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Organic and organo-mineral colloids in discontinuous permafrost zone

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Abstract

On-going permafrost thaw in discontinuous permafrost regions produces significant amounts of small permafrost subsidence and depressions, while large lakes are likely to drain into streams and rivers. The intensification of permafrost thaw may alter the size distribution and chemical composition of organo-Fe–Al colloids in lakes and rivers. We used a continuum of surface water bodies, from permafrost subsidence, small depressions and thaw ponds to large lakes and rivers that drain the Western Siberia Lowland (WSL), to assess OC, major and the trace element size distribution between the 20-μm, 5-μm, 1.2-μm, 0.45-μm, 0.22-μm, 0.025-μm and 1-kDa (~1.4 nm) size fractions. This approach allowed us to distinguish the organic and organo-ferric colloids that were responsible for the transport of trace elements in surface waters and address their evolution during possible physico-chemical and biological processes. Both conventionally dissolved (<0.22 μm) and low-molecular-weight (<1 kDa) fractions exhibited an order of magnitude decrease in DOC/Fe in the landscape continuum "depressions and permafrost subsidence → thaw ponds → thermokarst lakes → streams → rivers". Thermodynamic modeling and on-site size separation suggested that a number of trace elements (TEs), including alkaline earth elements and several micronutrients (Zn, Ba, Mn, and Ni), decreased the degree of their binding to DOM along the landscape continuum, whereas the majority of insoluble TEs (Al, Fe, Co, Cd, Cu, Pb, REEs, Th, and U) remained complexed with DOM in the $LMW_{<1\ kDa}$ fraction. Two primary sites of colloid generation included (i) ground vegetation and peat leaching, which supplied DOM complexes of divalent metals and organo-Al entities to thaw ponds and lakes; and (ii) Fe^{2+} oxidation and TE co-precipitation with Fe hydroxides in the presence of surface DOM at groundwater discharge sites within the riparian/hyporheic zones of rivers. Under a warming climate scenario, an increase in the thickness of the thawing depth will intensify the input of inorganic components from deep mineral horizons and possibly underground waters thus producing the enrichment of large lakes in Fe-rich colloids and particles. The speciation of divalent metal micronutrients (Cu, Ni, and Co) and toxic metals (Al, Cd, Pb, and U) that are complexed within DOM will most likely remain conservative. Overall, the WSL's surface water colloidal composition may shift from DOM-rich and DOM-Al-rich to Fe-rich, and the export of low-soluble trivalent and tetravalent hydrolysates from the soil to rivers will increase.

Keywords: peat; thaw; ponds; lakes; trace elements; metals; organic carbon

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1. INTRODUCTION

In contrast to the relatively good understanding of surface water colloid speciation and size fractionation in boreal and subarctic non-permafrost regions (Ingri et al., 2000, 2006; Andersson et al., 2001, 2006; Gundersen and Steinnes, 2003; Dahlqvist et al., 2004, 2007; Vasyukova et al., 2010; Pokrovsky et al., 2014b), knowledge concerning the colloidal distribution and transport within soil waters, rivers and lakes in permafrost regions has remained notably limited (Guo et al., 2003; Stolpe et al., 2013a,b). The evolution of landscapes in discontinuous permafrost zones, which are the most vulnerable to on-going climate warming, follows the continuum "permafrost subsidence and depression → thaw ponds → small lakes → large lakes → lake drainage to small streams → large rivers" (Kirpotin et al., 2009a,b, 2011) and exhibits two main tendencies: (i) the appearance of many new small permafrost subsidence events and depressions, which form young thaw ponds (<200 m^2, Polishchuk et al., 2014, 2015); and (ii) the disappearance of large lakes (Smith et al., 2005; Pokrovsky et al., 2014a,b) because of drainage into hydrological networks (Kirpotin et al., 2011). Changes in the colloidal status of DOM and trace metals among three contrasting surface water reservoirs that represent the hydrological continuum of discontinuous permafrost zones, namely, depressions, lakes and rivers, remains totally unknown within the framework of this evolution. The degree of the connection of surface waters to underground reservoirs may change during permafrost thawing. Thus, the relative contribution of dissolved organic matter and mineral (Fe and Al) fractions to the overall colloidal composition may also be affected to an unknown degree.

