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Carbon, nitrogen and their stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) records in two peat deposits of Central Siberia: raised bog of middle taiga and palsa of forest-tundra ecotone

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Abstract. The peatlands in the northern hemisphere accumulated substantially more atmospheric carbon (C) during the Holocene than other terrestrial ecosystems. In this study we applied a multi-proxy record to distinguish variations in dynamics of two peatlands in the boreal belt (raised bog) and the forest-tundra ecotone (palsa mire) in Central Siberia. Carbon and nitrogen content in peatland soils and their stable isotope composition ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) were used to trace likely changes of hydrothermal regimes, vegetation shifts and diagenetic alteration of accumulated peat. Several inter-related allogenic and autogenic forcings have influenced the changes in macroelement content and stable isotope composition of peat with depth. In particular, there were climate-induced and succession-driven vegetation community shifts in domination of plants characterized by specific nutrient requirements, nutrient stoichiometry and fractionation of stable isotope values. The climate and permafrost-mediated processes like hummock uplift affected ^{13}C uptake by *Sphagnum* mosses in wet and dry periods and changing hydrothermal conditions in peat profiles resulted in perturbations of the nitrogen cycle inducing N loss and enrichment ^{15}N abundance, as well as enhanced decomposition was responsible for enrichment of organic matter in the heavier isotopes. These findings confirm the hypothesis that combined use of elemental and stable isotope composition provide meaningful insights in tracing the hydrothermal conditions and the functional state of peatbogs for paleoecological and paleoclimate reconstructions.

1. Introduction

Peatlands are more efficient long-term organic carbon (OC) stores than upland forests as they burn much less frequently [1]. Thus, the peatlands in boreal and arctic regions represent large reservoirs of carbon and nitrogen, which, nevertheless, are vulnerable to its release under expected changes in



global climate and land use [2-4]. The global climate change with rising air temperatures and changing moisture conditions in the boreal (taiga) zone leads to changes in peatland productivity and vegetation composition [5, 6]. Particularly for the high latitudes, thawing of permafrost and an increase of the active layer thickness are expected to dramatically alter carbon balance of tundra peatlands. Such permafrost-driven peatlands, developed in cold circum polar regions during the Holocene, store about 277 Gt OC [7] and constitute around a fifth of total permafrost soil OC [8]. The climate models predict that the area occupied by tundra peatlands will decline by half by the 2030s, and likely disappear completely by the end of the 21st century [9].

The peatlands in the northern hemisphere have accumulated more atmospheric carbon during the Holocene than any other terrestrial ecosystem [1, 10, 11]. On the other hand, the peatland OC accumulation rates fluctuated over millennial, centennial, interannual and seasonal timescales. In this context high latitude peat cores serve as an important source of information about the variability of environmental conditions and vegetation changes in the past [3, 12]. Past climate and local shifts in hydrology can be estimated using a variety of biotic and biogeochemical proxies, including carbon and nitrogen contents and stable C, N and O isotope composition of organic material [2, 13-16]. However, the environmental (e.g. climate) and biotic (e.g. species) controls of isotope differentiation in the peatland-forming plant species as well as diagenetic changes in peat are still poorly understood and current assumptions regarding these controlling factors are still to be tested on larger spatial scales.

Both, the raised bogs in taiga zone and tundra peatlands in high latitudes of Siberia, are growing peatlands with different stages of development. However, with increasing active layer depth (annual thawing soil layer), tundra hummocks lose stability and are already subjected to collapse at the edges, subsequent subsidence [15] and could create thermokarst ponds [17]. Thus, there is a growing concern about the future of peatland development in the permafrost regions and there have been numerous attempts to analyze the response to ongoing climate change using the paleorecords stored in peat cores.

