COEVOLUTION OF ORGANIC SUBSTANCES AND SOILS

Stability of soil organic matter in two northeastern German fen soils: the influence of site and soil development

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Received: 3 October 2011 / Accepted: 5 March 2012 / Published online: 30 March 2012 © Springer-Verlag 2012

Abstract

Purpose Peatland soils play an important role in the global carbon (C) cycle due to their high organic carbon content. Lowering of the water table e.g. for agricultural use accelerates aerobic secondary peat decomposition and processes of earthification. Peatlands change from C sinks to C sources. We characterized soil organic matter (SOM) with special attention to human impact through drainage. Our aim was to gain knowledge of SOM quality and soil-forming processes in drained fen soils in northeastern Germany.

Materials and methods Through techniques of representative landscape analysis, we identified two typical and representative sampling sites in different stages of land use, representing the most important hydrogenetic mire types in northeastern Germany. We adapted chemical fractionation procedures which include hot water extraction (C_{hwe} and N_{hwe}) for determination of the labile fraction. Furthermore, a stepwise acid hydrolysis procedure was performed to measure the chemical recalcitrant part of SOM as it is more resistant to biodegradability.

Results and discussion Total organic C decreased with increasing human impact and intensity of drainage. Conversely, C_{hwe} and N_{hwe} concentrations increased with increasing drainage and human impact. In contrast, the more recalcitrant fractions increased with soil depth.

Conclusions Generally, there is a lack of existing data about SOM quality and the factors controlling its stability and decomposition in fen soils. For northeastern German fen soils, the data are even more inadequate. Influence of drainage

Responsible editor: Gabriele Schaumann

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Keywords Decomposition · Drained fen soils · Labile fraction · Soil organic matter

1 Introduction

Peatland soils play an important role in the global carbon (C) cycle. Although they cover a small area (about 3 % of the earth's surface), they store 15-30 % of the whole global terrestrial C in the form of soil organic matter (SOM) because of their waterlogged conditions, which constrain litter decomposition (Moore 1989; Limpens et al. 2008). By human impact such as drainage, peat mining, and agricultural use (often connected with tillage and/or the addition of fertilizers), processes of secondary peat decomposition and mineralization accelerate, thus resulting in a net release of carbon. Peatlands change from C sinks to C sources within the global C cycle. Decomposition of SOM and loss of C out of peatlands can reach vast amounts (Joosten and Clarke 2002; Oleszczuk et al. 2008). Especially in densely populated Middle and Western Europe, most of the former natural peatlands are strongly influenced by human impact. Less than 40 % of formerly pristine and undisturbed peatland areas are still intact. In Germany it is even less, only about 1 % (Couwenberg and Joosten 2001). About two thirds of national greenhouse gas emissions from peatlands are caused by degraded fens which are used for forestry or agriculture (Höper 2007). The mechanisms which control these processes are still not well understood (Laiho 2006; Limpens et al. 2008; Fenner et al. 2011). Many external factors like moisture, temperature, pH, etc. control the

intensity of SOM decomposition and mineralization, and therefore the loss of C out of peatlands. Besides these external factors, decomposition of SOM depends strongly on SOM quality and its labile and more recalcitrant fractions, respectively (e.g., Haider 1996; Berg and McClaugherty 2008; Torn et al. 2009; Straková et al. 2011). Cornwell et al. (2008) even rate different plant species traits as "a predominant control on the rate of decomposition in ecosystems."

