2015), researches devoted to the investigation of the links with permafrost dynamics are rare and mainly 405 based on short time series. Typically, mobilisation of trace elements to surface water during early spring is 406 attributed to snowmelt when precipitation that has accumulated during winter is released (McNamara et 407 al., 1997; Rember and Trefry, 2004; Pokrovsky et al., 2010), with trace elements also potentially 408 incorporated from upper-soil horizons and thawing ponds (Rember and Trefry, 2004). Differently, Barker 409 et al. (2014) reported increasing concentrations of trace elements (AI, Ba, Fe and Mn) in stream water 410 during late fall in Alaska (Brooks Range), correlated with increased ALT and weathering fluxes from 411 freshly-exposed mineral surface (metal sources). Bagard et al. (2011) discriminated two distinct seasonal 412 peaks of trace element fluxes in Central Siberia (Russia): the first one in the beginning of spring snowmelt 413 and related to the uppermost soil horizon rich in organics, and the second one occurring late in summer

414 and related to deeper mineral soil horizons. Permafrost gradient was found to be the most important 415 environmental parameter in controlling trace element concentrations in western Siberia (Russia), where 416 Pokrovsky et al. (2016) analysed approximately 60 large and small rivers (<100 to ≤150,000 km² 417 watershed area) during spring flood and summer, and winter baseflow, across a 1500-km latitudinal 418 gradient. The main factors controlling the shift of river feeding from surface and subsurface flow to deep 419 underground flow in the permafrost-bearing zone were the depth of the active layer and its position in 420 organic or mineral horizons of the soil profile. The authors also suggested that under climate warming 421 scenarios the change in the relative degree of the peat and mineral soil leaching to the river might cause a 422 decrease in divalent metal organic complexes and an increasing delivery of trivalent and tetravalent 423 hydrolysates in the form of organo-ferric colloids to the river via supra-permafrost flow and hyporheic 424 influx. Differently, a recent study performed by Raudina et al. (2017) in western Siberia (Russia) reported 425 that the concentration of most trace elements in peat porewater did not show any statistically significant 426 trend with latitude. Applying a space-for-time substitution approach for the climate warming scenario in 427 western Siberia, the authors also predicted a decrease in the feeding of small rivers and lakes by peat soil 428 leachates in transitional permafrost areas with frozen peatlands. Finally, similar to major elements, the use 429 of stable isotopes of inorganic solutes such as Fe (Hirst et al., 2017) will allow to improve the knowledge 430 about the impacts of future permafrost evolution on surface waters.

431 In a multi-decadal study (from 1980s to 2000s) performed in a mineralised alpine watershed with 432 natural acidic in the Colorado's Rocky Mountains (USA), Todd et al. (2012) provided evidence of 433 increasingly high concentrations (increase ranging from 100% to 400%) of Zn and other metals of 434 ecological concern (e.g., Mn) in the Upper Snake River during low-flow months (late summer-early fall) 435 (Fig. 6). Increased rock weathering on freshly-exposed mineral surfaces and sulphide oxidation due to the 436 degradation of permafrost and the opening of new subsurface pathways, causing the migration of 437 groundwater and oxygen into the subsurface, were indicated as driving factors. Acid drainage is indeed a 438 potential mechanism capable to strongly influence water quality, through the release of metals (e.g., Fe, 439 Zn, Pb, Cu) from sulphide-rich minerals due to the exposure to oxygen and water (e.g., He et al., 1997; 440 Nordstrom, 2011), in areas where permafrost is degrading. In northern Yukon Territory (Canada), Lacelle 441 et al. (2007) reported water quality deterioration due to acidity and high metal concentrations in a stream

442 affected by acid drainage. Here, acid drainage was a natural phenomenon which effects were amplified by 443 the construction of a road. The removal of the surficial sediments, and consequent deepening the active 444 layer, allowed seasonal thawing and oxidation of sulphide-rich minerals in the excavated area. Increase of 445 ALT under warmer climate scenarios might enhance acid drainage at sites with sulphide-rich minerals by 446 allowing access to atmospheric oxygen to penetrate deeper in the ground.

447

448 **5.2 Thermokarst**

449 Trace element dynamics in thermokarst ponds and lakes have been found to be primarily related to the 450 evolutionary stage of these features. For example, Manasypov et al. (2014) investigated the 451 hydrochemical characteristics of thermokarst ponds and lakes with different degrees of permafrost 452 influence located in the northern part of western Siberia, across a latitudinal gradient of ~900 km. The 453 authors evidenced a geographical gradient in trace element concentrations related to thermokarst lake 454 evolution (from small permafrost depressions to larger lakes), in relation to different degrees of carbon 455 and element leaching from frozen peat soils. They estimated that the acceleration of permafrost thaw in 456 Siberia might increase the amount of small thermokarst lakes and, in turn, increase the concentrations of 457 most trace elements by 200-400%. Shirokova et al. (2013) also reported a clear decrease in some trace 458 element concentrations (e.g., Fe, Al, Ti, Zr and rare earth elements) from thermokarst depressions, to 459 ponds, and finally, to lakes in the central part of western Siberia (Russia) (Fig. 7). They attributed this 460 pattern to two main factors: i) increase in water residence time in large lakes, which leads to more efficient 461 mineralisation of organo-mineral colloids by aerobic heterotrophic bacterioplankton; ii) decrease in peat 462 abrasion at the lake borders as the perimeter-volume ratio decreases with size. Furthermore, trace 463 element concentrations (e.g., Fe, Al, Ni, Pb) have been found to increase in hollows, depressions and 464 permafrost subsidences in an area characterised by thawing frozen peat in western Siberia. Russia (Loiko 465 et al., 2017). Here, the authors reported decreasing concentrations with increasing surface area of the 466 water body, along the hydrological continuum: soil water \rightarrow hollows \rightarrow depressions and permafrost 467 subsidences \rightarrow thaw ponds \rightarrow thermokarst lakes. Thermokarst lakes can also have an important role in 468 the storage of some trace elements (AI, Cr, Cd, Pb) comparable to, or even higher than, the transport of 469 these elements by rivers (western Siberia - Russia, Polishchuk et al., 2017). Hot summer periods, and 470 cycles of ice formation and melting have been reported to drive in-lake biological uptake and release of 471 some elements (Zn, Mn, Co, Mo, Cu, Si, Pb, Cd) (western Siberia - Russia, Pokrovsky et al., 2013), and 472 seasonal differences in trace element concentrations (western Siberia - Russia, Manasypov et al., 2015), 473 respectively. In addition, Audry et al. (2011) observed that in differently-developed thermokarst lakes in 474 western Siberia, sediments at the early stage of ecosystem development are a sink for water column Cu, 475 Zn, Cd, Pb and Sb due to authigenic sulphides precipitation, confirming the progressive depletion trends 476 of trace element concentrations in the water column during the chronosequence of lake maturation (from 477 permafrost subsidence to mature and drained lakes) reported by Pokrovsky et al. (2011), who analysed 478 20 lakes and small ponds of various sizes and ages in the same area. Conversely, the sediments are a 479 source of dissolved Co, Ni and As to the water column due to upward diffusive fluxes, regardless the 480 ecosystem development stage. However, the concentrations of these elements were found to be low due 481 to sorption processes on Fe-bounding particles and/or large-size organo-mineral colloids.

482 Several studies have been conducted focusing on Hg and Pb dynamics in thermokarst-affected areas. 483 For instance, Klaminder et al. (2008) assessed the impact of permafrost degradation on the increase in 484 Hg mobility from soils to lake surface water in a palsa peat complex in sub-Arctic Sweden. Main driving 485 factors were accelerated soil/peat erosion, increasing hydrological connectivity, and increased runoff 486 which led to the exposure of soluble elements. Gordon et al. (2016) (Northwest Territories - Canada) 487 further demonstrated that new hydrological pathways due to permafrost thaw can increase peatland 488 hydrological connectivity, creating areas of high Hg concentrations at critical points (fens) before water 489 discharged to a wider drainage system. Small permafrost thaw ponds also contribute in controlling the 490 local and regional fluxes of Hg, as demonstrated by MacMillan et al. (2015) in sub-Arctic and high-Arctic 491 Canada. Elevated concentrations of Hg and methylmercury have been found to be strongly related to 492 inputs of organic matter and nutrients into surface water. Moreover, Rydberg et al. (2010) reported that 493 long-term changes in climate, permafrost and mire dynamics had large effects on the release of Hg from 494 palsa mires to lakes in sub-arctic Sweden. Particularly, the recent thawing of permafrost has increased 495 thermokarst erosion, resulting in an enhanced Hg transport from the mire to lake water. In their study of 496 sub-Arctic Sweden, Klaminder et al. (2010) reported a similar process for Pb, attributing its increase to the 497 thermokarst erosion of peat. Conversely, Deison et al. (2012) found that lakes affected by the 498 development of retrogressive thaw slumps in the Mackenzie Delta (Canada) had lower Hg levels in 499 surface sediments when compared to not-affected lakes. The authors attributed these results to the 500 effects of thaw slumping of clay-rich permafrost tills, which resulted in high inorganic sedimentation rates 501 that caused a dilution of organic material and associated Hg in the sediments.

502

503 5.3 Rock-glacier thawing

504 An increase in trace element concentrations in high-elevation Alpine lakes (Central Eastern Alps, 505 Austria and Italy) has been observed, and it has been attributed to the influence of ice melting within rock 506 glaciers (Thies et al., 2007). For instance, unexpectedly high Ni, Mn and Al concentrations, exceeding the 507 European Union limits for drinking water by more than an order of magnitude, have been reported for a 508 remote high-mountain lake situated at the toe of an active rock glacier. In contrast, negligible 509 concentrations of these elements (and other solutes) have been recorded in an adjacent pond without a 510 rock glacier in the catchment (Central Eastern Alps - Italy, Ilyashuk et al., 2014). Surprisingly, the lithology 511 did not contain high Ni concentrations, thus the source of Ni remains unknown. In addition, other springs 512 derived from rock glaciers in the Central Eastern Alps exhibited high concentrations of trace elements 513 such as Ni, Co, Cu, Fe, Mn and Zn (Krainer, 2014), pointing to rock-glacier ice as a potential origin. 514 Increasing acidity of rock-glacier affected surface waters accompanied by high heavy metal 515 concentrations have been also reported to cause significant changes in aquatic ecosystems (Central 516 Eastern Alps - Austria, Thies et al., 2013) and severe ecological damages (Central Eastern Alps - Italy, 517 Ilyashuk et al., 2017).

