Mobilization of Geochemical Elements to Surface Water in the Active Layer of Permafrost in the Russian Arctic

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Abstract The predicted increase of ground temperatures in the Arctic results in the deepening of the active layer and intensification of geochemical processes. Determining the responses of riparian soil systems to surrounding hydrological flows is important for understanding seasonal changes in hydrological processes. In this study, one soil core from a polygon rim (close to the Taz River, TA) and two soil cores from a riverine terrace (close to the Syoyakha River, SY and Murtyakha River, MU) in Western Siberia, Russia, and their suprapermafrost water, adjacent surface flows, and river water were sampled for analysis of geochemical elements. Results showed that most elements above their respective detection limits began accumulating in the underlying gleyed layer during September-October in response to the deepest thaw in the active layer. This study focused on the highly mobile elements in the deepest layer; and found that the transport of organic matter in the upper layer carried these elements to both surface water ponds/flows and suprapermafrost water, and further, to the rivers. The efflux of released elements from surface soil to surrounding surface water appeared to be low. The best linear correlation for both surface flows and river water was with Mn; therefore, Mn may be a proxy for predicting the processes occurring within the active layer during the annual summer-autumn thaw. Moreover, landscapes with different ice contents may experience changes in the elements transported to surface waters. A general conceptual model for the response of elements to the thawing-freezing process of the active layer is established.

Plain Language Summary The rapidly increasing atmospheric temperature in the Arctic has led to the feedback of permafrost thawing, which increases the depth of the active layer and accelerates chemical weathering. These processes may cause a further release of chemical substances to adjacent aquatic landscapes. Here, we investigated the horizontal and vertical transport of geochemical elements through surface flow and suprapermafrost water to river water from three cryogenic soil cores in the Arctic tundra. The results showed that most elements accumulated in the gleyed layer, which was deepest in the active layer during the thawing season. Mn, Ca, Mg, Al, and Ti showed the highest mobility from soil to suprapermafrost water to the surface flows/rivers, while Mn was the only element that could migrate from topsoil and suprapermafrost water to surface water and river water, indicating that Mn may be a proxy for predicting the processes occurring in the active layer during summer-autumn thawing.

1. Introduction

Increasing atmospheric temperatures in the Arctic have led to permafrost thawing and vertical downward migration of the active layer into formerly frozen ground during the thawing season (Christiansen et al., 2010; Connon et al., 2018; Jorgenson et al., 2010; Romanovsky et al., 2010; Smith et al., 2010)). The active layer responds to changing climatic conditions by increasing its depth, thereby accelerating chemical weathering (Colombo et al., 2019; Keller et al., 2007, 2010) and potentially releasing geochemical components and organic carbon from the soil to adjacent aquatic landscapes (Barker et al., 2014; Grosse et al., 2016; Johnson et al., 2013, 2014; Loiko et al., 2017; Raudina et al., 2018; Schuur et al., 2015). This
would increase the movement of carbon dioxide (CO2) from the soil to aquatic reservoirs, such as rivers and lakes (Elder et al., 2019; Natali et al., 2015; Polishchuk et al., 2018; Wild et al., 2019), a phenomenon which occurs through the transport of solutes and water along surface streams and the permafrost table (known as “suprapermafrost flow”). Suprapermafrost water is found in the shallow subsurface of the active layer, where it is typically situated at the boundary between the frozen and thawed fractions of the soil profile (Cederstrom et al., 1953). Owing to the absence of groundwater discharge and low lateral groundwater flows in the permafrost-affected region, solutes being transported to lakes or rivers from adjacent soils originate primarily from suprapermafrost water.

Permafrost degradation has been associated with an increased contribution of groundwater to streams via surface flows or suprapermafrost water in Canadian Arctic rivers (Walvoord & Striegl, 2007). Ice wedge degradation has also been proven to be related to the water balance of lowlands across Arctic landscapes, and to increased streamflow (Liljedahl et al., 2016). Several studies have observed substantial increases in discharges from the major Eurasian Arctic rivers due to the warming climate (Browny et al., 2019; Feng et al., 2019; Lammers et al., 2001; Yang et al., 2002; Zheng et al., 2019). Raudina et al. (2018) observed a northward shift of the permafrost boundary under climate change scenarios, and that the concentrations of dissolved organic carbon (DOC), major and trace elements, and greenhouse gases are expected to decrease in the suprapermafrost waters at the border between the thawed and frozen parts from peat soils in the western Siberia lowland. Loiko et al. (2017) hypothesized that the direct mobilization of soil waters to hydrological networks and the transformation of autochthonous processes are controlled by physical factors in different landscapes. Overall, there appears to be considerable variability and uncertainty regarding how discharges of DOC, elements, and greenhouse gases in suprapermafrost waters/surface flows respond to permafrost thaw and are subsequently released to surface water ponds and rivers.

Several studies concerning the biogeochemical cycles of carbon and related metals focused on both the aquatic and the terrestrial parts of the continental permafrost-bearing ecosystem (Guo et al., 2007; McClelland et al., 2007; Olefldt & Roulet, 2012; Pokrovsky et al., 2011). More recently, the biogeochemistry of soil porewater and suprapermafrost water in mineral and organic/peat parts of soil profiles in permafrost areas have been studied (Barker et al., 2014; Jessen et al., 2014; Lamhonwah et al., 2017; Loiko et al., 2017; Raudina et al., 2018; Street et al., 2016). Previous studies concluded that the export fluxes of DOC, greenhouse gases, and trace metals from the active layer of permafrost to the surrounding hydrological landscapes are determined by the amount of water passing through the active layer down to the permafrost table, before being drained to a lake or river (Pokrovsky et al., 2016a, 2016b; Raudina et al., 2018). Barker et al. (2014) reported that the concentrations of metals in surface water were related to the increasing active layer thickness/degrading permafrost during late fall and early winter. These results revealed that the dynamics of trace metal concentrations in the transition from Arctic soils to surface water corresponded to top-down freezing processes in the active layer. However, there is a lack of information connecting geochemical tracers in both the underlying suprapermafrost flow and the upper soil layer to explain the transport of geochemical elements to surrounding hydrological networks, which can be used as a proxy for seasonal active layer dynamics.

Therefore, this study aims to provide knowledge of such geochemical element transport by analyzing suprapermafrost water, soil porewater, the water of surrounding small ponds/flows, and finally, river water from three typical soils close to rivers from continuous permafrost regions within the Yamal and Gydan peninsulas, Western Siberian Arctic. Tundra lakes and river floodplains are abundant in the Yamal and Gydan peninsulas; lakes cover, on average, 10% of the Yamal peninsula, occupying 20% of the floodplains of large rivers (Dvornikov et al., 2019). Approximately 90% of all lakes in the study region are small (<1 km²) water bodies. To analyze the effluxes from permafrost soils from relatively homogeneous landscapes, the sampling sites were set up next to the largest rivers flowing to the Kara Sea, such as the Syoyakha, Murtyyakha, and Taz Rivers.

