

Carbon in tundra soils in the Lake Labaz region of arctic Siberia

A. GUNDELWEIN^a, T. MÜLLER-LUPP^b, M. SOMMERKORN^c, E. T. K. HAUPT^d, E.-M. PFEIFFER^c
& H. WIECHMANN^c

^aCouncil for the Lindau Nobel Laureate Meetings, 88131 Lindau (B), Germany, ^bIFM-GEOMAR, Leibniz-Institute for Marine Science, 24148 Kiel, Germany, ^cThe Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK, ^dInstitute of Applied and Inorganic Chemistry, University of Hamburg, and ^eInstitute of Soil Science, University of Hamburg, 20146 Hamburg, Germany

Summary

Large amounts of carbon are stored in permafrost-affected soils of the Arctic tundra. The quantity, distribution and composition of this carbon are important, because much of the carbon is likely to be released as a result of global warming. We have studied soils of the central Siberian Arctic to determine the carbon content and the nature of the organic matter by density fractionation, and ¹³C-NMR- and ¹³C-stable-isotope analyses. There are pronounced differences in the profile and variations from place to place in the quantity and nature of soil organic matter. We estimated that the mean stock of carbon was 14.5 kg m⁻² within the active layer. We found a total of about 30.7 kg C m⁻³ in the entire upper metre of the soils. Carbon of the tussock tundra showed strong vertical differentiation, with a large proportion comprising decomposed, recalcitrant compounds. We identified within the soil several zones of aerobic and anaerobic decomposition. Mobile carbon fractions have precipitated under the influence of low temperatures.

Introduction

The Arctic region is expected to be affected by global warming more than other regions of the earth, and the Arctic in turn may exert a strong feedback on global climate (IPCC, 2001; AMAP, 2003). Based on current General Circulation Model (GCM) predictions, a rise of the mean global annual temperature of 0.8–2.6°C within the next 50 years and an increase in precipitation are expected for the polar regions (IPCC, 2001). Arctic soils are thought to be very sensitive to climate change, and possible consequences could be the loss of permafrost and increased decomposition of soil organic matter, resulting in increased emission of the greenhouse gases carbon dioxide and methane (Oechel & Billings, 1992; IPCC, 2001).

With an estimated 21% (Raich & Schlesinger, 1992) to 27% (Post *et al.*, 1982) of the global terrestrial organic carbon stored in tundra and taiga ecosystems, permafrost-affected soils will play an important role in determining the consequences of global warming for the whole terrestrial carbon cycle. Even though von Baer (1840) gave a first description of

the large amounts of organic carbon stored in permafrost soils of Siberia, 166 years later the current discussion about the size and dynamics of carbon in the permafrost-affected soils is still constrained by few data and large uncertainties of estimates (Post *et al.*, 1982; Batjes, 1996; Stolbovoi, 2002; Smith *et al.*, 2004). Data from Siberia, which has about 50% of the world tundra, are rare. Stolbovoi (2000, 2002) has recently reviewed the carbon contents of the soils of Russia and Smith *et al.* (2004) reviewed the carbon contents of the soils of the west Siberian lowland. Published means of the carbon stocks of Arctic tundra soils worldwide range from 9 to 44 kg C m⁻³ (Table 1).

To improve our understanding of the possible consequences of climate change on tundra ecosystems, we need more detailed knowledge about the quantity, nature and spatial distribution of soil carbon in these systems. Because the amount of carbon in Arctic soils is strongly related to short-range variations, any estimation of the carbon content in Arctic ecosystems can be solved only by detailed mapping of such patterns. Therefore we aimed to determine the quantity, nature and spatial distribution of soil organic carbon in a southern Arctic tundra environment by mapping the soils and patterned ground structures and determining the carbon in various parts of the structures.

Correspondence: A. Gundelwein. E-mail: andreas.gundelwein@lindau-nobel.de

Received 22 September 2004; revised version accepted 4 January 2007

Table 1 Carbon contents in Arctic soils

Author(s)	Region	Number of profiles	Carbon /kg C m ⁻²	Depth /m
< 100 cm				
Post <i>et al.</i> (1982)	Worldwide	48	11–37 (21.8)	Active layer
Oechel & Billings (1992)	Alaska	ND ^a	13–29	A and O horizon
Biryukova & Orlov (1993)	Russia	2	14.5	0.5
Tarnocai & Ballard (1994)	Canadian Arctic	ND ^a	26.2	Active layer
	Canadian Subarctic	ND ^a	21.7	
Nadelhoffer <i>et al.</i> (1997)	Alaska	ND ^a	20–25	Active layer (0.4)
Stolbovoi (2000, 2002)	Russia	< 163	11.6	0.3
This study	Siberia	10	14.5	Active layer
100 cm				
Tarnocai & Smith (1992)	Canada	14	4–63	1.0
Matsuura & Yefremov (1995)	Russia	7	11–20	1.0
Batjes (1996)	Worldwide	5	15.7–125	1.0
Ping <i>et al.</i> (1997, 2002)	Alaska	42	10–94	1.0
Stolbovoi (2000, 2002)	Russia	< 163	16.6	1.0
Post (2006)	Worldwide	ND ^a	14.2	1.0
This study	Siberia	10	30.7	1.0

^aND, no declaration.

Study region

The region we studied is in central Siberia on the Taimyr Peninsula at 72°N and 99°E, and extended over 8 km² at the northern shoreline of Lake Labaz. The climate is continental (Table 2). The vegetation is dominated by dwarf shrubs, sedges, mosses and lichens. The characteristic species are *Betula nana*, *Salix arctica*, *Cassiope tetragona*, *Dryas punctata*, *Vaccinium vitis-idea*, *Eriophorum vaginatum*, *Polytrichum strictum* and *Hylocomium splendens*, all typical of the boundary zone between the southern Arctic tundra and the Arctic tundra in the north (Walter & Breckle, 1986).

Stolbovoi (2000) summarizes the soil coverage, climatic and vegetation zones in Russia. According to him, a typical southern tundra in Russia has about 71% Dystric and Gelic Gleysols, 10% Terric and Fibric Histosols and 3% Gelic Podzols. In the Labaz region we found 70%, 10% and 3%, respectively, of these three soil types, and so we regard the region as representative of the southern arctic tundra. This tundra type covers 8.6% of the whole Arctic (CAVM, 2003).