In this study we attempted to apply a multi-proxy record to distinguish variations in the dynamics of two peatlands: a raised peatbog in the boreal belt (middle taiga subzone) and a tundra mire system of the forest-tundra ecotone in Central Siberia. Particularly, we have used C and N content in peatland soils and their stable isotope composition ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) to trace likely changes of hydrothermal regimes, vegetation shifts and diagenetic alteration of accumulated peat. The aim of this comparative study was to use depth profiles of boreal and arctic peatlands of Central Siberia as indicators of their specific temporal dynamics. Our hypotheses were as follows: (I) the boreal raised bogs and arctic tundra hummocks differ in their elemental and stable carbon and nitrogen isotope composition in respective depth profiles, (II) the changes from increasing to decreasing C and N isotope values in peat cores indicate temporal changes in vegetation composition, hydrothermal regimes and particularly the uplifting of hummocks by permafrost in tundra and (III) the raised peat bogs of the taiga biome has a higher variation of stable carbon and nitrogen isotopes in their depth profiles compared to tundra hummocks indicating enhanced degradation in a warmer environment.

2. Materials and methods

Two peatlands of Central Siberia have been selected for this study: raised peatbog (pine tundra) of the boreal belt (middle taiga subzone) and tundra mire located within the forest-tundra ecotone (figure 1).

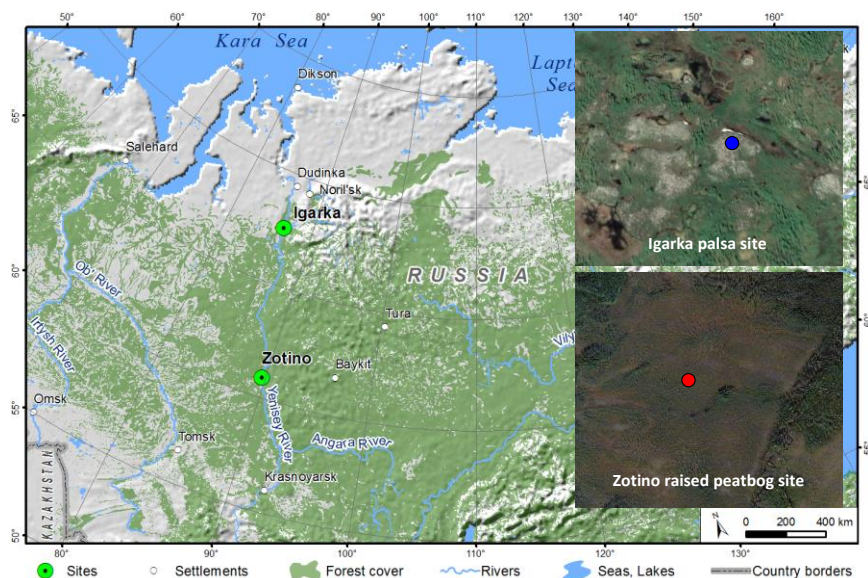


Figure 1. Location of study sites with high resolution images demonstrating raised peatbog in middle taiga subzone (Zotino raised peatbog site) and palsa mire in forest-tundra ecotone (Igarka palsa site).

The raised peatbog site is located on the Eastern edge of the Western Siberian Lowland (60°04'N, 89°23'E) near Zotino tall tower observatory (ZOTTO), 26 km to the west from Zotino settlement. The climate of the region is temperate continental according to the Alisov B.P. classification. The area lacks permafrost or contains rare relict permafrost islands. The average annual air temperature is -3.5 °C, the annual precipitation is 594 mm. The peat core (VB7-3) was obtained in the central part of oligotrophic mire on a *Sphagnum fuscum* hummock. The detailed description of this peatbog was given earlier [18]. Peat samples were collected at 5 cm intervals using the Eijkelkamp peat sampler (Netherlands) to a depth of 4.2 m ending with a gley clay layer.