We considered the conditions of geochemical transport in permafrost regions to be as follows: (i) When the active layer reaches its greatest depth during late autumn, the contribution of geochemical components and DOC from soils to rivers correspondingly reaches its yearly maximum values (Yang et al., 2002), a process that should be driven by surface flow and suprapermafrost rivers. (ii) The subsurface soils in the active layer receive the major mobilized components when mineral weathering processes continue advancing toward
the deeper active layer above the permafrost table. During the spring thaw of the following year, these components will be enhanced in suprapermafrost waters and transported further to surrounding surface waters. (iii) Due to the redox environment in the lower active layer, DOC and geochemical elements cannot be consumed by the biota or depleted by abiotic reactions. Therefore, they persist in suprapermafrost water and are transported to the surrounding hydrological networks. Based on these considerations, the specific objectives of this study were to (1) assess the mobility of released geochemical elements from upper soil layer water and suprapermafrost water to the surrounding water bodies (see Figure 1 for a conceptual graph); and (2) examine whether the concentrations of geochemical elements in surface water (i.e., the connected streams and receiving river) can explain active layer dynamics in permafrost riparian soils in different permafrost-affected landscapes.

**Figure 1.** Conceptual schematic of the transport of geochemical elements from surface flow or suprapermafrost water to surrounding water bodies.
2. Study Site and Methods

2.1. Geographical Setting

The study area was located in the northwestern area of the Yamal-Nets Autonomous Region, above 66°N, with continuous permafrost (Figure 2a). Sampling sites were located close to the lowlands of the Syoyakha, Murtyyakha, and Taz rivers. The Syoyakha and Murtyyakha rivers are situated in the Yamal Peninsula on the Western Siberian plain (Golovatin et al., 2011). The geographical features of this region are divided between river valleys, lake hollows, and streams (Golovatin et al., 2011). Cryogenic soils in this part of the Yamal Peninsula were formed due to the high ice content of Holocene alluvial sediments (Sidorchuk & Grigorev, 1998) and aeolian materials (Alekseev & Abakumov, 2018). This part of the lowland comprises very flat watersheds of the Syoyakha and Murtyyakha Rivers and is covered with frozen bogs and palsas. The Syoyakha is one of the largest rivers of the Yamal Peninsula (Bespalaya et al., 2018); its watercourse is 165 km long and its watershed covers an area of 4,400 km² (Bespalaya et al., 2018). The Murtyyakha River has roughly 580 watercourses and numerous lakes in its basin, which contains 70 rivers greater than 10 km in length. The Murtyyakha River flows into the Syoyakha River and then enters the Kara Sea. Syngenetic permafrost close to these two rivers contains massive Holocene ice deposits (Vasil’chuk et al., 2016). The 1,401-km-long Taz River is located in the Gydan Peninsula and drains a basin of 150,000 km²; it flows into the Taz Estuary and ends in the Gulf of Ob. Soils along the river developed from alluvial stratified parent deposits from an earlier stage of the Holocene (Tarnocai, 2009).

We investigated three poorly drained riparian soils with upper organic layers and a downward mineral profile adjacent to each river (Figure 2a). The soil close to the Taz River site (TA) was located at the top of the polygon rim (one of several well-developed low-center polygons with elevated rims and wet centers) where the landscape is a polygonal tundra, with the polygon centers featuring accumulations of poorly degraded organic matter under anaerobic conditions. The surrounding elevated polygon rims show evidence of cryoturbation for most of the horizons in the active layer (Figure 2b). The soil profile was gleyed with frost heaving of the clay stratum, while the surrounding vegetation consisted predominantly of wet acidic tussock sedge, grass, and sphagnum moss. Sampled soils were situated on the floodplain nearby the

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Figure 2. Location of the sampling area and installed thermometer (a). Soil pit profiles and their upper vegetation species near rivers: (b) Taz river (67°30’13.3″N, 78°40’56.2″E), (c) Syoyakha river (69°57’03.6″N, 71°23’15.2″E), and (d) Murtyyakha river (70°06’04.71″N, 68°40’24.1″E) in Yamal-Nets Autonomous Region. All soil profiles are gleyed and have oxidation/reduction horizons in the upper active layer, a thick top organic layer, and cryoturbation in the lower part of the active layer. The dotted line in A is the Arctic circle line (66°34’N).
Syoyakha (SY) and Murtyyakha (MU) rivers. The SY site was vegetated with moist, acidic moss, lichens, and sedges, and the MU site was vegetated with lingonberry, willow, moss, and sedges. Both soil profiles had shallow active layers that were strongly gleyed and under reducing conditions, while the deeper layers at the MU site showed obvious signs of cryoturbation (Figures 2c and 2d). The formation of the SY and MU stratified soils may have resulted from the constant changes in the river water levels. All three soil profiles for the TA, SY, and MU sites have been depicted as having a relatively light chroma color, with an oxidation of iron minerals, and are dominated by mineral substrates with either allochthonous organic matter or autochthonous peat.

2.2. Soil Core and Suprapermafrost Water Collection and Analysis

Three soil cores were extracted down to the permafrost table using a portable Snow-Ice Permafrost-Research-Establishment auger set (Jon’s Machine, Fairbanks, Alaska, USA) consisting of a coring auger powered by an engine. The location of each soil core was directly adjacent to the borehole, into which a string thermometer was inserted (Figure 2a). The thermometers, which were put in cases filled with grease as an inert material, were placed roughly 10 cm above the permafrost table for 24 h in July 2016 to reach thermal equilibrium with the surrounding soil material. The thermometers were connected to a data logger for recording hourly temperatures in degrees Celsius (Modular GM10, Yokogawa Electric Corporation, Tokyo, Japan), powered by a battery with a 3-year life time and attached to a stainless-steel stake inserted into the soil cores. After that, local soils were excavated to fill the soil cores for site remediation. The cores were collected in May 2016, sealed with Polyethylene covers, transported at a stable temperature of −4°C to inducing freezing, and stored in a refrigerator at the same temperature prior to analysis. We believe the cores partially reflect the deepest active layer during a year, with approximately 65 cm for Mu, 46 cm for Sy, and 90 cm for Ta, shown by the thawing materials. The soil pits were excavated in July 2017 adjacent to the coring location (Figure 2), and site restoration procedures followed the standard protocols for permafrost-affected soils (Ping et al., 2013). Excavating soil pits can provide insight into the zone between the active layer and permafrost that contains external flows to rivers. Each 35 × 35 cm soil pit was excavated with a shovel and hatchet until reaching frozen materials and the genetic horizon and name of each soil were identified using the World Reference Base for Soil Resources (WRB, 2015) classification system. The stagnic condition of the soils (i.e., soils were sufficiently saturated with surface water to show reducing conditions) meant that 2,2′-dipyridyl spray was required on the soils for 30 s to test for reducing conditions, as per the tests previously conducted on gleyed soils (Ping et al., 1998).