Materials and methods

Mapping and sampling

We identified landscape units within the region. For points on a 50 × 50 m grid we characterized the main vegetation units and tundra forms and recorded the dominant plant species. We then identified units of patterned ground and mapped them, a total of 74 soil profiles (six to 10 for each unit) described according to the US Soil Taxonomy (Soil Survey Staff, 1999). The steep shore of

Lake Labaz, with gradients up to 30° and covering about 6% of the study area, is characterized by a wide variety of different substrates, disturbed soils and strong thermokarst erosion. This shore area was not considered for the estimation of the carbon storage of the study area. The carbon content of the soil depends on the microrelief, and so we described the two extreme positions of the microrelief within the unit (named the a- and b-position of a profile, see Figure 1) and considered the spatial extent of the parts of the structures (see below). Both disturbed and undisturbed soil samples were taken from each horizon for determination of properties in the laboratory. The information gained was used to construct a map of the soil and patterned ground of the region. Then, we selected one reference profile based on the similarity of profiles within a landscape unit and determined the

Table 2 Physical environment of the Lake Labaz region (72°N, 99°E)

Botanical zone	Southern tundra (typical tundra)
Mean annual air temperature/°C	–13.4 ^a
Mean July air temperature/°C	+12.3 ^a
Frost free period/days year ⁻¹	73 ^a
Mean annual precipitation/mm	237 ^a
Mean thickness of active layer/m	0.20–0.50
Relief	Moderately hilly landscape with maximum altitude up to 150 m above sea level
Parent material	Quaternary, loamy-sandy lake sediments
Permafrost thickness/m	400

^aClimatic data for the Labaz Lake region from the Chatanga (Siberia) meteorological station (73°N, 102°E).

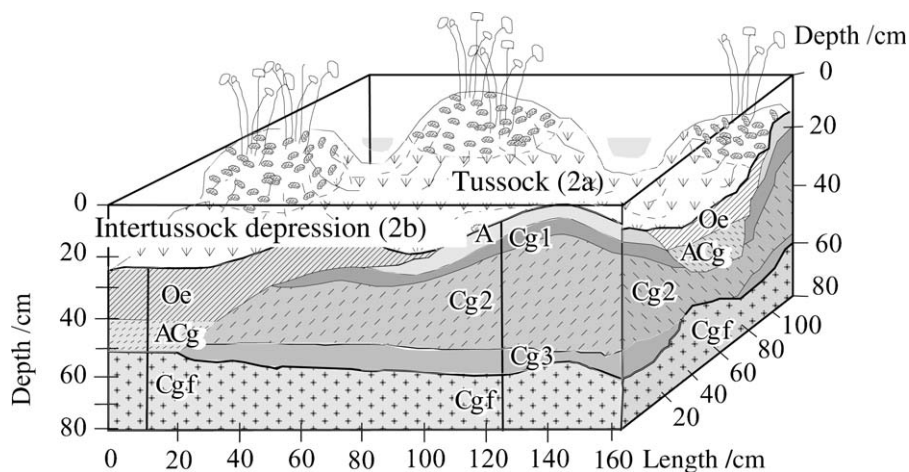


Figure 1 Ruptic Histoturbel of the tussock tundra (Profile 2). The vertical lines named 2a and 2b mark the position of the two different subprofiles in the extreme positions of the microrelief (2a at the Tussock summit, 2b at the Intertussock depression).

carbon content of it. Vegetation analysis for the tussock tundra was done on a 1-m² plot. Percentage cover for individual plant species was assessed on a 10 × 10 cm grid, i.e. at 100 points, of 1 m². Samples were taken from the dominant species, air dried and analysed for the carbon contents as for the soil samples.

Carbon quantification

We determined bulk density by taking five replicates of undisturbed soil from each horizon in 100-cm³ cylinders. The soil was dried at 105°C to constant weight. The bulk densities of the permanently frozen soil horizons were extrapolated from the bulk density of the layers above, partly corrected to smaller values from the volumetric extent of ice lenses.

Total organic carbon of oven-dried soil samples (< 2 mm), milled to < 63 μm, was determined with a CHN-Analyser (HERAEUS, Frankfurt-am-Main, Germany). In a few exceptional cases the carbon content of frozen layers was estimated in the field by colour. These data are marked in the Tables. The amount of soil organic C per square metre was determined based on the C contents of the individual horizons:

$$I = \frac{1}{100} \sum_{i=1}^n C_i L_i D_i, \quad (1)$$

where I is the C content of a soil with i horizons up to 1 m depth respective up to the top of the permafrost in kg m⁻², C_i is the C concentration in g kg⁻¹ soil (< 2 mm), L_i is the thickness of the layer in cm, and D_i is the bulk density in g cm⁻³. We calculated the mean carbon content of 1 m² of a soil type to either the top of the permafrost at maximum thaw (active layer) or to 1 m. For the calculation the different spatial extents of the ground patterns were considered (e.g. for the tussock tundra: tussocks represented 45% of the area, intertussocks represented 55% of the area; see Table 3).

These results of the single soil types were scaled up to the spatial extent of the various soil units within the region. For a better comparison with existing data, the carbon contents were

expressed in two ways: (a) in mass of carbon per square metre surface area and to permafrost level at maximum thaw (18 August, 1995) and (b) in mass of carbon per cubic metre of soil (Table 4).

The nature of the organic matter

The soil organic matter was fractionated into four fractions by density. We used the method of Beudert (1988), only modified by sodium-polytungstate instead of tri-chloro-bromomethane. The fractions represent undecomposed plant material (density < 1.6 g cm⁻³), decomposed, humified organic matter (1.6–2.0 g cm⁻³), organo-mineral complexes (2.0–2.4 g cm⁻³) and almost exclusively mineral soil (> 2.4 g cm⁻³). For this fractionation, 10 g of air-dry soil samples were added to the 1.6 g cm⁻³ sodium-polytungstate solution and sonicated for 1 minute (at 50 J s⁻¹), followed by 20 minutes of centrifuging (2000 g). This procedure was repeated for every density step.

The fractionation into humic and fulvic acids separated two dominant components of the medium-weight density fraction of the organic matter (1.6–2.0 g cm⁻³) and was conducted as defined by Ping *et al.* (1995), using XAD-resins (Rohm & Haas, Philadelphia, PA, USA). From each horizon of the selected soil profile, two 50-g portions of air-dry soil (< 2 mm) were taken, and the NaOH-soluble part of the organic matter extracted five times with 0.1 M NaOH for 2 hours on a rotary shaker and separated by centrifuge (20 minutes 2000 g). The solution was filtered on a 0.45-μm aperture polyethersulfone filter (SUPOR 450, Gelman Science, Ann Arbor, MI, USA) under N₂. The filtrate was fractionated into humic acids (HA) and fulvic acids (FA) by precipitation of HA from the solution at pH 1 with 1 M HCl. The precipitated HAs were separated by centrifugation (20 minutes 2000 g) and re-dissolved with 0.1 M NaOH. Also, the FA-solution was titrated with 0.1 M NaOH to pH 2–3. Finally, we purified the solution of the HAs and the FAs by passing them through two columns (3 litre) with XAD-8- and XAD-4-resins (XAD-8: poly methyl-methacrylate

Table 3 Organic carbon stocks of selected soils at Lake Labaz area calculated to 1-m depth