1.1 Factors controlling SOM quality in peatlands

Peat and SOM qualities in natural undisturbed peatlands ("mires" according to Joosten and Clarke 2002) are strongly dependent on hydrological and geomorphological building conditions which are controlled by climate, geology, surface topography, water table, and time. These building conditions constitute the kind of peat-forming vegetation through nutrient and water supply and various soil-forming processes like humification and decomposition as a result of distinct redox conditions. Characteristic peatlands with distinctive peat qualities have formed over time. Such qualities include specific stratigraphy, peat thickness, stages of primary peat decomposition during formation, botanical origin of peat, and chemical quality of organic and inorganic compounds (e.g., Cameron et al. 1989). One simple classification system for peatlands is the widely known concept of ombrotrophic bogs vs. minerotrophic fens. Bogs, which are only fed by atmospheric inputs (rainwater, nutrients) are reflecting their regional climate. Fens are particularly influenced by smallscale local groundwater impacts. Therefore, fens show much greater local variety in SOM quantities and qualities than ombrotrophic bogs (Vitt et al. 2009). Considering this aspect of local variety, peatlands can be further classified into different hydrogenetic mire types (HGMT) (Succow and Joosten 2001; Joosten and Clarke 2002, Koster and Favier 2005; Mueller et al. 2007; Zauft et al. 2010; see Fig. 1 for examples). The classification system considers individual size and hydrogeologic quality of above and below ground catchment areas and individual position within a landscape topography. These factors control water regime, mineral and oxygen supply, and determine the peat-forming vegetation and the quality and quantity of peat deposits. In northeastern Germany, about 99 % of entire peatland area is of minerotrophic origin (Couwenberg and Joosten 2001).

One HGMT of great importance in this region is named "terrestrialization mire" where peat primarily accumulates under water. Hydrology is dominated by an open water body, often shaped as a result of glacial activity during the late quaternary. After sedimentation of detritus and/or mineral gyttja, the water body becomes shallow enough to allow peat-forming plants (particularly *Phragmites australis*) to settle. Naturally occurring peats in this HGMT generally show medium to weak stages of primary decomposition. Schematic cross-section through different HGMT



,Terrestrialization mire' - formed by sedimentation of an open water body and following succession of peat-forming vegetation

Modified after Jeschke (1988)

Fig. 1 Schematic cross section through the hydrogenetic mire types "paludification mire" and "terrestrialization mire," modified after Jeschke (1988)

Peat thickness is below 2 m (Succow and Joosten 2001; Joosten and Clarke 2002).

Another widespread HGMT which is of great significance is the "paludification mire" (also named as "water rise mire"), where hydrology is dominated by rising groundwater levels. In contrast to terrestrialization mires, groundwater rises slowly over a mineral surface so that no open water body is formed. This often results in swamping with specific peat-forming vegetation, e.g., *Carex* sp. and/or *Alnus* sp., and peat deposits which are less thick and have peats of stronger primary decomposition (Succow and Joosten 2001). Within the federal state of Brandenburg, northeastern Germany, more than 150,000 ha are covered with paludification mires. This accounts for 73 % of total peatland area. Terrestrializaton mires cover approximately 20,000 ha, which is about 10 % of total peatland area, respectively (Schultz-Sternberg et al. 2000).

Beside local influences of site on SOM quality during mire formation, anthropogenic impact can influence and alter peat and SOM quality drastically. In addition to quantitative loss of C and SOM from drained peatlands, human impact also results in qualitative changes of SOM. A socalled secondary soil development leads to peat degradation, connected with peat subsidence caused by shrinking, secondary decomposition, and mineralization. Physical, chemical, and biological characteristics rapidly change, most of them irreversibly (e.g., Zeitz and Velty 2002; Ilnicki and Zeitz 2003; Sokołowska et al. 2005; Mueller et al. 2007).

1.2 Characterization of SOM decomposability through chemical fractionation

As mentioned briefly above, SOM quality in peatlands and its stability towards decomposition can be characterized by determination of the different SOM fractions of labile and more recalcitrant compounds. Particularly, the labile or decomposable carbon fraction is of great interest as it is part of SOM which can be potentially oxidized and released as CO_2 into the atmosphere (Khanna et al. 2001; Kalisz et al. 2010).

One reliable and solid method to characterize this labile SOM pool is hot water extraction (HWE) (e.g., Schulz and Körschens 1998; Chodak et al. 2003; Ghani et al. 2003). By weakly hydrolyzing SOM, the hot water extract [often measured as amount of hot water-extracted organic C (C_{hwe}) and/or total N (N_{hwe})] contains the readily mineralizable part of SOM. Chemical characterization by spectroscopic and pyrolytic analysis of HWE of different soils (e.g., Leinweber et al. 1995; Landgraf et al. 2006) has shown that this fraction contains simple carbohydrates, proteinous compounds, lignin monomers, and other soluble phenolics. Balaria et al. (2009) compared ¹³CNMR spectra of hot water extracts from organic layers with spectra of whole soils and noticed less aromacity and a greater carbohydrate content in the hot water extracts than in the whole soils. In addition, strong correlations between Chwe, microbial biomass, and enzymatic activity have been found (e.g., Sparling et al. 1998; Rinklebe et al. 2001). In comparison to the readily mineralizable pool, a more recalcitrant and chemically resistant part, resistant to biodegradation, can be fractionated by acid hydrolysis (Khanna et al. 2001; Rovira et al. 2010). Solid-state ¹³C NMR spectra of soils and humic substances after acid treatment have clearly shown the removal of labile compounds like amino acids and carbohydrates and a relative enrichment of lipid-like alkyl-C (Silveira et al. 2006).

