Quantifying exchangeable base cations in permafrost: a reserve of nutrients about to thaw

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Abstract. Permafrost ecosystems are limited in nutrients for vegetation development and constrain the biological activity to the active layer. Upon Arctic warming, permafrost thaw exposes large amounts of soil organic carbon (SOC) to decomposition and minerals to weathering, but also releases organic and mineral soil material that may directly influence the soil exchange properties (cation exchange capacity CEC and base saturation BS). The soil exchange properties are key for nutrient base cation supply (Ca^{2+}, K^+, Mg^{2+}, Na^+) for vegetation growth and development. In this study, we investigate the distribution of soil exchange properties within Arctic tundra permafrost soils at Eight Mile Lake (Interior Alaska, USA) because they will dictate the potential reservoir of newly thawed nutrients and thereby influence soil biological activity and vegetation nutrient sources. Our results highlight much lower CEC density in surface (~9 400 $cmol_c$ m^{-3}) than in the mineral horizons of the active layer (~16 000 $cmol_c$ m^{-3}) and in permafrost soil horizons (~12 000 $cmol_c$ m^{-3}). Together, with the overall increase in CEC density with depth and the overall increase in BS (percentage of CEC occupied by exchangeable base cations Ca^{2+}, K^+, Mg^{2+}, and Na^+) with depth (from ~19% in organic surface to 62% in permafrost soil horizons), the total exchangeable base cations density (Ca^{2+}, K^+, Mg^{2+} and Na^+ in g m^{-3}) is up to 5-times higher in the permafrost than in the active layer. More specifically, the exchangeable base cations density in the 20 cm upper part of permafrost about to thaw is ~ 850 g m^{-3} for Ca_{exch}, 45 g m^{-3} for K_{exch}, 200 g m^{-3} for Mg_{exch} and 150 g m^{-3} for Na_{exch}. This estimate is needed for future ecosystem prediction models to provide constraints on the size of the reservoir in exchangeable nutrients (Ca, K, Mg, Na) about to thaw.

1 Introduction

Northern ecosystems are characterized by low temperatures and the presence of ground underlain by permafrost. Within permafrost soils, the surface ground layer which thaws seasonally in summer and refreezes in winter is referred to as the active layer. Active layer thickness is crucial because it governs the soil volume for plant rooting systems, biogeochemical activity, hydrological processes, and the amount of soil organic and mineral constituents exposed to temperatures above freezing (Blume-Werry et al., 2019; Hinzman et al., 2003; Kane et al., 1991). In parallel, the presence of permafrost restricts downward movement of surface water and may create waterlogged soil conditions (Hinzman et al., 2003; Schuur et al., 2015). Together, cold temperatures, water-saturated conditions, and soil acidity reduce the decomposition rates of soil organic matter (SOM) mainly originating from dead plant tissues and lead to high SOM accumulation in surface (Schuur et al., 2008; Zimov et al., 2006).

Soil organic matter shows specific properties such as low bulk density, source of acidity, large amounts of negatively charged sites at the organic compound surface (Askin and Özdemir, 2003; Périé and Ouimet, 2008; Ping et al., 2005), and thereby largely influences multiple soil physical and chemical properties. In particular, SOM and clay minerals both contribute to the soil cation exchange capacity (CEC), which is a soil parameter that evaluates the soil complex ability to retain exchangeable

cations and prevent their lixiviation or further drainage (Doran and Safley, 1997; Feller et al., 1991; Oades et al., 1989;
40 Stevenson, 1994). Among exchangeable cations, the most common base cations Ca^{2+}, K^+, Mg^{2+} and Na^+ act as buffer against
soil acidification (Bowman et al., 2008; Tian and Niu, 2015; Ulrich, 1983). Some base cations are essential nutrients for plant
growth and development (Ca^{2+}, K^+ and Mg^{2+}) and the exchangeable soil fraction constitutes a pool of cations readily available
for plant uptake (Binkley and Vitousek, 1989; Marschner, 2012). More broadly, plant nutrient availability results from dynamic
interaction of soil processes (as weathering, atmospheric deposition, leaching and biological cycling; Jobbágy and Jackson,
45 2001) and the surface exchange reactions are especially important for the nutrient K, but also for the key nutrients Ca and Mg
(Havlin, 2005; Krull et al., 2004; Peverill et al., 1999).

Upon warming in Arctic, permafrost thaw results in active layer thickening, ground subsidence and changing soil moisture
conditions (Hirst et al., 2022; Olefeldt et al., 2016; Osterkamp, 2005; Osterkamp et al., 2009). Moreover, permafrost thaw may
50 influence organic constituents forming the soil exchange complex. In particular, increased SOM microbial degradation (Hobbie
and Chapin, 1998; Nadelhoffer et al., 1992; Schuur et al., 2015; Shaver et al., 2006) or lateral transport of organic soil material
from soils to streams (Plaza et al., 2019) generates massive loss of soil organic carbon (SOC). Although the SOC stock and
distribution in permafrost-affected soils is well characterized (Hugelius et al., 2014; Tarnocai et al., 2009; Strauss et al 2017;
Schuur et al 2018), its evolution is uncertain and partly depends on the vulnerability of organic constituents to decompose
55 upon soil warming and permafrost thaw (Schaefer et al., 2011; Schuur et al., 2008). Additionally, permafrost thaw exposes
soil material at depth (Beermann et al., 2017; Keuper et al., 2017; Salmon et al., 2016), with potential organic inclusions and
clay minerals that may contribute to the soil exchange complex in the active layer, and reservoirs of exchangeable cations with
readily available nutrients (Ca^{2+}, K^+, Mg^{2+}, Na^+) for plant uptake. Overall, changes in the active layer thickness (ALT) and in
the balance between organic and mineral constituents of the active layer are likely to influence the size of the reservoir and the
60 sources of available nutrients for plant uptake, and thereby promote the tundra vegetation productivity. However, these changes
in nutrient availability upon permafrost thaw remain poorly quantified and further estimation of the exchangeable nutrient
(Ca^{2+}, K^+, Mg^{2+}, Na^+) reservoir about to thaw relative to the current stock in the active layer is a needed step for ecosystem
models simulating the evolution of vegetation development and microbial activity upon permafrost thaw (Fisher et al., 2014;
Koyama et al., 2014; Sulman et al., 2021; van der Kolk et al., 2016a).
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The main objective of this study is to investigate the influence of permafrost thaw on the properties of the soil exchange
complex. We posit that permafrost thaw exposes a deep soil layer with contrasted properties of the soil exchange complex
relative to the seasonally thawing active layer, and we aim to quantify this contrast. Across a range of permafrost soil profiles
divided into two groups depending on their active layer thickness (ALT < 60 cm where ALT = 53 ± 5 cm and ALT > 60 cm
70 where ALT = 76 ± 12 cm), we investigate the difference in the constituents controlling the soil capacity to retain exchangeable
cations and the distribution of exchangeable cations retained, and we quantify the exchangeable cations density in the
seasonally thawed active layer and in the permafrost.

