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Carbon Accumulation and the Possibility of Carbon Losses by Vertical Movement of Dissolved Organic Carbon in West Siberian Peatlands

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Abstract: We studied peat stratigraphy at the Mukhrino peatland, which is a typical ombrotrophic bog for the middle taiga zone of Western Siberia, to gain insights about its history, hydrology and carbon fluxes. Seven cores were collected from locations chosen to represent the typical present-day vegetation types, for dating of separated dissolved (DOC) and particulate (POC) organic carbon fractions using the Accelerator Mass Spectrometer (AMS) radiocarbon (^{14}C) method. The oldest peat was found at the bottoms of an underlying lake (10,053 cal. year BP) and an ancient riverbed (10,989 cal. year BP). For the whole history of the peatland the average peat accumulation rate was estimated to be 0.067±0.018 cm yr^{-1} (0.013–0.332 cm yr^{-1}) and the carbon accumulation rate was 38.56±12.21 g m^{-2} yr^{-1} (28.46–57.91 g m^{-2} yr^{-1}). There were clear age differences between the separated samples of DOC and POC. DOC was older than POC in the uppermost 150 cm of the peat deposit, and younger in the deeper layers. The difference in age increased with depth, reaching 2,000–3,000 years at the bottom of the peat deposit (depth 430–530 cm). Following consideration of a range of factors that could potentially cause the dating discrepancy, we hypothesised that DOC continuously moves down into the mineral sediment beneath the peat, as an additional carbon flux that results in mixing of younger and older carbon. On this basis we estimated the apparent rate of DOC downward movement and the associated rate of carbon loss. The first estimate of the average rate of DOC downward movement in Western Siberia is 0.047±0.019 cm yr^{-1}.

Keywords: AMS radiocarbon dating; Mukhrino bog; peat accumulation rate; peatland stratigraphy; POC

1. Introduction

Unlike most other ecosystems, peatlands assimilate carbon and sequestrate it over thousands of years, as long as net primary production exceeds the rate of organic matter decomposition. It has been estimated that peatlands occupy 2.84% (4.23 million km^2) of the global land area [71] but have accumulated a disproportionally considerable amount of the world's soil carbon (∼30%) [73].

In this context, peatlands cover ∼22% [57] of the total area of West Siberia, where the waterlogging of some territories reaches 50–75% locally [49]. Indeed, this is one of the most waterlogged places globally, where peatlands occupy depressions in local relief, vast watershed areas and floodplains [8]. It is estimated that West Siberian peatlands contain ∼20% of the total world peat deposits, with the highest concentration in the taiga zone (55 °N to 65 °N) [40,57]. Moreover, they hold a carbon stock of approximately 70.2 Pg, representing up to ∼26% of the total terrestrial organic carbon (held in soils, detritus and vegetation) accumulated since the Last Glacial Maximum [58,70].

West Siberian peatlands developed mainly during the early Holocene (11,500-9,000 cal yr BP) due to postglacial warming [40,58]. The rates of carbon accumulation ranged from 12 g m^{-2} yr^{-1} to 39 g m^{-2} yr^{-1} throughout the Holocene, depending on latitude. The average accumulation rate for the middle taiga zone is 28.5 g m^{-2} yr^{-1} and it generally declines towards older dates [8,63,65].

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Exceptions are found in the uppermost 50 cm due to poorly decomposed and uncompressed peat. The amount of biomass input determines the rate of carbon transfer from the acrotelm (surface aerobic layer) to the catotelm (deep anoxic layer) [20] and is strongly correlated with climatic conditions [24] as well as with the plant species forming the peat [4].

During decomposition under waterlogged conditions, part of the litter and peat converts to a dissolved form that can pass through a 0.45 μm filter, known as dissolved organic carbon (DOC) [1,9,14,15,17,19,54], but 0.2-0.7 μm filter pore size are also common [38]. Expected global warming may increase the DOC concentrations in water discharged to streams [45] and thus, ultimately, increase DOC flux into the oceans [28,29], where a significant fraction is rapidly mineralised and returned to the atmosphere as a greenhouse gas. The paths and magnitudes of DOC fluxes are not accounted for in most estimates of contributions to the C cycle and, thus, require further scientific attention to support forecasting of climate change effects.

Most of the DOC released to streams and rivers [29,55] is derived from recently fixed carbon (∼50 years) in the upper peatland layers [5]. However, radiocarbon dating has shown that riverine DOC is much older than previously thought [52], suggesting that baseflow from deeper peats may also export DOC to streams. This DOC does not flow directly to the mineral floor beneath the peatland but moves vertically up and down in the peat profile, and there is significant redistribution of DOC in groundwater [69]. Also, any vertical DOC inflow from the upper peatland layers may be converted to CO_2 and CH_4 by microbial activity [1,2,13–15]. Thus, the waterborne flux of DOC is important in determination of the peatland carbon budget and in understanding the spatial and temporal variability of CO_2 and CH_4. Vertical movements of DOC would also lead to mixing of young and old carbon that may result in dating inversions and inaccuracies for bulk samples of peat. Inversed dates are usually excluded from the age-depth model, which may lead to a significant shift in the model shape that would affect interpretation [37,41]. Well-known reasons for dating inversions include root intrusion [31], slippage of neighbouring peat [35], peat fires [64], and other profile disturbances [37] such as dry years, cryoturbation and periodic flooding [67]. All of these happen occasionally; however, a permanent downward flux of DOC is implied by the dating discrepancies reported. This could cause a systematic under-estimation of bulk sample dates that may have affected previous estimates of carbon accumulation rates in peatlands. These considerations create a need for separate age determinations of DOC and the immobile particulate organic matter (POM).