518 Results from geochemical analyses of ice cores sampled from a medium-sized active rock glacier 519 (Lazaun) in Central Eastern Alps (Italy) are reported by Krainer et al. (2015). The ice near the base is 520 approximately 10,300 years old and trace elements (Ni, Co, Cu, Zn) are enriched in three horizons within 521 the ice at depths of 4.2 m (approx. 2600 yr BP), 9.9 m (approx. 3200y BP) and 12.4 m (approx. 3500 yr 522 BP), with Ni concentrations up to 0.49 mg L⁻¹. High Ni concentrations were also measured at the rock 523 glacier spring, indicating that Ni in spring water was derived from distinct depth intervals within the 524 permafrost ice (Krainer et al., 2011). Again, the lithology was reported to not contain high concentrations 525 of trace elements. However, only few rock glaciers in Central Eastern Alps display meltwater with

abnormally high trace element concentrations. Considerable uncertainty still exists about the origin of thehigh concentrations of trace elements in rock-glacier ice.

528

529 6. Research perspectives

530 Several studies report major ion distribution in near-surface permafrost, finding increasing 531 concentrations at the top of permafrost, generally corresponding with ice-rich layers. However, relatively 532 few researches have combined geochemical analyses on changing near-surface permafrost and resulting 533 effects on surface-water characteristics. Performing combined investigations may provide insight into the 534 relationship between concentrations of major ions in near-surface permafrost and modifications of 535 surface-water geochemistry in case of permafrost degradation, both on intra- and inter-annual bases. Few 536 studies in the Arctic also demonstrated that rainfall events can flush solutes from near-surface permafrost 537 to the surface and increase ion concentrations in surface water. Projected warming and rainfall 538 augmentation in Arctic areas (IPCC, 2013) might cause increases in major ion concentrations in surface 539 water in permafrost areas; in turn, increasing runoff might reduce ion concentrations since discharge is 540 generally negatively correlated with concentrations of major ions because of dilution effects (Petrone et 541 al., 2006, 2007), although the "chemostatic" behaviour in stream water (solute concentrations in stream 542 water are not determined by simple dilution, Godsey et al., 2009) should be also taken into account. The 543 ability to adequately incorporate these processes into models will be relevant for predicting the 544 hydrochemical impacts of climatic changes in transitional permafrost areas. Future studies should also 545 focus on the bedrock/sediment composition and particularly on the geochemical composition of 546 permafrost ice that might be locally enriched in ions (due to lithological characteristics), which can be 547 released when permafrost ice melts. Finally, research in highly sensitive areas such as watersheds where 548 acid drainage is possible due to lithological properties (e.g., pyritiferous shale presence) will help to 549 understand how permafrost degradation may cause a deterioration of surface water quality.

550 Major ion concentrations downstream of rock glaciers have mainly been investigated in the European 551 Alps and in mountain chains of North America. Extending these studies to areas such as in the Andes 552 (e.g., Brenning, 2005) and in the Hindu Kush Himalaya (e.g., Schmid et al., 2015; Gruber et al., 2017) will 553 allow better understanding the dynamics and potential effects of rock-glacier thaw on downstream water 554 quality. The establishment of baselines for future monitoring and the better understanding of processes of 555 solute export from rock glaciers will thereby be important elements of such studies. In this framework, 556 investigating the hydrological connections between rock glaciers and adjacent surface waters through the 557 application on non-invasive techniques (Colombo et al., 2017) could provide new insights on the rock-558 glacier role, and dynamics, in exporting concentrated chemical fluxes into high-elevation hydrological 559 systems. Moreover, it has been shown that melting of ice in active rock glaciers can increase their storage 560 capacity. May chemical composition of outflowing water be affected by this process? Fresh water stored in 561 rock glaciers can be important for local water management only during the melt season (summer) since 562 during the cold season (winter) discharge is extremely low or absent. Future studies on water quality 563 originating from rock glaciers should also focus on relict rock glaciers due to their higher storage capacity 564 and residence time for fresh water which can also be released during winter. Finally, extending 565 investigations to other common debris features with permafrost such as talus slopes (Sass, 2006; Lambiel 566 and Pieracci, 2008; Scapozza et al., 2011) will allow understanding the effects of thawing permafrost on 567 water quality in cold mountains more broadly. Do talus slopes with significant amount of ground ice (cf., 568 Gruber and Haeberli, 2009) behave like rock glaciers in their export of solutes during permafrost 569 degradation? Trends of major ions and ion-isotope ratios in surface water may be considered as important 570 additions to the permafrost monitoring conducted in mountains (c.f., PERMOS, 2016).

571 Given that most studies on geochemistry in near-surface permafrost and ground ice considered only 572 major ions, future research on trace element concentrations and their variations within the active layer, 573 permafrost and massive ground ice occurrences is necessary for evaluating the effect they might have on 574 ecosystems when thawing.

High trace element concentrations have been reported downstream of rock glaciers and in three horizons within the ice core of a rock glacier in the Central Eastern Alps. Since lithology was not found to contain high trace element concentrations, alternative hypotheses (e.g., atmospheric fallout) to chemical weathering should be tested in order to understand the origin and the potential for future release of trace elements.

580 Beside specific research needs, several broader questions emerge for the understanding of permafrost 581 degradation and its effects on inorganic chemistry of surface water. These are especially important in arid 582 areas, such as some areas in the Andes and Himalaya, where fresh water stored in permafrost can be 583 important for local water management (Brenning, 2005; Rangecroft et al., 2013; Rangecroft et al., 2015; 584 Gruber et al., 2017) in small catchments. What is the role of permafrost in controlling water quality in these 585 areas and what duration will the transient effects of permafrost thaw have? What will be the long-term 586 implications of permafrost degradation on water guality of local freshwater reservoirs? What are the 587 possible socioeconomic consequences of water quality deterioration due to permafrost degradation? What 588 are suitable adaptation strategies to mitigate the possible impacts of permafrost degradation on water 589 supply quality of local populations?

590

591 **7. Conclusion**

592 This review of permafrost-thaw impacts on inorganic chemistry of surface fresh water has revealed 593 several common patterns.

594 Spatially-distributed progressive increases of major ion delivery to surface fresh water have been 595 reported in both polar and mountain areas following permafrost degradation. This is the result of 596 increasing contributions of highly mineralised groundwater and enhanced interactions of soil water with 597 deep mineral strata. Localised releases of major ions to surface water due to the liberation of soluble 598 materials sequestered in permafrost and ground ice have been found in ice-rich terrains both at high 599 latitude (thermokarst features) and high elevation (rock glaciers). Generalisations must be considered 600 carefully though, because the intensity of hydrochemical modifications depends on several factors such as 601 the characteristics of the watersheds (e.g., physical and geochemical characteristics of permafrost), their 602 hydrological connectivity, the magnitude and type of disturbance in case of thermokarst, and the extent of 603 permafrost or rock glaciers in the catchment. Permafrost degradation can also increase the export of 604 inorganic N and P forms, and Si, from permafrost to surface water due to deeper flow paths that bypass 605 shallow organic layers where most retention and removal of nutrients occur (N), and because of enhanced 606 mineral weathering (P and Si). However, significant uncertainty has been shown on DIN dynamics, mainly 607 dependent on regional and landscape-scale differences in Arctic areas (e.g., Alaska and Siberia). In 608 addition, thermokarst can enhance the export of inorganic nutrients from permafrost to surface water, 609 although biological uptake, sedimentation and degradation of nutrients might mitigate these effects. 610 Increases in nitrate concentrations have been also attributed to rock glacier melt water flushing microbially611 active sediments.

612 Trace element dynamics in permafrost areas have been shown to exhibit two seasonal peaks in 613 geochemical fluxes: one at the beginning of the snowmelt (early spring), related to the flushing of surficial 614 soil horizons and previously mobilised species stored in them; the second occurring in late summer and 615 early fall, associated with deeper mineral-soil horizons. The formation of new thermokarst features (e.g., 616 ponds, lakes, palsa mires) and leaching from frozen peat can be relevant for increasing trace element 617 concentrations in permafrost catchments and for affecting the locations of high concentrations due to 618 newly-developing hydrological pathways. Alternatively, increasing sediment erosion due to thermokarst 619 processes has been reported to potentially mitigate these effects through increasing sedimentation rates 620 and dilution of concentrations. Moreover, stabilisation and increasing size of older thermokarst features 621 might lead to decreasing trends because of stabilising shorelines, reduced peat abrasion, and more 622 efficient mineralisation. Increasing trends in trace element concentrations have been also reported in 623 streams and lakes in mountain areas, where enhanced chemical weathering on fresh mineral surfaces 624 exposed by permafrost thaw and contribution of metal-enriched groundwater have been hypothesised to 625 be the main drivers. Nevertheless, in the Central Eastern Alps, high concentrations of trace elements 626 (e.g., Ni) in surface water have been found to be unrelated to the lithological setting, hence rejecting the 627 hypothesis of mineral weathering as the only process involved.

628 In conclusion, several factors influence the timing and magnitude of the impacts of permafrost 629 degradation on inorganic chemistry of surface fresh water. These include permafrost sensitivity to thawing 630 (e.g., amount of ground ice), modes of permafrost degradation (e.g., increasing ALT, thermokarst) and 631 environmental characteristics of watersheds (e.g., soil properties, lithology, land cover, topography, 632 hydrological connectivity). Further mobilisation of solutes and related transport to surface fresh water 633 appear reasonable under warming climatic conditions. This might develop through gradual concentration 634 increase in case of progressive and diffused thawing of permafrost, and/or through distinct temporal peaks 635 in case of localised thermokarst and rock glacier thawing. As a result, modifications of inorganic water 636 chemistry might have significant implications for ecological and human systems.