The frozen soil core was cut into 5-cm sections with a diamond wire saw (LKH-8, Kanghua Company, Guilin, China), which used a cutting section of diamond-impregnated wire mounted on idler pulleys, in a cold room in the laboratory of the Arctic Logistics Center, Salekhard, Yamal-Nenets Autonomous Region, Russia. The cut sections of each soil core were then placed in tightly sealed plastic bags (9.5 cm × 18 cm, Bag Whirlpak Clear 7 oz, Nasco, FL, US) and kept at room temperature (approximately 23°C) to thaw for 12 h. Completely thawed soils were used to collect soil porewater with an SPS 200 lysimeter soil solution sampler (SDEC, Reignac-sur-Indre, France). The collected water was filtered through a 0.45-μm polypropylene filter, decanted to glass test tubes, and acidified with 0.5 (wt.) % ultrapure nitric acid (HNO₃, CAS: 7697-37-2 Fisher Scientific, Hampton, USA) before processing through inductively coupled plasma-tandem mass spectrometry (8800 ICP-MS/MS, Agilent, Santa Clara CA, USA). To remove the spectral interferences of ions through ion/neutral reactions, the collision reaction cells (CRCs) mode in the ICP-MS was operated using He or NH₃ as the inert collision gas, following the protocol developed by McCurdy and Woods (2004). The elements V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and As were analyzed in CRCs mode with He gas to remove unidentified polyatomic particles arising from Cl⁻, S⁻, and C⁻. Ti was analyzed in CRCs mode with NH₃ to remove interferences from S-based polyatomic ions. The elements Sr, K, Ca, Mg, Al, Ba, Be, B, Cd, Pb, Au, Mo, P, Sc, Ag, Ti, Sn, and rare earth elements (REEs) were analyzed using normal (non-CRC) mode.

Four calibration standards (1 × 10⁻², 1 × 10⁻¹, 1 × 10⁰, 1 × 10³ μg L⁻¹) were prepared by diluting 1 × 10³ μg L⁻¹ stock standard solution for each element and mixed REEs (TraceCERT®) purchased from Sigma-Aldrich, St. Louis, MO, USA. Two percent of (w/w) ultrapure HNO₃ was taken as the blank. Calibration was performed before every analytical test with a good calibration curve (R² ≈ 0.999), and three blanks and check standards
were run before every 10 samples. The analytical uncertainty for each sample was determined by triplicate analysis within an error of ±3%. The detection limits for all elements were set at the level of 1 µg L⁻¹. To correct the magnitude of the signal suppression or enhancement, a standard mixture solution of Bi, Ge, In, Li, Sc, Tb, and Y (10 µg mL⁻¹) prepared in 2% ultrapure HNO₃ was used as the internal standard added to all standards, blanks, and samples.

Then, each soil core section was transported to the Applied Ecological Laboratory, Saint Petersburg State University. They were dried in a vacuum drying oven for 16 h, homogenized by grinding using a roller mill, processed through a 2-mm sieve, and finally, soils were pressed into a powder pellet with a vertical hydraulic jack. Each pellet was analyzed through scanning electron microscopy using energy dispersive X-ray spectroscopy (SEM-EDX) (JSM-6390 LA, EX2300, JEOL, Tokyo, Japan). EDX revealed the characteristic peak for each metal in each sample with atomic-level precision, which could be converted directly into concentrations in terms of mg kg⁻¹. The soil certified reference materials CRM027 and SQC001-30G (Sigma-Aldrich, St. Louis, USA) for trace metals were used for calibration. Samples and the reference material were analyzed in triplicate, and the detection limits were determined based on the minimum value of the reference material.

Stagnant suprapermafrost waters were collected adjacent to the previous soil cores (<10 cm) in September 2016. To prevent the contamination of water samples due to the previous methods of collecting suprapermafrost waters with soil pit excavation, an alloy probe rod was first inserted into the soil to confirm approximately the same depth of the active layer-permafrost boundary as the previous soil core. A direct push device (SP16 Groundwater Sampler, Geoprobe Systems®, Salina, KS, USA) comprising a polyvinyl chloride screen was driven to the permafrost table within a sealed steel sheath. Then, the water samples were pumped through the tube to the surface and stored in 25-mL PVC serum bottles by oscillating the tubing up and down.

For the lower floodplain (SY and MU), water samples were collected after pumping the tube for 15–20 min to flush water with permafrost materials. The time required for pumping water in TA was relatively longer than that for the other sites, by approximately 30 min, with less volume of inflowing water because of the greater depth of the polygon rims. For all sites, the first portion of water containing permafrost materials was discarded, and clearer water with fewer impurities was collected. Unfiltered water samples in the serum bottles were treated with 0.2 mL of mercuric chloride (HgCl₂, Sigma-Aldrich) and capped without air bubbles or headspace using butyl rubber stoppers pierced by a needle attached to a 3-mL syringe that allows air and water to escape from the bottle when the stopper is inserted. With the bottle inverted, 10 mL of methane-free helium (Sigma-Aldrich) was added, meanwhile 10 mL of water was removed through needle displacement and the syringe. Then, another 10 mL of methane-free He was added to the headspace without removing water, and water and headspace were equilibrated in the bottle by shaking for 2 min. Triplicates of subsample headspace gas (into the syringe) were analyzed for CH₄ and CO₂ by gas chromatography (GC-456, Bruker, Billerica, MA, USA), with a Flame-Ionization Detector (FID) and an Electron Capture Detector (ECD), respectively. After each set of 10 samples, the detectors were calibrated based on Air Liquide (CO₂ = 246.6 µmol mol⁻¹, CH₄ = 302.3 µmol mol⁻¹). The results of triplicate injection showed a repetition rate within ±2%. The gas solubilities of CH₄ and CO₂ (Kastanidis et al., 2018) were taken by calculating the total concentration of CH₄ and CO₂ in the vials and then converting to µmol L⁻¹ of the initial samples. All analysis procedures for analyzing CH₄ and CO₂ were carried out in the Center for Chemical Analysis and Materials Research of St. Petersburg State University. The water temperature, dissolved oxygen, pH, and specific conductivity were field-measured with a portable multiparameter meter (Orion Star™ A329, ThermoFischer Scientific, Waltham, MA, USA). Stagnant suprapermafrost waters in this study were oxygenated with an average O₂ saturation in samples ranging from 10.2% to 82.3%, with an uncertainty of 3–4%, which is very close to previous reports from the Western Siberian lowlands (Loiko et al., 2017; Raudina et al., 2018). No significant difference was observed in the O₂ concentrations from water samples at each soil site. The average temperature of suprapermafrost waters did not vary significantly, being 12.3 ± 1.8°C for SY, 13.4 ± 1.6°C for MU, and 15.6 ± 2.0°C for TA. The DOC concentrations were analyzed by a TOC-L TOC Analyzer (Shimadzu Kyoto, Japan) with an uncertainty of 5% and a detection limit of 4 µg L⁻¹.
2.3. Surface Water Collection and Analysis