Soil type	Microrelief and coverage /%	Horizon	Thickness /cm	C /%	BD ^a /g cm ⁻³	Soil /kg m ⁻²	C /kg m ⁻²
Ruptic-Histic Aquiturbel	Hummock (Profile 1a) 88%	A	1	10.3	0.9	9	0.9
		Cg	9	1.5	1.3	117	1.8
		Cg	40	1.3	1.3	520	6.8
		Cg	5	1.9	1.3	65	1.2
		Sum act. layer	–	–	–	–	10.7
		Cgf	45	1.4 ^b	1.2 ^b	540	7.6
		Sum/m ³	–	–	–	–	18.3
	Interhummock (Profile 1b) 12%	Oe	10	45.8	0.3–0.6	30–60	13.7–27.5
		Sum act. layer	–	–	–	–	13.7–27
		Oef	10	22.2	0.4 ^b	40	8.9
		Cgf	80	1.3 ^b	1.2 ^b	1040	13.5
		Sum/m ³	–	–	–	–	36.1–49.9
		Mean	–	–	–	–	20.4–22.1
		–	–	–	–	–	–
Ruptic Histoturbel	Tussock (Profile 2a) 45%	A	5	4.8	0.6	30	1.4
		Cg1	3	2.3	1.2	36	0.8
		Cg2	12	2.1	1.4	168	3.5
		Cg2	14	2.4	1.4	196	4.7
		Cg3	6	4.0	1.2	72	2.9
		Sum act. layer	–	–	–	–	13.3
		Cgf	60	2.4 ^b	1.2 ^b	720	17.3
	Sum/m ³	–	–	–	–	30.6	
	Intertussock (Profile 2b) 55%	Oe	17	33.6	0.2–0.5	34–85	11.4–28.6
		Acg	10	3.8	1.3	130	4.9
		Sum act. layer	–	–	–	–	16.4–33.5
		Cgf	73	2.0 ^b	1.2 ^b	876	17.5
		Sum/m ³	–	–	–	–	33.9–51.0
		Mean	–	–	–	–	32.4–41.8
–		–	–	–	–	–	
Glacic Histoturbel	Centre (Profile 3b) 60%	Oi	6	44.1	0.3	18	7.9
		Oe	14	34.2	0.5	70	23.9
		Bg	16	9.3	1.3	208	19.3
		Sum act. layer	–	–	–	–	51.1
		Cf	64	10.1	1.2 ^b	768	77.6
		Sum/m ³	–	–	–	–	128.7
		–	–	–	–	–	–
	Rim (Profile 3a) 40%	Oi	3	46.1	0.13	3.9	1.8
		Oa	8	38.7	0.3	24	9.3
		Oe	9	31.5	0.4	36	11.3
		Bg	9	9.3	1.3	117	10.9
		Sum act. layer	–	–	–	–	33.3
		Cf	71	10.1	1.2 ^b	852	85.2
		Sum/m ³	–	–	–	–	118.5
Mean	–	–	–	–	124.6		
Spodic Psammuturbel	AE	10	1.7	1.1	110	1.9	
	Bw	15	0.6	1.6	240	1.4	
	Bwg	35	0.1	1.9	665	0.7	
	Cg	20	0.2	1.4	280	0.6	
	Sum act. layer	–	–	–	–	4.6	
	Cgf	20	< 0.1	1.4 ^b	280	0.3	
	Sum/m ³	–	–	–	–	4.9	
Typic Aquorthel	Oi	12	16.8	0.5	60	10.1	
	ACg	40	1.8	1.4	560	10.1	
	ACg	2	3.5	1.4	28	1.0	
	Sum act. layer	–	–	–	–	21.2	
	Cgf	46	2.5	1.3 ^b	598	14.9	
	Sum/m ³	–	–	–	–	36.1	

^aBD, bulk density.^bEstimated.

Table 4 Mean carbon stock in different soil-units and in the mapped area

Profile number	Mean C content /kg C m ⁻²	Portion of the mapped area /%	Contribution of the soil unit to the mean carbon content /kg C m ⁻²
Active layer			
1	11.1–12.7	51	5.6–6.5
2	15.0–24.4	14.5	2.2–3.6
3	44.0	10.1	4.4
4	4.6	3	0.1
5	21.2	4.7	1.0
Sum			13.3–15.6
First 100 cm			
1	20.4–22.1	51	10.4–11.3
2	32.4–41.8	14.5	4.7–6.1
3	124.6	10.1	12.6
4	4.9	3	0.1
5	36.1	4.7	1.7
Sum			29.5–31.8

and XAD-4: styrene-divinylbenzene) to remove polysaccharides and low-molecular weight acids. The HA and FA residues were freeze-dried.

Additionally, the lignin fraction (Klason-lignin) was determined on some soil samples. We measured the amount of Klason-lignin as defined by Schlichting *et al.* (1995). This involved stepwise Soxhlet-extraction of two 50-g portions of air-dry soil (< 2 mm) with a 1:1 by volume ethanol-toluene mixture for 24 hours, followed by hot water (100°C) and 20 g l⁻¹ HCl at 100°C and 720 g l⁻¹ H₂SO₄ at 20°C and weighing of the dried residue.

$\delta^{13}\text{C}$ -signature

In contrast to decomposition under aerobic conditions, anaerobic decomposition discriminates against the heavy carbon isotope, ¹³C. When methane is produced, the residual organic matter becomes enriched in ¹³C (Heyer *et al.*, 1976). Therefore, the $\delta^{13}\text{C}$ -signature of organic matter can be used to characterize decomposition processes. For isotope analysis of organic carbon, the sample-C was combusted for 10 minutes at 900°C under an excess of oxygen and converted into CO₂ in a high-vacuum line. The isotopically interfering species of nitrogen oxides, NO_x, were reduced over copper at 450°C. The yield of CO₂ was determined volumetrically and analysed in a FINNIGAN MAT 250 isotope-ratio mass spectrometer (Thermo-Finnigan, Austin, TX, USA). The instrument was isotopically calibrated through the ISO-TOP standard (Messer-Griesheim, Frankfurt-am-Main), which is depleted against the PDB Standard (–20‰ PDB). The isotope composition is given as $\delta^{13}\text{C}$ with respect to PDB notation:

$$\delta^{13}\text{C} \left[\text{‰} \right] = \left[\left(\frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{PDB}}} - 1 \right) \right] \times 1000. \quad (2)$$

CPMAS ¹³C-NMR-spectroscopy

Fractions of HA and air-dried milled plant material were analysed by ¹³C-CPMAS spectroscopy. The samples contained between 0.6 and 1.6 g C kg⁻¹, which gives CPMAS ¹³C-NMR spectra with adequate signal-to-noise (S/N) ratios. The CPMAS ¹³C-NMR spectra were obtained on a Bruker MSL300 spectrometer (Bruker BioSpin GmbH, Rheinstetten), operated at 75.47 MHz, with Hartmann Hahn match with 90° pulses of 4.5 μs, contact times of 1 ms, and a 4-s recycle delay. Samples were examined in 4-mm rotors with spinning rates of about 5000 Hz. The spectra were usually obtained from overnight runs, and a standard line broadening of 50 Hz was applied. The chemical shift was given relative to tetramethyl silane (0 p.p.m.) and was standardized to the CO signal of solid glycine at 176.09 p.p.m. The spectra yielded a very broad, underlying signal shape over the whole chemical shift range, and so integration was omitted and the spectra were compared only by visual inspection of relative peak heights in the different areas (alkyl C, –10–45 p.p.m.; O alkyl C, 45–110 p.p.m.; aromatic C, 110–160 p.p.m., carbonyl C, 160–220 p.p.m.). We repeated some spectra to achieve comparable data for subtraction studies, but because of the large cost and time required, we made no systematic studies of reproducibility.