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644 **Reference list**

- Abbott, B.W., Jones, J.B., Godsey, S.E., Larouche, J.R., Bowden, W.B., 2015. Patterns and persistence
 of hydrologic carbon and nutrient export from collapsing upland permafrost. Biogeosciences 12, 37253740.
- ACGR (Associate Committee On Geotechnical Research), 1988. Glossary of Permafrost and Related
 Ground Ice Terms. Permafrost Subcommittee, National Research Council of Canada, Technical
 Memorandum 142.
- Åkerman, H.J.A., Johansson, M., 2008. Thawing permafrost and thicker active layers in subarctic
 Sweden. Permafrost and Periglacial Processes 19, 279-92.
- Andresen, C.G., Lougheed, V.L., 2015. Disappearing Arctic tundra ponds: Fine-scale analysis of surface
 hydrology in drained thaw lake basins over a 65 year period (1948-2013). Journal of Geophysical
 Researches 120, 466-479.
- Audry, S., Pokrovsky, O.S., Shirokova, L.S., Kirpotin, S.N., Dupré, B., 2011. Organic matter mineralization
- and trace element post-depositional redistribution in Western Siberia thermokarst lake sediments.
 Biogeosciences 8: 3341-3358.
- Azócar, G.F., Brenning, A., 2010. Hydrological and geomorphological significance of rock glaciers in the
 dry Andes, Chile (27°-33° S). Permafrost and Periglacial Processes 21, 42-53.
- Bagard, M.-L., Chabaux, F., Pokrovsky, O.S., Viers, J., Prokushkin, A.S., Stille, P., Rihs, S., Schmit, A.D.,
- 662 Dupre, B., 2011. Seasonal variability of element fluxes in two Central Siberian rivers draining high
- latitude permafrost dominated areas. Geochimica et Cosmochimica Acta 75, 3335-3357.

- Bagard, M.-L., Schmitt, A.-D., Chabaux, F., Pokrovsky, O.S., Viers, J., Stille, P., Labolle, F., Prokushkin,
 A.S., 2013. Biogeochemistry of stable Ca and radiogenic Sr isotopes in a larch-covered permafrostdominated watershed of Central Siberia. Geochimica et Cosmochimica Acta 114, 169-187.
- Barker, A.J., Douglas, T.A., Jacobson, A.D., McClelland, J.W., Ilgen, A.G., Khosh, M.S., Lehn, G.O.,
- 668 Trainor, T.P., 2014. Late season mobilization of trace metals in two small Alaskan arctic watersheds as 669 a proxy for landscape scale permafrost active layer dynamics. Chemical Geology 381, 180-193.
- Barnes, R.T., Williams, M.W., Parman, J.N., Hill, K., Caine, N., 2014. Thawing glacial and permafrost
 features contribute to nitrogen export from Green Lakes Valley, Colorado Front Range, USA.
 Biogeochemistry 117, 413-430.
- Baron, J.S., Schmidt, T.M., Harman, M.D., 2009. Climate-induced changes in high-elevation stream
 nitrate dynamics. Global Change Biology 15 (7), 1777-1789.
- Barsch, D., 1996. Rockglaciers: Indicators for the Present and Former Geoecology in High Mountain
 Environments. Springer-Verlag: Berlin-Heidelberg.
- 677 Bense, V.F., Ferguson, G., Kooi, H., 2009. Evolution of shallow groundwater flow systems in areas of 678 degrading permafrost. Geophysical Research Letters 36, L22401 (doi:10.1029/2009GL039225).
- Berger, J., Krainer, K., Mostler, W., 2004. Dynamics of an active rockglacier (Ötztal Alps, Austria).
 Quaternary Research 62, 233-242.
- Berthling, I., 2011. Beyond confusion: Rock glaciers as cryo-conditioned landforms. Geomorphology 131,
 98-106.
- Boeckli, L., Brenning, A., Gruber, S., Noetzli, J., 2012. Permafrost distribution in the European Alps:
 calculation and evaluation of an index map and summary statistics, The Cryosphere 6, 807-820.
- Bowden, W.B., Gooseff, M.N., Balser, A., Green, A., Peterson, B.J., Bradford, J., 2008. Sediment and
 nutrient delivery from thermokarst features in the foothills of the North Slope, Alaska: Potential impacts
 on headwater stream ecosystems. Journal of Geophysical Research 113, G02026
- 688 (doi:10.1029/2007JG000470).
- Brenning, A., 2005. Geomorphological, hydrological, and climatic significance of rock glaciers in the
 Andes of Central Chile (33-35 S). Permafrost and Periglacial Processes 16, 231-240.

- Burger, K.C., Degenhardt, J.J., Giardino, J.R., 1999. Engineering geomorphology of rock glaciers.
 Geomorphology 31, 93-132.
- Burn, C.R., Zhang, Y., 2009. Permafrost and climate change at Herschel Island (Qikiqtaruk), Yukon
 Territory, Canada. Journal of Geophysical Research 114, F02001 (doi: 10.1029/2008JF001087).
- 695 Caine, N., 2010. Recent hydrologic change in a Colorado alpine basin: an indicator of permafrost thaw?
 696 Annals of Glaciology 51 (56), 130-134.
- 697 Clark, I.D., Lauriol, B., Harwood, L., Marschner, M., 2001. Groundwater contributions to discharge in a 698 permafrost setting, Big Fish River, N.W.T., Canada. Arctic Antarctic and Alpine Research 33, 62-69.
- 699 Colombo, N., Sambuelli, L., Comina, C., Colombero, C., Giardino, M., Gruber, S., Viviano, G., Vittori
- Antisari, L., Salerno, F., 2017. Mechanisms linking active rock glaciers and impounded surface water
- formation in high-mountain areas. Earth Surface Processes and Landforms, doi:10.1002/esp.4257.
- Corte, A., 1976. The hydrological significance of rock glaciers. Journal of Glaciology 17, 157-158.
- 703 Cremonese, E., Gruber, S., Phillips, M., Pogliotti, P., Boeckli, L., Noetzli, J., Suter, C., Bodin, X., Crepaz,
- A., Kellerer-Pirklbauer, A., Lang, K., Letey, S., Mair, V., Morra di Cella, U., Ravanel, L., Scapozza, C.,
- Seppi, R., Zischg, A., 2011. Brief Communication: "An inventory of permafrost evidence for the
 European Alps". The Cryosphere 5, 651-657.
- 707 Deison, R., Smol, J.P., Kokelj, S.V., Pisaric, M.F.J., Kimpe, L.E., Poulain, A.J., Sanei, H., Thienpont, J.R.,
- Blais, J.M., 2012. Spatial and temporal assessment of mercury and organic matter in thermokarst
 affected lakes of the Mackenzie Delta Uplands, NT, Canada. Environmental Science & Technology 46,
 8748-8755.
- Douglas, T.A., Blum, J.D., Guo, L., Keller, K., Gleason, J.D., 2013. Hydrogeochemistry of seasonal flow
 regimes in the Chena River, a subarctic watershed draining discontinuous permafrost in interior Alaska
 (USA). Chemical Geology 335, 48-62.
- 714 Dugan, H.A., Lamoureux, S.F., Lewis, T., Lafrenière, M.J., 2012. The Impact of permafrost disturbances
- and sediment loading on the Limnological characteristics of two High Arctic lakes. Permafrost and
 Periglacial Processes 23 (2), 119-126.
- Fegel, T.S., Baron, J.S., Fountain, A.G., Johnson, G.F., Hall, E.K., 2016. The differing biogeochemical
- and microbial signatures of glaciers and rock glaciers. Journal of Geophysical Research 121, 919-932.

- Fountain, A.G., Campbell, J.L., Schuur, E.A.G., Stammerjohn, S.E., Williams, M.W., Ducklow, H.W., 2012.
 The Disappearing Cryosphere: Impacts and Ecosystem Responses to Rapid Cryosphere Loss.
 BioScience 62, 405-415.
- 722 Frauenfeld, O.W., Zhang, T.J., Barry, R.G., Gilichinsky, D., 2004. Interdecadal changes in seasonal freeze 723 depths Russia. Journal Geophysical D05101 and thaw in of Research 109, 724 (doi:10.1029/2003JD004245).
- 725 French, H.M., 2007. The Periglacial Environment. Third edition, John Wiley & Sons, Chichester.
- Frey, K.E., McClelland, J.W., 2009. Impacts of permafrost degradation on arctic river biogeochemistry.
 Hydrological Processes 23, 169-182.
- Frey, K.E., McClelland, J.W., Holmes, R.M., Smith, L.C., 2007b. Impacts of climate warming and
 permafrost thaw on the riverine transport of nitrogen and phosphorus to the Kara Sea. Journal of
 Geophysical Research 112, G04S58 (doi:10.1029/2006JG000369).
- Frey, K.E., Siegel, D.I., Smith, L.C., 2007a. Geochemistry of west Siberian streams and their potential
 response to permafrost degradation. Water Resources Research 43, W03406
 (doi:10.1029/2006WR004902).
- Giardino, J.R., Vitek, J.D., DeMorett, J.L., 1992. A model of water movement in rock glaciers and
 associated water characteristics. Proceedings of the 22nd Annual Binghamton Symposium in
 Geomorphology, 159-184.
- 737 Giesler, R., Lyon, S.W., Mörth, C.-M., Karlsson, J., Karlsson, E.M., Jantze, E.J., Destouni, G., Humborg,
- C., 2014. Catchmentscale dissolved carbon concentrations and export estimates across six subarctic
 streams in northern Sweden, Biogeosciences 11, 525-537.
- Godsey, S.E., Kirchner, J.W., Clow, D.W., 2009. Concentration-discharge relationships reflect chemostatic
 characteristics of US catchments. Hydrological Processes 23 (13), 1844-1864.
- Gooseff, M.N., Balser, A., Bowden, W.B., Jones, J.B., 2009. Effects of hillslope thermokarst in Northern
 Alaska. Eos, Transactions American Geophysical Union 90 (4), 29-30.
- Gooseff, M.N., Van Horn, D., Sudman, Z., McKnight, D.M., Welch, K.A., Lyons, W.B., 2016. Stream
- biogeochemical and suspended sediment responses to permafrost degradation in stream banks in
- Taylor Valley, Antarctica. Biogeosciences 13, 1723-1732.