2. Material and methods

2.1 Study area and sampling

75 The study is conducted within the Eight Mile Lake (EML) watershed close to Healy, in Interior Alaska, USA (63°52'42N,
149°15'12W; Schuur et al., 2009). The research site is underlain by degrading permafrost in the discontinuous permafrost zone
(Natali et al., 2011; Osterkamp et al., 2009) and covers a natural gradient in permafrost thaw (Gradient site). Long-term (1977-
2015) mean annual air temperatures range between 10 ± 3.8 °C (for the growing season from May to September; Natali et al.,
2012) and -17 ± 2.5°C (for the non-growing season) and the mean annual precipitation is about 381 mm (Natali et al., 2011;

80 Vogel et al., 2009). Soils at EML are classified as Histic Turbic Cryosols (IUSS Working Group WRB, 2015) and characterized by a thick organic layer up to 55 cm (SOC ≥ 20%) in surface. This organic horizon overlays a cryoturbated mineral soil (SOC < 20%) composed of glacial till and loess parent material (Hicks Pries et al., 2012; Osterkamp et al., 2009; Vogel et al., 2009) with dominant amounts of quartz and feldspars (Plaza et al., 2019). The site is located on moist acidic tundra, with a dominance of sedges (as *Eriophorum vaginatum* L. and *Carex bigelowii* Torr. ex Schwein), evergreen shrubs (e.g., *Andromeda polifolia*

85 L., *Rhododendron tomentosum* Harmaja, *Vaccinium vitis-idaea* L., and *Empetrum nigrum* L.), deciduous shrubs (e.g., *Vaccinium uliginosum* L. and *Betula nana* L.) and forbs (e.g., *Rubus chamaemorus* L.). Non-vascular plant cover is dominated by mosses (mainly *Sphagnum* spp., *Dicranum* spp., and feather mosses including *Hylocomium splendens* and *Pleurozium schreberi*) and lichen species (e.g., *Nephroma* spp., *Cladonia* spp., and *Flavocetraria cucullata*; Deane-Coe et al., 2015; Natali et al., 2012; Schuur et al., 2007). Since the start of the thermokarst development, vegetation cover changed with the evergreen

90 and deciduous shrubs (as *V. uliginosum* and *R. tomentosum*), and forbs (as *R. chamaemorus*) being dominant at the expense of the sedges (Jasinski et al., 2018; Mauclet et al., 2022a; Schuur et al., 2007; Villani et al., 2022).

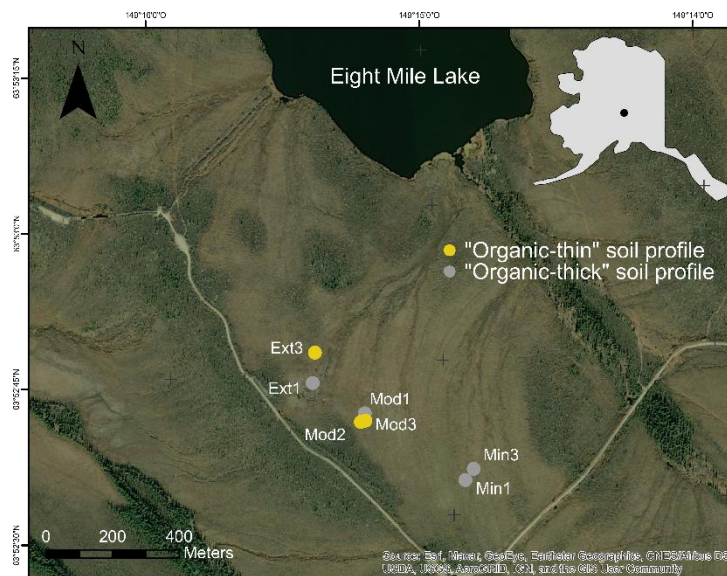



Figure 1: Study site at Eight Mile Lake, in Central Alaska, USA (inset). The Gradient site is a natural thermokarst gradient originally
95 **composed of areas of minimal (Min), moderate (Mod), and extensive (Ext) permafrost thaw. According to the active layer thickness measurement, we separate the seven soil cores into two groups: "organic-thin" soil profile (ALT > 60 cm; in yellow) and "organic-thick" soil profile (ALT < 60 cm; in grey). Source: Esri, HERE, Garmin, OpenStreetMap contributors, and GIS user community.**

A field campaign took place on the natural and monitored gradient of permafrost thaw at EML (Gradient Site; Fig 1; Osterkamp et al., 2009; Vogel et al., 2009) at the late season period between mid-August and early-September in 2019 to sample
100 permafrost soil profiles with contrasted thaw depth from 48 to 88 cm depth. Seven soil cores were collected along the permafrost gradient and their respective active layer thicknesses (ALT) were measured with a metal probe (Table S1). This measurement highlights that ALT no longer follows the gradient of permafrost thaw defined in the literature (Schuur et al., 2021). We then divided our seven soil cores according to ALT with the "organic-thin" soil profile (ALT > 60 cm, corresponding to an organic layer thickness OLT < 40 cm) and "organic-thick" soil profile (ALT < 60 cm, corresponding to
105 OLT > 40 cm). This relationship between ALT and OLT can be explained by the low thermal diffusivity and conductivity of the organic matter (Adams, 1973; Farouki, 1981) that insulates the soil (Decharme et al., 2016; Lawrence and Slater, 2008) and thereby influences the permafrost thaw depth. The mineralogy of the soils from this site is similar and mineral phases observed are plagioclase, K-feldspath, amphibole, quartz, muscovite, vermiculite, kaolinite and illite (Mauclet et al., 2023). Soils were sampled to a maximum depth of 120 cm and subdivided into 5 cm to 10 cm horizons. Active layer samples were
110 collected using a hammer and chisel as deep as possible (up to 45 cm, unless water table was higher than 45 cm). Below 45 cm depth, active layer and permafrost samples were collected using a steel pipe (diameter 4.5 cm) that was manually hammered

into the soil using a sledgehammer (Palmtag et al., 2015). The demarcation between organic and mineral horizons (organic layer thickness OLT) was determined visually and confirmed by %OC analysis (section 2.2) when the %OC of the soil decreased to less than 20% (Hicks Pries et al., 2012). For each soil core, we kept separated samples from organic active layers, mineral active layers, and permafrost soil layers. In the lab, soil samples (n=85) were dried at air temperature in a ventilated and temperature-controlled room. Mineral horizons (SOC ≤ 20%) were sieved at 2 mm and organic horizons (SOC > 20%) free of large roots were ground.