A specific feature of the huge territory of the western Siberia peatlands (close to 2 million km^2 including the northern Siberian lowland) is the relatively low concentration of inorganic salts in all surface waters, including rivers (total dissolved solids, TDS, is <50 mg/L), which stems from the dominance of organic (peat) rather than mineral (clay and sand) soil substrates. This feature is especially prominent in permafrost-bearing zones, where the maximal active layer depth is lower than the peat thickness (Baulin et al., 1967; Tyrtikov, 1973, 1979; Baulin, 1985; Khrenov, 2011). Both low TDS and high DOC from peat leaching can enhance colloidal stability in aqueous solutions. Thus, trace elements (TEs) such as metal micronutrients (Fe, Mn, Zn, Co, and Cu) and toxicants (Pb, Cd, Al, U...) in the low-TDS, DOC-rich surface waters of the Western Siberia Lowland are likely to be strongly influenced by colloids compared to those in other continental regions.

Despite the widely accepted definition of the colloidal fraction as 1 kDa–1 μm (Buffle and Leppard, 1995; Gustafsson and Gschwend, 1997), a significant part of the DOM is smaller than 1 kDa (Hedges et al., 1994; Amon and Benner, 1996) or even <100–500 Da (Remucal et al., 2012). Nevertheless, the colloidal transport of metal nutrients and contaminants remains an issue of high concern (Lead et al., 1997; Shiller, 2003; Bauer and Blodau, 2009; Neubauer et al., 2013a,b; Philippe and Schaumann, 2014). This problem is especially important for continental waters in northern latitudes, which contain high concentrations of DOM and experience both human impacts and climate change. Previous works in western Siberia established a first-order picture of the trace element distributions among particles (0.45 μm–5 μm), colloids (1 kDa–0.45 μm) and "truly dissolved" low molecular weight fractions ($LMW_{<1\ kDa}$) during peat abrasion and the formation of thaw ponds and thermokarst lakes in continuous permafrost zones (Pokrovsky et al., 2011) and assessed the role of thawing permafrost in the colloidal migration of trace metals in surface waters in discontinuous permafrost regions (Shirokova et al., 2013a). In the latter study, however, a continuum of different size fractions (from LMW to submicron particles >0.45 μm) was not considered; therefore, the transformation of colloids in the landscape context of interconnected water bodies from depressions to small thaw ponds, large thermokarst lakes, streams and rivers could not be assessed. The on-going intensification of the permafrost thawing in western Siberia (i.e., Anisimov et al., 2002, 2013; Zhang et al., 2005; Romanovsky et al., 2010) may shift the size distribution and chemical composition of the colloids that are responsible for the transport of metal micronutrients and toxicants from the land to the Arctic Ocean. However, neither the direction nor the magnitude of this change is currently known. Our main working hypothesis is that the colloids of thermokarst confined water bodies, located within frozen peat and isolated from mineral substrate and underground taliks, will be distinctly different from rivers of the discontinuous permafrost zone. We further expect that characterizing the geochemistry of surface waters within the natural continuum of permafrost thaw events should allow, using substitution "space for time" approach (i.e., Frey and Smith, 2005; Frey et al., 2007), to foresee possible changes of aquatic colloids in case of intensification of permafrost thaw. The present study is built on background information regarding surface fluids in discontinuous permafrost zones and new measurements from on-site size-separation techniques that cover a wide range of colloids (0.002–0.45 μm) and particles (1–20 μm) and aims to fulfill the following:

(1) Characterize the colloid and particle transformation in the landscape continuum from surface flow-fed small depressions, thaw ponds and thermokarst lakes to groundwater-fed rivers.
(2) Quantify the role of major water chemistry parameters (pH, DOC, TDS) in the colloidal status of TEs and the chemical composition of colloids and particles.

To resolving these issues, we chose to sample a discontinuous permafrost zone in August 2014, which corresponds to summer baseflow and exhibits the greatest impact from groundwater and the maximal active layer thickness. We believe that the general features of the DOM, metal transport and fractionation in the studied landscape continuum can be scaled to considerably larger frozen peatland territories in Siberia.