- Gorbunov, A.P., 1978. Permafrost investigations in high-mountain regions. Arctic and Alpine Research 10,
 283-294.
- Gordon, J., Quinton, W., Branfireun, B.A., Olefeldt, D., 2016. Mercury and methylmercury biogeochemistry
- in a thawing permafrost wetland complex, Northwest Territories, Canada. Hydrological Processes 30,
 3627-3638.
- Gruber, S., 2012. Derivation and analysis of a high-resolution estimate of global permafrost zonation. The
 Cryosphere 6, 221-233.
- 754 Gruber, S., Fleiner, R., Guegan, E., Panday, P., Schmid, M.-O., Stumm, D., Wester, P., Zhang, Y., Zhao,
- L., 2017. Review article: Inferring permafrost and permafrost thaw in the mountains of the Hindu Kush
- Himalaya region. The Cryosphere 11, 81-99.
- Gruber, S., Haeberli, W., 2009. Mountain permafrost. In R. Margesin (Ed.), *Permafrost Soils*. Berlin,
 Heidelberg: Springer Berlin Heidelberg, 33–44. (doi: 10.1007/978-3-540-69371-0).
- Gruber, S., Hoelzle, M., Haeberli, W., 2004. Permafrost thaw and destabilization of Alpine rock walls in the
 hot summer of 2003. Geophysical Research Letters 31, L13504 (doi:10.1029/2004GL020051).
- Guglielmin, M., Cannone, N., 2012. A permafrost warming in a cooling Antarctica? Climatic Change 111,
 177-195.
- Guglielmin, M., Dalle Fratte, M., Cannone, N., 2014. Permafrost warming and vegetation changes in
 continental Antarctica. Environmental Research Letters 9, 045001 (doi:10.1088/17489326/9/4/045001).
- Haeberli, W., Hallet, B., Arenson, L., Elconin, R., Humlum, O., Kääb, A., Kaufmann, V., Ladanyi, B.,
 Matsuoka, N., Springman, S., and Vonder Mühll, D., 2006. Permafrost creep and rock glacier
 dynamics. Permafrost and Periglacial Processes 17, 189-214.
- Hansen, J., Sato M., 2016. Regional climate change and national responsibilities. Environmental
 Research Letters 11: 034009 (doi:10.1088/1748-9326/11/3/034009).
- Harden, J.W., Koven, C.D., Ping, C., Hugelius, G., McGuire, A.D., Camill, P., Jorgenson, T., Kuhry, P.,
 Michaelson, G.J., O'Donnell, J.A., Schuur, E.A.G., Tarnocai, C., Johnson, K., Grosse, G., 2012. Field
 information links permafrost carbon to physical vulnerabilities of thawing. Geophysical Research
 Letters 39, L15704 (doi:10.1029/2012GL051958).

- Harms, T.K., Abbott, B.W., Jones, J.B., 2014. Thermo-erosion gullies increase nitrogen available for
 hydrologic export. Biogeochemistry 117 (2-3), 299-311.
- Harms, T.K., Jones Jr., J.B., 2012. Thaw depth determines reaction and transport of inorganic nitrogen in
 valley bottom permafrost soils. Global Change Biology 18, 2958-2968.
- Harris, H., Arenson, L.U., Christiansen, H.H., Etzelmüller, B., Frauenfelder, R., Gruber, S., Haeberli, W.,
 Hauck, C., Hoelzle, M., Humlum, O., Isaksen, K., Kääb, A., Kern-Lütschg, M.A., Lehning, M.,
 Matsuoka, N., Murton, J., Noetzli, J., Phillips, M., Ross, N., Seppälä, M., Springman, S.M., Vonder
 Mühll, D., 2009. Permafrost and climate in Europe: Monitoring and modelling thermal,
 geomorphological and geotechnical responses. Earth-Science Reviews 92, 117-171.
- Harris, K.J., Carey, A.E., Lyons, W.B., Welch, K.A., Fountain, A.G., 2007. Solute and isotope
 geochemistry of subsurface ice melt seeps in Taylor Valley, Antarctica. Geological Society of America
 Bulletin 119 (5-6), 548-555.
- He, M., Wang, Z., Tang, H., 1997. Spatial and temporal patterns of acidity and heavy metals in predicting
 the potential for ecological impact on the Le An river polluted by acid mine drainage. Science of the
 Total Environment 206, 67-77.
- Heginbottom, J.A., Dubreuil, M.A., Harker, P.A., 1995. Canada-Permafrost. National Atlas of Canada, 5th
 Edition. National Atlas Information Service, Natural Resources Canada, Ottawa, Plate 2.1 MCR 4177.
- Hinzman, L.D., Bettez, N.D., Bolton, W.R., Chapin, F.S., Dyurgerov, M.B., Fastie, C. L., Griffith, B.,
- Hollister, R.D., Hope, A., Huntington, H.P., Jensen, A.M., Jia, G.J., Jorgenson, T., Kane, D.L., Klein,
- D.R., Kofinas, G., Lynch, A.H., Lloyd, A.H., McGuire, A.D., Nelson, F.E., Oechel, W.C., Osterkamp,
- 795 T.E., Racine, C.H., Romanovsky, V.E., Stone, R.S., Stow, D.A., Sturm, M., Tweedie, C.E., Vourlitis,
- G.L., Walker, M. D., Walker, D.A., Webber, P.J., Welker, J.M., Winker, K.S., Yoshikawa, K., 2005.
- Evidence and implications of recent climate change in northern Alaska and other Arctic regions.Climatic Change 72, 251-298.
- Hirst, C., Andersson, P.S., Shaw, S., Burke, I.T., Kutscher, L., Murphy, M.J., Maximov, T., Pokrovsky,
 O.S., Mörth, C-M., Porcelli, D., 2017. Characterisation of Fe-bearing particles and colloids in the Lena
 River basin, NE Russia. Geochimica et Cosmochimica Acta 213, 553-573.

- Hobbie, J.E., Peterson, B.J., Bettez, N., Deegan, L., O'Brien, W.J., Kling, G.W., Kipphut, G.W., Bowden,
 W.B., Hershey, A.E., 1999. Impact of global change on the biogeochemistry and ecology of an Arctic
 freshwater system. Polar Research 18 (2), 207-214.
- Humlum, O. (2000). The geomorphic significance of rock glaciers: estimates of rock glacier debris
 volumes and headwall recession rates in West Greenland. Geomorphology 35, 41-67.
- 807 Ikeda, A., Matsuoka, N., 2006. Pebbly versus bouldery rock glaciers: Morphology, structure and
 808 processes. Geomorphology 73, 279-296.
- 809 Ilyashuk, B.P., Ilyashuk, E.A., Psenner, R., Tessadri, R., Koinig, K.A., 2014. Rock glacier outflows may
 810 adversely affect lakes: lessons from the past and present of two neighboring water bodies in a
 811 crystalline-rock watershed. Environmental Science & Technology 48, 6192-6200.
- 812 Ilyashuk, B.P., Ilyashuk, E.A., Psenner, R., Tessadri, R., Koinig, K.A., 2017. Rock glaciers in crystalline
 813 catchments: hidden permafrost-related threats to alpine headwater lakes. Global Change Biology,
 814 doi:10.1111/gcb.13985.
- Ishikawa, M., Sharkhuu, N., Zhang, Y., Kadota, T., and Ohata, T., 2005. Ground thermal and moisture
 conditions at the southern boundary of discontinuous permafrost, Mongolia. Permafrost and Periglacial
 Processes 16: 209-216.
- 818 IPCC, 2013. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the
 819 Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University
 820 Press, Cambridge, United Kingdom and New York, NY, USA.
- Jessen, S., Holmslykke, H.D., Rasmussen, K., Richardt, N., Holm, P.E., 2014. Hydrology and pore water
 chemistry in a permafrost wetland, Ilulissat, Greenland. Water Resources Research 50 (6), 4760-4774.
- Jones Jr., J.B., Petrone, K.C., Finlay, J.C., Hinzman, L.D., Bolton, W.R., 2005. Nitrogen loss from
 watersheds of interior Alaska underlain with discontinuous permafrost. Geophysical Research Letters
- 825 32, L02401 (doi:10.1029/2004GL021734).
- Jorgenson, M.T., Osterkamp, T.E., 2005. Response of boreal ecosystems to varying modes of permafrost
 degradation. Canadian Journal of Forest Research 35, 2100-2111.
- 828 Jorgenson, M.T., Racine, C.H., Walters, J.C., Osterkamp, T.E., 2001. Permafrost degradation and
- ecological changes associated with a warming climate in Central Alaska. Climatic Change 48, 551-579.