Results

Soil-patterned ground units

We identified five different soil patterned ground units within the mapped region. More than 75% of the area was covered by poorly drained soils (Ruptic-Histic Aquiturbels, Profile 1; Ruptic Histoturbels, Profile 2; Glacic Histoturbels, Profile 3), in association with tussocks, hummocks and ice-wedge polygons. Drier soils such as Spodic Psammenturbels represented only 3% of the study area. Figure 2 gives an overview of the distribution of soil patterned ground units and the location of the reference profiles.

In contrast to the wet soils associated with patterned ground structures, Typic Aquorthels (Profile 5) with no patterned ground structure, dominated wet-sedge tundra, which occupied < 5% of the mapped area. On the exposed hilltops and the riverbanks of Tolton Creek (in the centre of the study area), Spodic Psammenturbels (Profile 4) without patterned ground structures are developed and cover 3% of the total mapped area on dry, sandy and gravelly substrates with thaw-depths up to 100 cm, and sparse vegetation.

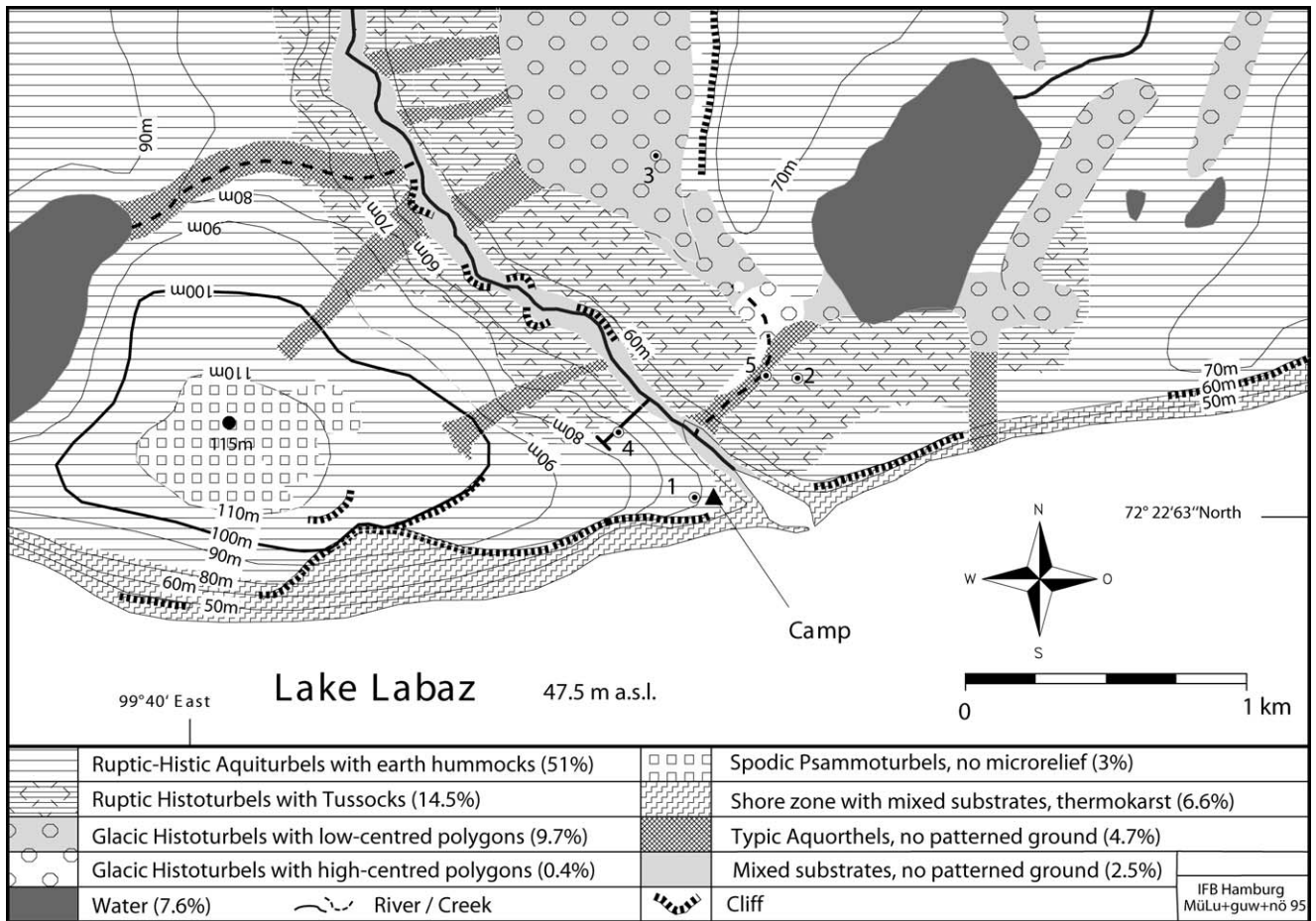


Figure 2 Soil-patterned ground units of the Lake Labaz Region; extent in brackets. Profiles are shown as numbered circles. The T-line near Profile 4 marks a studied transect, the dotted line near Profile 5 a temporary watercourse.

Horizontal and vertical distribution of organic carbon

The carbon content of the soils varied greatly with depth, with position in the soil microrelief, and between different soil units. Due to these variations we described and sampled soil profiles in both extreme positions of the microrelief, named a and b in the description (Table 3). The amount of carbon increases from dry to wet sites. The largest C contents (up to 44 kg C m^{-2}) were found in the low-centred polygons (polygons with a depressed centre), while the smallest carbon contents (4.6 kg C m^{-2}) were found in the dry, sandy soils. The large variation of C can be seen from Tables 3 and 4.

The mean total soil C was 14.5 kg C m^{-2} within the active layer and 30.7 kg C m^{-3} in total. The organic layers alone contained 6.3 kg C m^{-2} (Table 3). Thus, 47.2% of the carbon within the first metre was in the active layer, 52.8% was sequestered in the upper permafrost, 20.5% was in the organic horizons, and 79.5% was stored in the mineral horizons. In wet sites, a small accumulation of carbon was found in the mineral soil near the permafrost table at maximum thaw depth in August. However, the carbon content of the frozen horizons

below maximum thaw depth (Cf and Cgf horizons) was not significantly larger than in the mineral soil of the thawed horizons.