2.2 Characterization of the total soil fraction

2.2.1 Soil pH

The soil pH_{H2O} and pH_{KCl} were measured on all soil samples (n=85) with the pH probe (Inlab micro) connected to the pH-meter (Mettier Toledo SevenCompact DuoS213). Mineral soil samples were mixed in the 1:5 proportion with H_2O or 1M KCl (Peech, 1965), whereas organic soil samples required adaptation and were mixed in 1:15 proportion with H_2O or 1M KCl in order to have enough liquid solution for the insertion of the pH probe. Although dilution increases the pH of the soil suspension, regardless of the initial pH value of the soil or the distilled water used in preparation of the suspensions (Peech, 1965), we obtained lower pH in organic soil samples (4.0 ± 0.25 for pH_{H2O} and 3.3 ± 0.29 for pH_{KCl}) than in mineral soil samples (5.0 ± 0.66 for pH_{H2O} and 4.2 ± 0.66 for pH_{KCl}). The pH probe was calibrated for pH 4 and 7 before measurement.

2.2.2 Soil organic carbon content measurement and estimation of soil bulk density

The total soil carbon content was measured on all soil samples (n=85) with the C, N, S elemental analyzer vario EL CUBE (ELEMENTAR ®, Germany). The C measurements on soil samples (n=85) are reported to the dry soil matrix (105°C). Each sample was measured twice and the average standard deviation for C content ~5%, with the detection limit <0.1%. As the presence of carbonates was not detected by X-ray diffraction, the total soil carbon content is considered equivalent to soil organic carbon (SOC) content. The SOC content analysis was used to confirm the limit between organic (SOC > 20%) and mineral (SOC ≤ 20%) soil horizons (OLT, Hicks Pries et al., 2012).

Given that bulk densities were not measured upon sampling, bulk densities were estimated based on measured SOC content. Because of the strong correlation between the soil organic matter content and the soil bulk density (Askin and Özdemir, 2003; Chaudhari et al., 2013; Périé and Ouimet, 2008), we established a linear regression (Figure 2; Eq. 1; R² = 0.73) to relate the SOC content (g_C kg_{soil}^{-1}) to soil bulk density (BD, in g_{soil} cm^{-3}) based on 443 paired measurements on active layer and permafrost samples from a previous study at the EML research site (Interior Alaska, USA; Plaza et al., 2017). This regression reflects the higher bulk density in mineral horizons than in organic horizons (Figure 2), even if the variability in bulk density is higher in soils with low SOC content (mineral horizons). We applied the resulting empirical equation of correlation between the two parameters (Eq. 1) to our SOC data for soil samples collected at the Gradient site in 2019.

$$BD_i = 0.92 - 0.0018 \times SOC\ content_i \qquad (1)$$

With i the sample horizon considered, and $SOC\ content$ in (g_C kg_{soil}^{-1}).

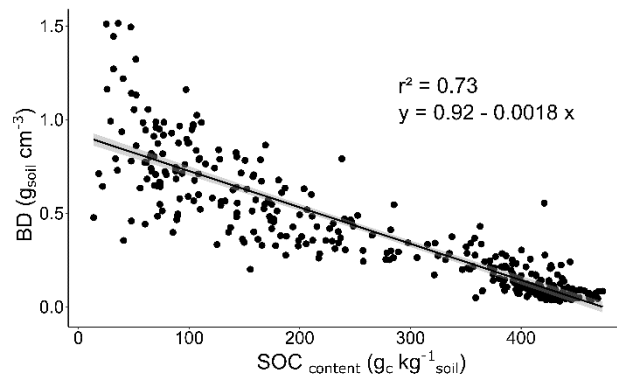



Figure 2: Linear correlation between soil organic carbon content (SOC content in g_C kg_{soil}^{-1}) and bulk density (BD in g_{soil} cm^{-3}) in Eight Mile Lake, Alaska, USA (n=443; adapted from Plaza et al., 2017).

2.2.3 Soil elemental composition

150   On two selected soil profiles (n = 25) with contrasted permafrost thaw states (one "organic-thick" soil profile Min1 where ALT = 55 cm and one "organic-thin" soil profile Mod3 where ALT = 75 cm) the total concentration in Ca, K, Mg, and Na in bulk soils was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6500 ThermoFisher Scientific, Waltham, USA) after alkaline fusion (Chao and Sanzolone, 1992). For the fusion, a portion of the ground sample (80 mg) is mixed with lithium metaborate and lithium tetraborate and heated up to 1000°C for 10 minutes. Then, the fusion

155   bead is dissolved in HNO_3 2.2 N at 80°C and stirred until complete dissolution. The loss on ignition is assessed at 1000°C, and the total element content is expressed in reference to the dry weight at 105°C. The accuracy on mineral element (Ca, K, Mg, and Na) analyses was assessed using trueness (± 2%, ± 5%, ± 2%, and ± 2%; respectively) on the USGS basalt reference material BHVO-2 (Wilson, 1997) and the analytical precision (± 0.5%) for each element. The limits of detection (LOD) were 0.05 mg L^{-1}, 0.01 mg L^{-1}, 0.001 mg L^{-1}, and 0.02 mg L^{-1} for Ca, K, Mg, and Na, respectively. The blank levels were below the

160   detection limit for Ca, K, Mg, Na. The sum the total concentration in Ca, K, Mg, and Na was calculated as the total reserve in bases (TRB expressed in cmol$_c$ kg^{-1}; Herbillon, 1986).

2.3 Characterization of the exchangeable soil fraction

2.3.1 Potential soil cationic exchange capacity, concentration in exchangeable base cations, and base saturation

165   The concentration in exchangeable base cations and the potential CEC of soil were determined on all soil samples (n=85). The exchangeable base cations (Ca^{2+}, K^+, Mg^{2+}, Na^+) were collected at neutral pH by ammonium acetate extraction (1M NH_4OAc, Metson, 1956) and their concentration within the extracts was determined by ICP-OES. The potential soil CEC (expressed in reference to the dry weight at 105°) was determined by desorbing the ammonium from the soil exchange complex and measuring the amount of ammonium recovered by spectrophotometry (Spectroquant® ammonium test kits). The base

170   saturation (BS; percentage of CEC occupied by exchangeable base cations Ca^{2+}, K^+, Mg^{2+}, and Na^+) was calculated with the equation Eq. 3:

$$BS = \frac{\sum(Ca^{2+} + K^+ + Mg^{2+} + Na^+)}{CEC} \tag{3}$$

2.3.2 Estimates for CEC density, exchangeable base cations stock and density

175   While the usual soil CEC (cmol$_c$ kg^{-1}) is relative to soil mass, we evaluated here the CEC density relative the soil volume (in cmol$_c$ m^{-3}) along permafrost soil profiles. For the calculation, we relied on the soil CEC (in cmol$_c$ kg^{-1}) and bulk density (BD in g cm^{-3}) with the equation Eq. 4:

$$CEC\ density_i = CEC_i \times BD_i \times 1000 \tag{4}$$

With i the sample horizon considered.