The objectives of the study described here were (1) to describe stratigraphy and measure historical peat and carbon accumulation rates at the Mukhrino bog in West Siberia; (2) to date dissolved (DOC) and particulate (POC) organic carbon separately throughout the peat profile; and (3) in the eventuality that differences in the ages of DOC and POC at the same depths were revealed, to explore potential causes and implications.

2. Materials and Methods

2.1. Study Site

The Mukhrino peatland is located 20 km south-west of Khanty-Mansiysk city in the middle taiga zone [32] of West Siberia near the confluence of two major rivers, the Irtysh and the Ob' (60.889 °N, 68.702 °E). It covers a local watershed between the two smaller rivers "Mukhrina" and "Bolshaya rechka" (Figure 1), within a zone of ombrotrophic (rain-fed) *Sphagnum* raised bogs on the left terrace of the River Irtysh [34]. The total area of the Mukhrino peatland is 65 km^2. The Mukhrino field station is operated by the UNESCO Chair of Environmental Dynamics and Global Climate Change at Yugra State University.

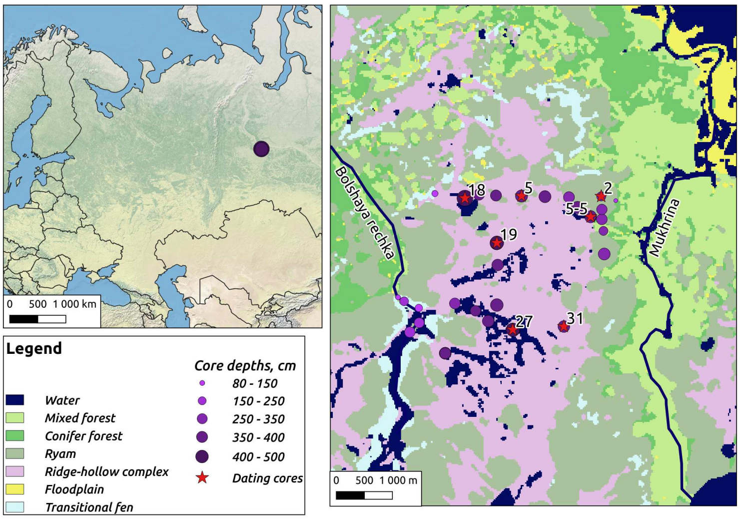

Figure 1. Maps showing the location of the Mukhrino peatland on the map of Eurasia (**left**) and the distribution of peat cores in relation to the main ecosystems of the study area and bounding rivers (**right**). Several cores, both collected at the adjacent hollow and ridge, are presented as a single dot on the map.

The climate of the region is moderately continental. According to Russian Weather Service observations at their Khanty-Mansiysk weather station, the mean annual air temperature is -1.0 °C. Winters are cold with mean January temperature -21.5 °C and summers are short with mean July temperature 17.4 °C [23]. Mean annual precipitation is 480 mm and most (307 mm) of this falls during the summer–autumn season (August–September). The remaining precipitation falls as snow, starting in October. The snow begins to melt in mid-April and disappears completely in May. The area is characterised by the absence of permafrost, but in some places frozen soil can be found at depths of 50–100 cm until the end of June.

The peatland is surrounded by taiga forest dominated by *Pinus sibirica*, *Picea obovata* and *Abies sibirica* mixed with *Populus tremula* and *Betula pubescens*, which occupies the mineral islands and slopes along the rivers and streams. The following contemporary peatland vegetation types are present:

- **typical ryam** (pine—dwarf shrub—peat moss community) is characterised by a low Scots pine layer (*Pinus sylvestris f. litwiniwii*, height 1.5–4 m), a well developed dwarf shrub layer (*Ledum palustre*, *Chamaedaphne calyculata*), and a moss layer dominated by *Sphagnum fuscum* with minor admixture of *S. angustifolium* and *S. divinum*;
- **tall ryam**, found on shallower peat near the outer edges of the peatland, is similar to typical ryam except that it has tall pine trees (*Pinus sylvestris f. uliginosa*, height 6–10 m) and *Sphagnum angustifolium* dominates the moss layer;
- **the ridge-hollow complex** which features ridges, elongated perpendicular to the water flowlines and occupied by typical ryam communities, alternating with waterlogged sedge—peat moss hollows (*Carex limosa*, *Scheuchzeria palustris*, *Eriophorum russeolum*, *Sphagnum balticum*, *S. majus*, *S. jensenii*); and
- **treeless throughflow fens**, as well as *Sphagnum* lawns with hollow vegetation and occasional scattered hummocks, located within limited areas in the lower reaches of the peatland's water catchment [25].

The peatland has a domed shape with a difference in elevation of 1.2 metres between the central part and the edge [9]. The central part of the dome is relatively flat and occupied by the ridge-hollow complex, whereas towards the edge it becomes more inclined and better drained with ryam and tall ryam communities.

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The Mukhrino peatland receives water as rainfall and melting snow. Usually, meltwater is retained on the peatland surface in local depressions or upstream of ridges until the upper peat layer has thawed. During surface ice break down, the meltwater rapidly seeps into the peat, raising the water table dramatically. The lowest water level is recorded at the end of summer (in August). The water table rises again in response to precipitation during the autumn season, which is characterised by low air temperature and reduced evapotranspiration. Discharge from the peatland stops in the middle of October when water freezes. For more information see Bleuten [8].

2.2. Field Sampling

To describe the peatland's stratigraphy, 34 peat cores were collected in 2010–2016 using a Russian peat corer (chamber length 0.5 m, inside diameter 5.0 cm). Each core was extracted from a single borehole and sampling continued through the entire depth of peat until the bottom sediment was reached. The locations of the cores were chosen to include the most typical and the most unique habitats of the Mukhrino peatland (Figure 1). The uppermost 50 cm layer was extracted in the same way but with some gaps due to the fragile structure of litter and living mosses. The gaps were mostly related to the first 20-30 cm layer. In case of lower gap occurred the peat sample was cut out by a knife and dating was not provided.