Nature of organic matter

To assess vertical differences in the nature of the organic matter we fractionated the organic matter of the tussock tundra-site (Profile 2). We chose the Tussock tundra because it represented a dominant unit in our region, covers large areas of the Arctic (Aleksandrova, 1980), and represented an intermediate moisture regime.

Density fractions

Within the top 5 cm, 59% of the total organic C was in the lightest fraction, which by definition consists only of weakly decomposed plant material (Figure 3). The relative contribution of this lightest fraction to the organic matter was less in the deeper horizons (5–20 cm depth, < 30%) but increased again

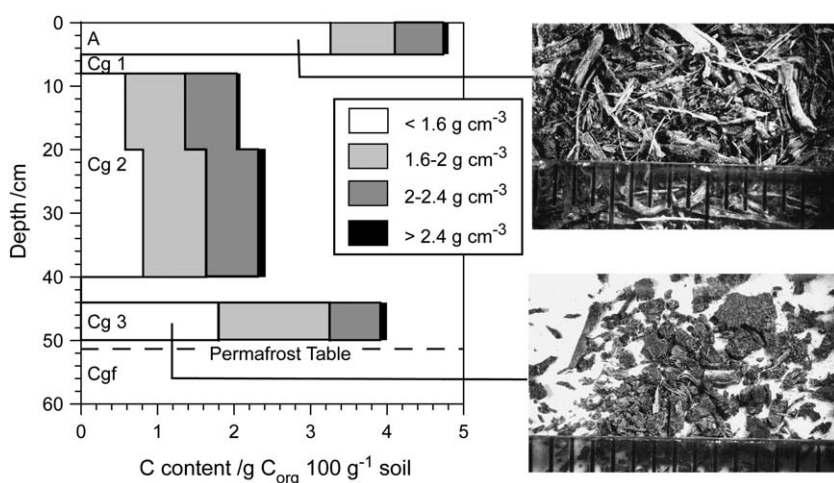


Figure 3 Distribution of organic matter in density fractions (Profile 2). The photographs illustrate the differences between organic material with density $< 1.6 \text{ g cm}^{-3}$ from the soil surface (upper photograph) and from the permafrost boundary (lower photograph). Scale is in mm.

near the permafrost-boundary to 39%. Despite the predominantly cold and wet conditions of the central part of the soil profile (5–20 cm depth), more than 70% of the C in this part of the profile was part of the well-decomposed fractions, with a density in the range $1.6\text{--}2.4 \text{ g cm}^{-3}$.

The C/N ratio of the light fraction of the top 5 cm was 40, which is similar to undecomposed plant material. In contrast, the C/N ratio of the light fraction near the permafrost boundary was 20. This distinct qualitative difference within this fraction is the result of increased decomposition of the original plant litter. The micrograph shows the differences in decomposition between the light fraction from the soil surface and near the permafrost (Figure 3). The C/N ratio of the fraction $> 2.4 \text{ g cm}^{-3}$ was 6; a substantial proportion of the organic part of this fraction can be interpreted as microbial biomass (Beudert, 1988).

Humic and fulvic acids

In the top 5 cm of the soil, 35% of the C (1.7 g of 4.8 g C) was humic acids (HA). The proportion of this fraction decreased to 10–14% (0.2–0.3 g of 2.1–2.4 g C) in the deeper horizons and increased again to 35% (1.4 g of 4.0 g C) immediately above the permafrost boundary (Figure 4). The relative amount of the fulvic acid (FA) fraction showed an even distribution throughout the profile, with a small increase in the deeper horizons. This fraction accounted for 6–9% of the C (0.2–0.4 g of 2.1–4.8 g C, Figure 4). The HA and FA fractions had C/N ratios ranging from 13.6 to 18.1, and from 15.1 to 21.7, respectively, with generally larger ratios found near the surface and again near the permafrost boundary.

Lignin

In surface horizons, the Klason-lignin fraction represented 33% of the C, whereas in deeper horizons this fraction represented up to 46% of the C.

CPMAS ^{13}C -NMR-spectroscopy

The fresh, undecomposed plant material showed, in parts, well-structured signals of significant strength in the CPMAS ^{13}C -NMR spectra (Figure 5a). The mosses, grasses and roots showed a strong predominance of signals in the O alkyl C area, the birch-bark spectrum differed greatly with a strong signal in the alkyl C region, indicating lignin-bound components or waxes. These signals accord with the signals of the HAs near the soil surface, which were dominated by prominent resonance peaks in the 40 p.p.m. and 170 p.p.m. regions. This suggests that there is material derived from shrubs such as birch with large lignin contents. With increasing depth, the contents of alkyl C and also the carbonyl C of the HA decreased, and near the permafrost boundary the signals vanished completely (Figure 5b).

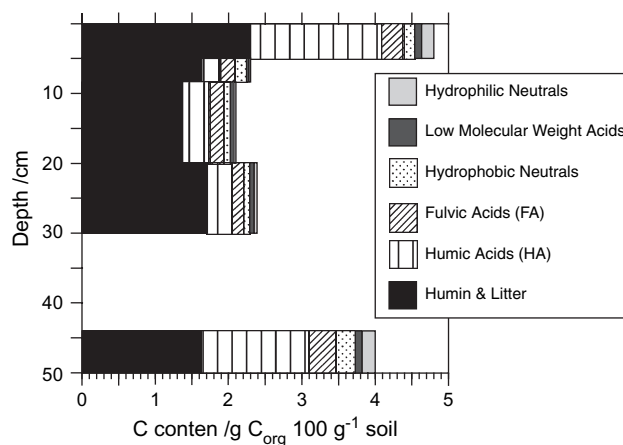


Figure 4 Distribution of organic C in HA, FA and other fractions by XAD-fractionation (Profile 2).

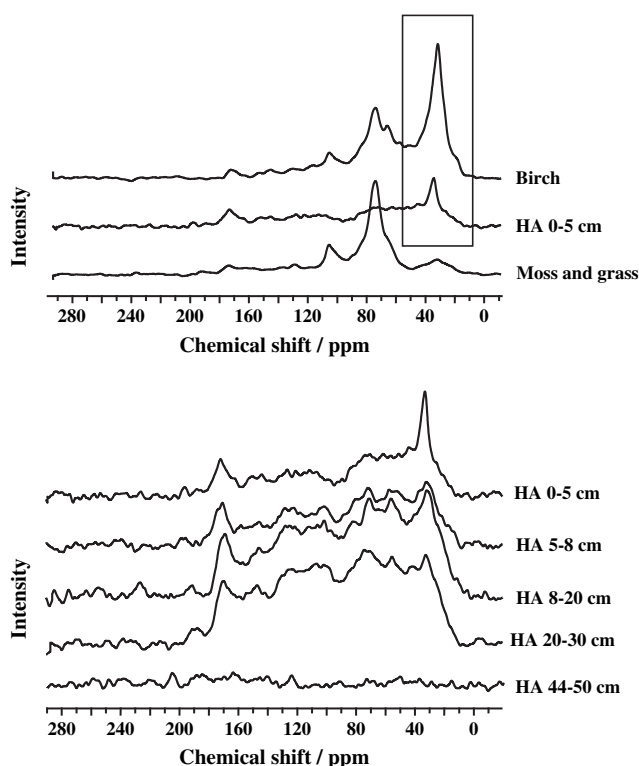


Figure 5 (a) CPMAS¹³C-NMR spectra of the plant source material (birch-bark [*Betula nana*], grass and mosses) and the near-surface HA fraction (HA 0–5 cm) of profile 2; (b) CPMAS¹³C-NMR spectra of the HA fractions from soil surface (HA 0–5 cm) to permafrost (HA 20–30 cm) of profile 2 and below (HA 44–50 cm).