On four soil profiles (n = 47) that have samples of each horizon down to 1 m (two "organic-thick" soil profiles Min3 and Mod1, and two "organic-thin" soil profiles with Mod2 and Mod3), we evaluated the exchangeable base cations density (Ca^{2+}, K^+, Mg^{2+}, and Na^+; in g m^{-3}) using the mineral element concentration of soil [X] (g kg^{-1}) and the bulk density (BD in g cm^{-3}) with the equation Eq. 5:

$$exchangeable\ base\ cations\ density\ X_i = [X]_i \times BD_i \times 1000 \tag{5}$$

With i the sample horizon considered. This exchangeable base cations density is independent of the depth of each horizon considered and allows us to compare the density of horizons that have different thicknesses.

From this exchangeable base cations density (in g m^{-3}), we also estimated the exchangeable base cations (Ca^{2+}, K^+, Mg^{2+}, and Na^+) stocks (in g m^{-2}) using the thickness of each horizon (HT; in m) with the equation Eq. 6:

$$stock\ X_i = exchangeable\ base\ cations\ density\ X_i \times HT_i \tag{6}$$

All statistics were performed using R 4.2.1 (RStudio Inc., Boston, Massachusetts, USA; R Core Team, 2018) and plots using the ggplot2 package. The significant differences between organic active layer, mineral active layer and permafrost were evaluated using the non-parametric Kruskal-Wallis test (α = 0.05). If significant differences were observed at a p-value $< \frac{\alpha}{2}$, a post hoc Dunn's test was carried out.

3. Results and discussion

3.1 Distribution of the organic and mineral constituents from the soil exchange complex within permafrost soil profiles

The soils from EML accumulate organic matter, and show contrasts in SOC contents between the organic surface (SOC > 20%) and deep mineral (SOC ≤ 20%) soil horizons (Fig. 3). This is consistent with expectations for typical sub-Arctic tundra soils (Christensen et al., 1999; Hugelius et al., 2014; Michaelson et al., 1996). On average, organic soil horizons hold about 43% OC, whereas mineral soil horizons hold about 4.5% OC (Table S2). For some soil profiles, increase in SOC content at the bottom of the active layer (60-80 cm depth; up to 30% OC) may reflect the presence of old organic matter inclusions within the soil mineral phase. This supports that the transient layer, that may contain thaw unconformities reflecting previous periods of exceptional permafrost thaw, is sensitive to cryoturbation that can mix soil material by repeated freezing and thawing (Fig. 3; Bockheim and Hinkel, 2007; Ping et al., 2008; Shur et al., 2005).

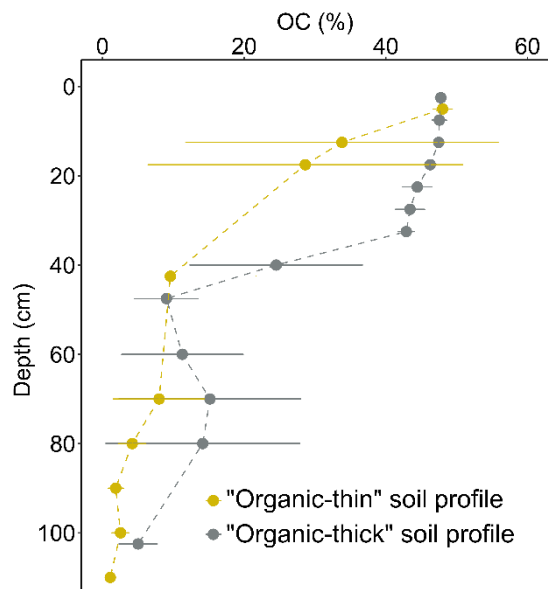



Figure 3: Distribution of soil organic carbon content (%OC) into permafrost soil. The "organic-thin" (in orange) soil profiles present more shallowly distributed high values for OC content, and the "organic-thick" (in grey) soil profiles present more deeply distributed high values for OC content. The error bars (horizontal lines) represent the standard deviation on the mean values (of 3 to 7 samples).

In parallel to the decrease in OC content with depth, the analysis of the soil composition in mineral elements reveals a significant increase in the Ca, K, Mg, and Na total concentrations between the organic and the mineral active layer (3 to 9 times; p-value < 0.01), and permafrost (3 to 9 times; p-value < 0.01); whereas concentrations are not significantly different between mineral active layer and permafrost layer (p-value > 0.1; Fig. 4). On average, organic active layers contain ~2.5 ± 0.26 g kg^{-1} Ca, ~1.4 ± 0.31 g kg^{-1} Mg, ~4.4 ± 1.9 g kg^{-1} K, and ~1.3 ± 0.66 g kg^{-1} Na, and mineral active layer and permafrost layers contain about ~8.1 ± 1.0 g kg^{-1} Ca, ~7.5± 0.78 g kg^{-1} Mg, ~16 ± 0.58 g kg^{-1} K, and ~11 ± 0.54 g kg^{-1} Na (Table S3). Moreover, Ca, Mg, K and Na concentrations are not significantly different (p-value > 0.1) between the organic-thick and the organic-thin soil profiles.

This net difference in the total concentrations in Ca, K, Mg and Na between surface and deep soil horizons reflects the transition between organic and mineral soil horizons (Fig. 4), with higher elemental concentrations in the mineral soil horizons originating from the mineral constituents. In particular, the mineral phases observed at EML include primary minerals (i.e., quartz, micas, feldspar-K, plagioclase, and amphibole) and secondary minerals (i.e., kaolinite, vermiculite, and illite; Mauclet et al., 2023). While some secondary minerals (as clay minerals, Al and Fe oxides) may directly contribute to the soil exchange complex, primary minerals constitute a soil reserve in potentially weatherable minerals that may release base cations into the soil solution. Therefore, the soil composition and distribution in minerals within permafrost will directly influence the soil exchange properties upon active layer thickening.

Overall, our data support the hypothesis of changing balance between organic and mineral constituents forming the soil exchange complex upon permafrost thaw. A thinner organic layer in more thawed permafrost soils leads to a lower contribution from organic constituents to the soil exchange complex in active layer relative to less thawed permafrost soils. In addition, permafrost thaw exposes mineral layers containing proportionally less organic matter and more clay minerals than the above active layer, leading to an increasing contribution from clay minerals to the soil exchange complex at increasing depth, and providing new sites for cation exchange.

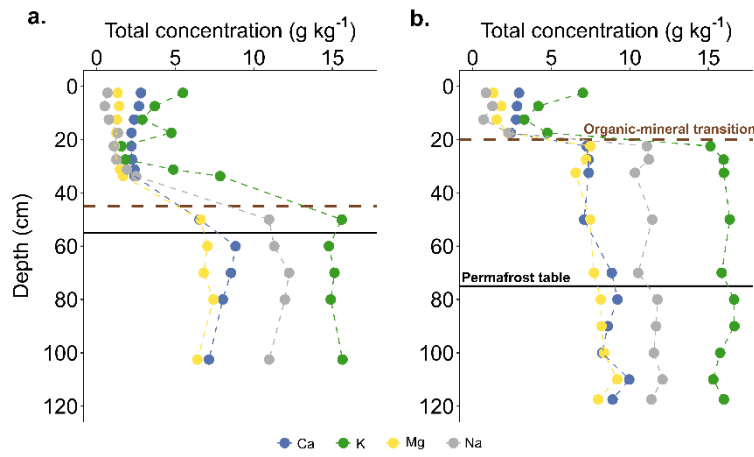



Figure 4: Distribution of total concentrations in Ca, K, Mg, and Na (g kg⁻¹) in an "organic-thick" soil profile (Min1) and an "organic-thin" soil profile (Mod3). Permafrost table is indicated by the straight black line, and the transition between the organic (SOC ≥ 20%) and mineral (SOC < 20%) soil is indicated by the dotted brown line.