In the summer of 2016, seven additional peat cores were extracted from the most typical bog habitats (Table 1) using the same methodology. From near the lower end of each half-metre section of each core we cut a 1 cm thick slice (in total, 67 samples; see the Supplement for exact depths, Table S1). These pieces were moved by a clean knife and packed into labelled plastic zip-bags, minimising contact with the environment to avoid contamination. The remainder of each core section was placed in a plastic cassette and wrapped in plastic film. All samples were then transported to the laboratory of Yugra State University (Khanty-Mansiysk, Russian Federation). The zip-bags with contents were immediately frozen then sent in insulated packaging to the Max-Plank Institute of Biogeochemistry in Jena (Germany), where they were kept frozen until analysis (separation of DOC and POC followed by AMS radiocarbon dating) in January 2018. The fresh material from the cassettes was divided into 10 cm subsamples for the other analyses, which were conducted in Khanty-Mansiysk.

Table 1. Habitat descriptions for the seven dating cores (for their locations, see Figure 1). WT = water table.

Core	Habitat Description	WT Depth (cm)	Peat Depth (cm)
2	Typical transition from ryam to dry peatland; covered by pine trees up to 3 m tall, dwarf shrubs (*Ericaceae*) and *Sphagnum fuscum*.	20–30	530
5, 19	Ridge in ridge-hollow complex; covered by low pine (up to 2 m tall), dwarf shrubs (*Ericaceae*) and *Sphagnum fuscum*.	15–20	390, 400
5-5	Ecotone between ridge and hollow; covered by mixed species from both habitats: cottongrass, *Sphagnum* mosses (*S. fuscum*, *S. balticum*), dwarf shrubs (*Ericaceae*).	5–10	310
18	Floating *Sphagnum* mat close to the lake; covered by *Scheuchzeria*, sedges (*Carex limosa*) and *Sphagnum* mosses (*S. papillosum*, *S. balticum*).	2-5	480
27	Ridge in ridge-pool complex; treeless ridge with dwarf shrubs and *Sphagnum* mosses.	10-15	400
31	Hollow in ridge-hollow complex; covered by sedges (*Carex limosa*) and *Sphagnum balticum*.	5-10	380

2.3. Identification of Peat Types

Plant macrofossils were analysed in contiguous 10 cm subsections of all cores. For this purpose a subsample of 10 cm^3 (10 cm height, 1 cm width, 1 cm thickness) was washed with flowing water on a 0.25 mm mesh sieve. We identified plant remains under a binocular microscope (10–40× magnification; Zeiss Axiostar, Jena, Germany) using both our own experience and the key samples data bank, i.e., collection of plant remains used for peat botanical composition identification (unpublished).

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The abundance of each type of plant remains was expressed as a percentage, and peat types were identified based on the dominance of plant species according to Matukhin [48].

2.4. Bulk Density, Carbon and Ash Content

The bulk density, carbon and ash content of each 10 cm subsample were determined on 50 cm^3 of peat taken from the middle 5 cm (2.5–7.5 cm) of the core section. Bulk density (BD; g cm^{-3}) was measured by drying this peat at 105 °C for 24 hours, weighing, and dividing by the initial volume. The dried subsample was ground and divided into two parts. Ash content was determined (for one part) by ignition (Nabertherm L9/11/SKM, Lilienthal, Germany) at 525 °C for nine hours. The second part was used to determine total carbon content (elemental analyser EA-3000; EuroVector, Pavia, Italy). When the samples are introduced to this analyser and combusted, the carrier gas helium is temporarily mixed with pure oxygen. The gases are separated by a system similar to that of gas chromatography (purge and trap principle). After carbon dioxide is released from the adsorption column, it is measured by the thermal conductivity detector (TCD). The instrument was calibrated with Atropine (C = 70.56%, N = 4.84%, H = 8.01%, O = 16.59 %). Concerning the seven dating cores collected in 2016, bulk density and ash content were measured only on Cores 5, 5-5, 19 and 27, while carbon content was measured on Cores 2, 5, 5-5 and 19 (Figure 1).

2.5. Separation of DOC and POC

At the laboratory in Germany, DOC was separated from POC by dispersing the peat samples in distilled water using the approach from Schulze et al. (2015). Dissolved organic carbon (DOC) is operationally defined as organic molecules that can pass through a 0.45 μm filter [38]. In our separation setup for the peat samples we choose the smallest available glass fibre filter of 1.6 μm. This is specifically required for ^{14}C analysis. Therefore, in our setup, DOC is considered as organic particles that can pass through a 1.6 μm glass fibre filter. First, the frozen peat sample was thawed carefully, weighed, dispersed in distilled water, and shaken for two hours. The suspension was then wet-sieved (63 and 36 μm mesh) and the residues were freeze-dried (Piatkowski, Munich, Germany). The sieved suspension (< 36 μm) was adjusted to pH 9 by adding NaOH, shaken for another 20 minutes and centrifuged at 2900 g for 30 min (Megafuge 3.0, Heraeus, Hanau, Germany). The supernatant was vacuum filtered through a 1.6 μm glass fibre filter (Sartorius) that had been baked at 500 °C beforehand, and the filtrate (< 1.6 μm) was freeze dried. The residue from the filter and the pellet remaining from the centrifugation were combined and freeze-dried. This fraction (> 1.6 < 36 μm) was defined as particulate organic carbon (POC).

