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Does soil organic matter in mollic horizons of central/east European floodplain soils have common chemical features?

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ABSTRACT

Soils on riverine floodplains in temperate climate may be characterized by a mollic epipedon, i.e. by dark colour, enhanced content of soil organic matter (SOM), high 'base' saturation and developed structure in the topsoil. We studied 124 soil samples from ten central/east European countries to investigate whether SOM in mollic horizons has similar chemical features. We determined carbon contents with a thermal-gradient method to differentiate SOM with varying thermal stability, and carbonates. We characterized SOM by diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy. According to the World Reference Base for Soil Resources, 102 of the samples fulfilled all criteria of a mollic horizon. Mollic features were not restricted to the uppermost horizon but also detected in buried former surface horizons. Soil colour was mostly the criterion to exclude non-mollic samples. Mollic and adjacent non-mollic horizons contained thermostable SOM, indicating SOM stabilized by interaction with minerals or as black carbon (BC), to very similar extent, up to 20.4% of total soil organic carbon (SOC). However, the correlation between the contents of thermostable SOC and total SOC, the SOC:N ratios of the thermostable fraction, and the smaller extent of metal complexation of carboxyl groups, pointed to a larger contribution of BC to SOM of mollic samples than to SOM in non-mollic samples. Thus, like in mollic horizons in Chernozems and Phaeozems not affected by fluviatile dynamics, SOM in mollic horizons of floodplain soils seemed to consist of SOM affected by natural or anthropogenic fires, constituting a common chemical feature of SOM. Thus, BC may contribute to soil colour and SOM stability in mollic horizons of floodplain soils. However, apart from BC contribution, SOM in mollic horizons of floodplain soils may have further pathways of formation and development, as SOM may be inherited from deposited material or form/transform by degradative or constructive processes.

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1. Introduction

Soil formation and development on riverine floodplains comprises a variety of potentially highly dynamic geomorphic and pedogenic processes including deposition of material, erosion, flooding, and water saturation by high groundwater tables (e.g. Du Laing et al., 2009; Rinklebe et al., 2007). A common feature of floodplain soils in the temperate zone is accumulation of soil organic matter (SOM), causing enhanced contents and stocks of soil organic carbon (SOC) as compared to terrestrial soils outside of the fluviatile environment (e.g. Eisenmann et al., 2003; Graf-Rosenfellner et al., 2016; Rennert et al., 2018; Szombathová et al., 2008; Zehetner et al., 2009). Accumulation of SOM in floodplain soils is interconnected with processes typical of the fluviatile system (Graf-Rosenfellner et al., 2016; Gurwick et al., 2008; Sutfin et al., 2016; Tobiašová et al., 2015). Because of flooding events, SOM, including particulate OM, SOM adsorbed on soil minerals and occluded within aggregates, is periodically deposited on floodplain soils. Periodical cycles of drying and re-wetting facilitate the formation of aggregates (Denef et al., 2002; Totsche et al., 2018), which stabilize SOM. Further, SOM-enriched topsoil horizons may be buried by deposition of mineral material during longer phases of sedimentation (Rinklebe, 2004). Finally, water saturation, caused by flooding or by high groundwater tables or both, induces depletion of oxygen and thus decelerated decomposition of SOM. Thus, SOM in floodplain soils partially consists of poorly degraded plant residues, which are potentially oxidizable, but microbial oxidation is hampered owing to the water budget (Blazejewski et al., 2005; Gurwick et al., 2008; Mayer et al., 2019; Rennert et al., 2017).

Rather the contrary, SOM accumulated in floodplain soils may be characterized by a mollic epipedon, i.e. by a surface horizon with, among further criteria, dark colour, enhanced OC content, high 'base' saturation (>50%) and frequently carbonates present (Soil Survey Staff, 2014). The World Reference Base for Soil Resources WRB (IUSS Working Group WRB, 2007, 2015) defines a mollic horizon by very similar criteria and additionally by thickness and structure/aggregation of the horizon. Consequently, soils on riverine floodplains with a horizon fulfilling the mollic criteria, can be classified for instance as Mollic Fluvisol (IUSS Working Group WRB, 2007) or Fluvic Phaeozem (IUSS Working Group WRB, 2015), depending on the edition of the WRB system.