3.2 Variation of the soil exchange properties along permafrost soil profiles

3.2.1 Change in CEC distribution and CEC density with soil constituents

Given that the distribution of soil CEC follows the SOC content distribution (R^2 = 0.91), high CEC values are more deeply distributed in the "organic-thick" (OLT ≥ 40 cm) than in the "organic-thin" (OLT < 40 cm) permafrost soil profiles (Fig. 5a). Moreover, CEC in the organic active layer is significantly higher than in the mineral active layer (4 times, p-value < 0.001) and significantly higher than in permafrost (5 times, p-value < 0.001); whereas CEC are not significantly different (p-value > 0.1) between the mineral active layer and permafrost. Overall, our CEC values measured in organic horizons (~91 ± 24 cmol$_c$ kg⁻¹) and mineral horizons (~20 ± 6 cmol$_c$ kg⁻¹; data from Table S2) are in the same range than the values reported in arctic tundra soils underlain by permafrost (Ping et al., 2005, 1998; CEC ~88 ± 36 cmol$_c$ kg⁻¹ for organic soil layers and ~24 ± 12 cmol$_c$ kg⁻¹ for mineral soil layers). Locally, we observe CEC values at 60-80 cm 1.5-times higher in "organic-thick" than in "organic-thin" soil profiles (Fig. 5a), and this reflects deep organic inclusions in "organic-thick" soil profiles (Fig. 3). Below the organic-mineral transition, given that the concentration in organic carbon decreases and the presence of clay minerals is verified (vermiculite, kaolinite, illite; Mauclet et al., 2023), the contribution from the clay minerals to the CEC increases.

Furthermore, soil CEC is dictated by the presence of variable charges provided by organic matter, some clay minerals, and Fe and Al oxides. While the organic matter is usually associated with a variable charge, clay minerals are assumed to have both constant and variable charges (Kamprath and Smyth, 2005; Weil and Brady, 2016). As the strength of the variable charge depends on ionic strength and pH, chemical soil environment directly influences the soil variable charge and thereby the soil CEC. In our soils, the average pH$_{H2O}$ oscillates between ~4.0 in surface and ~5.3 at depth (Table S2). The low pH in the organic-rich soil surface (pH$_{H2O}$ ~ 4) is expected to reduce the number of negatively charged exchange sites on the variable charge components (i.e., organic matter and clay minerals as kaolinite) and thereby reduce the effective CEC compared to the deep mineral horizons with higher pH (pH$_{H2O}$ ~5.3) and less variable charge components (Bigorre et al., 2000).

We observe peaks in potential CEC at about 25 cm depth in "organic-thick" soil profiles (Fig. 5a) that seem to be correlated with the water table depth (27 ± 8.4 cm). An accumulation of Fe-oxides at the level of the water table (Fig. S1) can be explained by the translocation of reduced Fe upon water saturated condition and Fe oxide precipitation in favorable oxic conditions at the redox interface (Herndon et al., 2017; Monhonval et al., 2021). The increase in potential CEC can therefore be explained by a methodologically induced potential CEC associated to negative charges created on Fe-oxides at the pH buffered at 7 in the method (Metson, 1956) but not present in the soil at pH ~4.

Unlike the distribution of CEC values within soil profile, CEC density shows lower values in the organic active layers (~9 400 ± 6 300 cmol$_c$ m^{-3}) than in the mineral soil horizons (~16 000 ± 4 000 cmol$_c$ m^{-3} for mineral active layer; ~12 000 ± 3 500 cmol$_c$ m^{-3} for permafrost) (Table S2). More specifically, estimates for CEC density increase along the organic active layer and stabilize in the mineral soil horizons (Fig. 5b). When we integrate the CEC density over the permafrost soil profile top meter, "organic-thick" soil profiles have lower CEC stock (~12 000 cmol$_c$ m^{-2}) than the "organic-thin" soil profiles (~14 000 cmol$_c$ m^{-2}). This is mainly explained by the difference in organic matter contribution to the total CEC stock: the uppermost 40 cm of "organic-thick" soil profiles have lower CEC stock (~3 500 cmol$_c$ m^{-2}) than the "organic-thin" soil profiles (~5 000 cmol$_c$ m^{-2}).

The major increase in the estimates for CEC density in mineral horizons relative to organic horizons is driven by the massive change in bulk density. The increase in soil bulk density with depth overcomes the lower CEC values, and results in higher estimates for CEC density. Within the top soil meter, the organic active layer in "organic-thin" soil profile generates a higher contribution of clay mineral to the CEC density than the organic active layer in "organic-thick" soil profile. Overall, our results support that SOM accumulation in surface influences the distribution of CEC density in permafrost soil profiles (Fig. 5b).

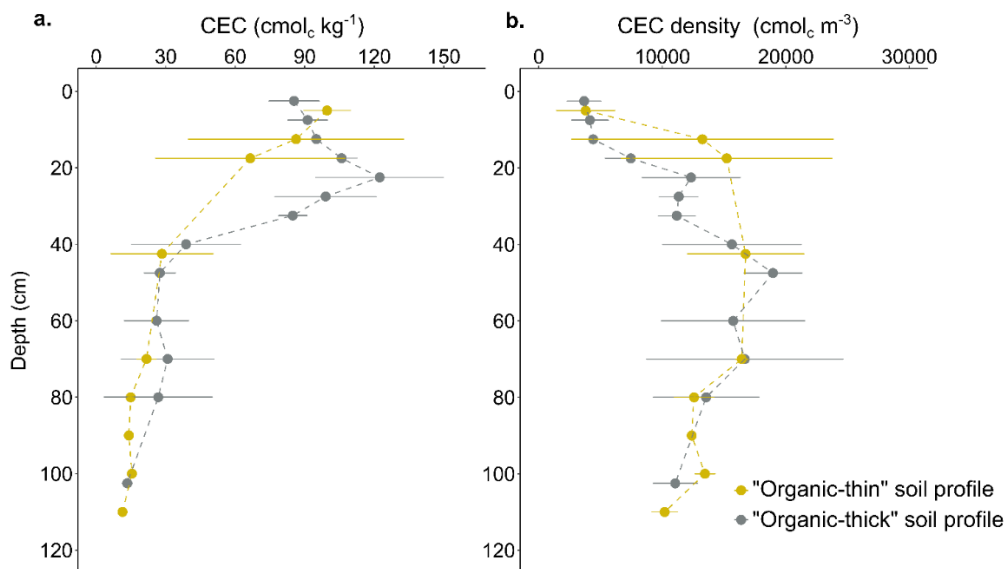



Figure 5: (a) Distribution of the soil cation exchange capacity (CEC, in cmol$_c$ kg^{-1}) and (b) distribution of the density of soil cation exchange capacity (CEC density, in cmol$_c$ m^{-3}) with depth between "organic-thin" (in orange, n=34) and "organic-thick" (in grey, n=51) permafrost soil profiles. The error bars (horizontal lines) represent the standard deviation on the mean values (of 3 to 7 samples).