2.6. AMS ^{14}C Analysis

The DOC and POC samples from the peat cores were analysed using the Accelerator Mass Spectrometer (AMS) radiocarbon (^{14}C) method [59,60]. For one measurement, 0.7 mg of carbon (C) is required. The samples were chemically prepared by combustion to produce CO2 which was trapped and catalytically reduced to graphite in the presence of Fe^{2+} powder and H_2. The resulting graphite was pressed into targets for measurement in the AMS system. In the AMS system the graphite was ionised (negative charge) and accelerated within an electric field to a final energy of 400 keV. The ^{14}C isotope ratios were corrected using the measured 13/12C AMS values [60]. The radiocarbon dates were calibrated (see the Supplement Table S1) with the IntCal20 [53] and NH1 post-bomb [33] atmospheric curves using the package 'clam' [6]. The age-depth model was developed using the Bayesian-based package 'rbacon' [7] with 95% confidence intervals.

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2.7. Calculation of Accumulation Rates

The peat accumulation rate (PA) was calculated along the entire core, for each of the dating steps (usually at intervals of approximately 50 cm, but more widely spaced in cases of missing age data; see Supplement) using Equation (1):

$$PA_i = \frac{(d_l - d_u)}{(a_l - a_u)}, \tag{1}$$

where PA_i (cm yr^{-1}) is the peat accumulation rate for the ith time interval between dated samples; while d_l , d_u (cm) are the depths and a_l , a_u (years) are the ages (dates) of the lower and upper surfaces of the corresponding peat layer, respectively.

The short-term apparent carbon accumulation rate (ACAR) was calculated for each 10 cm depth interval (slice) of the cored profile using Equation (2):

$$ACAR_j = (BD_j \times LOI_j \times CC_j) \times PA_i \times 10^4, \tag{2}$$

where $ACAR_j$ (g m^{-2} yr^{-1}) is the short-term carbon accumulation rate for the j^{th} 10 cm slice, BD_j (g m^{-3}) is the bulk density of peat in the j^{th} 10 cm slice, LOI_j is the loss on ignition expressed as a proportion (e.g. 0.9), CC_j is the proportion of carbon in the organic part of the peat, PA_i (from Equation (1)) is assumed to apply to all 10 cm core slices that accumulated during the the ith time interval, and 10^4 is a conversion factor (the number of cm^2 in a one metre square). The equation is adapted from [66] by adding LOI as a correction factor to convert the ACAR results to ash-free organic matter values. In the case of low ash content (i.e. LOI close to unity) this correction has almost no effect; but in the case of high ash content (i.e. LOI is 0.5–0.7) it reduces the ACAR to reflect the fact that carbon is accumulated in the organic matter but not in the mineral fraction. Bulk density, ash content and carbon content were not all measured in Cores 2, 18, 27 and 31 (see above), so for these cores ACAR was calculated at least partly on the basis of peat types, using the mean values of bulk density, carbon and ash contents for each peat type derived from a statistical analysis of 34 cores from the Mukhrino peatland (see the Supplement, Table S2).

Long-term rate of carbon accumulation (LORCA) was calculated according to Borren [10] using Equation (3):

$$LORCA = \frac{C_{total}}{A_{bottom}}, \tag{3}$$

where LORCA is the long-term rate of carbon accumulation (g m^{-2} yr^{-1}) and A_{bottom} is the bottom age of the core (years). C_{total} is the total carbon storage per unit area (g m^{-2}) and was calculated via the cumulative sum of carbon storage in contiguous 10 cm slices of the peat profile, working from bottom to top (see the Supplement, Table S2).

Long term peat accumulation rate (lPA) was calculated using Equation (4):

$$lPA = \frac{D_{total}}{A_{bottom}}, \tag{4}$$

where lPA is the long-term peat accumulation rate (cm y^{-1}) and D_{total} is the total depth of the core (cm).

2.8. Calculation of DOC Downward Velocity

We hypothesised that, if a dating discrepancy between DOC and POC at the same depth was found, it could be caused by vertical movement of DOC within the peat profile. Specifically, if it emerged that DOC was systematically younger than POC, this might reflect a continuous downward movement of DOC relative to the peat matrix. Assuming that POC is stationary and associated with

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the solid phase (peat), whereas DOC is mobile and associated with the liquid phase (peatland water), the apparent rate of DOC downward movement could then be calculated according to Equation (5):

$$v = \frac{(d_i - d_{doc_i})}{(a_{poc} - a_{doc})}, \tag{5}$$

where v is the apparent rate of DOC movement (cm yr^{-1}), d_i (cm) is the ith depth from which DOC was extracted, d_{doc_i} (cm) is the depth at which POC is of the same age as the DOC at d_i, while a_{poc} and a_{doc} (years) are the respective ages of POC and DOC at d_i. Equation (5) calculates how fast the horizontal front of DOC moves downward during the time period under consideration, regardless of the physical processes involved—whether sorption/desorption, dissolution/sedimentation, microorganism consumption or changes in substrate porosity. Then, the amount of carbon lost as a result of the DOC downward movement is given by Equation (6):

$$cc = C \times v \times 10^4, \tag{6}$$

where cc (mg m^{-2} yr^{-1}) is the amount of carbon lost per square metre, C (mg cm^{-3}) is the DOC concentration in the deep peatland water, which ranges between 0.06 mg cm^{-3} [26] and 0.2 mg cm^{-3} (based on our unpublished estimation), and 10^4 is a conversion factor as above.