- Kääb, A., Haeberli, W., 2001. Evolution of a high mountain thermokarst lake in the Swiss Alps. Arctic,
 Antarctic and Alpine Research 33(4), 385-390.
- Kane, D.L., Yoshikawa, K., McNamara, J.P., 2013. Regional groundwater flow in an area mapped as
 continuous permafrost, NE Alaska (USA). Hydrogeology Journal 21, 41-52.
- Keller, K., Blum, J.D., Kling, G.W., 2007. Geochemistry of soils and streams on surfaces of varying ages
 in Arctic Alaska. Arctic, Antarctic, and Alpine Research 39, 84-98.
- Keller, K., Blum, J.D., Kling, G.W., 2010. Stream geochemistry as an indicator of increasing permafrost
 thaw depth in an arctic watershed. Chemical Geology 273 (1–2), 76-81.
- Klaminder, J., Hammarlund, D., Kokfelt, U., Vonk, J.E., Bigler, C., 2010. Lead contamination of subarctic
 lakes and its response to reduced atmospheric fallout: can the recovery process be counteracted by
 the ongoing climate change? Environmental Science & Technology 44, 2335-2340.
- Klaminder, J., Yoo, K., Rydberg, J., Giesler, R., 2008. An explorative study of mercury export from a
 thawing palsa mire. Journal of Geophysical research 113, G04034 (doi:10.1029/2008JG000776).
- Koch, J.C., Runkel, R.L., Striegl, R., McKnight, D.M., 2013. Hydrologic controls on the transport and
 cycling of carbon and nitrogen in a boreal catchment underlain by continuous permafrost. Journal of
 Geophysical Research 118, 698-712.
- Kokelj, S.V., Burn, C.R., 2003. Ground ice and soluble cations in near-surface permafrost, Inuvik,
 Northwest Territories, Canada. Permafrost and Periglacial Processes 143, 275-289.
- Kokelj, S.V., Burn, C.R., 2005. Geochemistry of the active layer and near-surface permafrost, Mackenzie
 delta region, Northwest Territories, Canada. Canadian Journal of Earth Sciences 42, 37-48.
- Kokelj, S.V., Jenkins, R.E., Milburn, D., Burn, C.R., Snow, N., 2005. The influence of thermokarst
 disturbance on the water quality of small upland lakes, Mackenzie Delta region, Northwest Territories,
- 852 Canada. Permafrost and Periglacial Processes 16, 343-353.
- Kokelj, S., Jorgenson, M.T., 2013. Advances in thermokarst research. Permafrost and Periglacial
 Processes 24, 108-119.
- Kokelj, S.V., Lacelle, D., Lantz, T.C., Tunnicliffe, J., Malone, L., Clark, I.D., Chin, K.S., 2013. Thawing of
 massive ground ice in mega slumps drives increases in stream sediment and solute flux across a
 range of watershed scales. Journal of Geophysical Research 118, 681-692.

- Kokelj, S.V., Lewkowicz, A.G., 1999. Salinization of permafrost terrain due to natural geomorphic
 disturbance, Fosheim Peninsula, Ellesmere Island. Arctic 52, 372-385.
- Kokelj, S.V., Smith, C.A.S., Burn, C.R., 2002. Physical and chemical characteristics of the active layer and
- permafrost, Herschel Island, western Arctic coast, Canada. Permafrost and Periglacial Processes 13,
 171-185.
- Kokelj, S.V., Zajdlik, B., Thompson, M.S., 2009. The impacts of thawing permafrost on the chemistry of
 lakes across the subarctic boreal tundra transition, Mackenzie Delta region, Canada. Permafrost and
 Periglacial Processes 20, 185-200.
- Kolosov, R.R., Prokushkin, A.S., Pokrovsky, O.S., 2016. Major anion and cation fluxes from the Central
 Siberian Plateau watersheds with underlying permafrost. IOP Conference Series: Earth and
 Environmental Science 48, 012018, doi:10.1088/1755-1315/48/1/012018.
- Krainer, K., 2014. Permafrost and Climate Change in North and South Tyrol. In: permAfrost, Austrian
 Permafrost Research Initiative, Final Report, 51-67.
- 871 Krainer, K., Bressan, D., Dietre, B., Haas, J.N., Hajdas, I., Lang, K., Mair, V., Nickus, U., Reidl, D., Thies,
- H., Tonidandel, D., 2015. A 10,300-year-old permafrost core from the active rock glacier Lazaun,
 southern Ötztal Alps (South Tyrol, northern Italy). Quaternary Research 83(2), 324-335.
- Krainer, K., Mostler, W. 2002. Hydrology of active rock glaciers: Examples from the Austrian Alps. Arctic,
 Antarctic, and Alpine Research 34, 142-149.
- Krainer, K., Mostler, W., Spötl, C., 2007. Discharge from active rock glaciers, Austrian Alps: a stable
 isotope approach. Austrian Journal of Earth Sciences 100, 102-112.
- Krainer, K., Nickus, U., Thies, H., Tessadri, R., 2011. Geochemical analyses of permafrost ice and of
 permafrost water springs. PermaNET Project report, WP7.
- Kurylyk, B.L., MacQuarrie, K.T.B., McKenzie, J.M., 2014. Climate change impacts on groundwater and
 soil temperatures in cold and temperate regions: Implications, mathematical theory, and emerging
 simulation tools. Earth-Science Reviews 138, 313-334.
- Lacelle, D., Doucet, A., Clark, I.D., Lauriol, B., 2007. Acid drainage generation and seasonal recycling in
 disturbed permafrost near Eagle Plains, northern Yukon Territory, Canada. Chemical Geology 243,
- 885 157-177.

- Lacelle, D., Fontaine, M., Forest, A.P., Kokelj, S.V., 2014. High-resolution stable water isotopes as tracers
 of thaw unconformities in permafrost: A case study from western Arctic Canada. Chemical Geology
 368, 85-96.
- Lacelle, D., Juneau, V., Pellerin, A., Lauriol, B., Clark, I.D., 2008. Weathering regime and geochemical
 conditions in a polar desert environment, Haughton impact structure region, Devon Island, Canada.
- 891 Canadian Journal of Earth Sciences 45, 1139-1157.
- Lafrenière, M.J., Lamoureux, S.F., 2013. Thermal perturbation and rainfall runoff have greater impact on
 seasonal solute. Permafrost and Periglacial Processes 24, 241-251.
- Lambiel, C., Pieracci, K., 2008. Permafrost distribution in talus slopes located within the alpine periglacial
 belt, Swiss Alps. Permafrost and Periglacial Processes 19, 293-304.
- Lamhonwah, D., Lafrenière, M.J., Lamoureux, S.F., Wolfe, B.B., 2017. Evaluating the hydrological and
 hydrochemical responses of a High Arctic catchment during an exceptionally warm summer.
 Hydrological Processes 31(12), 2296-2313.
- Lecomte, K.L., Milana, J.P., Formica, S.M., Depetris, P.J., 2008. Hydrochemical appraisal of ice- and rockglacier meltwater in the hyperarid Agua Negra drainage basin, Andes of Argentina. Hydrological
 Processes 22, 2180-2195.
- Leibman, M.O., Streletskaya, I.D., 1997. Landslide induced changes in the chemical composition of
 active-layer soils and surface-water runoff, Yamal Peninsula, Russia. Proceedings of the International
 Symposium on Physics, Chemistry and Ecology of Seasonally Frozen Soils, 120-126.
- 905 Levy, J.S., Fountain, A.G., Gooseff, M.N., Welch, K.A., Lyons, W.B., 2011. Water tracks and permafrost in
- 906 Taylor Valley, Antarctica: Extensive and shallow groundwater connectivity in a cold desert ecosystem.
- 907 Geological Society of America Bulletin 123 (11-12), 2295-2311.
- Levy, J.S., Fountain, A.G., Welch, K.A., Berry Lyons, W., 2012. Hypersaline "wet patches" in Taylor
 Valley, Antarctica. Geophysical Research Letters 39, L05402 (doi:10.1029/2012GL050898).
- 910 Ley, R.E., Williams, M.W., Schmidt, S.K., 2004. Microbial population dynamics in an extreme environment:
- 911 controlling factors in talus soils at 3,750 m in the Colorado Rocky Mountains. Biogeochemistry 68 (3),
- 912 313-335.

- Lewis, T., Lafrenière, M.J., and Lamoureux, S.F., 2012. Hydrochemical and sedimentary responses of
 paired High Arctic watersheds to unusual climate and permafrost disturbance, Cape Bounty, Melville
 Island, Canada. Hydrological Processes 26 (13), 2003-2018.
- Liljedahl, A.K. Boike, J., Daanen, R.P., Fedorov, A.N., Frost, G.V., Grosse, G., Hinzman, L.D., Iijma, Y.,
 Jorgenson, J.C., Matveyeva, N., Necsoiu, M., Raynolds, M.K., Romanovsky, V.E. Schulla, J., Tape,
 K.D., Walker, D.A., Wilson, C.J., Yabuki, H., Zona, D., 2016. Pan-Arctic ice-wedge degradation in
 warming permafrost and its influence on tundra hydrology. Nature Geoscience 9,
 (doi:10.1038/NGEO2674).
- Loiko, S.V., Pokrovsky, O.S., Raudina, T.V., Lim, A., Kolesnichenko, L.G., Shirokova, L.S., Vorobyev,
 S.N., Kirpotin, S.N., 2017. Abrupt permafrost collapse enhances organic carbon, CO₂, nutrient and
 metal release into surface waters. Chemical Geology 471, 153-165.
- Louiseize, N.L., Lafrenière, M.J., Hastings, M.G., 2014. Stable isotopic evidence of enhanced export of
 microbially derived NO3- following active layer slope disturbance in the Canadian High Arctic.
 Biogeochemistry 121, 565-580.
- Luo, D., Wu, Q., Jin, H., Marchenko, S.S., Lü, L., Gao, S., 2016. Recent changes in the active layer
 thickness across the northern hemisphere. Environmental Earth Sciences 75:555 (doi:10.1007/s12665015-5229-2).
- MacLean, R., Oswood, M.W., Irons, J.S., McDowell, W.H., 1999. The effect of permafrost on stream
 biogeochemistry: A case study of two streams in the Alaskan (U.S.A.) taiga. Biogeochemistry 47, 239267.
- MacMillan, G.A., Girard, C., Chételat, J., Laurion, I., Amyot, M., 2015. High methylmercury in Arctic and
 subarctic ponds is related to nutrient levels in the warming eastern Canadian Arctic. Environmental
 Science & Technology 49, 7743-7753.
- Malone, L., Lacelle, D., Kokelj, S., Clark, I.D., 2013. Impacts of hillslope thaw slumps on the geochemistry
 of permafrost catchments (Stony Creek watershed, NWT, Canada). Chemical Geology 356, 38-49.
- 938 Manasypov, R.M., Pokrovsky, O.S., Kirpotin, S.N., Shirokova, L.S., 2014. Thermokarst lake water across
- 939 the permafrost zones of western Siberia. The Cryosphere 8, 1177-1193.