3.2.2 Variation in base saturation (BS), pH and total reserve in bases (TRB) along soil profiles

Within permafrost soils at EML, we observe a significant decrease in the base saturation (BS; percentage of CEC occupied by exchangeable base cations Ca^{2+}, K$^+$, Mg^{2+}, and Na$^+$) of the soil exchange complex in the organic active layer relative to the mineral active layer (2 times, p-value < 0.001) and relative to permafrost (3 times, p-value < 0.001); whereas permafrost is 2-times lower (p-value < 0.01) the mineral active layer and permafrost (Fig. 6a). On average, active layers show base saturation around ~19% in the organic soil surface and ~35% in the underlying mineral horizons, while permafrost soil horizons show base saturation around ~62% (Table S3).

The distribution of BS along permafrost soil profiles shows a positive linear relation with soil pH (R² = 0.67; Fig. 6b), well in line with previous studies across various ecosystems (Beery and Wilding, 1971; Binkley et al., 1989; Giesler et al., 1998;

Thomas, 2019) including the Arctic (Ping et al., 2005). This reflects the balance between acid cations and base cations on the soil exchange complex. As the BS contributes to the soil buffer capacity (Bowman et al., 2008; Tian and Niu, 2015; Ulrich, 1983), the more acidic conditions in permafrost soil surface (pH_{H2O} ~ 4.0) reveal lower soil buffer capacity and thereby lower BS (black dots on Fig. 7). In contrast, less acidic soil conditions at depth (pH_{H2O} ~5.3) reflect higher soil buffer capacity and thereby higher BS. The lower values of pH_{KCl} (between 3.29 in surface and 4.47 at depth) than pH_{H2O} (between 4.02 in surface and 5.27 at depth; Table S2) also support the presence of exchangeable acid cations adsorbed onto the soil exchange complex.

The difference in BS between the organic soil surface and the deep permafrost soil likely reflects the increase in the weatherable mineral reserve in the soil with depth, quantified by the total reserve in bases (TRB, sum of total concentration in Ca, K, Mg, and Na; Herbillon, 1986). The TRB is significantly lower (3 times, p-value < 0.01) in the organic active layer than in the mineral active layer and than in permafrost (4 times, p-value < 0.01); whereas TRB is no significantly different (p-value > 0.1) between the mineral active layer and permafrost. The net increase in TRB with depth (higher values in the mineral active layer and permafrost ~180 $cmol_c$ kg^{-1} than in the organic active layer ~52 $cmol_c$ kg^{-1}; Table S3) follows the organo-mineral transition and reflects higher soil reservoirs of total Ca, K, Mg, and Na in the mineral soil layers compared to the organic active layer. In particular, BS in the mineral soil horizons increases gradually between the mineral active layer, the upper permafrost horizons and the deep permafrost horizons (Fig. 6a) whereas the TRB remains constant (Fig. 6c). This likely reflects the influence of permafrost thaw on the leaching of exchangeable base cations (Ca^{2+}, K^+, Mg^{2+}, and Na^+) that are soluble cations. The seasonally thawed mineral active layer is subject to more cation leaching than the upper permafrost (potentially thawed upon exceptional previous warming), and more than the deep permafrost.