1.3 Lack of knowledge and the need for data

Numerous publications present data on SOM quality in peatlands. Most of them investigated boreal and subboreal peatland sites (e.g., the works of Bohlin et al. 1989; Turetsky 2004; Domisch et al. 2006; Wieder and Vitt 2006; Straková et al. 2011, etc.) or sites with temperate bogs (e.g., Bragazza and Iacomin 2009; Delarue et al. 2011; Kracht and Gleixner 2000; Schellekens et al. 2009). Studies presenting SOM data with special regard to decomposition stability in warm temperate fen sites are more scarce (e.g., Szajdak et al. 2007; Gogo 2010; Kalisz et al. 2010; Reiche et al. 2010). For northeastern German Fen Sites under agricultural use, only a few studies on SOM quality and its stability towards decomposition exist (e.g., Kalbitz 2001; Mueller et al. 2007). As described above, most of the peatland areas in northeastern Germany are influenced by human impact. About 200,000 ha of the peatland areas in Brandenburg are used for agriculture. This accounts for 7 % of the total state area (Schultz-Sternberg et al. 2000). In the future, a growing demand e.g. for renewable energy increases the pressure to utilize peatland sites for energy plant production (MLUV Brandenburg 2006). Under these circumstances, intensification of agriculture will lead to increasing C losses from peatlands. Thus, it is of crucial importance to gain more knowledge about SOM quality and decomposition stability of peatland soils used for agricultural purposes.

In the present study, we investigated SOM stability in two northeast German fens with special attention to human impact through drainage. Therefore, we adapted chemical fractionation procedures which include HWE for determination of the labile fraction as it is part of SOM which can be potentially oxidized. Furthermore, a stepwise acid hydrolysis procedure was performed to measure the chemical recalcitrant part of SOM as it is more resistant to biodegradability. Through techniques of representative landscape analysis, we identified two sampling sites in different stages of land use, representing the most important HGMT in northeastern Germany.

We tested if influences of natural mire formation and/ or changes in land use intensity affected the amounts of labile and recalcitrant fractions of SOM. Our aim was to gain knowledge of SOM quality and soil-forming processes in drained fen soils in northeastern Germany. In addition, the obtained results may contribute to a better understanding of organic soils which are threatened by loss of SOM and C.

2 Materials and methods

2.1 Site selection procedure

In preliminary work, sampling sites were chosen by representative landscape analysis, using comprehensive backfile data (peatland mapping and drilling data). The selected sites had to reflect different aspects of landscape and human impact and therefore had to fulfill the following criteria:

- Sites are within fen areas and have organic soils (Histosols according to IUSS Working Group WRB 2006)
- 2. Sites differ in HGMT
- 3. Sites are drained for agricultural use
- Sites differ in intensity of drainage and degree of secondary soil development
- 5. Peats differ in botanical origin between sites
- 6. Peats differ in degree of decomposition
- 7. Every site contains peats of only one botanical origin within soil profile (no mixed peats).

The representative landscape analysis included evaluation of more than 30,000 ha and 3,000 soil profiles [according to the method of Schultz-Sternberg et al. (2000) and Zeitz et al. (2008)]. Two typical and representative sampling sites, which fulfilled the criteria mentioned above, were chosen.

2.2 Soil sampling

Peat samples were collected in May and July 2010. Both sites are situated within the pleistocene area of the federal state of Brandenburg, northeastern Germany (Fig. 2). The climate in Brandenburg is semi-continental with an average temperature of approximately 9 °C. Average amount of rainfall is about 550 mm p. a. The first sampling site "Gadsdorf" (G), a weakly acidic fen with *Carex* peat is situated 30 km south of Berlin (15°12′N, 13°19′E). The HGMT is a paludification mire and the peat is underlain by fluvial sands from glacial outwash. The site is drained through ditches and is used extensively for grassland and pasture for at least 40 years.