All surface water samples were collected in September 2016. All sampling sites were adjacent to the location of the soil cores. We collected water samples (streams connected to each river) from shallow (<10–30 cm) permafrost subsidence areas and hollows of size < 1 m²; deep depressions (<1 m) of palsa bogs with sizes ranging from 5 to 15 m²; small thaw ponds (ca. 1–2 m) with sizes ranging from 10 to 150 m²; and each river closest to the soil core within 5–10 m (depth < 5 m). These surface streams were downslope from the soil cores, with a short distance of about 30–40 m, and their distance to the river was about 10–30 m. Neoprene gloves were used during water sampling, and water from the shoreside was collected by a standard PVC MP2 two-stop peristaltic pump tubing (1.09 mm I.D., White/Red, Pkg. 12, PerkinElmer, Waltham, MA, USA) outfitted with a pre-sterilized Durapore® 0.45 µm capsule filter (MilliporeSigma, Burlington, MA, USA). The water passing through the tubing and filter capsules for the first 30 s was not collected, and polypropylene (PPCO) bottles with white PP closures precleaned by 2% nitric acid were used for water collection. The analysis of trace metals in water samples was the same as in section 2.2.

3. Results

3.1. Characteristics of Soil Profiles and Chemical Composition in the Soil Column

Detailed horizon and vegetation information in the soil pit profiles in the photographs for SY, MU, and TA are shown in Figure 2. The soil groups belong to Histic Gleysols (Stagnic), Histic Gleysols (Turbic), and Turbic Cryosols for SY, MU, and TA, respectively. The top fractions of the soil horizons from three soil pits all show a high chroma color, with TA being relatively lighter (Figure 2b), and all the lower fractions show strongly gleyed conditions, which may indicate a redox boundary. The lower fractions of the soils were further tested by a few drops of alpha-alpha-dipyridyl for 30–40 s, showing that no pink color was observed for SY at the depth of 6–9 cm, with a strip-shaped iron oxidized boundary leading to the next horizon. A positive pink color was observed during the reaction in the next gray color horizon (9–18 cm), suggesting the occurrence of reduced ferrous oxides under reducing conditions. Compared with the previous horizon, this horizon had few plant roots and little accumulation of organic matter. The lowest section (18–35 cm depth) had a sporadic positive pink color. This difference may be due to the different redox spots visually observed in the excavated soil pit (Figure 2c). The lower 18–35 cm showed a heterogeneous rusty-gray color, suggesting the presence of ferric iron as well as aluminum, and inclusions of organic materials due to cryogenic mass exchange through bottom-up flow of water by thawing/freezing processes that bring parent materials to the upper layers, where cracks could be observed in the top 18–35 cm. In the upper 6–9 cm horizon, the oxidation of ferrous iron to ferric iron is mostly due to the leaching process within the upper water thawing zone containing oxygen. Therefore, the low density of the strictly reduced gleyed horizon (6–9 cm) separated the two different geochemical transport pathways between the upper and lower horizons.

For soil pit MU, a pink reaction color was observed at a depth of 7–25 cm (note the shape shown as “Bg@ horizon” in Figure 2d, for which the subscripts g and @ represent stagnic conditions and evidence of cryoturbation, respectively), and in certain middle parts at depths of 30–40 cm. In the Bg@ horizon, there were more disbursed rust-orange spots and stains that followed the path of roots; these ferrous irons were oxidized when exposed to the atmosphere due to the pore spaces caused by the vegetation’s growing roots. An apparent presence of cryoturbation with a gray-brown color was observed in the deeper parts alongside the dark-gray inclusions from the lower permafrost. The oxidized iron in this horizon likely resulted from the multiyear freezing/thawing and lower activities of congeliturbation (i.e., repeated cycles of freezing and thawing) in which materials were transported from both the upper and lower layers. The 60–65 cm depth was completely under reducing conditions, with loamy soil in gray color.

For soil pit TA, reducing conditions, indicated by a positive pink color, were observed below 55 cm. TA showed a mixed O-and-A horizon within 30 cm that had a brownish-gray color and very few roots, which is common under hummocks in Western Siberia. Within the depth of 0–55 cm, lateral ring-shaped layers and mud spots could be observed, which were caused by frost heave when a rounded knoll of ice rises during freezing. Evidence of cryoturbation could be seen below 55 cm, with a dark-gray color, and some moss residues were observed in the fragments of cryoturbation clusters.
The vertical distributions of elemental concentrations in the three soil cores measured by EDX are listed in Table S1 and plotted as logarithmic concentrations versus soil core depth in Figure 3. The other elements not shown in Figure 3 did not exhibit a regular pattern under reducing conditions within the soil cores. Mn and Co were enriched in the top mineral layer with organic matter accumulation, likely because of their...

Figure 3. Vertical metal/element distribution in soil cores collected from Taz river (TA), Syoyakha river (SY), and Murtyyakha river (MU) sites in the Yamal-Nets Autonomous Region in the beginning May 2016. The logarithmically transformed distribution shows the element enrichment relevant to the top layer, with humus accumulation under oxidizing conditions (Mn and Co) and the lower gleyed layer under reducing conditions.
complexation with natural organic matter. In contrast, Cr, V, Sr, Ca, Mg, Al, Ti, Cd, Mo, Zr, and Sc increased in lower mineral soil horizons in the three soil cores. In particular, for the MU site, Fe, Cr, and V were only higher in the first gleyed horizon with cryoturbation (7–25 cm) and decreased gradually with increasing depth. Al, Ti, Cd, and Sc kept increasing until 40 cm depth (second gleyed horizon) and then decreased gradually or maintained relatively comparable levels in the deeper layers. As, Mo, and Zr decreased until the depth of 40 cm and then increased in both the deeper mineral horizons mixed with frozen material, and at the frozen horizon. Zn, Sr, K, Ca, Na, Mg, and Y were higher in all gleyed horizons.

For the SY site, three trends were observed: (i) a relatively slight decrease from top to bottom within the gleyed horizons for As, Cr, V, Mo, Zr, and Se; (ii) a continuous increase in the gleyed horizon with depth for Sr, K, Ca, Va, Mg, Al, Ti, and Pb; and (iii) only the Cd content increased sharply in the upper gleyed horizon (9–18 cm) and decreased significantly below 18 cm. For the TA site, the maximum concentration was observed in the gleyed horizon for Cr, V, Sr, Ca, Mg, Al, Ti, Cd, Pb, Mo, Zr, Y, and Sc. These elements were apparently enhanced in reducing fractions, concentrations of which, with respect to the upper layers of the soil column, can reflect soils with increased reducing conditions. This obvious demarcation between elements with concentrations either increasing in the upper layers of the soil column or accumulating in the lower part of the soil column correlated with the variation in reducing conditions in the soil pit profile as well. The fluctuation of elemental concentrations in the lower soil cores may have also been caused by the effect of cryoturbation.