3. Results

3.1. Stratigraphy

After the last glaciation, the Mukhrino peatland started as a minerotrophic fen dominated by trees (birch, pine, fir) and herbs (fern, horsetail and tussock-forming sedges). Remains of these plants are found in the bottom layer of minerotrophic peat. The thickness of this layer does not exceed 1.7 m and is 0.65 m on average. It is overlain by ∼0.5 m of transitional peat containing minerotrophic plant remains (*Scheuchzeria* palustris, sedges, dwarf shrubs and *Sphagnum* mosses). Ombrotrophic peat forms the main upper part of the peatland. About two-thirds of the peat deposit is composed of *Sphagnum* peat with thin interlayers of cottongrass—*Sphagnum* or sedge—*Scheuchzeria*—*Sphagnum* peat types (Figure 2), as formed by dynamic changes in the ridge-hollow complex. The most abundant types are *Sphagnum fuscum* peat (22.5% of the peat deposit), *Sphagnum* hollow peat (*S. balticum*, *S. papillosum*; 12.0%) and mixed *Sphagnum* ombrotrophic peat (*S. fuscum*, *S. angustifolium*, *S. divinum*, *S. papillosum*, *S. balticum*; 5.7%).

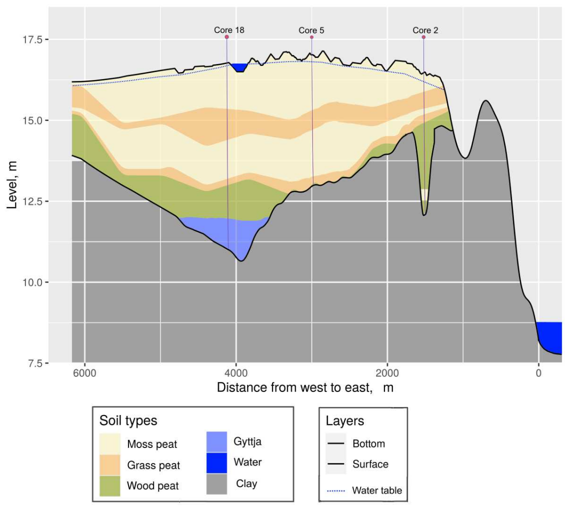

Figure 2. Section through the Mukhrino peatland showing stratigraphy and shape of the mineral bottom.

3.2. Peat Ages and Accumulation Rates

The average depth of the Mukhrino peatland is 340 cm based on 34 cores ranging in length from 85 to 530 cm (Figure 1–3, see Supplement Table S2). The two deepest points were found in the northern part of the peatland: Core 18 is located in the basin of a primary lake (peat depth 480 cm) partly infilled by gyttja (100 cm) covered with peat (380 cm); and Core 2 (peat depth 530 cm) is associated with an ancient stream bed with rush peat at the bottom. Other cores have 40–60 cm of minerotrophic grass—woody peat at the bottom, at depths of 350–400 cm.

Shallow peat deposits (∼100 cm and less) are present at the edges of the peatland bordering with forest and mineral islands. The peatland is still expanding by paludification of the surrounding forest area, where an abundance of tall, dry and dead conifer trunks is found on shallow peat deposits. The abundance of charcoal in the peat may be attributed to frequent fire events at the bog edge, and the presence of *Carex globularis* in the modern vegetation is also an indicator of fires [41]. Usually this fire type does not reach the central part of the peatland and destroys only treed areas at the border with forest growing on mineral soils.

The average PA is 0.067±0.02 cm yr^{-1} (data used for this calculation can be found in the Supplement). The lowest average value (0.04±0.02 cm yr^{-1}) was found for Core 31 (hollow) and the highest average value (0.10±0.08 cm yr^{-1}) was found for Core 2 (ryam). PA was highest for ombrotrophic peat (0.080±0.038 cm yr^{-1}), lower in minerotrophic peat (0.062±0.033 cm yr^{-1}), and lowest for transitional peat (0.061±0.027 cm yr^{-1}). Apparently, the type of water (rainwater or groundwater) and nutrient availability are amongst the main limiting factors in the peat accumulation process.

The range of average lPA values was 0.03–0.048 cm yr^{-1} (mean value 0.041±0.007 cm yr^{-1}), depending on the total depth; i.e., peat accumulation over 10–11 kyr was 1.2–1.6 times faster for the deepest cores than for the shallow cores. The average PA based on 64 dates over different peat layers across all cores had the higher value of 0.067±0.018 cm yr^{-1} (0.013–0.332 cm yr^{-1}), mostly owing to increased rates (0.137–0.332 cm yr^{-1}) of recent (from 600 BP to present day) peat accumulation for several cores.

High rates of peat accumulation were found in the bottom minerotrophic layers of Core 2 (0.086–0.277 cm yr^{-1}). The PA value started to decrease to 0.049 cm yr^{-1} at approximately 9800 cal years BP when the vegetation changed from minerotrophic to a transition type. The highest PA values during the last ∼1200 years were calculated for Core 5-5 (0.332 cm yr^{-1}) and Core 19 (0.336 cm yr^{-1}), which were located on *Sphagnum fuscum* ridges (water table depth 30–40 cm) in the ridge-hollow complex. During the same period, increased PA values were calculated for Cores 18 and 27 (0.137 and 0.147 cm yr^{-1}, respectively), where water levels were apparently higher because *Sphagnum papillosum* dominated the moss layer. In general, the PA values decreased between 6500 and 3000 cal yr BP and increased for older and younger dates, reaching maximum values in current times (Figure 3-4).

The oldest peat layers were found in Cores 2 and 18 (∼11,000 and 10,000 cal yr BP), which means the peat accumulation process started from the eastern and western edges of the area now occupied by peatland and encroached onto its central part during the next 1,500–2,500 years. Thus, the lateral rate of peatland expansion can be estimated at 0.65–1.0 m yr^{-1} during the period 11,700–8,200 cal yr BP.

The oldest peat was formed 10,989 cal yr BP and the oldest gyttja was deposited 10,053 cal yr BP. In general, peat growth started via terrestrialisation after lake sediments had filled the lake basin, around 7,000 and 6,000 cal yr BP. Based on eight dates from the deepest peat layers, the average date of peatland initiation was 10,265 cal yr BP (see Supplement, Table 1S).