The second sampling site "Uckerwiesen" (U) (53°13'N, 13°52'E), a calcareous fen with *Phragmites* peat, is located in the "Uckermark" region, 90 km northeast of Berlin. Its HGMT is a terrestrialization mire. The peat is underlain by calcareous gyttja and marl from glacial till. The site is also drained through ditches and is used for very extensive grassland for at least 45 years. A schematic cross section of these two HGMT is given in Fig. 1. Composite samples out of six individual samples, representing each diagnostic soil horizon (G1 to G4, U1 to U4), were taken, placed into



Fig. 2 Location map of the study sites Gadsdorf and Uckerwiesen within the federal state of Brandenburg, northeast Germany

sealed plastic bags, and stored frozen. Before analysis, each composite sample was freeze dried, homogenized, and finely ground. In addition to the sampled soil, fresh rhizomes of *P. australis* (common reed) and *Carex* sp. (sedge)—two below ground parts of two peat-forming plants which are typical for the two sites—were dug out, cleaned, freeze dried, and finely ground.

2.3 Basic chemical parameters

The pH values were measured using a mobile pH meter (PCE Instruments GmbH, Meschede). Total nitrogen (Nt), organic C (TOC), and total C (Ct) contents were determined by a CNS analyzer (Variomax, Elementar GmbH, Hanau). Nt and Ct were determined by dry combustion at 900 °C, whereas TOC was determined by dry combustion at 600 °C. Inorganic C (TIC) was calculated by subtraction of TOC from total C. C/N ratios were calculated from TOC and Nt. All data are presented on a dry mass basis (oven-dried subsamples at 105 °C), performed as duplicates (Table 1).

2.4 Chemical fractionation

2.4.1 Hot water extraction

To estimate the labile soil pool of the sampled horizons, hot water extraction (HWE) was carried out. Furthermore, HWE of the *Phragmites* sample was performed to compare the labile soil pool with the readily mineralizable part of the undecomposed rhizomes. A modified method after the German technical rule for mineral soils (Schulz et al. 2004) was used. This method includes a 1-h treatment at 100 °C and a soil/solution ratio from 1:5 (w/v). Because of the high organic amounts occurring in peatland soils and undecomposed plants, we did various detailed preliminary dilution series with different sample/solution ratios (data will be published elsewhere). The most effective ratio that we found was 1:800 (w/v). Due to these results, 0.5 g of the dried and ground sample was boiled under reflux with 400 ml of TOC-free water for 1 h in a flat-bottomed flask. After cooling down to room temperature, the extract was filtered (MN 615 ¼, Macherey-Nagel GmbH & Co. Kg, Düren). The filtrate was frozen prior to analysis of TOC and Nt with an automated analyzer (LiquiToc, Elementar GmbH, Hanau). Chwe and Nhwe ratio was calculated. All data are presented on a dry mass basis (oven-dried subsamples at 105 °C), performed as duplicates (Table 2).

2.4.2 Acid hydrolysis

A method after Goering and van Soest (1970) was slightly adapted to measure this fraction. Therefore, we determined the amount of ADF ("acid detergent fiber") and ADL

Table 1	Diagnostic	attributes	of the	two	study	sites
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Horizon (sample depth)	Diagnostic attributes	Degree of decomposition	pН	Ct (% dry mass)	TOC (% dry mass)	TIC (% dry mass)	Nt (% dry mass)	C/N
G1 (0–15 cm)	Drained and earthified, grainy structure	9–10 (sapric)	5.8	21.0	20.4	0.6	1.5	13.6
G2 (15–30 cm)	Drained and shrank with aggregates, <i>Carex</i> peat	5-6 (hemic)	5.9	26.4	26.4	0.0	1.8	14.7
G3 (30–55 cm)	Drained and shrank, no aggregates, <i>Carex</i> peat	5-6 (hemic)	6.0	40.5	39.9	0.6	2.7	14.9
G4 (60–75 cm)	Groundwater oscillation range, <i>Carex</i> peat	5-6 (hemic)	5.9	47.5	47.2	0.3	2.5	18.6
U1 (4–15 cm)	Drained and earthified, grainy structure	9-10 (sapric)	7.2	23.1	16.3	6.8	1.3	17.2
U2 (15–40 cm)	Groundwater oscillation range, <i>Phragmites</i> peat	7-8 (hemic to sapric)	6.9	24.5	18.8	5.7	1.1	21.4
U3 (40-65 cm)	Groundwater oscillation range, <i>Phragmites</i> peat	5-6 (hemic)	6.8	26.8	19.8	7.0	1.4	19.3
U4 (70–80 cm)	Beneath groundwater level, <i>Phragmites</i> peat, rhizomes remain clearly visible	3–4 (fibric)	6.6	48.8	48.4	0.4	2.4	20.0