The elemental concentrations of the soil porewater are listed in Table S2 and plotted as a function of depth along the cores (not containing suprapermafrost water) in Figure 4. These plotted data reveal that the soluble fraction of geochemical elements was likely transported to the surrounding surface and suprapermafrost water. The results showed that Ca, Mg, and Ti were soluble species that may be available for transport in suprapermafrost water for all three sites because of the increased concentrations in the deeper fraction of the soil core. Additionally, Al in the TA site, Mg in the MU site, and Fe in the SY site may also have had the same potential. To some extent, Mn, Ca, Mg, Al, Ti, and Fe all can be soluble species in both upper and deeper fractions of the soil core, indicating both the transport capability from surface flows and suprapermafrost waters to the river.

### 3.2. Thermal Dynamics in the Active Layer

The temperatures at multiple depths from the installed thermometers are provided in Figure 5. In general, the surface (0 cm) soil temperature corresponds to the variation in ambient temperature in this region. The soils at four different depths in TA, MU, and SY were completely frozen by the end of April, when our measurements were initiated. In TA, the thawing of frozen soils (temperature rose above 0°C) occurred on 30 May 2016 at 0 cm, on June 7, 2016 at 20 cm, on June 18, 2016 at 40 cm, and on June 30, 2016 at 75 cm. In MU, the thawing occurred on June 2, 2016 at 0 cm, on July 14, 2017 at 25 cm, on June 25, 2016 at 40 cm, and on July 4, 2016 on 59 cm. In SY, thawing occurred on June 1, 2016 at 0 cm, on June 11, 2016 at 18 cm, on June 22, 2017 at 26 cm, and on July 2, 2016 at 38 cm. It should be noted that frozen soils in the Arctic thaw from the top down during the spring-summer season. The lower latitude of TA resulted in a relatively earlier thawing time than that of MU and SY.

### 3.3. Chemical Composition in the Suprapermafrost Water

All measured elemental concentrations are plotted as a function of sampling time in Figure 6, and the pH values for suprapermafrost water in TA, SY, and MU for different sampling months are presented in Figure S1, with a detailed description in Text S1. In TA, the contents of Zn, Mn, Ti, and Sr increased generally from the beginning of summer (June), while Sr and Ti increased slightly with an obvious increasing trend at the end of summer (September 15, 2016). Zn reached its highest concentrations (15.93–17.50 μg L⁻¹) at the beginning of autumn, and this level was maintained until October 2016. Unlike Zn, the peak value of Mn was observed in October. Fe concentrations started to rise significantly at the end of September and peaked at the end of October 2016 (2049.71 μg L⁻¹). Mg, Cr, V, Pb, Al, and Ca concentrations exhibited less fluctuation over summer, with low concentrations until an increasing trend was observed at the beginning of
autumn. Na was the only element that showed a gradual increase in concentration over time until October 15, 2016. Cd and Mo had no particular trend, and exhibited low levels. SY and MU essentially followed the pattern of TA, while the highest Fe concentration in SY occurred at the end of October 2016.

### 3.4. Chemical Composition in the Surrounding Hydrological Streams and Rivers

We measured the elemental concentrations of the surface water surrounding the soil cores, including the connected hydrological flows (i.e., shallow, depression, and thaw ponds) and rivers (flow receptors), which are shown in Figure 7. The pH values for TA, MU, and SY for different months are shown in Figure S2, with a detailed description in Text S2. The concentrations of CO₂, CH₄, and DOC in the surrounding streams are plotted as a function of sampling time in Figure S3 and described in Text S3.

![Figure 4. Distributions of soluble metals along the vertical soil water extracted from the soil cores collected adjacent to the TA, SY, and MU rivers in the Yamal-Nets Autonomous Region. TA, Taz river, SY, Syoyakha river, and MU, Murtyyakha river.](image-url)
The remaining detected elements are not shown here because they were below the detection limit. All three sites showed strong similarity in the distribution of elements in the connected surface flows and the adjacent rivers with time. Most elements (i.e., Fe, Mn, Zn, Na, Pb, Al, and Ca) showed an increasing trend from the beginning of September to the beginning of October, while Co, V, and Sr significantly increased beginning in August, and only Cr increased starting in July. These elements in the surrounding hydrological streams or rivers reached their highest concentrations at the beginning of October, except for Mo, Cd, and Ti, which had very low concentrations over all timescales and slightly increased only in October. The concentrations of Fe, Zn, Al, Co, and Sr were consistent with the observation of enhanced soluble concentrations in suprapermafrost water for each of the corresponding months. This may be because of the solubility of these metals, except for Co and Mn, which remained at low levels in the top layers of the soil cores, and because of the different solubilities of the metals during snow melting, which are related to the bonding mechanism in the soil, especially for top soil layers with increased organic matter. The highest to lowest concentrations for metals were approximately Fe > Mn > Zn > Sr > Ti > V ≈ Na ≈ Al ≈ Pb > Cd ≈ Mo.

4. Discussion

4.1. Variability of Elemental Concentrations in Soil and Soil Porewater

In the TA soil column, higher elemental concentrations in soil porewater, such as Mn, Mg, and Ti, were found in the oxidizing zone (~10–15 cm, i.e., the layer with organic matter accumulations). Compared with the deeper depths of the soil column (~30–83 cm, i.e., the reducing zone), enhanced elemental accumulations were also observed, especially for Mg and Ti. The lower Ca and Al concentrations in the top organic layer (Figure 4), which may be due to the excess of Ca in the soil solutions, accounted for a greater proportion of the total cation concentration (Leckie, 1986). Ca cations can control the soluble stage of trace elements in soils, due to the fact that Ca is an organic complex in soil solutions, preventing the precipitation of soil deposits (Leckie, 1986). For instance, fulvic acid in this organic layer could potentially interfere with the crystallization of aluminum hydroxide polymorphs to a significant degree (Kodama & Schnitzer, 1980). In addition, the aqueous Ti concentrations in both the oxidizing and reducing zones were similar, while Mn was relatively higher in oxidizing zones, and Mg was more enhanced in the reducing zone. Compared with the distribution of these elements in the solid soil core, only Ca and Al showed a similar trend. This difference was likely due to the soluble and chemical fractions of species.

In the MU soil column, the concentrations of Mn, Ca, Mg, Al, Fe, and Ti in soil porewater were increased below 7 cm in the reduced zones. However, the solid soil phase showed high levels of Mn in the oxidizing zones (~0–7 cm), with the other elements’ distribution corresponding to the soluble forms. In the SY soil column, Mn, Mg, and Fe contents in the soil porewater were enhanced in the upper oxidizing zones, and the Ca content was only obviously enhanced in the reduced zones, while Al and Ti both accumulated in the oxidizing and reduced zones. The Mn concentrations were found to be highest in the oxidizing zones in the solid phase, whereas other elements (Ca, Mg, Al, Ti, and Fe) increased in the reduced zones.
Figure 6. Soluble element concentrations (μg L⁻¹) in the suprapermafrost water collected from the TA, SY, and MU sites as a function of date in 2016, respectively, TA, Taz river, SY, Syoyakha river, and MU, Murtyyakha river.
Figure 7. Soluble element concentrations (μg L⁻¹) in the surface water from connected hydrological streams to rivers and rivers from the TA, SY, and MU sites as a function of date in 2016, respectively. TA, Taz river, SY, Syoyakha river, and MU, Murtyyakha river.
In both the MU and SY sites, Mn concentrations were found to be higher in the top layer of the soil, which is consistent with the low solubility of Mn in lower pH soils (pH = 4.7 for Mu and 4.8 for Sy) (Scholz & Kahlert, 2015). We speculate that this was because of a more integral gleyed layer (~10–40 cm) caused by cryoturbation, which could result in a shared origin for the different soils. SY revealed more heterogeneous materials that divided several soil layers through cryoturbation, resulting in elemental fluctuations in terms of soluble elements.