Several national classification systems in central and eastern European countries consider soil types that reveal similarities with floodplain soils with a mollic horizon/epipedon. For instance, the 'Feuchtschwarzerde' (literally 'moist Chernozem') of the Austrian classification describes a floodplain soil that has developed from carbonate-containing sediments under semi-terrestrial conditions but that fell dry in the course of soil formation (Blum and Solar, 1986). The humus form of these soils may be mull, which shares features with a mollic horizon. Similarly, the German soil type 'Tschernitza' (described as a 'Chernozem-like floodplain soil') may have formed in a bog-like semi-terrestrial environment (Rinklebe, 2004), characterized by intensive bioturbation and high microbial activity (Moche et al., 2015; Rinklebe and Langer, 2006).

In the Croatian soil classification (Husnjak, 2014), 'Humofluvisol' ('Livadsko fluvijalno tlo') is a soil type that developed from a Fluvisol and usually comprises dark coloured, structured SOC-rich surface horizon with high 'base' saturation, very similar to the WRB mollic horizon. Mollic Fluvisols appertain to the soil type 'Fluvizem modální' of the Czech classification, which is defined more broadly as a soil developed from stratified fluviatile sediments with a SOC-rich surface horizon (Němeček et al., 2011). In the Hungarian soil classification, 'alluvial meadow soils' and 'alluvial chernozems' ('öntés csernozjom talajok') can correspond to Mollic Fluvisols (Krasilnikov et al., 2009), like the 'dark-humus alluvial soils' in the Russian soil classification from 2004 and the 'Čiernica' in the Slovakian soil classification (Krasilnikov et al., 2009; Societas pedologica slovaca, 2014). The Polish soil classification defines 'chernozemic alluvial soils' ('mady czarnoziemme') as alluvial soils with a mollic-like ('mollik') epipedon (Systematyka Gleb Polski, 2019), which is very close to Mollic Fluvisols (according to IUSS Working Group WRB, 2007). Similarly, the Romanian soil classification defines a 'Mollic Aluviosol', equivalent to a Mollic Fluvisol developed from alluvial parent material (Florea, 2012). The 'Humofluvisol' in the Serbian soil classification refers to a floodplain soil affected by groundwater with SOM accumulation (Pavlović et al., 2017), similar to a Fluvisol with a 'humic' supplementary qualifier in the WRB system and the Croatian 'Humofluvisol'.

In North America, soils with a mollic epipedon have formed on the floodplains of rivers with Mollisols (partially corresponding to the WRB Chernozem and Phaeozem) distributed in the catchment area (Soil Survey Staff, 2014). Then, mollic SOM on the floodplains would be inherited from SOM in formerly eroded Mollisols/Chernozems. A special feature of SOM in these soils is that fire-derived black carbon (BC) may amount to up to 45% of the SOC (Schmidt et al., 1999). 'Typical' mollic horizons are characterized by SOM stabilized by interactions with minerals after rapid transformation in soil with enhanced microbial and faunal activity and by occlusion of SOM in aggregates (Łabaz and Kabała, 2016). These authors alternatively suggested that 'mollic-like' or mollic horizons may have formed by agricultural practice, i.e. after drainage and ploughing, thus by mixing of organic layers with sandy subsoil. However, Łabaz and Kabała (2016) did not provide any analytical data on the chemical composition of SOM reflecting the transition of histic (organic horizon with poorly aerated SOM) to mollic material. This kind of SOM transition is in line with the assumption that mollic floodplain soils along the Rhine and the Danube may have developed from Histic Gleysols and Histosols that have fallen dry (Rehfuess, 1990).