Degree of decomposition after von Post and WRB. Data are presented on a dry mass basis, performed as duplicates

Basic chemical parameters (Ct total carbon, TOC total organic carbon, TIC total inorganic carbon, Nt total nitrogen, C/N TOC/Nt ratio) of the sampled soil horizons of Gadsdorf (G1 to G4) and Uckerwiesen (U1 to U4)

("acid detergent lignin") from soil and plant samples. The fractionation procedure included a stepwise hydrolysis of a 0.5-g sample with boiling H_2SO_4 and cetyl trymethyl ammonium bromide for 1 h in the first step. This treatment removes cell constituents, carbohydrates, hemicelluloses, and proteins. In a second step, the residue was treated for 3 h with concentrated H_2SO_4 (72 % *w/v*) to hydrolyze crystalline cellulose. The non-hydrolyzable residue (ADL) consists of lignin or lignin-like phenolic macromolecules (Laiho 2006; Yanni et al. 2011) and other more recalcitrant fractions like cutin, suberin, and waxes (von Lützow et al. 2007). All data is

presented on a dry mass basis (oven-dried subsamples at 105 °C), performed as duplicates (see Table 1).

3 Results and discussion

3.1 Diagnostic description

A summarized description of the sampled soil horizons (including sampling depth, diagnostic attributes and state of soil development; degree of decomposition according to

 Table 2
 Chemical fractions of labile and recalcitrant organic matter of composite peat samples from soil horizons of the two study sites Gadsdorf (G1 to G4) and Uckerwiesen (U1 to U4) and of undecomposed rhizomes of *P. australis* and *Carex* sp.

Sample	C _{hwe} (g/kg)	N _{hwe} (g/kg)	C _{hwe} /N _{hwe}	ADF (% ash-free dry mass)	ADL (% ash-free dry mass)
G1	25.7	1.1	22.9	See Fig. 3	See Fig. 3
G2	18.3	1.5	12.1	See Fig. 3	See Fig. 3
G3	15.6	0.8	20.7	See Fig. 3	See Fig. 3
G4	12.6	0.5	24.9	See Fig. 3	See Fig. 3
U1	15.4	2.0	7.8	See Fig. 4	See Fig. 4
U2	14.3	1.4	10.1	See Fig. 4	See Fig. 4
U3	13.3	1.2	11.3	See Fig. 4	See Fig. 4
U4	11.3	0.9	12.0	See Fig. 4	See Fig. 4
Phragmites	68.1	5.0	13.7	44.1	11.2
Carex	n.d.	n.d.	n.d.	32.3	6.0

Data are presented on a dry mass basis, performed as duplicates

 C_{hwe} hot water-extracted organic carbon, N_{hwe} hot water-extracted nitrogen, C_{hwe}/N_{hwe} C_{hwe}/N_{hwe} ratio, ADF acid detergent fiber, ADL acid detergent lignin, n.d. not determined

the method of von Post (1924) and structure according to WRB classification) together with the basic chemical parameters are presented in Table 1. Both sites are clearly influenced by human impact (drainage and conversion to grassland). Thus, both topsoils (G1 and U1) underwent a massive secondary soil development, including shrinkage, aeration, and decomposition, which resulted in physical and chemical alteration, named as "earthification" (see e.g., Zauft et al. 2010). Both topsoils had disaggregated and very loose structures and seemed to have high bulk densities, which is typical for degraded fen topsoils. These diagnostic soil attributes of degraded fens were also described by other authors (e.g., Zeitz and Velty 2002 or Mueller et al. 2007). The pedogenetic process of earthification includes increase in bulk density and loss of pore volume. Zauft et al. (2010) analyzed soil physical data of 316 soil horizons of northeast German fens under different anthropogenic impact. Lowest bulk densities (average of 0.12 g cm⁻³) were measured in subsoils, which had the least human impact and were mostly groundwater saturated. In contrast, bulk densities of strongly drained and earthified topsoils were sometimes more than four times higher with an average of 0.44 g cm⁻³. These densities are extremely high compared to bulk densities of relatively undisturbed fens. Vitt et al. (2009) reported mean values of bulk densities in boreal fen sites with maxima up to 0.12 g cm⁻³.