Manasypov, R.M., Vorobyev, S.N., Loiko, S.V., Kritzkov, I.V., Shirokova, L.S., Shevchenko, V.P., Kirpotin,
S.N., Kulizhsky, S.P., Kolesnichenko, L.G., Zemtzov, V.A., Sinkinov, V.V., Pokrovsky, O.S., 2015.
Seasonal dynamics of organic carbon and metals in thermokarst lakes from the discontinuous
permafrost zone of western Siberia. Biogeosciences 12, 3009-3028.

- Mast, M.A., Turk, J.T., Clow, D.W., Campbell, D.H., 2011. Response of lake chemistry to changes in
 atmospheric deposition and climate in three high-elevation wilderness areas of Colorado.
 Biogeochemistry 103 (1-3), 27-43.
- Mavromatis, V. Prokushkin, A.S., Pokrovsky, O.S., Viers, J., Korets, M.A., 2014. Magnesium isotopes in
 permafrost-dominated Central Siberian larch forest watersheds. Geochimica et Cosmochimica Acta
 147, 76-89.
- Mavromatis, V., Rinder, T., Prokushkin, A.S., Pokrovsky, O.S., Korets, M.A., Chmeleff, J., Oelkers, E.H.,
 2016. The effect of permafrost, vegetation, and lithology on Mg and Si isotope composition of the
 Yenisey River and its tributaries at the end of the spring flood. Geochimica et Cosmochimica Acta 191,
 32-46.
- McClelland, J.W., Stieglitz, M., Pan, F., Holmes, R.M., Peterson, B.J., 2007. Recent changes in nitrate
 and dissolved organic carbon export from the upper Kuparuk River, North Slope, Alaska. Journal of
 Geophysical Research 112: G04S60 (doi:10.1029/2006JG000371).
- McNamara, J.P., Kane, D.L., Hinzman, L.D., 1997. Hydrograph separations in an Arctic watershed using
 mixing model and graphical techniques. Water Resources Research 33 (7), 1707-1719.
- Millar, C.I., Westfall, R.D., Delany, D.L., 2013. Thermal and hydrologic attributes of rock glaciers and
 periglacial talus landforms: Sierra Nevada, California, USA. Quaternary International 310, 169-180.
- Muller, S.W., 1943. Permafrost or permanently frozen ground and related engineering problems. U.S.
 Engineers Office, Strategic Engineering Study, Special Report No. 62.
- 963 Nelson, F.E., Anisimov, O.A., Shiklomanov, N.I., 2001. Brief communication: Subsidence risk from
 964 thawing permafrost. Nature 410, 889-890.
- 965 Nelson, F.E., Anisimov, O.A., Shiklomanov, N.I., 2002. Climate change and hazard zonation in the circum-
- 966 Arctic permafrost regions. Natural Hazards 26, 203-225.

- Nordstrom, D.K., 2011. Hydrogeochemical processes governing the origin, transport and fate of major and
 trace elements from mine wastes and mineralized rock to surface waters. Applied Geochemistry 26,
 1777-1791.
- 970 Oelke, C., Zhang, T.J., Serreze, M.C., 2004. Modeling evidence for recent warming of the Arctic soil
 971 thermal regime. Geophysical Research Letters 31, L07208 (doi: 10.1029/2003GL019300).
- 972 Parham, L.M., Prokushkin, A.S., Pokrovsky, O.S., Titov, S.V., Grekova, E., Shirokova, L.S., McDowell,
- W.H., 2013. Permafrost and fire as regulators of stream chemistry in basins of the Central Siberian
 Plateau. Biogeochemistry 116, 55-68.
- 975 PERMOS, 2016. Permafrost in Switzerland 2010/2011 to 2013/2014. Noetzli, J., Luethi, R., and Staub, B.
- 976 (Eds.), Glaciological Report (Permafrost) No. 12-15 of the Cryospheric Commission of the Swiss977 Academy of Sciences.
- Petrone, K.C., Hinzman, L.D., Shibata, H., Jones, J.B., Boone, R.D., 2007. The influence of fire and
 permafrost on sub-arctic stream chemistry during storms. Hydrological Processes 21 (4), 423-434.
- Petrone, K.C., Jones, J.B., Hinzman, L.D., Boone, R.D., 2006. Seasonal export of carbon, nitrogen, and
 major solutes from Alaskan catchments with discontinuous permafrost. Journal of Geophysical
 Resources 111, G02020 (doi:10.1029/2005JG000055).
- Pokrovsky, O.S., Manasypov, R.M., Loiko, S.V., Krickov, I.A., Kopysov, S.G., Kolesnichenko, L.G.,
 Vorobyev, S.N., Kirpotin, S.N., 2016. Trace element transport in western Siberian rivers across a
 permafrost gradient. Biogeosciences 13, 1877-1900.
- Pokrovsky, O.S., Manasypov, R.M., Loiko, S.V., Shirokova, L.S., Krickov, I.A., Pokrovsky, B.G.,
 Kolesnichenko, L.G., Kopysov, S.G., Zemtzov, V.A., Kulizhsky, S.P., Vorobyev, S.N., Kirpotin, S.N.,
 2015. Permafrost coverage, watershed area and season control of dissolved carbon and major
 elements in western Siberian rivers. Biogeosciences 12 (21), 6301-6320.
- Pokrovsky, O.S., Reynolds, B.C., Prokushkin, A.S, Schott, J., Viers, J., 2013. Silicon isotope variations in
 Central Siberian rivers during basalt weathering in permafrost-dominated larch forests. Chemical
 Geology 355, 103-116.

- Pokrovsky, O.S., Shirokova, L.S., Kirpotin, S.N., Audry, S., Viers, J., Dupré, B., 2011. Effect of permafrost
 thawing on organic carbon and trace element colloidal speciation in the thermokarst lakes of western
 Siberia. Biogeosciences 8, 565-583.
- Pokrovsky, O.S., Shirokova, L.S., Kirpotin, S.N., Kulizhsky, S.P., Vorobiev, S.N., 2013. Impact of western
 Siberia heatwave 2012 on greenhouse gases and trace metal concentration in thaw lakes of
 discontinuous permafrost zone. Biogeosciences 10, 5349-5365.
- Pokrovsky, O.S., Viers, J., Shirokova, L.S., Shevchenko, V.P., Filipov, A.S., Dupré, B., 2010. Dissolved,
 suspended, and colloidal fluxes of organic carbon, major and trace elements in the Severnaya Dvina
 River and its tributary. Chemical Geology 273, 136-149.
- Polishchuk, Y.M., Bogdanov, A.N., Polishchuk, V.Y., Manasypov, R.M., Shirokova, L.S., Kirpotin, S.N.,
 Pokrovsky, O.S., 2017. Size Distribution, Surface Coverage, Water, Carbon, and Metal Storage of
 Thermokarst Lakes in the Permafrost Zone of the Western Siberia Lowland. Water 9, 228,
 doi:10.3390/w9030228.
- Rangecroft, S., Harrison, S., Anderson, K., 2015. Rock glaciers as water stores in the Bolivian Andes: an
 assessment of their hydrological importance. Arctic, Antarctic, and Alpine Research 47(1), 89-98.
- Rangecroft, S., Harrison, S., Anderson, K., Magrath, J., Castel, A.P., Pacheco, P., 2013. Climate change
 and water resources in arid mountains: An Example from the Bolivian Andes. Ambio 42, 852-863.
- 1010 Raudina, T.V., Loiko, S.V., Lim, A.G., Krickov, I.V., Shirokova, L.S., Istigechev, G.I., Kuzmina, D.M.,
- 1011 Kulizhsky, S.P., Vorobyev, S.N., Pokrovsky, O.S., 2017. Dissolved organic carbon and major and trace
- elements in peat porewater of sporadic, discontinuous, and continuous permafrost zones of westernSiberia. Biogeosciences 14, 3561-3584.
- 1014 Rember, R., Trefry, J., 2004. Increased concentrations of dissolved trace metals and organic carbon 1015 during snowmelt in rivers of the Alaskan arctic. Geochimica et Cosmochimica Acta 68, 477-489.
- 1016 Roberts, K.E., Lamoureux, S.F., Kyser, T.K., Muir, D.C.G., Lafrenière, M.J., Iqaluk, D., Pieńkowski, A.J.,
- 1017 Normandeau, A., 2017. Climate and permafrost effects on the chemistry and ecosystems of High Arctic
 1018 Lakes. Scientific Reports 7, 13292 (doi:10.1038/s41598-017-13658-9).
- 1019 Roer, I., Kääb, A., Dikau, R., 2005. Rock glacier acceleration in the Turtmann valley (Swiss Alps):
- 1020 Probable controls. Norsk Geografisk Tidsskrift 59, 157-163.