The palsa site is located 10 km North-East of Igarka settlement (67°31'N, 86°38'E) on the second terrace of the Yenisei River within the Gravijka River watershed. The Igarka-site climate is continental subarctic with mean annual air temperature -7.8 °C and mean annual precipitation of 647 mm. The area is underlain by discontinuous permafrost. The peat core was obtained in the central intact part of an eroding dry hummock (>4.5 m height) surrounded by hollows and mixed forests. The active layer or seasonal thaw layer, at the coring site, was about 0.6 m (at the end of August, 2020). The depth of peat deposit was 8.6 m, but interrupted by ice lenses. Thawed and frozen peat samples of 0.5-5.0 cm thickness (mean=2.8 cm) were collected at 2.0-12.0 cm intervals, depending on the amount of peat material.

The collected samples were dried at 60 °C for 48 h in an oven and subjected to elemental and stable isotope (C and N) analysis with TOC Macro cube (Elementar, Germany) connected to an Isoprime 100 IRMS (Isoprime Ltd., UK). These measurements were further accompanied by radiocarbon dating, measurements of loss on ignition, plant macrofossil and macro-charcoal analyses. Radiocarbon dating of the bulk samples of palsa site was performed in the Laboratory of Radiocarbon Dating & Electronic microscopy of Institute of Geography Russian Academy of Science (Moscow) and the Center for Applied Isotope Studies of University of Georgia (USA). Zotino raised bog peat sample radiocarbon was obtained from the Max Planck Institute for Biogeochemistry in Jena (Germany) with accelerator mass spectrometry (AMS) based on a 3MV Tandemtron accelerator as described earlier [19]. The ^{14}C dates were calibrated using the Calib 8.2. software and the calibration dataset Intcal20 [20]. All calculations were done at the 2σ level. We used the Bacon age-modelling software [21] to construct an age-depth model for the peat cores.

Macrofossil analysis of the peat samples was carried out under microscope (Leitz Wetzlar) at magnification 20× and 40×. Plant species macrofossil identification in the peat cores was carried out according to [18].

3. Results and discussion

3.1. Peat cores characteristics

Peat core depths varied among selected sites between 420 cm in the hummocks of raised peat bog (pine ryam) in the Zotino area and 860 cm at Igarka's palsa mire. However, the onset of the peatland formation at the study sites has been dated at about 13.6 ± 0.2 ka BP in Zotino area and only 6.29 ± 0.02 ka BP in Igarka palsa site. This discrepancy between the age and depth in the latter case was caused by an uplift of hummock due to water intrusions and segregated ice lens formation through the entire peat column. There were several segregated ice lenses (0.2-0.3 m thick) and the entire peat core was generally ice-rich (peat moisture content $\gg 1000\%$).

Both peatlands were initiated with brown and feather moss-dominated plant communities (5-6 ka BP and 12-13 ka BP in Igarka and Zotino sites, respectively) and went through several shifts in plant community composition over time. Woody plant (birch and pine) macrofossils were abundant (30-60% of macrofossils) at the bottom layers of the Zotino site peatland (355-395 cm depths). Similarly, high portions of wood remnants (up to 85%) were found in the bottom of Igarka site palsa deposits (830-860 cm depth). For both sites, grassy vascular plant domination stages ($>50\%$ of macrofossils) were relatively short in time, but rather frequent throughout the peatland development. Domination by *Sphagnum* spp. was site specific: in palsa mire, this stage occurred in two periods at 220 – 377 cm depth (ca. 4.49-4.97 ka BP) and 413-510 cm (ca. 5.06-5.33 ka BP), while in raised bogs, they dominate for the last 1.7 ka (0-145 cm depth). *Sphagnum fuscum* dominated in upper 100 cm at the Zotino site peat core (70-90% of macrofossils) reflecting the ombrotrophic stage of peatland development which started ca. 1.28 ka BP. Similar peatland development patterns for the Zotino area reported in an earlier study [22]. The upper 10 cm of the peat layer from the palsa mire was composed of lichens and remnants of the ericoid dwarf shrub *Ledum palustre*, indicating extreme dry conditions in the recent past.