The depths of the three soil cores represent the typical maximum vertical depth during the thawing period in autumn. Among the three soil cores, differences between elemental concentrations in soil porewater and solid soil were still substantial. Taking the concentrations of Mn in the TA soil column as an example, the concentration of Mn in the oxidizing layer was 1039 mg kg\(^{-1}\), with approximately 0.11 mg L\(^{-1}\) in soluble form. There were approximately 0.045 mg L\(^{-1}\) of Mn mobilized within the thawing water to the reduced zones, with 388 mg kg\(^{-1}\) presented in the solid soil of this layer.

To better understand the solubility of elements, partitioning coefficients (K\(d\)) were calculated, as shown in Figure 8. A small K\(d\) value suggests high partitioning from the soil to the aqueous phase. Despite an increasing solubility of certain elements that was observed below the top layer (i.e., Mn, Ca, and Mg in all three soil columns), a decreasing solubility of these elements could also be observed within the gleyed layers, which is consistent with the theory that metal movement would be hindered in this layer (Antcibor et al., 2014). However, Al and Mn were observed to have a clearly increasing solubility in all soil cores above the permafrost table. In addition, a high partitioning from the solid to the aqueous fraction was observed in Ti for the SY site, and in Fe and Mn for the MU site. Unlike the top organic-rich layers, which mainly reflect biogeochemical cycles, minerogenic layers tend to reflect mineralogical weathering. Therefore, the difference between the sites may be due to the differences in soil textures and frost processes.

It should be noted that the enrichment of Mn and Al for soil materials in Western Siberia has been previously investigated (Abakumov et al., 2017; Antcibor et al., 2014; Evgeny et al., 2017; Ji et al., 2019a, 2019b). Findings have shown that with increased soil water flow into suprapermafrost water, the input of elements, such as Mn and Al, is more consistent from soil to solution. One previous study showed that the solubility of Mn increases with increasing soil acidity (Andrade et al., 2002), which is consistent with our observation. Further, Barker et al. (2014) first reported that trace metal concentrations (Al, Ba, Fe, and Mn) were correlated with the seasonal thawed active layer in the Alaskan Arctic. These findings further support that elemental transport likely occurred through the mechanism of thawing soil porewater, and that the potential existed for these elements to enter surrounding water bodies.

4.2. Elemental Fluctuation in Suprapermafrost Water and Surface Water by Seasonal Controls

Our study focused primarily on surface water from top organic layers and suprapermafrost water from lower mineral layers in a low gradient tundra stream flowing through thawed glacial till. We investigated whether elements could represent the seasonal dynamics from different permafrost-affected soils to drainages (streams and rivers) as endmembers. The soluble elements with the highest concentration in the bottom of
the three soil cores were Mn and Al (Figure 4). We expected to see a high mobilization of Mn and Al to the suprapermafrost water during spring snow thawing. However, except for Mn, no or very slightly increasing concentrations in late May-early June were found in the suprapermafrost water (Figure 6), which may have been due to the low volume of thawing water or the equilibrium between the elemental pool size in solid soils and snowmelt water in the reducing zones at this time. We found that the peak concentration time for most elements was in late autumn-early winter. With respect to elements in the soil porewater, more elements were above the detection limit and at significantly higher levels during the August-October time period. This indicates that the origin of elements in suprapermafrost water may not only originate from the dilution of snowmelt water within the soil core, but also from external water flows through the slope of the permafrost table in the landscape. The relatively higher levels of elements such as Mn, Zn, and Fe in the TA site than those in the SY and MU sites could have resulted from frost heaving of the polygon rim, which would have released more frozen material. During summer, thawing begins with the permafrost-affected soils, which leads to a deeper active layer, and this was reflected by the slight increase in Mn, Fe, and other elemental concentrations in the suprapermafrost water over the course of June, July, and August. This increase was also correlated with the low Kd values in the bottom of the soil core (Figure 8) and with the soil temperature. The soil thermal stratification showed that soil temperatures were above 0°C at 0, 20, and 40 cm for TA from late June; at 0, 25, and 40 cm for MU from the beginning of June; and at 0, 18, and 25 cm for SY from late June, whereas the deeper depths (75 cm for TA, 59 cm for MU, and 38 cm for SY) were still frozen at that time.

Most elements revealed a relatively high solubility with small Kd values at the deepest depth. At the TA site, Mn followed this trend at depths of 18–35 cm, whereas at the deeper depth of 35–40 cm, the solubility decreased. The high mobility of these elements in the deeper soil column, along with the later thawing for these layers, could account for the high concentrations in suprapermafrost water and surface water in late September and early October. This pattern is relatively comparable to that of the other elements in the TA, MU, and SY sites, except for Ca and Ti in the MU site. Generally, elemental fluctuations in the surface flow and rivers were the same as those in the suprapermafrost water. The concentrations of Zn, Mn, and Ti in the rivers from July to October were higher than those of the surface flow, indicating a transport of these elements to the rivers from the surface flow, and suggesting the possibility of contribution from this input from suprapermafrost water. One previous study also showed that metals such as Fe, Al, Mn, and Ba decreased in the active layer, with subsequent thawing and increasing surface water concentrations during summer to autumn, which could indicate elemental transport signals corresponding to the depth dynamics of the active layer (Barker et al., 2014). Our results are consistent with the theory that major and trace elements are transported to lakes and rivers through the boundary between the thawed and frozen layers (Raudina et al., 2018). However, we cannot exclude the possibility of an abrupt permafrost collapse in the surrounding water body and rivers, which has been shown to enhance metal release into the surface water (Loiko et al., 2017). This may also be the reason why not all elements in the surface water were above the detection limit in the soil porewater.