3.3. Bulk Density and Ash Content

BD values increased linearly with depth from 0.016 to 0.348 g cm^{-3} (see Supplement, Table 2S). This was caused mainly by changes in peat stratigraphy; ombrotrophic *Sphagnum* moss peat types have the lowest BD values because they have a low decomposition rate and thus retain more of their initial volume [44]. In the Mukhrino peatland, many well-preserved *Sphagnum fuscum* peats

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(decomposition degree 5–10%, H1-H2 von Post) were found at depths greater than 200 cm, overlain by more decomposed layers. On the other hand, minerotrophic peat contains a lot of woody and sedge remains which, over time, lose structure to create dense peat layers, and which may mix with mineral sediments at the bottom [47].

Ash content changed irregularly with a maximum (5–8%) at 100 cm depth followed by a subsequent decline (∼2.5%), then slowly increased again towards the mineral bottom (5–7%). These variations are related to the composition of plant remains. The ombrotrophic *Sphagnum* peat types have the lowest ash content while herb and wood peats normally show high ash content values [47].

In all of the Mukhrino peat cores we measured high ash content in the upper peatland layers (50–100 cm) [41,63]. This might be explained by mineral sediments covering the peatland during an extreme flooding event 1,000–2,000 years ago, or by a surface fire. However, analysis of soil and peat composition to elucidate the fire history of the Mukhrino peatland gave no indication of a large fire event during the last 1,300 years [41].

3.4. Carbon Accumulation Rate

The range of LORCA values was 24.80-28.92 g m^{-2} yr^{-1} (average 26.93±1.76 g m^{-2} yr^{-1}). ACAR is determined by high PA (0.15–0.33 cm yr^{-1}) in the upper peat layers and by high BD (0.4-1.4 g cm^{-3}) in the lower layers. The average ACAR for all seven cores was 37.99±11.4 g m^{-2} yr^{-1} and the median value was 26.17 g m^{-2} yr^{-1}. These values are similar to average values for the middle boreal zone of West Siberia (24.8±5.5 g m^{-2} yr^{-1}) [42]. Average C content for the 10 cm peat slice was 6.16±1.46 kg m^{-2}. The total amount of C stored up to the average depth (4.3 m) was 264.9±62.8 kg m^{-2}.

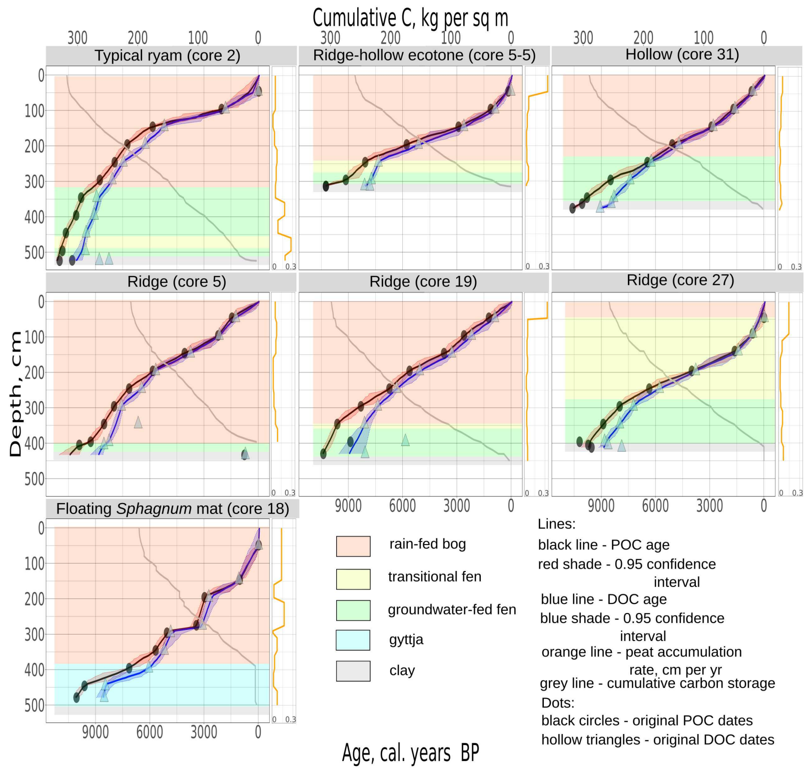

Figure 3. The age-depth models, carbon accumulation curves and peat types for the seven dating cores from the Mukhrino peatland.

3.5. POC and DOC

The DOC and POC dates were closely correlated (Pearson linear correlation, r^2=0.98, slope 0.93) from the present time until ∼6000 cal year BP, when they started to diverge (Figure 4). In older peat layers, the slope of the relationship between DOC and POC ages (Figure 4) decreased (to

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0.7), with increasing variation (r^2=0.75). Differences between DOC and POC ages showed a linear relationship with depth (Pearson linear correlation, r^2=0.55, slope 0.14) and ranged from 80 yr at 50 cm to 2000–3000 yr in the bottom layers (430–530 cm). Linear (Cores 5, 5-5, 18, 19, 27 and 31) and exponential (Core 2) models were used in calculations of the downward movement of DOC, to derive d_{doc_i} as the depth of collection of POC. The average apparent rate of DOC downward movement was 0.047$\pm$0.019 cm yr^{-1}, range -0.24–0.97 cm yr^{-1}. Negative values mean upward DOC movement, which was found for ten samples (sim15%). The minimum ($\sim$0.52 cm yr^{-1}) and maximum (17.7 cm yr^{-1}) values were found in the uppermost 50 cm, and likely to be influenced by the calibration uncertainty for modern dates (Figure 3, 4).