3.2. Elemental (C and N) composition of peat profiles

According to a compiled dataset of 268 published and unpublished Holocene peat records from 215 sites [10], carbon content in organic matter in Northern peatlands was estimated at $42 \pm 3\%$ (standard deviation) for *Sphagnum* peat, $51 \pm 2\%$ for non-*Sphagnum* peat, and at $49 \pm 2\%$ overall. Nitrogen content is the lowest in *Sphagnum* peat ($0.7 \pm 0.3\%$) and the highest in herbaceous vascular plants ($1.7 \pm 0.6\%$), while the mean is estimated at $1.2 \pm 0.7\%$.

Organic carbon (OC) content in peat profile of the raised peatbog (pine ryam) at the Zotino site varied from 23.3 to 58% (figure 2a). The lowest OC content (23-30%) was found in the bottom of peat deposit dominated by brown and feather moss macrofossils. An elevated OC content was characteristic to woody peat (55-58% OC) and peat composed of remnants of the vascular plants *Scheuchzeria palustris* L., *Eriophorum vaginatum* L. and *Carex* spp. (49-52% OC). Vascular plant peat was also enriched in nitrogen: 1.1-1.9% in the peat bed layer and up to 3.9% in the middle of the peat profile (145-200 cm depths) (figure 2b). *Sphagnum* spp. peat contained 43-49% of OC and 0.3-1.2% of N. Thus, the entire peat profile varied by 10-fold in its N content, from 0.35 to 3.86%. The C:N ratio in peat profiles varied also substantially from 13 to 129 (figure 2c). The highest C:N ratios (88-129) occurred in the upper 25 cm of *Sphagnum fuscum* layers along with their lowest N content. As C:N ratios have been reported to decrease with progressing decomposition due to relatively faster release of C over N, these findings reflect preservation of OM in top 25 cm of the raised bog. The lowest C:N ratios were characteristic for vascular plant peat (13-32) and peat near the bottom of profile (ca. 20), though not related to accelerated decomposition, but rather the dominance of N-rich vegetation. These findings corroborate our earlier observations in the Zotino area demonstrated by

dramatic C:N ratio shifts at the transition zone from the initial stage with vascular minerotrophic type of peat to ombrotrophic stage with *Sphagnum* spp. dominance [23].