- Rogger, M., Chirico, G.B., Hausmann, H., Krainer, K., Brückl, E., Stadler, P., Blöschl, G., 2017. Impact of
 mountain permafrost on flow path and runoff response in a high alpine catchment. Water Resources
 Research 53(2), 1288-1308.
- 1024 Rowland, J.C. Jones, C.E., Altmann, G., Bryan, R., Crosby, B.T., Hinzman, L.D., Kane, D.L., Lawrence,
- 1025 D.M., Mancino, A., Marsh, P., McNamara, J.P., Romanovsky, V.E., Toniolo, H., Travis, B.J., Trochim,
- 1026 E., Wilson, C.J., Geernaert, G.L., 2010. Arctic landscapes in transition: responses to thawing 1027 permafrost. Eos 91 (26), 229-230.
- Rudy, A.C.A., Lamoureux, S.F., Kokelj, S.V., Smith, I.R., England, J.H., 2017. Accelerating thermokarst
 transforms ice-cored terrain triggering a downstream cascade to the ocean. Geophysical Research
 Letters, doi:10.1002/2017GL074912.
- 1031 Rühland, K.M., Smol, J.P., Wang, X., Muir, D.C.G., 2003. Limnological characteristics of 56 lakes in the 1032 Central Canadian Arctic Treeline Region. Journal of Limnology 62 (1), 9-27.
- Rydberg, J., Klaminder, J., Rosén, P., Bindler, R., 2010. Climate driven release of carbon and mercury
 from permafrost mires increases mercury loading to sub-arctic lakes. Science of the Total Environment
 408, 4778-4783.
- Salerno, F., Rogora, M., Balestrini, R., Lami, A., Tartari, G.A., Thakuri, S., Tartari, G., 2016. Glacier
 melting increases the solute concentrations of Himalayan glacial lakes. Environmental Science &
 Technology 50(17): 9150-9160.
- Sass, O., 2006. Determination of the internal structure of alpine talus deposits using different geophysical
 methods (Lechtaler Alps, Austria). Geomorphology 80, 45-58.
- 1041 Scapozza, C., Lambiel, C., Baron, L, Marescot, L., Reynard, E., 2011. Internal structure and permafrost 1042 distribution in two alpine periglacial talus slopes, Valais, Swiss Alps. Geomorphology 132(34), 208-221.
- Scapozza, C., Lambiel, C., Bozzini, C., Mari, S., Conedera, M., 2014. Assessing the rock glacier
 kinematics on three different timescales: a case study from the southern Swiss Alps. Earth Surface
 Processes & Landforms 39, 2056-2069.
- Schmid, M.O., Baral, P., Gruber, S., Shahi, S., Shrestha, T., Stumm, D., Wester, P., 2015. Assessment of
 permafrost distribution maps in the Hindu Kush Himalayan region using rock glaciers mapped in
 Google Earth. The Cryosphere 9, 2089-2099.

- 1049 Schuur, E.A.G., McGuire, A.D., Schädel, C., Grosse, G., Harden, J.W., Hayes, D.J., Hugelius, G., Koven,
- 1050 C.D., Kuhry, P., Lawrence, D.M., Natali, S.M., Olefeldt, D., Romanovsky, V.E., Schaefer, K., Turetsky,
- M.R., Treat, C.C., Vonk, J.E., 2015. Climate change and the permafrost carbon feedback. Nature 520,
 1052 171-179.
- Sharkhuu, N., 1998. Trends of permafrost development in the Selenge River Basin, Mongolia.
 Proceedings of the 7th International Conference on Permafrost, 979-985.
- Shirokova, L.S., Pokrovsky, O.S., Kirpotin, S.N., Desmukh, C., Pokrovsky, B.G., Audry, S., Viers, J., 2013.
 Biogeochemistry of organic carbon, CO2, CH4, and trace elements in thermokarst water bodies in
 discontinuous permafrost zones of Western Siberia. Biogeochemistry 113, 573-593.
- St-Jacques, J.M., Sauchyn, D.J., 2009. Increasing winter baseflow and mean annual streamflow from
 possible permafrost thawing in the Northwest Territories, Canada. Geophysical Research Letters 36,
 L01401 (doi:10.1029/2008GL035822).
- 1061 Stottlemyer, R., 2001. Biogeochemistry of a treeline watershed, northwestern Alaska. Journal of 1062 Environmental Quality 30 (6), 1990-1998.
- Streletskiy, D.A., Shiklomanov, N.I., Nelson, F.I., 2012. Permafrost, infrastructure and climate change: A
 GIS based landscape approach to geotechnical modeling. Arctic, Antarctic and Alpine Research 44(3),
 368-380.
- Striegl, R.G., Aiken, G.R., Dornblaser, M.M., Raymond, P.A., Wickland, K.P., 2005. A decrease in
 discharge-normalized DOC export by the Yukon River during summer through autumn. Geophysical
 Research Letters 32, L21413 (doi:10.1029/2005GL024413).
- 1069 Szopińska, M., Szumińska, D., Polkowska, Z., Machowiak, K., Lehmann, S., Chmiel, S., 2016. The 1070 chemistry of river-lake systems in the context of permafrost occurrence (Mongolia, Valley of the
- Lakes). Part I. Analysis of ion and trace metal concentrations. Sedimentary Geology 340, 74-83.
- 1072 Tank, S.E., Frey, K.E., Striegl, R.G., Raymond, P.A., Holmes, R.M., McClelland, J.W., Peterson, B.J.,
- 1073 2012. Landscape-level controls on dissolved carbon flux from diverse catchments of the circumboreal.
- 1074 Global Biogeochemical Cycles 26, GB0E02 (doi:10.1029/2012GB004299).

- 1075 Tank, S.E., Striegl, R.G., Frey, K.E., McClelland, J.W., Kokelj, S.V., 2016. Multi-decadal increases in
 1076 dissolved organic carbon and alkalinity flux from the Mackenzie drainage basin to the Arctic Ocean.
 1077 Environmental Research Letters 11 (5), 1-10.
- 1078 Thies, H., Nickus, U., Tessadri, R., Psenner, R., 2007. Unexpected response of high Alpine Lake water to 1079 climate warming. Environmental Science & Technology 41, 7424-7429.
- Thies, H., Nickus, U., Tolotti, M., Tessadri, R., Krainer, K. 2013. Evidence of rock glacier melt impacts on
 water chemistry and diatoms in high mountain streams. Cold Regions Science and Technology 96, 77 85.
- Thompson, M.S., Wrona, F.J., Prowse, T.D., 2012. Shifts in plankton, nutrient and light relationships in
 small tundra lakes caused by localized permafrost thaw. Arctic 65, 367-376.
- Todd, A.S., Manning, A-H., Verplanck, P.L., Crouch, C., McKnight, D.M., Dunham, R., 2012. Climate change-driven deterioration of water quality in a mineralized watershed. Environmental Science &
 Technology 46 (17), 9324-9332.
- Toohey, R.C., Herman-Mercer, N.M., Schuster, P.F., Mutter, E., Koch, J.C., 2016. Multi-decadal increases
 in the Yukon River Basin of chemical fluxes as indicators of changing flowpaths, groundwater, and
 permafrost. Geophysical Research Letters, (doi:10.1002/2016GL070817).
- 1091 Vieira, G., Bockheim, J., Guglielmin, M., Balks, M., Abramov, A.A., Boelhouwers, J., Cannone, N.,
- 1092 Ganzert, L., Gilichinsky, D., Goryachkin, S., López-Martínez, J., Meiklejohn, I., Raffi, R., Ramos, M.,
- 1093 Schaefer, C., Serrano, E., Simas, F., Sletten, R., Wagner, D., 2010. Thermal state of permafrost and
- active-layer monitoring in the Antarctic: advances during the International Polar Year 2007-2008.
 Permafrost and Periglacial Processes 21, 182-197.
- 1096 Vonk, J.E., Tank, S.E., Bowden, W.B., Laurion, I., Vincent, W.F., Alekseychik, P., Amyot, M., Billet, M.F.,
- 1097 Canário, J., Cory, R.M., Deshpande, B.N., Helbig, M., Jammet, M., Karlsson, J., Larouche, J.,
- 1098 MacMillan, G., Rautio, M., Walter Anthony, K.M., Wickland, K.P., 2015. Reviews and syntheses:
- 1099 Effects of permafrost thaw on Arctic aquatic ecosystems. Biogeosciences 12, 7129-7167.
- 1100 Voss, B.M., Peucker-Ehrenbrink, B., Eglinton, T.I., Spencer, R.G.M., Bulygina, E., Galy, V., Lamborg,
- 1101 C.H., Ganguli, P. M., Montluçon, D.B., Marsh, S., Gillies, S.L., Fanslau, J., Epp, A., Luymes, R., 2015.

- 1102 Seasonal hydrology drives rapid shifts in the flux and composition of dissolved and particulate organic 1103 carbon and major and trace ions in the Fraser River, Canada. Biogeosciences 12, 5597-5618.
- Walter Anthony, K.M., Zimov, S.A., Chanton, J.P., Verbyla, D., Chapin, F.S., 2006. Methane bubbling from
 Siberian thaw lakes as a positive feedback to climate warming. Nature 443, 71-75.
- Walvoord, M.A., Kurylyk, B.L., 2016. Hydrologic impacts of thawing permafrost-A review. Vadose Zone
 Journal 15(6) (doi:10.2136/vzi2016.01.0010).
- Walvoord, M., Striegl, R., 2007. Increased groundwater to stream discharge from permafrost thawing in
 the Yukon river basin: Potential impacts on lateral export of carbon and nitrogen. Geophysical
 Research Letters 34, L12402 (doi:10.1029/2007GL030216).
- Watanabe, S., Laurion, I., Chokmani, K., Pienitz, R., Vincent, W.F., 2011. Optical diversity of thaw ponds
 in discontinuous permafrost: A model system for water color analysis. Journal of Geophysical
 Research 116, G02003 (doi:10.1029/2010JG001380).
- Williams, M.W., Knauf, M., Caine, M., Liu, F., Verplanck, P.L., 2006. Geochemistry and source water of
 rock glacier outflow, Colorado Front Range. Permafrost and Periglacial Processes 17, 13-33.
- Williams, M.W., Knauf, M., Cory, R., Caine, N., Liu, N., 2007. Nitrate content and potential microbial
 signature of rock glacier outflow, Colorado Front Range. Earth Surface Processes and Landforms 32,
 1032-1047.
- Williams, P.J., Smith, M.W., 1989. The frozen earth. Fundamentals of geocryology. Cambridge University
 Press, Cambridge.
- 1121 Woo, M., (2012). Permafrost hydrology. Springer-Verlag Berlin Heidelberg.
- Wu, J.C., Sheng, Y., Wu, Q.B., Wen, Z., 2010. Processes and modes of permafrost degradation on theQinghai-Tibet Plateau. Science in China 53 (1), 150-158.
- 1124 Wu, Q., Zhang, T., Liu, Y., 2012. Thermal state of the active layer and permafrost along the Qinghai-1125 Xizang (Tibet) railway from 2006 to 2010. Cryosphere 6 (3), 607-612.
- Yang, Y., Wu, Q., Hou, Y., Zhang, Z., Zhan, J., Gao, S., Jin, H., 2017. Unravelling of permafrost
 hydrological variabilities on Central Qinghai-Tibet Plateau using stable isotopic technique. Science of
- 1128 the Total Environment 605-606: 199-210.