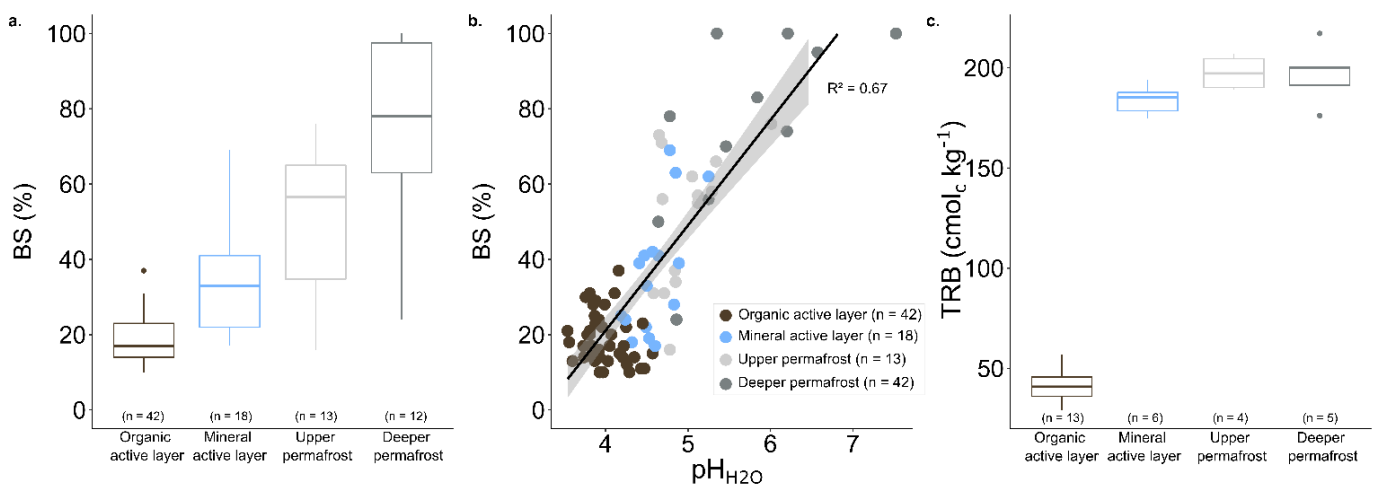



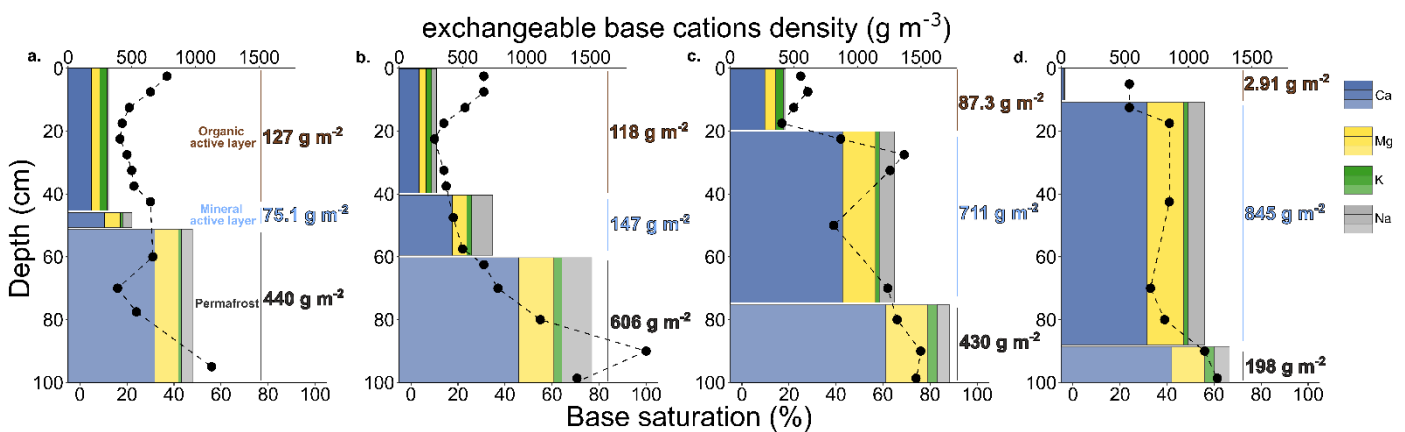
Figure 6: (a) Distribution of base saturation (BS, in %) represented as boxplots, (b) linear correlation between BS and soil pH, and (c) distribution of the total reserve in base (TRB in $cmol_c$ kg^{-1}; Herbillon, 1986) represented as boxplots in organic (brown) and mineral (blue) active layers, and in upper (light grey) and deeper (dark grey) permafrost. The upper permafrost consists of soil samples less than 20 cm below the permafrost table and the deeper permafrost consists of soil samples at least 20 cm below the permafrost table. In each box plot, the horizontal line represents the median, the end of the box is the 25-75% quartiles, and whiskers are 1.5 interquartile ranges from the median. Data points outside of the 1.5 interquartile ranges are represented as dots.

3.2.3 Change in the distribution of exchangeable base cations

The fractions of exchangeable base cations (considered as readily available for plant uptake) over the total concentration of these elements in soils are significantly higher in organic than in mineral active layer (between 3 and 17 times, p-value < 0.001), and than in permafrost (between 6 and 35 times, p-value < 0.001; whereas these fractions are not significantly different between mineral active layer and permafrost (p-value > 0.1) . On average, from the total Ca, K, Mg, Na concentrations, we

observe that ~74%, ~16%, ~47% and ~32% is exchangeable in organic soil layers, and ~17%, <1%, ~5.5% and ~2.1% is exchangeable in mineral soil layers, respectively (Table S3). These results are well in line with the proportions of exchangeable base cations reported for an Alaskan tundra site, such as >70% for Ca_{exch} and 18% of K_{exch} in organic soil horizons, and ~23% for Ca_{exch} and 1% for K_{exch} in mineral soil horizons (Chapin et al., 1979).

We observe the same trend for the stock (in g m^{-2}; numbers in Fig. 7) where exchangeable base cations stock in organic layer is significantly lower than in mineral active layer (8 times, p-value < 0.001), and than in permafrost (7 times, p-value < 0.001); whereas stocks are not significantly different (p-value > 0.1) between the mineral active layer and permafrost. The stocks are higher where layers are thicker: mineral active layer is enriched in exchangeable cations from 75 to 845 g m^{-2} (from 5 to 78 cm thick; Fig. 7 a to d) and permafrost layer is depleted in exchangeable cations from 606 to 198 g m^{-2} (from 40 to 12 cm thick; Fig. 7 a to d). These results are mainly explained by the layer thicknesses that are different between soil profiles: stock is higher where layers are thicker. To be able to investigate the "potential" stocks of exchangeable cations independent to the soil thickness, we converted the concentrations in exchangeable base cations into exchangeable base cations density (in g m^{-3}; Fig. 7). At EML, permafrost soil profiles show an increase in exchangeable base cations density (Ca^{2+}, K^{+}, Mg^{2+} and Na^{+} in g m^{-3}) with depth that follows the increase in BS (Fig. 7). On average, each exchangeable base cations density significantly increases from organic active layer to permafrost (5 times, p-value < 0.001) as: from 180 to 900 g m^{-3} for Ca^{2+}; from 51 to 55 g m^{-3} for K^{+}; from 62 to 250 g m^{-3} for Mg^{2+}; and from 22 to 140 g m^{-3} for Na^{+} (Table S4), considering a higher variability in the estimation for mineral than for organic soils according to the bulk density estimates (Figure 2). Furthermore, we observe a difference between the "organic-thick" soil profiles (Fig. 7a-b) and "organic-thin" soil profiles (Fig. 7c-d): exchangeable base cations density of the organic layer is 1.3-times higher in "organic-thick" than "organic-thin" soil profiles whereas exchangeable base cations density of the mineral layer is 1.5-times lower in "organic-thick" than "organic-thin" soil profiles.

Overall, the distribution of exchangeable base cations density follows the soil distribution of CEC density and BS, and results in a reserve in exchangeable base cations (Σ Ca^{2+}+K^{+}+Mg^{2+}+Na^{+}) 5-times higher at depth than in surface. Upon warming, permafrost thaw exposes deeper permafrost soil horizons to above zero temperatures and thereby increases the potential soil capacity to retain base cations readily available for plant uptake (i.e., soil CEC density). This provides newly thawed pool of nutrient base cations that can be sensitive to leaching. There is an increase in exchangeable cations density (independent of the thickness layer) in the mineral active layer at the "organic-thin" (~1100 g m^{-3}) compared to "organic-thick" (~500 g m^{-3}) soil profiles. As Arctic ecosystems only rely on active layer thickness in providing essential nutrients to sustain vegetation growth and development (Iversen et al., 2015; Ping et al., 1998), the contrast in nutrient base cation between the organic and the mineral parts of the active layer is of great importance for changes in tundra vegetation productivity.

 Figure 7: Distribution of exchangeable base cations density (Ca^{2+}, Mg^{2+}, K^+, Na^+; bar plots; in g m^{-3}) and stock (numbers; in g m^{-2}), and base saturation (black dots) along (a-b) two "organic thick" (Mod1 n=13 and Min3 n=14, respectively) and (c-d) two "organic-thin" soil profiles (Mod3 n=12 and Mod2 n=8, respectively).

3.3 Influence of vegetation nutrient cycling on the exchangeable base cations density within permafrost soil profiles

In this section, we investigate the ecological influence of vegetation nutrient uptake and cycling on the distribution of specific exchangeable base cation density (Fig. 7; in g m^{-3}) within permafrost soil profiles. When looking at the density of the four exchangeable base cations individually, we observe different trends in their vertical distributions into active layer soil horizons. Density in exchangeable Ca, Mg, and Na is low in the organic part of the active layer, and significantly increases (p-value < 0.001) with depth, even if the variability in bulk density is higher in mineral horizons (Figure 2). On average, these densities are about 4 (for Ca_{exch} and Mg_{exch}) and 5 (for Na_{exch}) times lower in organic than in mineral active layer horizons. Conversely, density in K_{exch} is 1.4-times higher in the organic than in mineral active layer horizons. As the exchangeable base cation densities follow the transition between organic and mineral soil horizons, the low (for Ca_{exch}, Mg_{exch}, Na_{exch}) and high (for K_{exch}) values of density are more deeply distributed in "organic-thick" than in "organic-thin" permafrost soils.