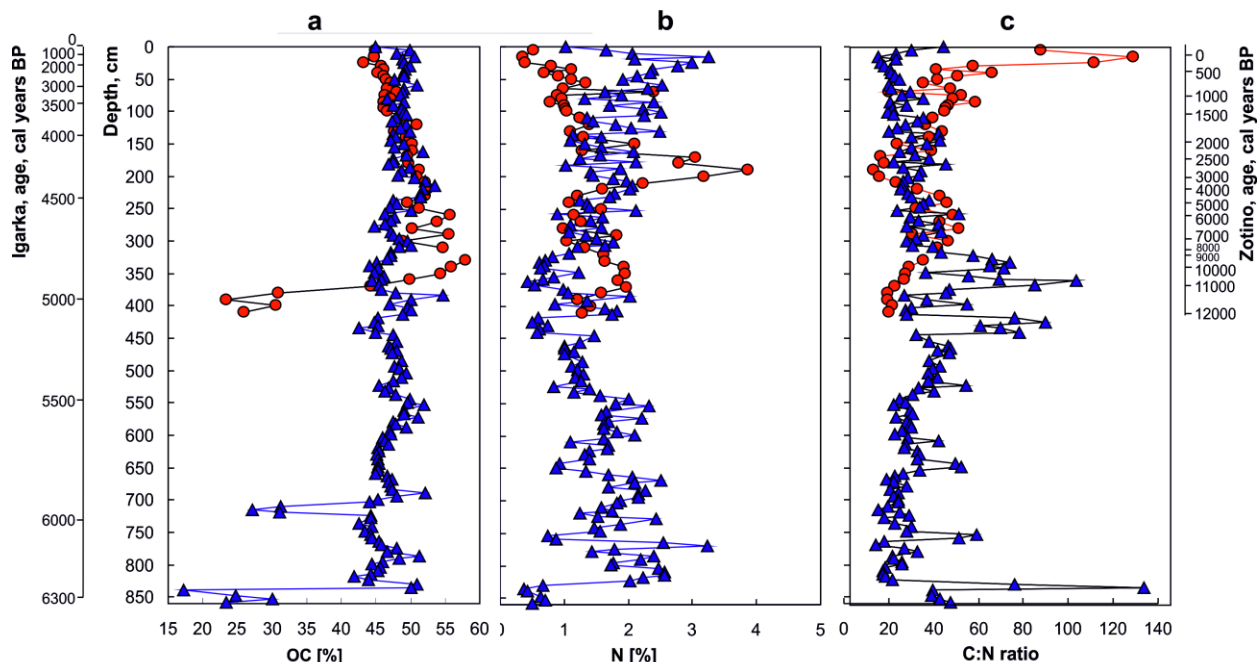


Figure 2. Depth profiles of organic carbon (OC) (a), nitrogen (b) content and C:N ratio (c) in peatland soils developed in the hummocks at the Zotino site raised peatbog (red circles) and the palsa mire site at Igarka (blue triangles).

The palsa mire peat profile in the forest-tundra ecotone demonstrated surprisingly similar contents of OC (17.3-54.7%), N (0.37-3.26%) and the C:N ratios (14-134) (figures 2a-c) relative to raised peatbog in taiga. Palsa peat OC and N fluctuations generally corresponded with the vegetation shifts described earlier for the raised peatbog. Particularly, vascular peat layers demonstrated an enrichment in both OC and N content, and a respective decrease of C:N ratios. All macroelemental concentrations of the respective plant end-members (*Sphagnum* spp., true mosses, vascular plants and wood) were in the range of variation found for the raised peatbog cores. However, the depth patterns of the macroelemental composition differ significantly between the compared peatlands, reflecting depth-specific differences in peat-forming plant composition and different peatland dynamics under various environmental factors. Particularly, narrower C:N ratios of palsa peat in the upper 100 cm, indicating the higher degree of decomposition of organic matter (OM), correspond the surprisingly higher OC and N content and suggest a deeper and well-aerated thawed active layer in the recent past. Such fluctuations in the active layer thickness have occurred after the peat core formation. Nitrogen enrichment in the upper 50 cm is unprecedented for dominant peat-forming end-members (i.e. dominant macrofossils are lichens and *Ledum palustre* roots) and reflect large diagenetic changes of peat OM and/or a large portion of fungal biomass containing obviously larger N quantities relative to plant and lichen tissues [24]. Moreover, the aged topsoil OM of the palsa peat deposit (1930±20 cal years BP at 15 cm depth) suggests significant surface erosion and/or its perturbation by fires resulted in a greater loss of the upper peat. In contrast, decreased N content and increased C:N ratios in the middle of the peat profile (ca. 300-450 cm depths), corresponding to the stage of *Sphagnum* spp. domination, indicate only small diagenetic changes of OM and its preservation, likely due to a permafrost effect, anaerobic or colder conditions. The OC content also indicated short periods at the initial stages of paludification (ca. 840 cm and 700 cm depths) when peat OM accumulation was interrupted and the surface has been covered with lacustrine clay-rich sediments. In this context,

highest C:N ratios at the peatbed (figure 2c) occurred right above the deepest clay layer coinciding with high content of wood macrofossils (80-85%), which remained almost unaltered.

3.3. Stable isotope composition ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$)

The depth profiles of stable isotopes in the peat soil cores reflect organic matter dynamics influenced by autogenic and allogenic forcings. Particularly, the ratio of ^{13}C to ^{12}C has been used to study plant composition (e.g. C3 vs. C4 vegetation), productivity, water availability, water use efficiency and soil OM degradation in different environments [15]. The ratio of ^{15}N to ^{14}N is shown to reveal biogeochemical processes such as decomposition rates of soil OM [25], perturbations in the ecosystem N cycle and specifically mycorrhizal N transfer [24].