- Zhang, T., Barry, R.G., Knowles, K., Heginbottom, J.A., Brown, J., 1999. Statistics and characteristics of
 permafrost and ground-ice distribution in the Northern Hemisphere. Polar Geography 23, 132-154.
- 1131 Zhang, T., Barry, R.G., Knowles, K., Ling, F., Armstrong, R.L., 2003. Distribution of seasonally and
- perennially frozen ground in the Northern Hemisphere. Proceedings of the 8th International Conference
- 1133 on Permafrost, 1289-1294.



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Figure 1 - TIS (total inorganic solutes, defined as sum of Ca²⁺, K⁺, Mg²⁺, Na⁺, Si, Cl⁻, SO₄²⁻ and HCO₃⁻) as a function of latitude. Permafrost limit is approximately located at 61°N (from Frey et al., 2007a).



Figure 2 - Annual flux increases in the Yukon River with Thiel-Sen trend lines (adapted from Toohey et al.,2016).





Figure 3 - Percentage of catchment area influenced by thermokarst disturbance (slumping) and specific conductivity (as index of total solute concentrations, mainly represented by Ca²⁺, Mg²⁺, and SO₄²⁻) of lake water, upland lakes, Mackenzie Delta region. The (*) indicates the mean specific conductivity of the 11 pristine lakes measured by Kokelj et al. (2005). The (-) indicates maximum and minimum values for pristine lakes (from Kokelj et al., 2005).



Figure 4 - Electrical conductivity, sulphate, calcium and magnesium concentrations in lake water of Rasass See (black triangles) and Schwarzsee ob Sölden (open circles) lakes (1985-2005). Values for each lake represent mean values of four to seven discrete samples along the lake vertical profile taken during holomixis. Variability among single values is <5 %. Horizontal lines show break in vertical scale (adapted from Thies et al., 2007).



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Figure 5 - a) Time series of nitrate in surface water of the Green Lakes Valley, for 2003. Arik is Arikaree Glacier outflow; GL5 is the outlet of Green Lakes 5; Mart is the outlet of the Martinelli catchment; RG5 is the Green Lake 5 rock glacier outflow; talus is the blockfield site (for site details refer to Williams et al., 2007). b) Time series of nitrate concentrations in the outflow of RG5 during the snow-free season from 1998 to 2004. c) Comparison of nitrate concentrations from the outflow of 7 rock glaciers and co-located surface waters, August 2003 (adapted from Williams et al., 2007).



Figure 6 - Trends in September dissolved Zn (a) and Mn (b) concentrations (µg/L) in the Upper Snake River. Different colours represent different data sources (further details in Todd et al., 2012). p-values were computed using the Mann-Kendall Test, and lines shown are Kendall-Theil lines (adapted from Todd et al., 2012).





Figure 7 - Iron (<0.45 μ m) concentration as a function of water body surface area in depressions, ponds and lakes. Uncertainties (±2 σ) are the same or smaller than symbol sizes (from Shirokova et al., 2013).

Author	Year	Study area	Permafrost configuration	Analytes
Bagard et al.	2013	Central Siberia - Russia	PD	М
Caine	2010	Colorado Rocky Mountains - USA	PD	Μ
Douglas et al.	2013	Chena River - Álaska	PD	Μ
Frey et al.	2007a 2007b	Western Siberia - Russia	PD	Μ
Giaslar at al	2007.0	Sub-Arctic - Sweden	חס	M
Harms and Jones	2014	Caribou Poker Creeks Research	PD	M
	2012	Watershed, Upper Kuparuk River Basin - Alaska	. 2	
Harris et al.	2007	McMurdo Dry Valleys - Antarctica	PD	Μ
Hobbie et al.	1999	MilkyWay stream - Alaska	PD	Μ
Jones et al.	2005	Caribou Poker Creeks Research Watershed - Alaska	PD	Μ
Keller et al.	2007	Brooks Range - Alaska	PD	Μ
Koch et al	2010	Richardson Catchment - Alaska	PD	М
Kolosov et al	2015	Central Siberian Plateau - Russia		M
L afrenière and	2010	Melville Island - Canada	PD	M
Lamoureux	2013			
Lamhonwah et al.	2017	Melville Island - Canada	PD	M
Levy et al.	2011	McMurdo Dry Valleys - Antarctica	PD	M
Lewis et al.	2012	Melville Island - Canada	PD	M
MacLean et al.	1999	Caribou-Poker Creeks Research Watershed - Alaska	PD	М
Mast et al.	2011	Colorado Rocky Mountains - USA	PD	Μ
Mavromatis et al.	2014	Central Siberia - Russia	PD	Μ
	2016	Yenisey River - Russia		
McClelland et al.	2007	Upper Kuparuk River - Alaska	PD	Μ
Parham et al.	2013	Central Siberia - Russia	PD	Μ
Petrone et al.	2006	Caribou-Poker Creeks Research	PD	Μ
Dekroveky et el	2007	Control Siboria Bussia	חס	Ν.4
POKIOVSKY EL al.	2013	Western Siberia - Russia	FD	IVI
Poharts at al	2015	Melville Island - Canada	חס	N/L
Rübland at al	2017	Control Conadian sub Arctic		N/
Stottlemver	2003	Nostak National Preserve - Alaska		N/
Stried et al	2001	Yukon River basin - Alaska	PD	M
Striegi et al. Szonińska ot al	2005	Central Mongolia		M
Tank of al	2010	Siberia - Russia, Vukon - Alaska		M
	2012	Mackenzie - Canada	ΓD	IVI
Todd et al.	2012	Colorado Rocky Mountains - USA	PD	M / T
Dugan et al.	2012	Melville Island - Canada	PD / TK	Μ
Baron et al.	2009	Colorado Rocky Mountains - USA	PD / RG	Μ
Abbott et al.	2015	Brooks Range - Alaska	ТК	Μ
Bowden et al.	2008	Brooks Range - Alaska	ТК	Μ
Gooseff et al.	2016	McMurdo Dry Valleys -Antarctica	ТК	Μ
Harms et al.	2014	Brooks Range - Alaska	ТК	Μ
Kokelj and Lewkowicz	1999	Ellesmere Island - Canada	ТК	Μ
Kokelj et al. Kokelj et al.	2005 2009	Northwest Territories - Canada Mackenzie Delta - Canada	ТК	Μ

Kokelj et al.	2013	Peel Plateau, Mackenzie Mountains - Canada		
Loiko et al.	2017	Western Siberia - Russia	ТК	M / T
Louiseize et al.	2014	Melville Island - Canada	ТК	Μ
Malone et al.	2013	Northwest Territories - Canada	ТК	Μ
Rudy et al.	2017	Banks Island - Canada	TK	М
Thompson et al.	2012	Mackenzie Delta uplands - Canada	ТК	М
Barnes et al.	2014	Colorado Rocky Mountains - USA	RG	Μ
Berger et al.	2004	Central Eastern Alps - Austria	RG	Μ
Fegel et al.	2016	Cascade Mountains, Rocky Mountains, Sierra Nevada - USA	RG	М
Giardino et al.	1992	San Juan Mountains of Colorado - USA	RG	М
Krainer and Mostler	2002	Central Eastern Alps - Austria	RG	Μ
Krainer et al	2007	Central Eastern Alps - Austria	RG	Μ
Lecomte et al.	2008	Agua Negra river basin - Andes of Argentina	RG	Μ
Thies et al.	2007	Central Eastern Alps - Austria, Italy	RG	M/T
	2013	Central Eastern Alps - Austria		
Williams et al.	2006	Colorado Front Range - USA	RG	Μ
	2007	-		
Bagard et al.	2011	Central Siberia - Russia	PD	Т
Barker et al.	2014	Brooks Range - Alaska	PD	Т
Hirst et al.	2017	Lena River Basin - Russia	PD	Т
Lacelle et al.	2007	Northern Yukon Territory - Canada	PD	Т
Pokrovsky et al.	2016	Western Siberia - Russia	PD	Т
Raudina et al.	2017	Western Siberia - Russia	PD	Т
Audry et al.	2011	Western Siberia - Russia	ТК	Т
Deison et al.	2012	Mackenzie Delta - Canada	TK	Т
Gordon et al.	2016	Northwest Territories - Canada	ТК	Т
Klaminder et al.	2008 2010	Sub-Arctic - Sweden	ТК	Т
MacMillan et al.	2015	Sub-arctic, high-Arctic - Canada	ТК	Т
Manasypov et al.	2014	Western Siberia - Russia	ТК	Т
	2015			
Pokrovsky et al.	2011	Western Siberia - Russia	TK	Т
	2013			
Polishchuk et al.	2017	Western Siberia - Russia	TK	Т
Rydberg et al.	2010	Sub-Arctic - Sweden	TK	Т
Shirokova et al.	2013	Western Siberia - Russia	ТК	Т
llyashuk et al.	2014	Central Eastern Alps - Italy	RG	Т
	2017			
Krainer	2014	Central Eastern Alps - Austria, Italy	RG	Т
Krainer et al.	2011	Central Eastern Alps - Italy	RG	Т

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Table 1 - Selected papers reporting information on the impacts of permafrost degradation on inorganic
chemistry of surface fresh water globally. PD: Pervasive permafrost degradation, TK: Thermokarst, RG:
Rock-glacier thawing, M: Major ions, T: Trace elements.