This short literature survey shows that soils located on floodplains with a 'mollic-like' mineral topsoil horizon are distributed along rivers in the temperate/steppe zone in the northern hemisphere, and their presence is reflected by the definition of soil types in various national soil classification systems. Classification and identification of these soils is mainly based on SOC quantity and soil physical and morphological properties such as soil colour, humus form, aggregation, 'base' saturation, and bioturbation. However, information on qualitative SOM composition in mollic horizons of floodplain soils is still very limited, in contrast to Mollisols/Chernozems/Phaeozems not developed on floodplains (e.g. Schmidt et al., 1999; Thiele-Bruhn et al., 2014). Although all these soils have a mollic-like horizon in common, the formation/transformation of SOM may differ between these groups of soils, as in non-floodplain Mollisols/Chernozems/Phaeozems SOM commonly forms in situ, while mollic floodplain soils are affected by fluviatile dynamics. These dynamics may include sedimentation of SOM-containing eroded soil material (i.e. with SOM formed ex situ) and flooding and high groundwater tables, which affect SOM transformation (Graf-Rosenfellner et al., 2016).

Mollic Fluvisols in Slovakia contained more SOM than spatially related Chernozems, and based on acid hydrolysis, SOM in the Fluvisols was more persistent than in the Chernozems (Jonczak et al., 2017). Rinklebe et al. (2016) have detected BC in bulk soils and Rennert et al. (2018) in physical fractions of horizons of Mollic Fluvisols along the Elbe River (Germany). The question arises whether SOM properties, particularly its stabilization, in mollic horizons of floodplain soils are rather common features so that joint soil classification reflects similar chemical SOM composition and properties, irrespective of still debated processes responsible for their initial formation and subsequent development.

The aim of this study was to answer this research question by quantitative and qualitative SOM characterization using a thermal-gradient method and by diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy. We took advantage of a collection of supposed mollic floodplain soils formed along various rivers in ten central/east European countries. We have chosen these soils as examples, not for a comprehensive survey of mollic floodplain soils in Europe. The results of this approach may expand our knowledge of SOM stabilization and transformation in mollic horizons of floodplain soils.

2. Materials and methods

2.1. Soils and sampling

We took 124 soil samples from 101 soils/locations on fluvial terraces in ten central/east European countries (Table 1), either in excavated pits or with an auger. When sampling in excavated pits, we sampled the profiles' horizons separately, i.e. at least 1 kg from the entire area of each mineral horizon as a composite sample with a gardening trowel. Sampling with an auger was often restricted to the topsoil. The choice of the spots for sampling was based on soil maps, previous field surveys and publications, and regional expert knowledge on the distribution of mollic horizons. However, when soils suspected to have a mollic horizon later turned out to be non-mollic, we did not exclude them from analysis and interpretation. Instead, they were used as reference soils to adjacent ones with a mollic horizon and designated as 'non-mollic' in the following.

Although the mollic horizon is defined as a surface horizon (IUSS Working Group WRB, 2015), we also included 41 deeper lying horizons in our study (Table 1), taken from soil profiles. We consider this approach appropriate, as former, potentially mollic surface horizons, may have become subsoil horizons, buried by subsequent sedimentation (Graf-Rosenfellner et al., 2016; Rinklebe, 2004). In these horizons, we also aimed to analyse the chemical SOM composition, which is the consequence of processes, rather than classification.