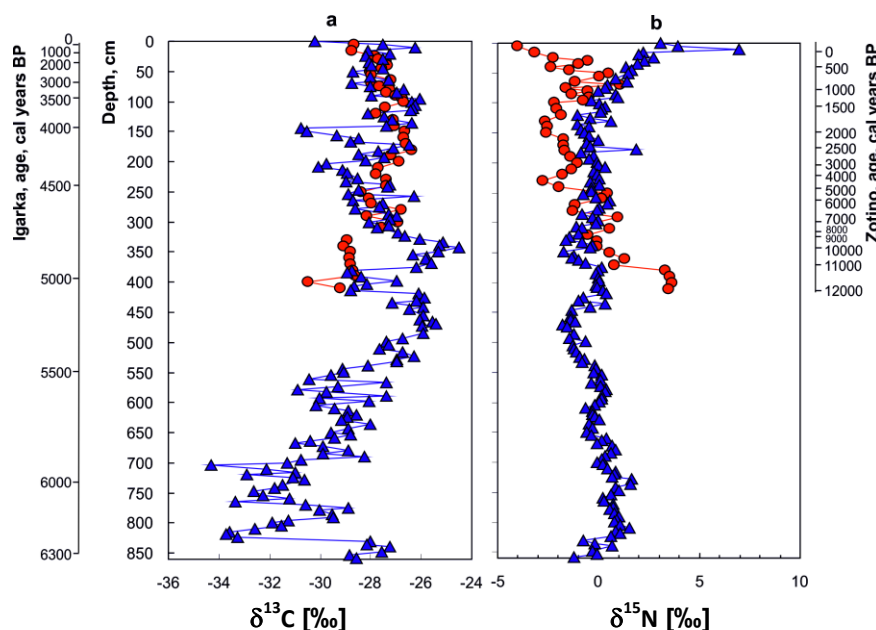


Figure 3. Depth profiles of $\delta^{13}\text{C}$ (a) and $\delta^{15}\text{N}$ (b) in peatland soils developed in the hummock of Zotino site raised peatbog (red circles) and palsa of Igarka site (blue triangles).

The peat $\delta^{13}\text{C}$ profile in the raised peatbog (pine ryam) of the Zotino area ranged from -25.0 to -30.5‰ and from -25.4 to -34.3‰ in the palsa mire (figure 3a). Obviously, soil OM of both peatlands were composed of isotopically light C3 plants, though much larger variations in latter case suggest more frequent fluctuations in the development of the palsa mire. Predominantly, more depleted isotopes layers ($\delta^{13}\text{C} < -30$ ‰) correspond to the dominance of brown and feathermosses, while enriched values ($\delta^{13}\text{C} > -28$ ‰) coincided with *Sphagnum* spp. dominance. Other peat types were within the ranges reported earlier for the vascular plants [14, 15].

In regard to $\delta^{13}\text{C}$ values of *Sphagnum* mosses, the highest (less discrimination against isotopically heavier $^{13}\text{CO}_2$) are reported when the plants are covered by diffusion limiting water films resulting in a less negative $\delta^{13}\text{C}$ signature. Alternatively, $\delta^{13}\text{C}$ is more negative when the moss plants are drier and diffusion and photosynthetic rates are maximized [15]. Thus, the biomass generated under different environmental conditions might produce a unique stable isotopic signature that is subsequently retained in subfossil material. In this context, ^{13}C enrichment with depth in *Sphagnum fuscum* peat (from -28.7 to -26.8‰) in the top 100 cm of taiga raised bog peat suggests wetter conditions during a shift to an ombrotrophic stage of the peatland development and a continuing drying pattern. Earlier findings from Western Siberian peatlands reported a range of $\delta^{13}\text{C}$ values from -27.1 to -29.6‰ for

Sphagnum fuscum, which also corresponded to the moisture conditions of the habitats [13, 16]. On the other hand, the $\delta^{13}\text{C}$ signature of *Sphagnum fuscum* has shown to respond less to wetter conditions (i.e. height of water table) in comparison with more hydrophilic mosses like *Sphagnum magellanicum* [3, 16] and *Sphagnum balticum* [13], which are reported to be more enriched isotopically.