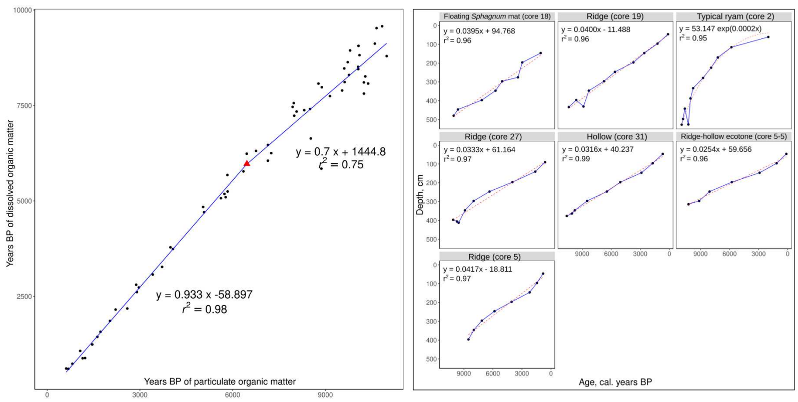

Figure 4. A scatter plot of the correlation coefficient between the DOC and POC ages (**left**). The red triangle is a breaking point of linear regression. The age-depth models of POC with the regression equations and r^2 (**right**).

4. Discussion

The study is aimed to describe the stratigraphy to explore the behaviour of DOC in a peat profile in Western Siberia and to estimate the apparent rate of DOC downward movement. Thus, it contributes to improving our understanding of the carbon cycle by considering the importance of a hitherto neglected long term carbon flux pathway, along with the implications for ^{14}C dating of peatlands and the temporal and spatial variation of greenhouse gas dynamics.

Sphagnum peat bogs are dominant in the middle taiga zone [49], covering $\sim$28% of the entire zonal area [61] and mostly occupying watersheds. Generally, the development histories of these peatlands are similar, involving initial waterlogging via paludification or terrestrialisation resulting in formation of a eutrophic peat layer, followed by a short stage producing minerotrophic peat, then an abrupt change to the ombrotrophic stage [34,46,74].

The ACAR, PA and hydrology of peatlands are all related to the stratigraphy [63]. In this study it has been shown that about two-thirds of the Mukhrino peat body consists of ombrotrophic *Sphagnum* peat with low ash content and low bulk density, which matches existing data for the West Siberian lowland [8]. These properties are mostly the result of the composition of plant communities from which the peat formed, along with climatic conditions at the time of peat formation, rather than peat age [12]. In [50] showed similar PA values for the Great Vasyugan mire, where PA was higher for ombrotrophic *Sphagnum* peat (0.115 cm yr^{-1}) than for minerotrophic peat (0.059 cm yr^{-1}). These data may be explained by the location in the southern taiga, which offers the most favourable meteorological conditions for peatland development [34]. In [42] concluded that the average PA for the middle taiga zone is 0.056 cm yr^{-1}, whereas the average PA in the southern taiga zones is 0.074-0.08 cm yr^{-1}. This underlines the importance of different external conditions during peat accumulation.

The majority of published peat age-depth models show a concave shape, meaning that decomposition is ongoing in the catotelm [72]. The age-depth models derived for the Mukhrino peatland were almost linear for Cores 19 and 31, s-shaped for Cores 5, 27, and 5-5, convex for Core

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2, and broken for Core 18 (Figure 3-4). The absence of concave shape models at this peatland may have been caused by the dominance of peat moss (ombrotrophic *Sphagnum*) remains (comprising 90% of the cores), which are the most resistant bog plant species to decomposition [62]. Despite the different shapes of the age-depth models, all of the carbon accumulation curves have similar positive exponential shapes. It seems that the rate of peat accumulation does not greatly affect ACAR, which is influenced more strongly by other factors such as the diversity and biochemical content of vegetation remains, bulk density, carbon content, and local topography and hydrology [42–44,51].

Regarding the eutrophic phase of peatland development, the peat accumulation process is influenced by proximity to the mineral soil, which leads to favourable geochemical conditions and fast peat accumulation [30] due to higher litter input [62]. Moreover, fen vegetation is less sensitive to climate conditions and thus has more stable PA values [30]. Nonetheless, the initial rate of mass loss for fen vegetation and increasing age (i.e. longer period of decomposition) result in a lower PA value. When the fen-to-bog succession proceeds to the transitional phase it features low PA (0.037 cm yr^{-1}) and slow ACAR (30.46 g m^{-2} yr^{-1}). This is probably related to the composition of the vegetation—including lack of *Sphagnum* species—and high decomposition rates [68]. On the other hand, the highest ACAR values were measured for eutrophic (63.1∼48.0 g m^{-2} yr^{-1}) peat, due to the abundance of grass and woody debris, which is rich in carbon. Ombrotrophic peats consist mostly of the remains of *Sphagnum* mosses, which contain the lowest carbon levels. Thus, the lowest value of ACAR (34.4∼12.1 g m^{-2} yr^{-1}) is found for ombrotrophic peat.

In this study we discovered a clear pattern of age differences between DOC and POC sampled from the same peat depth. It seems that processes leading to the separation of DOC and POC occur in the peatland although detailed mechanisms are still unclear. Possible reasons for the date differences that can be largely excluded include:

1. Sedge and *Scheuchzeria* roots growing down through the peat to a depth of two metres [31] were not found in any of the dated samples (which were visually controlled) and cannot penetrate into deeper layers. This would cause extreme inversions of the age-depth model (for example, when the modern roots reached ancient peat layers), which were not found in the current study. The roots of trees and dwarf shrubs occupy only the surface aerobic layer because they lack aerenchyma.
2. Cryoturbation causing intensive and ubiquitous date discrepancy could not occur because permafrost has been absent from the Middle Taiga zone in recent centuries.
3. Periodical flooding of the Mukhrino peatland should form a repeated alluvium layers, of which only one has been detected, in the upper layer only.
4. Peat fires, which occur only during extremely hot and dry years in the Taiga zone, do not explain the pattern of DOC and POC ages or the peat profile.