4.3. Potential Elemental Signatures as a Function of Organic Matter in Surface Flow

The discharge amount and source of water are important for influencing the transport of geochemical components, such as elements and organic carbon, to surface waters. However, it is difficult to determine water sources in cryogenic landscapes with large amounts of ice and multiple flows. In the present study, DOC was used as the “participating medium” to estimate elements transported to surface water, as this parameter is considered to be the major carrier of trace elements in boreal and permafrost-affected organic-rich surface waters (Lyvén et al., 2003; Ma et al., 2019; Neubauer et al., 2013; Rember et al., 2004; Vasyukova et al., 2010). Due to the absence of pollution from domestic and industrial activities at our sampling sites, the riverine organic carbon can be subdivided into two origins: an allochthonous pool derived from terrestrial organic matter (i.e., topographical erosion and soil leaching) and an autochthonous pool derived from in situ phytoplankton production (Hope et al., 1994). Additionally, an empirical model for exports of organic carbon has shown that DOC exports to surface runoff are largely driven by unfrozen zones during permafrost thawing (Fabre et al., 2019). Therefore, surface streams with smaller water volumes connected...
between the soils and the rivers were also investigated to determine the relationships between DOC and elements, as well as the elemental relationships among the streams, rivers, and suprapermafrost waters.

All three study sites all had a top soil layer of organics, with sporadic organic distributions in the mineral layers. Previous studies have reported that precipitation can result in rapid surface runoff through the upper soil layers at depths of approximately 15–20 cm (Bishop et al., 1993; Hope et al., 1994); therefore, DOC could be exported to the surface water from the top layer without infiltration in the riparian zone. At the TA site, the highest concentrations of CO$_2$ and CH$_4$ were observed in the summer snowmelt season, showing an increasing thawing degree but with low concentrations (Figure 9), which may have been due to an abrupt thawing process from the top organic layer. This is consistent with previously reported maximum microbial metabolism occurring at the boundary between thawed and frozen permafrost soils in the Western Siberia lowland (Morgalev et al., 2017). However, Dillon and Molot (1997) reported that the release of CO$_2$ into boreal waters increased when the DOC concentration was elevated in thermokarst lakes. We found a slight decrease in CO$_2$ and CH$_4$ when the DOC concentrations reached their peak in autumn at the TA site. However, a different pattern was observed at the SY and MU sites, in that CO$_2$ and CH$_4$ did not increase significantly during snow-ice melting in the spring and summer seasons, while an increasing trend was observed for DOC contents in the surface water. Manasypov et al. (2015) reported no significant enrichment of CO$_2$ and CH$_4$ in thermokarst water bodies through base flow during the spring flood and further observed that CO$_2$ levels only increased in small depressions (<10 m$^2$), which is consistent with the ponds (approximately 1 m$^2$) that we sampled. Although some obvious build-up of CO$_2$ was found in the summer for the SY site, overall, the results are comparable to the nonenrichment phenomena in high latitude lakes.

Figure 9. Elements/CO$_2$/CH$_4$-dissolved organic carbon (DOC) relationships for the surrounding hydrological streams in TA, SY, and MU sites over the course of spring to autumn 2016. TA, Taz river, SY, Syoyakha river, and MU, Murtyyakha river.
The reason for the contrast between TA and the other sites (SY and MU) could have been caused by the relatively low water volume of the pond at SY, as well as the low ice contents and relatively short time period that would be required for this type of accumulation at low elevations in MU. However, there is also a possibility that more ice from the polygon rims and buried taliks would lead to higher volumes of unfrozen water flowing to the surrounding streams. The combined results of all three sites show that the response mechanism of enhanced CO$_2$ concentrations in the streams during snowmelt is the heterotrophic respiration of allochthonous DOM (Shirokova et al., 2017; Textor et al., 2019), as suggested by the constantly elevated DOC concentrations observed in this period. However, we suggest that the bioutilization of these carbon types within the small ponds may vary according to the contents of materials owing to different water volumes.

The elements with high mobility in the bottom gleyed layer of the soil column and obvious higher concentrations during the snowmelt period were plotted against DOC (Figure 9). In the TA site, the concentrations of Mn increased sharply in the summer while those of Al, Ca, and Mg did not significantly increase. Peak values of Mn, Al, Ca, and Mg with DOC were observed in autumn. The same pattern was observed for the SY and MU sites, especially for Mn. This may indicate the release of micronutrients, such as Mn, during vegetation activity and upper moss litter leaching in the warmer water, which allows for a higher mobility within the soil column. Because we did not observe a high concentration of Mn in the uppermost soil layer (Figure 3), we speculate that this contribution of Mn may be from the suprapermafrost water.

Another difference found at the TA site was that elemental concentrations (Al, Ca, and Mg) in autumn were significantly higher in comparison to the MU and SY sites, which may have been a result of upwelling via ice cracks, beginning as early as October, which would have produced organic-accumulated and Fe-accumulated allochthonous ice at the pond surface. The maximum values of these elements which peaked during autumn in the surface water were about 2–3 times greater than those in spring and summer, and can be thought to represent the highest water flows, including DOC and dissolved elements.

Additionally, a strong linear correlation of Mn between surface streams and rivers was found for all three sites, and between the surface streams and river in the TA site for Al (Figure S4). However, when comparing the surface streams and suprapermafrost water, Mn was correlated for all three sites; Al only in TA and SY; and Ca only in TA (Figure S5). For Mn, the snowmelt flows had higher Mn contents, attributed to the increasing mobility of Mn species as compared to other elements in the superficial layers of the soil, as previously reported (Barker et al., 2014). Further, suprapermafrost water initially contributes to the surface flows, and then to flows in the river. Therefore, the differences for Al and Ca may have been due to different water-soil interactions, suggesting that Mn could be a seasonal signature for autumn, representing the dominance of overland surface flow and maximum interactions with the active layer when the active layer is deepest.

4.4. Water Movement and Diffusive Element Fluxes

The seasonal groundwater flow dynamics above the permafrost table begins from the end of May when the daily air temperature is above 0°C (Figure 5). At that time, the active layer begins thawing from the surface downwards, which would increase the hydraulic activity in the active layer. Due to the fact that the permafrost table functions as an impermeable base, when the active layer reaches its maximum depth, the groundwater flow would still be shallow (Jessen et al., 2014). When the daily air temperature falls to values below 0°C at the end of September, freezing would occur, resulting in a decline of the hydraulic conductivity in the active layer by several orders of magnitude. The movement of remaining unfrozen porewater would then be confined by icy pores due to saturation at most depths of the active layer (Fox, 1992).