$\delta^{13}\text{C}$ signature

In general, we found an increase in $\delta^{13}\text{C}$ of the soil organic matter with progressive decomposition of the fractions. The most distinct increase of $\delta^{13}\text{C}$, by 1‰, was found in the horizon 5–20 cm below the soil surface (Figure 6a). The only exceptions were the HAs and FAs which showed smaller contents of ¹³C than the average (Figure 6b). Even near the permafrost, the HAs did not show enrichment in ¹³C, which was unexpected in relation to the degradation shown by the CPMAS ¹³C-NMR analyses.

Discussion

Quantity and patterns of carbon storage

Our data show a general increase of the amount of carbon in the soils with increased soil moisture content. The largest amounts were in tussock tundra, ice-wedge polygon tundra and wet-sedge tundra (Profiles 2, 3 and 5; Tables 3 and 4). At these sites, decomposition is slow because the soil is wet and anaerobic and plant growth is large. In ice-wedge polygons (Profile 3), we found about 125 kg C m⁻³. This value is identical to that reported by Batjes (1996) as an average for Gelic Histosols worldwide. Our

results show that in wet-tundra soils, large amounts of carbon are stored not only in the surface organic layers but also in the deeper horizons. We found 53% of the C in the permafrost. One possible reason for such a large carbon content in deeper horizons could be increased activity of frost processes. Ping *et al.* (1997) explained the accumulation of soil carbon near the permafrost table by a more active transport of carbon into deeper parts of the soil profile by cryoturbation followed by better conservation. They describe the combined mechanisms to be the main mechanism for carbon sequestration in Arctic tundra. However, cryoturbation at our wet sites was moderate, as judged from the almost continuous plant cover. Mud-boils (circular zones where cryogenically induced turbation results in the absence of vegetation) were rare. The observed characteristics of the organic matter suggest that the accumulation of organic carbon near the permafrost is the result of transport of water-soluble organic compounds down to the frozen ground, where they precipitated under the influence of low temperature (see below).

Soil carbon on a landscape scale

The carbon stores of tundra soils in other studies vary from 9 to 125 kg C m⁻³ in the whole soil, down to 1 m, and 11–29 kg C m⁻² in the active layer only (Table 1). Our results, with a mean of 14.5 kg C m⁻² in the active layer are at the lower end of this broad range and correspond well with the data of other studies from Siberia (Matsuura & Yefremov, 1995; Stolbovoi, 2002) and Alaska (Nadelhoffer *et al.*, 1997) and the global estimation of carbon in tundra soils by Batjes (1996). They are distinctly smaller than the 21.8 kg C m⁻² determined by Post *et al.* (1982) for tundra ecosystems worldwide. In our study, the amounts increased two-fold, to 30.7 kg C m⁻³, if the permanently frozen ground was considered.

Nature of soil organic matter fractions

The analysis of the fractions shows strong vertical differentiation into distinct decomposition zones.

In the surface horizons of the tussock tundra, we had distinct indications of aerobic decomposition with HA formation. Here 68% of the organic matter was part of the undecomposed, light-carbon fraction (based on the density fractionation; Figure 3), while 35% of the organic matter was well-decomposed humic acids (based on the XAD fractionation; Figure 4). The surface horizons are comparatively well-aerated, dry and warm, which is a necessary condition for aerobic decomposition of lignin by fungi and for HA-formation. As a result of the aerobic decomposition, the lignin content was small whereas the $\delta^{13}\text{C}$ signature of the organic matter was little different from that of the plants from which it derived. The CPMAS¹³C-NMR spectra identified the plants with large lignin contents (*Betula nana*) as the main source of HA. Thus, we interpret the accumulation of HAs near the soil surface as the result of aerobic decomposition,