At the Gadsdorf site, anthropogenic influence is stronger than at the Uckerwiesen site, resulting in a deeper drainage and a stronger secondary soil development. This could be observed by occurring aggregate formation in the G2 horizon and shrinking cracks in the G2 and G3 horizons, which is typical for peat soils in an intermediate level of drainage (see also Zeitz and Velty 2002).

Human-induced changes could not be observed in the deeper horizons at the Uckerwiesen site, where only the topsoil (U1) showed diagnostic attributes of secondary soil development. Soil horizons within the groundwater oscillation range (G4, U2, and U3) and beneath the permanently groundwater saturated zone at the Uckerwiesen site (U4) had not undergone any visible secondary soil development. In these soil horizons, the occurring peats obviously kept their original structures and remained relatively undecomposed with Carex peats at the Gadsdorf site and Phragmites peats at the Uckerwiesen site. Lowest degree of peat decomposition (3 to 4 after von Post 1924, fibric peat after WRB) was found in the U4 horizon. Well-preserved rhizomes, probably of P. australis, remained clearly visible. In addition, remains of various fossil mollusc shells were found in all soil horizons of the Uckerwiesen site, which indicates a former temporary water level above ground. This is typical for the HGMT "terrestrialization mire," where peat develops in open water. In contrast, peat accumulation in "paludification mires" starts directly over a mineral soil which is periodically swamped e.g. by rising groundwater table (Joosten and Clarke 2002; see Fig. 1).

3.2 Basic chemical parameters

Both soil profiles have high TOC contents, ranging from 16 to 48 % dry mass, which is characteristic for Histosols. TOC concentrations were lowest in topsoils of both profiles and increased with decreasing soil depth. In well-drained and aerated topsoils, where intensive secondary soil development took place, originally accumulated SOM disappears. The decrease of TOC concentrations with increasing anthropogenic influence is in line with the findings of Sajdak et al. (2007) and Zauft et al. (2010) who reported similar trends for fen soils under agricultural use. Ongoing secondary soil development and loss of C out of drained peatlands can lead to drastic SOM changes. Kalbitz et al. (1999) reported about massive C losses out of an intensively used fen site, which lost more than 60 % of its former 28,000 ha. In turn, only about 40 % of the former fen area is still covered by Histosols. Degradation through intensive agriculture within the last 200 years led to the formation of mollic Gleysols with only relictic amounts of peat and TOC concentrations of 4 to 5 % (w/w).

Higher TIC contents up to 7 % (w/w) appeared in upper horizons of Uckerwiesen site, whereas the sampled soil at Gadsdorf contained nearly no TIC. In this region, TIC originates almost completely from CaCO₃-C (Mueller et al. 2007). Fossil mollusc shells, found in soil horizons at Uckerwiesen site, might be an important biogenic source of TIC in this "terrestrialization" mire (see Section 3.1).

Nt concentrations ranged from 1.1 to 2.7 % (w/w) with a maximum detected in the Gadsdorf subsoils (G3, G4) and a minimum in the Uckerwiesen topsoils (U1, U2). These amounts of Nt are probably in the lower range and slightly below the average of N concentrations for fens. Koppisch (2001) reported of typical Nt concentrations ranging from 1.3 to 3.5 %. Kuntze et al. (1988) reported of average Nt concentrations in fens of 2 to 4 % dry mass. Nt concentrations in subsoils of both profiles were higher than in topsoils. This fits into the results of e.g. Malawska et al. (2006) for southern Polish fens. Our results showed no clear trend of Nt concentrations in relation to secondary soil development. This is in contrast to the results of Mueller et al. (2007) who clearly found increasing N concentrations with increasing soil development.