While the distributions in Ca_{exch}, Mg_{exch}, and Na_{exch} densities with depth reflect a depletion in nutrient base cations within the organic soil surface relative to the mineral soil horizon, the singular vertical distribution of K_{exch} across the active layer suggests a nutrient uplift through plant nutrient uptake and cycling, known as biolifting process (Jobbágy and Jackson, 2001). Our results are consistent with the vertical distribution reported in the literature for available nutrients from shallowest to deepest soil horizons in the following order $K_{exch} > Ca_{exch} > Mg_{exch} > Na_{exch}$ across a wide variety of ecological conditions (Jobbágy and Jackson, 2001). This supports the key role of plant cycling on the vertical distribution of plant nutrients such as K, and thereby on the vegetation production and development within nutrient-limited ecosystems (Flanagan and Cleve, 1983; Hobbie, 1992; Hobbie et al., 2002; Nadelhoffer et al., 1992; Poszwa et al., 2000).

3.4 Projection exchangeable base cations upon permafrost thaw: a new source of nutrients for vegetation

Upon projected permafrost thaw at EML (Garnello et al., 2021), the upper permafrost (0-20 cm below the permafrost table) will undoubtedly thaw and expose soil (total and exchangeable) constituents by 2100. In the upper permafrost layer (0-20 cm below the permafrost table), we measured exchangeable base cations density up to 850 g m^{-3} of Ca_{exch}, 45 g m^{-3} of K_{exch}, 200 g m^{-3} of Mg_{exch} and 150 g m^{-3} of Na_{exch} (Table S4). This represents a stock in exchangeable base cations up to 340 g m^{-2} in the 20 cm thick permafrost layer (170 g m^{-2} from Fig. 7a; 320 g m^{-2} for Fig. 7b; 340 g m^{-2} for Fig. 7c; and 200 g m^{-2} for Fig. 7d). Upon permafrost thaw, these reservoirs of nutrient base cations initially locked will progressively be released and available for plants and microbial activity.

Plants need essential (such as Ca, Mg, K, N, S, P) and beneficial (such as Na, Si, Co) nutrients for their growth because they support physiological functions in the vegetation, such as biomolecule formation, process regulation, and metabolic reactions (Marschner, 2012). The potential release of available nutrient stocks at depth is then expected to increase vegetation production and contribute to the ongoing Arctic greening (Keuper et al., 2017; Keyser et al., 2000; Nadelhoffer et al., 1991; Sistla et al., 2013). More specifically, nutrient addition can decrease species richness and diversity and shifted the plant community toward dominance by dwarf birch, *Betula nana*, and a forb, *Rubus chamaemorus* (Gough et al., 2015). With different nutrient requirements for each species, changes in nutrient distribution (higher at depth) may also influence the tundra plant species and thereby also contribute to the shift in vegetation observed across the Arctic (Chapin et al., 1995; Schuur et al., 2007; Mauclet et al., 2022a; van der Kolk et al., 2016b; Villani et al., 2022). For instance, the more deeply rooted graminoids access

first the newly thawed soil horizons at depth (Hewitt et al., 2019) and thereby benefit first from these newly thawed pools of nutrients. Nevertheless, plant strategies are complex and woody shrubs may also benefit from the deep release of nutrients upon further graminoid nutrient cycling and the nutrient transfer from deep soil horizons to surface litterfall deposition (Mauclet et al., 2023). Permafrost thaw also creates localized variability in moisture conditions as thermokarst areas accumulate moisture while higher areas become drier (Jorgenson and Osterkamp, 2005). This has direct effects on plant species composition that follows the altered moisture regime and thereby influencing spatial variability of nutrients. As changes in Arctic tundra vegetation composition and productivity may generate important feedbacks on climate change (Heijmans et al., 2022), our estimations in exchangeable cations within permafrost may be useful for future ecosystem models simulating the evolution of vegetation development and microbial activity upon permafrost thaw (Fisher et al., 2014; Koyama et al., 2014; Sulman et al., 2021; van der Kolk et al., 2016a).

4 Conclusion

We characterized the variability with depth of the soil exchange complex properties across a permafrost thaw gradient (constituents, cation exchange capacity, base saturation), and we quantified the exchangeable cations stocks and densities in the permafrost relative to the seasonally thawed active layer (organic and mineral active layer). The main conclusions are:

(i) The base saturation of the soil exchange complex is the highest in permafrost (~62%). In the active layer, the base saturation is lower in the organic part (~19%) than in the mineral part (~35%).

(ii) Despite their low OC content and low CEC values, the mineral active layer and the permafrost present a higher CEC density (~16 000 $cmol_c$ m^{-3} for mineral active layer; ~12 000 $cmol_c$ m^{-3} for permafrost) than the organic active layer horizons (~9 400 $cmol_c$ m^{-3}). This can be explained by the higher bulk density in mineral than in organic soil horizons, even if the bulk density estimation is more variable in mineral than in organic horizons.

(iii) As a result of the overall increase in base saturation with depth and the overall increase in CEC density with depth, exchangeable base cations density (Ca^{2+}, K^+, Mg^{2+} and Na^+ in g m^{-3}) is more than 5-times higher in the permafrost than in the active layer. These findings highlight that the availability of nutrients base cations increases with active layer deepening.

(iv) The permafrost layer which is predicted to thaw by 2100 (i.e., up to 20 cm below the permafrost table) contains 860 g m^{-3} of Ca_{exch}, 45 g m^{-3} of K_{exch}, 200 g m^{-3} of Mg_{exch} and 150 g m^{-3} of Na_{exch} as exchangeable base cations density. These values are needed for ecosystem models to better constrain the size of the reservoir in exchangeable nutrients (Ca^{2+}, K^+, Mg^{2+}, Na^+) in the upper permafrost about to thaw.

This study provides a first order estimate of a reservoir about to thaw and expected to contribute to supply nutrients for vegetation development and microbial activity. The contrast highlighted here in nutrient base cations density between the organic and the mineral parts of the active layer and the permafrost about to thaw, is key for changes in tundra vegetation productivity, given that Arctic ecosystems depend on active layer thickness in providing essential nutrients to sustain vegetation growth and development (Iversen et al., 2015; Ping et al., 1998).

Data availability

All data described in this paper are stored in Dataverse, UCLouvain's Online Repository and accessible through the following DOI: https://doi.org/10.14428/DVN/FQVMEP (Mauclet et al., 2022b).

Authors contribution

EM and SO conceived the project. EM, AM and CH collected the samples in Alaska, USA. EM and AM did the element analysis and the total organic carbon measurements. MV and EM did the measurements of pH, CEC and exchangeable bases. EM and MV analyzed the data and calculated to the stocks/densities. EM and MV wrote the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

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