Sphagnum mosses in the palsa mire profile appeared at 220–377 cm depth (ca. 4.49–4.97 ka BP) and 413–510 cm (ca. 5.06–5.33 ka BP) demonstrating significant variations in $\delta^{13}\text{C}$ signatures ranging from -24.51 to -28.98‰. Most depleted *Sphagnum* peat ($\delta^{13}\text{C} < -28\text{‰}$) corresponded to borders with other plant peat, like brown mosses and vascular plants, reflecting the changes in hydrological conditions (i.e. higher dryness). In contrast, the central layers of *Sphagnum* peat were significantly enriched in the heavier isotope, suggesting a wet environment prevailed in the period between 4.49 and 5.33 ka BP. This pattern is most likely due to wetter hydrological conditions as C:N ratios in that soil layers (up to 90) correspond with slightly altered OM content.

Despite the fact that peatlands differ substantially in patterns of $\delta^{15}\text{N}$ along depth profiles (figure 3b), their $\delta^{15}\text{N}$ values are within the range of reported values for peatlands from the Subarctic/Arctic region [14] and soils developed under the tundra vegetation [2]. The raised bogs in our study demonstrated the variation of $\delta^{15}\text{N}$ from -4.05 to 3.65‰, and in the palsa peat $\delta^{15}\text{N}$ ranged from -1.77 to 6.96‰.

The most depleted isotope value (up to -4.05 ‰) was in the upper 25 cm layer of the raised bog, which is close to $\delta^{15}\text{N}$ of NO_3 deposited in the northern latitudes with precipitation (-1 to -3‰). In contrast, the upper 50 cm of palsa peat contained extremely enriched $\delta^{15}\text{N}$ OM along with the highest N content (figure 2b), despite a dominance of *L. palustre* in peat, known to be highly depleted by ^{15}N (<-5‰) due to N supply from ericoid mycorrhiza. Increased portion of ^{15}N -rich fungal biomass (though unidentified in fossils) might be responsible for such enrichment of OM by N and ^{15}N [24]. On the other hand, as the light ^{14}N isotope is preferentially lost during the decomposition of organic matter and transformations of N species, our findings suggest an accelerated loss of mobile inorganic forms of N of palsa topsoil, which are usually depleted in ^{15}N . Such pattern was demonstrated earlier at permafrost-induced uplift and/or cryoturbation of palsa mires in Sweden [2]. A less obvious turning point in stable isotope profiles was observed at the Igarka palsa mire site during two periods of *Sphagnum* spp. dominance described above. At this relatively short phase, the peat was formed primarily by brown mosses, indicating drier conditions. Similar patterns in the N cycle, i.e. enrichment by ^{15}N , occurred in the bottom layer of the raised bog (figure 3b), which is also dominated by brown mosses. In general, we observed a positive trend of $\delta^{15}\text{N}$ with depth in boreal zone raised bog systems and a similar tendency in forest-tundra palsa mire starting at ca. 450 cm depth. In contrast, $\delta^{15}\text{N}$ tended to decrease from 0 and 350 cm depth.

According to a previous study [25], the soil $\delta^{15}\text{N}$ remains within a relatively narrow range of C:N ratios in unperturbed soils. An accelerated turnover of organic matter (e.g. mineralization, nitrification, denitrification) either increases or decreases $\delta^{15}\text{N}$ beyond the observed narrow range and reflects recent or past soil perturbations. Generally, the samples above the uncertainty envelope (set at $\pm 2.4\text{‰}$) indicate an accelerated N loss, whereas the samples below indicate an accelerated N gain [25]. Central Siberian peatlands showed different patterns in N-cycle perturbations. Despite that the majority of the soil samples appeared within this uncertainty envelope (figure 4), our findings demonstrated that permafrost-induced uplift of palsa mires led predominantly to a net loss of N (above the uncertainty envelope), and, vice versa. N gain appeared only in raised peatbog samples. Specifically, excessive N leaching (loss) occurred in palsa mire in the topsoil and at several deeper layers: 323–440, 643–649, 754–760 and 830–835 cm. Those perturbations may have different causes as topsoil receives only little input of fresh OM due to declined productivity and more wildfire impact in the recent period. Turning points [2] in deeper layers are more likely if severe changes in hydrological conditions occurred.