TOC/Nt ratios were in the range of 14 to 21 with widest ratios at the Uckerwiesen site (U2, U4). The nearest ratios were found in the drained horizons at the Gadsdorf site (G1 to G3) which probably points to a better decomposability. These values are in the same range of C/N ratios calculated for four different fen sites in northwestern Germany by Kuntze et al. (1988). Lower pH values were found at the Gadsdorf site, ranging from 5.8 to 6.0 which is weakly acid. In contrast, the Uckerwiesen site had pH ranging from 6.6 to 7.2 which is typical for neutral to calcaric fens (Succow and Stegmann 2001).

3.3 Chemical fractionation of labile and recalcitrant compounds

Total extracted amounts of C_{hwe} , N_{hwe} , the calculated C_{hwe}/N_{hwe} ratios, and the ADF and ADL residues of the plant samples are listed in Table 2. C_{hwe} amounts in relation to TOC, ADF, and ADL residues of the two sampling sites were plotted against soil depth (Figs. 3 and 4).

3.3.1 Hot water extractions

The highest Chwe and Nhwe concentrations were extracted from the undecomposed Phragmites rhizomes, which probably had higher amounts of solubles, and therefore higher amounts of readily mineralizable C and N in comparison to the sampled and decomposed peat soils. Total Chwe concentrations of the sampled soils ranged from 11 to 26 g kg^{-1} soil. Generally, Chwe concentrations in organic soils are higher compared to mineral soils due to higher TOC contents. For mineral soils, e.g. Plante et al. (2011) described Chwe concentrations of grassland soils, which were ranging from 0.5 to 1.9 g kg⁻¹ soil. Spohn and Giani (2007) measured Chwe concentrations of mineral soils under pasture and under forest. The extracted amounts ranged from 0.5 to 5.5 g kg⁻¹ soil. Relative amounts of C_{hwe}, extracted from TOC, varied between 2 and 13 % (w/w) of TOC with an average of 6.5 % (w/w) of TOC. Our findings are in contrast with the data of Mueller et al. (2007) who investigated topsoils of degraded fens and Kalisz et al. (2010) who compared northeastern Polish fens under different stages of drainage. Both reported lesser Chwe amounts ranging from 0.7 to 2.1 % (w/w) of TOC. Probably these different results are caused by methodical differences in extraction time, temperature, and soil/solution ratios. For mineral soils and humus layers in boreal forest stands, Vanhala et al. (2008)



Fig. 3 Chwe, ADF, and ADL profiles at the Gadsdorf site



Fig. 4 Chwe, ADF, and ADL profiles at the Uckerwiesen site

reported relative extracted amounts of 3 to 6 % (w/w) of TOC. Landgraf et al. (2005) reported relative extracted amounts ranging from 10 to 13 % of TOC (w/w) in humus layers and sandy soils in temperate forest sites.

In our study, C_{hwe} concentrations in both profiles (absolute and in relation to TOC) increased with decreasing soil depth and increasing influence of drainage. These results are in general agreement with findings from the literature. Mueller et al. (2007) found significant relationships between different stages of soil development of fen topsoils. Kalisz et al. (2010) found correlations between C_{hwe} amounts and individual stages of drainage and soil development. In addition, Kalisz et al. (2010) found correlations between C_{hwe} , TOC, Nt and a so-called oxidizable C fraction, measured by the amount of C oxidized with KMnO₄.

 N_{hwe} concentrations ranged from 0.5 g kg⁻¹ in the Gadsdorf subsoil (G4) to 2.0 g kg⁻¹ in the Uckerwiesen topsoil (U1). N_{hwe} concentrations tended to decrease with increasing soil depth and decreasing degree of decomposition at the whole Uckerwiesen profile. At the Gadsdorf site, a clear vertical gradient could not be observed. Šlepetiene et al. (2010) measured N_{hwe} concentrations in topsoils from a raised bog in Lithuania under different stages of land use and drainage. The reported concentrations differed widely from our own results, ranging between 0.06 and 0.11 g kg⁻¹, probably due to lower N contents occurring in bog sites. According to our knowledge, no further data of actual N_{hwe} of fen sites exist.

Our calculated C_{hwe}/N_{hwe} ratios tended to increase with depth (except G1 and G2) and were larger at the Gadsdorf site. This was also observed for C_{hwe}/N_{hwe} ratios in humic horizons in a forest floor recorded by Landgraf et al. (2006).