2.2. Analyses

The samples were sieved to $\leq$ 2 mm, homogenized, and air-dried. We determined Munsell colours in both air-dried and moist state. Soil pH was determined potentiometrically in H_2O at a soil-to-solution of 1:2.5. We analysed the samples for total carbon (C) and nitrogen (N) by dry combustion, using an elemental analyser (vario macro, Elementar Analysensysteme, Langenselbold, Germany). We obtained a further discrimination of total C by a thermal-gradient method (Rennert and Herrmann, 2020), using a SoliTOC elemental analyser (Elementar Analysensysteme). At a heat rate of 70 K min^{-1}, 50 mg of soil were heated to 450 °C (and the temperature was held constant for 500 s), then to 600 °C (temperature constant for 450 s), and finally to 900 °C (temperature constant for 150 s; Fig. 1). An infrared detector quantified the CO_2 evolved in each temperature interval. We attributed CO_2 detected at T = 20–450 °C (C-450) and T = 451–600 °C (C-600) to organic C (OC), and that detected at 601–900 °C (C-900) to inorganic C (IC). We have chosen 450 °C as the upper limit of the first analytical interval, as this temperature is a threshold to differentiate between thermolabile and stable SOM (Wilcken et al., 1997). We increased the temperature for the first interval to 450 °C, as the frequently used thermal-gradient method by Schwartz (1995) allowed quantifying soot BC, but strongly overestimated the contents of charcoal BC (Roth et al., 2012). Roth et al. (2012) have shown that oxidation at 350 °C (Schwartz, 1995) was not sufficient to distinguish between woody non-BC SOM and BC. At 600 °C, decomposition of SOM is largely completed, and thermal decomposition of calcite and dolomite occurs at higher temperatures, i.e. at 850–925 °C (Leinweber and Schulten, 1992; Vuong et al., 2016). We also increased the duration of the entire analysis (2250 s), as we used the smallest heating rate (70 K min^{-1} versus 70–120 K min^{-1}) compared to Roth et al. (2012) and deployed prolonged intervals of constant temperature (1100 s altogether).

In addition, we characterized the SOM composition by DRIFT spectroscopy (DRIFT module of a LUMOS infrared microscope; Bruker, Ettlingen, Germany). We used 75 mg of each sample and diluted it with 75 mg of potassium bromide (KBr). We recorded 200 spectra per sample at a resolution of 4 cm^{-1} in the spectral range of 4000 to 600 cm^{-1}, with background spectra recorded with pure KBr. For a qualitative evaluation of the spectra, we used the intensities of the absorption bands at 1724 cm^{-1} and 1395 cm^{-1}, respectively, divided by the SOC content and multiplied by 100, resulting in ratios designated as r1724 and r1395 (Rennert, 2018). Absorption at 1395 cm^{-1} increases with increasing extent of complexation of carboxyl groups with metals and metal oxides (Kaiser et al., 1997), and so does the r1395 ratio (Rennert, 2018). Absorption at 1724 cm^{-1} is proportional to the content of carboxyl groups. Their absorption decreases by metal complexation (Kaiser et al., 1997) and thermal decomposition, i.e. when BC forms (Guo and Bustin, 1998; Rennert et al., 2008).

3. Results and discussion

3.1. General properties of mollic and non-mollic horizons

All soil samples under study fulfilled the WRB criteria (IUSS Working Group WRB, 2015) for a mollic horizon regarding structure. In addition, 'base' saturation $\geq$ 50% is demanded, but we did not determine it explicitly. According to Kabała and Łabaz (2018), soil pH measured in H_2O provides a sufficient approximation, as soil pH (H_2O) > 5.5 indicates 'base' saturation > 50%. This applied for all samples, as the minimum pH was 5.7 (Table 1).

We could not consider the WRB criterion of the thickness of the horizon ($\geq$20 cm), as we partially sampled using an auger. In addition, almost two-thirds of the samples originated from arable land, which implies homogenization by ploughing, so that the thickness of the A horizon would be an artefact. Finally, the required minimum thickness of a mollic horizon does not derive from a processual point of view so that we did not exclude horizons with lower thickness. As pointed out before, we neither excluded buried former (mollic?) surface horizons, which are no recent mollic horizons sensu stricto WRB, too. The texture of the vast majority of samples was loamy (117 out of 124; Table 1).