Despite a substantially less pronounced perturbation of the ecosystem N-cycle in this boreal raised bog system, there seems to be an apparent period of net N gain (values below the uncertainty envelope) which corresponds to depths between 145 and 200 cm. This period is characterized by the dominance of *Scheuchzeria palustris* L., which remnants constitutes 50–70% of all macrofossils.

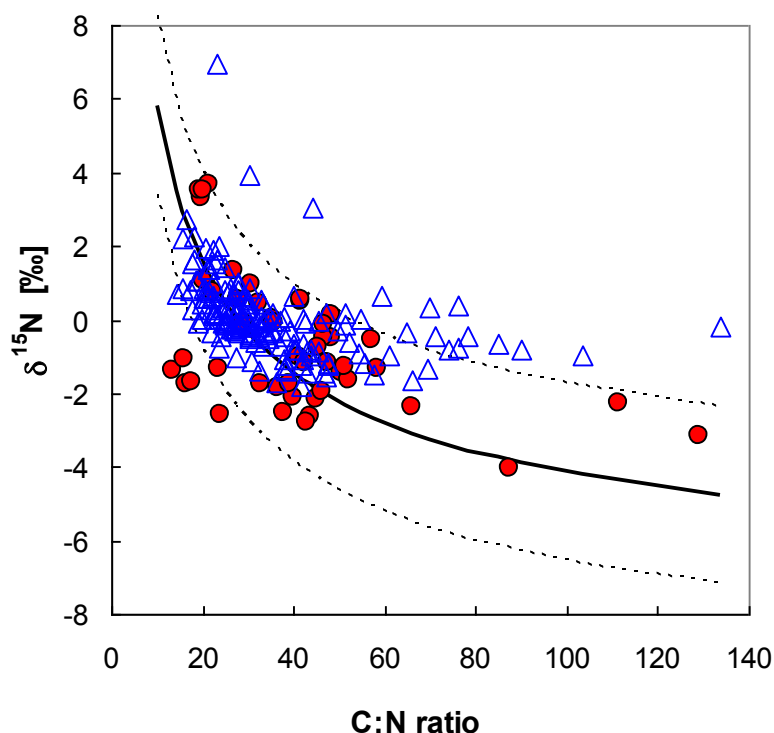


Figure 4. Relationship between $\delta^{15}\text{N}$ and C:N ratio of peat soil of raised bog of the taiga zone (red circles) and the palsa mire of forest-tundra ecotone (blue triangles) in Central Siberia. The relationship is given according to empirical equation from [25] to classify unperturbed samples (located inside the uncertainty envelope $\pm 2.4\%$) versus perturbed samples (located outside the uncertainty envelope $\pm 2.4\%$).

4. Conclusions

There are several inter-related allogenic and autogenic forcings influencing the changes in macroelemental content and stable isotope composition of peat OM with depth: 1) climate-induced and succession-driven vegetation community shifts, characterized by specific requirements for nutrient supply, nutrient stoichiometry and stable isotope fractionation (e.g. moss vs. vascular plants), 2) climate affecting ^{13}C uptake in wet and dry periods (opposite in mosses and vascular plants), 3) perturbations of the nitrogen cycle inducing enrichment or depletion of ^{15}N abundance, 4) organic matter decomposition responsible for enrichment in heavier isotopes and 5) permafrost-mediated processes like hummock uplift and/or cryoturbation changing hydrothermal regimes in peat profiles. Given these complex influences on the elemental and isotopic composition of peat profiles, important questions concerning the past climate reconstruction remain unanswered yet and, thus, require further investigations. Focused studies on the variability of peat composition and degradation based on a single functional plant trait will help in this regard.

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