3.3.2 Acid hydrolysis

In all soil and plant samples, concentrations of insoluble ADF fractions were greater than insoluble ADL concentrations due to stronger acid treatment during the ADL procedure. At both sites, the non-hydrolyzable fractions (ADF ranging from 13 to 78 %, ADL ranging from 9 to 58 %) relatively increased with soil depth. Particularly, the distinct

vertical increase of ADF and ADL, at the point of reaching the permanently water saturated zone at the Uckerwiesen profile (see Fig. 4, U3 to U4), is noteworthy. These fractions contain non-hydrolyzable lignin and/or other more recalcitrant macromolecular fractions, which can only be decomposed relatively slowly in oxygen-limited environments (Kögel-Knabner 2002; Thevenot et al. 2010). In contrast to the Uckerwiesen site. ADF and ADL concentrations tend to increase relatively constant. The subsoil (G4) is periodically above the water table. Thus, there might be more favorable oxic conditions for the aerobic decomposition of these complex macromolecules. According to our knowledge, there is no actual data from acid treatments of fen soils under agricultural use, but we found some data from bog sites. Williams and Yavitt (2003) e.g. reported about increasing amounts of an acid-insoluble fraction with depth in the upper peat horizons of three relatively undisturbed peatlands in the northeastern part of USA, mainly consisting of Sphagnum and herbaceous peats. The concentrations of nonhydrolyzable amounts (named as lignin) ranged from 10 to over 60 % (w/w) which is in line with our results. Updegraff et al. (1995) fractionated Sphagnum peat from an undisturbed peat bog in Minnesota, USA. Peats were treated with 72 % H₂SO₄. The non-hydrolyzable residues increased with soil depth from 29 to 46 % (w/w).

In contrast to these findings, studies of acid treatments for mineral soils show different results in vertical distributions. Paul et al. (2006) reviewed data of acid hydrolysis from approximately 1,100 data points of different (mineral) soils under different land use. They found general decreases of the non-hydrolyzable fractions with soil depth. Probably, these fractions can be better decomposed as a function of time due to more favorable oxic conditions. ADF and ADL concentrations in the undecomposed living rhizomes of *P. australis* were higher than the measured concentrations of the *Carex* rhizomes. This could suggest a higher chemical recalcitrance and a higher resistance to biodegradation of *P. australis* compared to *Carex* sp., which fits the results of litterbag experiments conducted by Hartmann (1999) and Richert et al. (2000).

Our study indicates a diminution and change in SOM quality towards decomposition in two fen sites of northeastern Germany. The intensity of drainage determined TOC concentrations at both sites. TOC decreased with increasing human impact and intensity of drainage. Conversely, C_{hwe} and N_{hwe} concentrations increased with increasing drainage and human impact. In contrast, the more recalcitrant fractions increased with depth. The results of this study indicate a relationship between soil depth, study site, secondary soil development, degree of primary and secondary decomposition, and the amount of labile and recalcitrant fractions of SOM at two fen sites of different HGMT.

4 Conclusions

- A comprehensive review of the literature showed a lack of existing data about SOM quality and its stability in fen soils. Especially for fen soils of northeastern German, the data are even more inadequate. In addition, general knowledge about the factors controlling SOM stability and decomposition in peatlands is limited.
- Influences of drainage seem to overlap natural influences of site on SOM quality.
- Further investigations in fen sites of northeastern Germany are important to gain knowledge about the influences of land use on regional SOM quality.
- The used extraction scheme was suitable for the chemical fractionation of SOM into labile and more recalcitrant parts. It can be incorporated into future studies.
- Additional investigations of SOM by using of spectroscopic and/or pyrolytic techniques could help to elucidate soil-forming processes in fens on a molecular scale.

Acknowledgments We acknowledge support for this research from the DBU (Deutsche Bundesstiftung Umwelt, Osnabrück) which provided funding. We thank Manuela Alt, Ines Dutschke, and the Common Laboratory of Analytics of the Humboldt-Universität zu Berlin, Faculty of Agriculture and Horticulture for their support with the laboratory analyses. We would especially like to thank Niko Roßkopf and Florian Beuthner for the field support. And we thank three anonymous reviewers for their constructive comments and ideas.

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