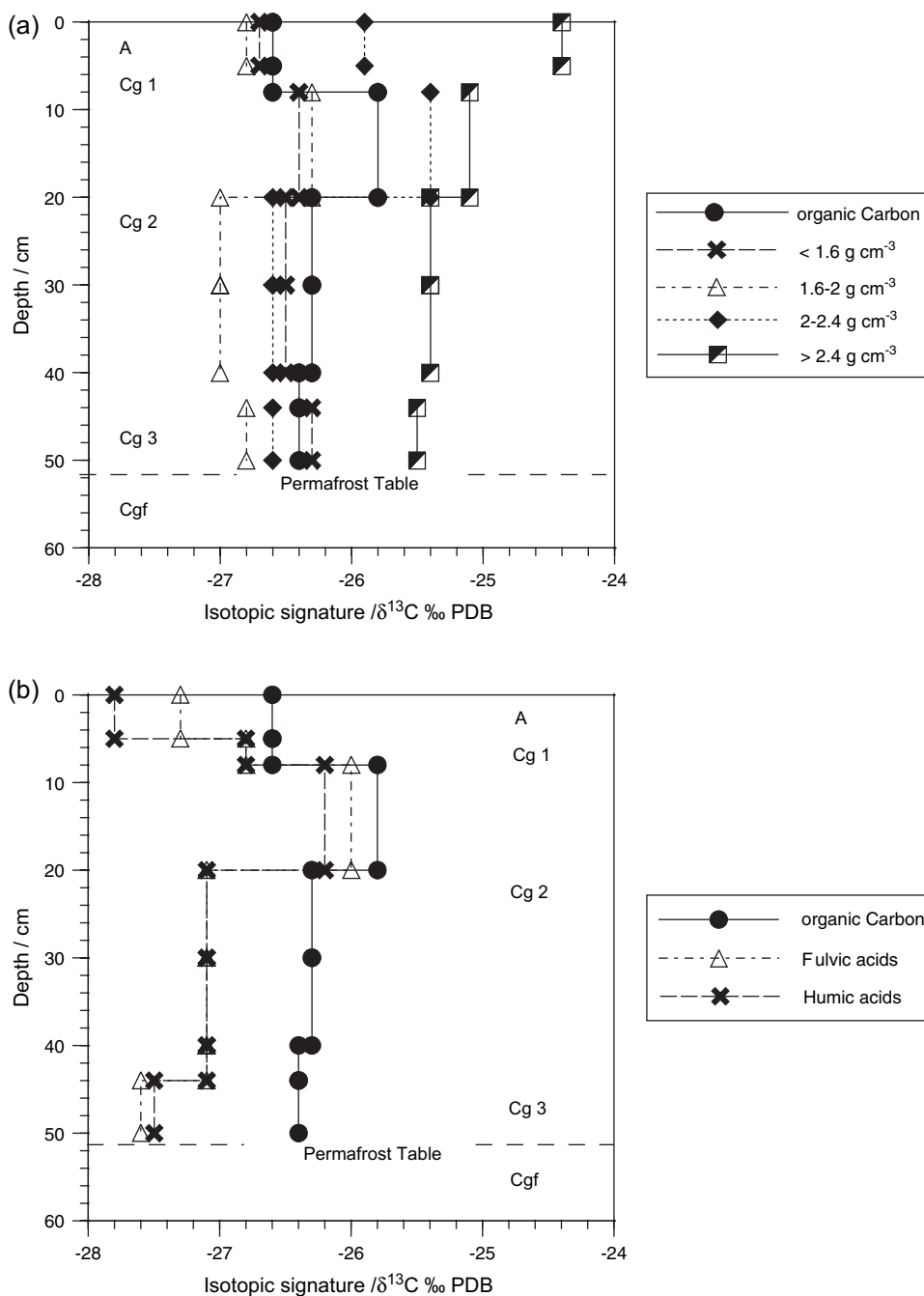


Figure 6 (a) $\delta^{13}C$ signature of organic matter and of the density-fractions (Profile 2); (b) $\delta^{13}C$ signature of organic matter and of the HA- and FA-fractions (Profile 2).

given that HAs are widely considered as immobile. This zone of aerobic decomposition within the top 5 cm of wet soils corresponds with the results of respiration measurements. We found that up to 90% of the respiration and decomposition took place in the upper 2 cm of the tussock-tundra soil.

The lower parts of the active layer, 5–20 cm below the surface, are cooler and wetter than near the surface. Here, organic matter decomposes anaerobically, and lignin does not degrade to form

HAs. Consequently the concentration of the immobile HAs is much smaller there than near the surface, whereas the distribution of the mobile FA fraction was nearly even throughout the profile.

As a result of the anaerobic decomposition, the organic matter is enriched in ^{13}C , especially in the denser fractions. The $\delta^{13}C$ signatures of HAs and FAs were very similar and followed the general $\delta^{13}C$ trend of the organic matter. However, because

formation of HAs and FAs requires aerobic conditions both were less enriched in ^{13}C than the organic matter as a whole.

Despite the low temperatures and the anaerobic conditions, the soil between 5 and 20 cm seemed to be a zone of very active decomposition. There is a remarkably large amount of carbon in the well-decomposed fractions. The HA/FA ratio of 1.2–1.7 was larger than other investigations have found with non-purified humic and fulvic acids (Karavayeva & Targulian, 1960; Grishina & Todorova, 1970; Biryukova & Orlov, 1993). The advanced decomposition of the organic matter in our study was also characterized by the weakening of the CPMAS ^{13}C -NMR signal of the HA fraction and the decreasing alkyl C content with increasing depth (Figure 5b).

Accumulation and alteration of organic matter

Directly above the permafrost, well-decomposed organic matter with a large portion of HAs was accumulated. Enrichment of organic carbon directly above the permafrost table is explained by Ping *et al.* (1997) as the result of intensive cryoturbation. But we found no signs of recent intensive cryoturbation at our tussock tundra site. Also, the structure, general appearance, small amount of undecomposed plant litter, and the large amount of HAs are inconsistent with this theory. Rather, the narrow C/N-ratio of the precipitated material, its slight enrichment in ^{13}C and its altered, weak CPMAS ^{13}C -NMR signal compared with other HAs, all indicate a great degree of decomposition of this fraction. We argue here that the C accumulation near the permafrost table derived from aerobically decomposed, dissolved organic carbon that was transported by water from upper soil horizons to the permafrost boundary and precipitated there under the influence of low temperatures. This so-called cryochemical precipitation (Kowalkowski *et al.*, 1986) is caused by the dehydration of the solvate shell of the dissolved carbon due to the water movement to the cryofront, followed by precipitation of the colloid-complexes. In a laboratory experiment, we found that nearly 20% of the dissolved carbon precipitated irreversibly under the influence of a simulated frost thaw cycle. This process has already been described in other studies in permafrost-affected soils (Ostroumov *et al.*, 2001; Polubesova & Shirshova, 1992). This cryochemical process is an important pathway for forming stable and HA-like organic matter out of dissolved organic carbon near the permafrost boundary with its near-zero temperatures.

Conclusions

The amount of organic matter in tundra soils is huge (Post *et al.*, 1982), and our estimate of it indicates that it is even larger than previously estimated, especially when the entire soil is considered. Further, an unexpectedly large portion of the soil carbon in tussock tundra soil was found to be part of the passive carbon fraction: between 60 and 90% of the carbon in the

soils we studied was sequestered in well-decomposed, passive fractions. The precipitation of dissolved organic carbon under the influence of low temperatures contributes substantially to this carbon sequestration. This passive C pool is of great importance in the context of the feedbacks that tundra soils can have on atmospheric greenhouse gas concentrations in a changing climate.

Acknowledgements

This study was part of the multidisciplinary German Russian project Environmental Development of Central Siberia during late Quaternary. Research funds were provided by the German Federal Ministry of Education and Research (BMBF), grant 03PLO14B. We thank the Alfred-Wegener-Institute for Polar Research (AWI) and the Arctic and Antarctic Institute (AARI) in St Petersburg for logistic support and German and Russian partners for their excellent co-operation. C. L. Ping and G. J. Michaelson of the University of Alaska Fairbanks generously introduced the XAD-method to us. We also thank Volodya Samarkin of the Pushino Institute for his co-operation and Julia Gebert, Birgit Grabellus, Susanne Kopelke, Sumita Rütli, Thomas Nöthen and Jens Hartmann of the Institute of Soil Science at the University of Hamburg for their assistance. Finally, we thank Peter Millard, Peter Loveland, David W. Hopkins, Richard Webster and two anonymous reviewers for valuable comments on our script.