From the above considerations, lateral groundwater flow could be measured during the thawing period, which lasted for approximately 4 months (from June to September). The software Rosetta Lite 3.01 within the freeware Hydrus-1D modeling program (Nelson & Rittenour, 2015) was employed to calculate the hydraulic conductivity of the upper organic and lower mineral active layer. The soil textural classes (i.e., the percent sand, silt, and clay and bulk density in the different soil layers, Table S3) was input to Rosetta Lite 3.01 to model approximate water retention parameters of the soil. Lateral flows and fluxes were obtained...
from the Darcy velocities divided by porosity. Darcy velocities were calculated from an online free software “Darcy Flux and Average Linear Groundwater Velocity” (https://www.groundwatersoftware.com/) by applying the gradient, conductivity, and porosity. Based on Rosetta Lite 3.01, the hydraulic conductivity values for the unsaturated organic layer were $2.8 \times 10^{-6}$, $4.3 \times 10^{-6}$, and $5.6 \times 10^{-6}$ m s$^{-1}$ for TA, SY, and MU, respectively. Lower values of hydraulic conductivity were obtained for the saturated mineral layers, with $5.7 \times 10^{-6}$ m s$^{-1}$ for TA, $1.2 \times 10^{-6}$ m s$^{-1}$ for SY, and $1.1 \times 10^{-6}$ m s$^{-1}$ for MU, respectively. Considering the 4 months thawing period, the velocities were approximately equivalent to annual lateral travel distances of 29 m for TA, 45 m for SY, and 58 m for MU in the organic layers, while all three soil cores showed differently saturated mineral layers with differing textures, i.e., clay loam (TA), sandy loam (SY), and silty loam (MU) with annual lateral travel distances of 5.9, 12, and 11 m, respectively (Figure 10). The flushing of the upper

![Diagram](image)

**Figure 10.** Water flow velocities in the active layer (lateral advective transport in the organic layer and vertical diffusive flux from the loam to the organic layer) for TA, SY, and MU sites. TA, Taz river, SY, Syoyakha river, and MU, Murtyyakha river.
organic layers was faster than that of the lower layers of the active layer, and clay loam had a relatively lower flushing speed as compared to sandy loam and silty loam.

Considering the lateral transport of water in Figure 10 and that solute concentrations dropped below the top organic layer, such as Mn in the TA and SY soil cores (Figure 4), an upward diffusive flux of single elements from the lower loam layers to the organic layer could be calculated according to Fick’s Law:

\[ F_i = -D \frac{c_i}{h} \frac{dh}{dh} \]

where \( F_i \) is the flux of solute \( i \) (mol m\(^{-2}\) s), \( D \) is the free ion diffusion coefficient, taken as \( 0.65 \times 10^{-9} \) m\(^2\) s\(^{-1}\) at \( 2^\circ C \), \( \varepsilon^2 \) is the correction factor for effects of tortuosity and porosity (Appelo & Postma, 2005), and \( h \) is the elevation (m). For the example of Mn in TA, the maximum upward diffusive flux was 0.23 mol m\(^{-2}\) yr. When the soluble element reached the organic layer, it was scattered into the porewater of this layer, amounting to 128 L m\(^{-2}\), with an organic layer depth of 0.16 m and a porosity of 0.8. Therefore, the diffusive flux caused an input concentration of \( 1.8 \times 10^{-3} \) mol L\(^{-1}\) yr\(^{-1}\). The retention time of the porewater in the organic layers was ca. 1.4 years, based on calculations of an annal lateral transport distances of 29 and 40 m to the surrounding surface flows. The maximum Mn concentration in the organic layer, therefore, yielded 0.32 moles, which is two orders of magnitude higher than the value of 0.01 mol in the soil layer. For SY, the maximum Mn concentration in the organic layer was 0.02 mol, calculated based on the same processes. This number is similar to the values observed in the organic layer, ca. 0.01 mol. This difference between TA and SY may have been due to the faster lateral flux in SY than in TA (Figure 10), which would also be associated with the layer’s soil texture. Moreover, in our calculation, both the soil-porewater chemical interaction and the lower vertical Mn gradient in the loam were negligible. If restrictions are imposed, the calculated concentration would be further reduced.

### 4.5. Conceptual Model of Active Layer Dynamics

A conceptual model representing the thawing-freezing process, with changes in active layer depth, is shown in Figure 11. This model indicates that the upper fraction of the organic layer begins to thaw with snowmelt from late May and is completely thawed by early July. At that time, soluble geochemical elements would form during oxidation and weathering processes of exposed surface soil, further flushing them laterally to surrounding surface waters. As soon as the organic layer and subsurface soil begin to thaw, the active layer expands downward and acidic porewater flows to the gleyed layers and finally gathers above the permafrost table. These processes mobilize elements. The soil begins to freeze in late September from the top...
downwards. This top-down freezing drives porewater flows down to deeper areas, where the reducing conditions of the gleyed layers prevail and where Mn, Mg, Al, and Ca become mobilized (Figures 4 and 8) with low relative partition coefficients. The acidic flows to deeper regions of the active layer, along with larger elemental concentrations, result in the relatively higher elemental concentrations of the suprapermafrost water (Figure 6). Except for Cd and Mo, most elements above the detection limit showed an increasing concentration during the autumn season, with the highest concentration in late autumn. Mn and Fe showed apparently higher concentrations than the other elements, which is attributed to the complex mineral weathering dynamics of Fe/Mn in late autumn. Moreover, Mn is known to actively migrate as a typomorphic element under tundra conditions and plays an important role in biological processes (Kataeva, 2013; Raudina et al., 2017). When the active layer reaches the greatest annual depth, the surface soil is frozen during September and October. Geochemical elements in the surface flows and suprapermafrost waters approximately correspond to the element concentrations in the porewater of unfrozen soil.

As an increase in the active layer depths in Russian Siberia is anticipated (Romanovsky et al., 2010), the downward moving trend of the thawed active layer will expose previously frozen soil, which will be intensively involved in mineral weathering processes, so that there will be strong correlations between geochemical elements in the surrounding surface and suprapermafrost waters and the thawing degree of the active layer. Therefore, this correlation, caused by the complex dynamics of soil and mineral weathering sources, a reducing environment, and elemental oxidation, indicates that perennial monitoring is needed.

5. Conclusions

This study investigated changes in the concentration of geochemical elements in the active layer during the permafrost thaw period and their transport to surface waters by way of lateral surface flows and suprapermafrost water. The patterns for surrounding water ponds, adjacent river surface waters, and suprapermafrost waters were generally comparable for most elements above the detection limit (Zn, Mn, Sr, Fe, Mg, Cr, Co, V, Pb, Al, and Ca), and concentrations were highest during the period from September to October, corresponding to the deepest depth of the active layer. Although a geochemical barrier in the reducing gleyed layers was observed in the soil column, certain elements (Mn, Ca, Mg, Al, and Ti) still retained high mobility above the permafrost table. Although Mn is thought to preferentially flow into surrounding waters (i.e., to the river) by way of both upper soil and suprapermafrost waters, thereby transporting organic matter such as CH₄ and CO₂ in the present study, heterogeneous landscapes with high amounts of ice and degrees of cryoturbation may have caused an additional efflux of elements to migrate into the surface waters. Nevertheless, Mn in surface flows may be a proxy for active layer processes during the period from summer to autumn. Despite the fact that geochemical elements and DOC from permafrost soils can be delivered to adjacent hydrological systems, the lateral efflux of the released elements to surface waters was still low. Future climate conditions are expected to further intensify the processes of soil-stream-river dynamics due to permafrost degradation and the complexities of active layer transport mechanisms.

Data Availability Statement

Data sets for this research are available through Ji, Xiaowen (2020), “Data of Chemical analysis from soil cores and surface waters from Yamal-Nets Area,” Mendeley Data, v1 http://dx.doi.org/10.17632/hhhns8sptr.1.

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