We suppose that the main reason for the age discrepancy is DOC downward movement. This would mean there is an additional pathway of carbon efflux from peatland that has not been properly studied so far. Numerous studies have analysed DOC fluxes from peatlands into streamwater [9,11,27,29], but few of these have considered DOC downward movement. On the other hand, the process has been considered by authors who found that the ^{14}C ages of carbon dioxide and methane are younger than those of the surrounding peat [1,2,13–15]. Results from south-west England have shown that DOC is 830–1260 yr younger than the surrounding peat [15], while [19] published results from a 7 m deep peatland in Scotland showing age differences between DOC and peat that increased with depth from 80 to 1,835 yr. One possible explanation is that young DOC which is transported from upper to lower peat layers is then converted to CO_2 and CH_4 by microbial activity.

Only [54] have previously taken DOC downward movement into account for peatlands in Western Siberia, where they recorded a maximum age difference of 6,500 years between DOC and POC. In the study reported here, the difference between DOC and POC ages increased with depth, from 9 to 3,044 yr (excluding three negative differences found in the uppermost 50 cm). The date discrepancy appeared at 100 cm depth, i.e., at the lowest position of the water table (Figures 3 and 4) where no active water flow takes place and DOC is, therefore, not affected by mixing with surrounding water layers.

We can suggest several possible causes for DOC downward movement and age delay specifically in the Mukhrino peatland:

1. This process might be fostered by the location of the Mukhrino peatland, which occupies the second high terrace and is drained by the small rivers "Mukhrina" and "Bolshaya Rechka" located 6–8 m lower from the eastern and western sides. This creates a piezometric gradient that enables the water from the peatland to penetrate through the mineral bottom (clay layer with hydraulic conductivity in the range 10^{-10} to 10^{-6} cm s^{-1}; [21] and discharge to the streams (Figure 2). The water deficit thus created in the lower layers must be compensated by the water influx from the upper peatland horizons, resulting in a vertical flow of water transporting DOC.
2. The temperature profile measured in the south taiga zone shows maximum temperature differences of 18 °C between the upper and lower layers of the peat body over the year [36]. This gradient may initiate a convection process that causes vertical movement of the labile phase. The opposite was shown by [16], where the decreased amount of porewater caused by thermal stratification in autumn caused rapid diffusion of CO_2 from deeper porewater to the peatland's surface.
3. In [39] showed a possible path of methane displacement into deeper soil horizons due to the freezing of thick strata of epigenetic permafrost. The same mechanism might potentially operate in peatlands since high peat porosity is favourable for vertical water movement. The surface layer of the Mukhrino peatland freezes from the end of September to the beginning of November and water discharge stops completely at that time. Thus, the peatland becomes a huge reservoir consisting of a high porosity substrate filled with water and completely confined by the ice pack above. The freezing of water may produce additional pressure, pushing the labile dissolved carbon downwards.
4. Another possible mechanism of DOC downward movement is the complete saturation of pore water by DOC (i.e. the highest possible concentration in given conditions), whereby concentration systematically increases with depth by diffusion. A few publications cover this topic [17,19,22] and report concentrations $\sim$2 mmol dm^{-3} at the surface and 6–22 mmol dm^{-3} at the bottom. However, the information specifically about Western Siberian peatlands is limited, reporting concentration in range 80-860 mL l^{-1} [56].
5. The negative values of the DOC movement rate may result from an upward flux that could be caused by water table movement in the surface layers. The rising water table may catch some of the DOC produced in the lower layers and lift it towards the surface, making DOC age older than POC age on the same depth [54]. Several negative DOC movement rates were found in the deeper layers (200–300 cm) that might be caused by methodological flaws in value calculations when the s-shaped age-depth models for the cores 5 and 27 were approximated by linear regression.

In our study we estimated an average apparent rate of DOC downward movement of 0.047 ± 0.019 cm yr^{-1}. There was a slight tendency for the rates to decrease, by 2–10 times, towards the mineral bottom. The most likely reason is low vertical hydraulic conductivity in the deep, dense and well-decomposed basal peat [3]. A limited number of publications estimate the rates of DOC vertical movement. In [15] used a vertical hydraulic conductivity value of 31.5 cm yr^{-1} to estimate DOC vertical transport in the UK. This value exceeds our results by $\sim$600 times because the study was based on potential water movement that varies significantly with degree of saturation and due to the physical properties of peat [18]. However, this value might be used as a potential rate of DOC downward movement. It has to be regarded as a maximum possible velocity, i.e., as a limiting factor.

This result provides a possible explanation for date delay between DOC and POC ages at the same depth, and quantifies the apparent rate of DOC vertical movement in West Siberian

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ombrotrophic peatlands for the first time. In long-term processes of peatland development during the last 10,000–12,000 yr [40], DOC downward movement could potentially make a significant additional contribution to the global carbon cycle and should, therefore, be considered for inclusion in the peatland carbon balance calculation. However, our estimate of the amount of carbon lost through DOC vertical movement (28–404 mg m^{-2} yr^{-1}) is equivalent to only 0.07–1.07% of the ACAR and 0.4–5.2% of the average DOC export through runoff [9]. Thus, the vertical movement of DOC may cause age discrepancies between mobile (DOC) and immobile (POC) peat fractions at the same depth but, based on our estimates, it forms an additional flux in the carbon balance of the peatland.

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