References

- Aleksandrova, V.D. 1980. *The Arctic and Antarctic: Their Division Into Geobotanical Areas*. Cambridge University Press, Cambridge.
- AMAP 2003. *AMAP Assessment 2002: The Influence of Global Change on Contaminant Pathways to, within, and from the Arctic*. Arctic Monitoring and Assessment Programme (AMAP), Oslo.
- von Baer, K.E. 1840. Materialien zur Kenntnis des unvergänglichen Boden-Eises in Sibirien. Unveröffentlichtes Typoskript. *Berichte und Arbeiten Aus der Universitätsbibliothek und Dem Universitätsarchiv Giessen*, **51**, 1–234.
- Batjes, N.H. 1996. Total carbon and nitrogen in the soils of the world. *European Journal of Soil Science*, **47**, 151–163.
- Beudert, G. 1988. *Morphologische, nasschemische und ^{13}C -NMR-spektroskopische Kennzeichnung der organischen Substanz von Waldhumusprofilen nach Dichtefraktionierung*. Bayreuther Bodenkundliche Berichte 8. Lehrstuhl für Bodenkunde und Bodengeographie, Bayreuth.
- Biryukova, O.N. & Orlov, D.S. 1993. Reserves of organic matter and types of humus in soils and peats in the north of the European part of Russia. *Eurasian Soil Science*, **25**, 26–42.
- CAVM 2003. *Circumpolar Arctic Vegetation Map. Scale 1: 7.500.000. Conservation of Arctic Flora and Fauna (CAFF) Map No 1*. US Fish and Wildlife Service, Anchorage, Alaska.
- Grishina, L.A. & Todorova, N.I. 1970. Fraktionii sostav gumusa putshch Taimirskoi tundrui. *Vestnik MGU, Series 6* **25**, 80–85.

- Heyer, J., Hübner, H. & Maaß, I. 1976. Isotopenfraktionierung von Kohlenstoff bei mikrobieller Methanproduktion. *Isotopenpraxis*, **5**, 202–205.
- IPCC 2001. *Climate Change 2001 Synthesis Report*. Cambridge University Press, Cambridge.
- Karavayeva, N.A. & Targulian, V.O. 1960. Humus distribution in the tundra soils of northern Yakutia. *Soviet Soil Science*, **3**, 1293–1300.
- Kowalkowski, A., Brogowski, Z. & Kocon, J. 1986. Properties of cryogenic horizons in the profile of rusty soil. *Quaternary Studies in Poland*, **7**, 25–37.
- Matsuura, Y. & Yefremov, D.P. 1995. Carbon and nitrogen storage of soils in a forest-tundra area of northern Sakha, Russia. In: *Proceedings of the Third Symposium on the Joint Siberian Permafrost Studies Between Japan and Russia in 1994* (eds K. Takahashi, A. Osawa & Y. Kanazawa), pp. 97–101. Forest & Forest Products Research Unit, University of Sapporo, Sapporo, Japan.
- Nadelhoffer, K.J., Shaver, G.R., Giblin, A. & Rastetter, E.B. 1997. Potential impacts of climate change on nutrient cycling, decomposition and productivity in Arctic ecosystems. In: *Global Change and Arctic Terrestrial Ecosystems (Ecological Studies 124)* (eds W.C. Oechel, T. Callaghan, T. Gilmanov, J.I. Holten, B. Maxwell, U. Molau & B. Sveinbjörnsson), pp. 349–364. Springer, Berlin.
- Oechel, W.C. & Billings, W.D. 1992. Effects of global change on the carbon balance of Arctic plants and ecosystems. In: *Arctic Ecosystems in a Changing Climate* (eds F.S. Chapin, R.L. Jefferies, J.F. Reynolds, G.R. Shaver & J. Svoboda), pp. 139–168. Academic Press, San Diego, CA.
- Ostroumov, V.E., Hoover, R., Ostroumova, N.V., Van Vliet-Lanoe, B., Siegert, C. & Sorokovikov, V. 2001. Redistribution of soluble components during ice segregation in freezing ground. *Cold Regions Science and Technology*, **32**, 175–182.
- Ping, C.L., Michaelson, G.J. & Kimble, J.M. 1997. Carbon storage along a latitudinal transect in Alaska. *Nutrient Cycling in Agroecosystems*, **49**, 235–242.
- Ping, C.L., Michaelson, G.J., Kimble, J.M. & Everett, L.R. 2002. Organic carbon stores in Alaska soils. In: *Agricultural Practices and Policies of Carbon Sequestration in Soils* (eds R. Lal, J.M. Kimble & R. Follet), pp. 485–494. Lewis Publishers, Boca Raton, FL.
- Ping, C.L., Michaelson, G.J. & Malcolm, R.L. 1995. Fractionation and carbon balance of soil organic matter in selected Cryosols in Alaska. In: *Advances in Soil Science: Soils and Global Change* (eds R. Lal, J. Kimble, E. Levine & B.A. Stewart), pp. 307–314. Lewis Publishers, Chelsea, MI.
- Polubesoova, T.A. & Shirshova, L.T. 1992. Effect of prolonged freezing on chemical properties of soils and clays. In: *Proceedings Joint Russian American Seminar on Cryopedology and Global Change, Pushchino 1992* (ed. D.A. Gilichinsky), pp. 140–145. Russian Academy of Sciences, Pushchino, Russia.
- Post, W.M. 2006. Organic matter, global distribution in world ecosystems. In: *Encyclopedia of Soil Science*, 2nd edn (ed. R. Lal), pp. 1216–1221. Taylor & Francis, New York.
- Post, W.M., Emanuel, W.R., Zinke, P.J. & Stangenberger, A.G. 1982. Soil carbon pools and world life zones. *Nature*, **298**, 156–159.
- Raich, J.W. & Schlesinger, W.H. 1992. The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate. *Tellus*, **44(B)**, 81–99.
- Schlichting, E., Blume, H.-P. & Stahr, K. 1995. *Bodenkundliches Praktikum*. Blackwell, Berlin.
- Smith, L.C., MacDonald, G.M., Velichko, A.A., Beilman, D.W., Borisova, O.K., Frey, K.E. et al. 2004. Siberian peatlands: a net carbon sink and global methane source since the early Holocene. *Science*, **303**, 353–356.
- Soil Survey Staff 1999. *Soil Taxonomy*, 8th edn. US Department of Agriculture Handbook No 436. US Government Printing Office, Washington, DC.
- Stolbovoi, V. 2000. Carbon pools in tundra soils of Russia: improving data reliability. In: *Global Climate Change and Cold Regions Ecosystems* (eds R. Lal, J.M. Kimble & B.A. Stewart), pp. 39–58. CRC Press LLC/Lewis Publishing, Boca Raton, FL.
- Stolbovoi, V. 2002. Carbon in Russian soils. *Climatic Change*, **55**, 131–156.
- Tarnocai, C. & Ballard, M. 1994. Organic carbon in Canadian soils. In: *Soil Processes and Greenhouse Effect* (eds R. Lal, J.M. Kimble & E. Levine), pp. 31–45. USDA Soil Conservation Service, Lincoln, NE.
- Tarnocai, C. & Smith, C.A.S. 1992. The formation and properties of soils in the permafrost regions of Canada. In: *Cryosols: the Effect of Cryogenesis on the Processes and Peculiarities of Soil Formation. Proceedings of the 1st International Conference on Cryopedology. November 10–16, Pushchino, Russia* (ed. D.A. Gilichinsky), pp. 21–42. Russian Academy of Sciences, Pushchino, Russia.
- Walter, W. & Breckle, S.W. 1986. *Ökologie der Erde. Spezielle Ökologie der Gemäßigten und Arktischen Breiten Euro-Nordasiens (3)*. G. Fischer, Stuttgart.