Of the 124 samples under study, 102 fulfilled the WRB criteria of mollic horizons. As we partially sampled soil profiles, 16 subsoil horizons out of the 102 horizons fulfilled the criteria, too. The most frequent criterion to prevent the classification as a mollic horizon was soil colour. With these samples (10 topsoil, 12 subsoil horizons), the Munsell value or the chroma or both were too high, i.e. the colour was too light or its saturation was too low or both. The WRB requires mollic horizons to have both value and chroma $\leq$ 3 (moist) or value $\leq$ 5 and chroma $\leq$ 3 (dry). The SOC content of only three samples (#08, #10, #25) was too small for a mollic horizon, i.e. SOC content < 6 g kg^{-1}. Six samples (#01, #04, #23, #44, #96, #111) fulfilled the colour criteria for a mollic horizon in dry state, but not in moist state. Mollic horizons may have a Munsell value in moist state > 3 and $\leq$ 5, but only when fulfilling the criteria of SOC content $\geq$ 25 g kg^{-1} and a $CaCO_3$ equivalent of $\geq$ 40% by mass (corresponding to $\geq$ 48 g IC kg^{-1}). Calculating the IC contents to $CaCO_3$ equivalents, only one sample under study (#65) fulfilled the carbonate criterion with an IC content of 50 g kg^{-1} (Tabs. 1, S1). More than half of the mollic samples (59 out of 102) were carbonate-free or did not contain>1 g IC kg^{-1} (Table 1). Similarly, the SOC contents of the mollic samples varied in a wide range, from 6.1 to 90 g kg^{-1}, with an arithmetic mean of 28 g kg^{-1}. The range of the non-mollic reference samples was narrower, 1.7 to 38.1 g kg^{-1}, arithmetic mean 12.8 g kg^{-1}.

3.2. Qualitative characterization of soil organic matter

The previous section revealed that mostly soil colour caused the differentiation between darker mollic and lighter non-mollic samples, according to classification criteria. Acksel et al. (2016) reported that soil lightness, as derived from diffuse reflectance of soil, was inversely related to the proportion of BC of total SOC. These authors studied mollic horizons of (Luvic) Chernozems and quantified BC via benzene polycarboxylic acids. Their findings on soil colour and BC content was consistent with previous studies (e.g. Glaser et al., 2000; Schmidt and

Table 1
Selected properties of soil samples taken from floodplain sites in central/eastern Europe. Sample numbers marked with an asterisk indicates sampling of corresponding horizons of a soil profile.

	Country	River	Coordinates[1]	Sampling depth (cm)	Land use[2]	Mollic horizon[3]	Colour (dry)[4]	pH[5]	Texture[6]	C-450[7] (g kg^{-1})	C-600[8]	IC[9]
#01	Austria	Danube	48°07′44″; 16°43′21″	0–13	F	–	10 YR 5/2	7.6	L	34.0	4.0	29.2
#02		Danube	48°07′59″; 16°43′56″	0–24	F	x	10 YR 5/2	7.5	L	46.8	4.6	27.2
#03		Danube	48°07′39″; 16°47′01″	0–25	F	x	10 YR 5/2	7.6	L	34.4	3.6	27.8
#04		Danube	48°07′26″; 16°40′42″	0–19	F	–	10 YR 5/2	7.8	SiL	26.7	3.4	26.3
#05		Danube	48°07′34″; 16°40′08″	0–12	F	x	10 YR 5/2	7.6	SiL	35.8	3.8	27.
#06	Belarus	Western Berezina	54°07′60″; 26°25′00″	0–20	NG	x	10 YR 5/3	5.7	LS	8.7	0.1	–
#07*	Croatia	Drava	46°12′12″; 17°0′14″	0–26	A	x	10 YR 4/3	6.7	SiL	27.8	1.2	0.5
#08*		Drava	46°12′12″; 17°0′14″	40–57	A	–	10 YR 5/3	8.1	Si	4.3	0.9	7.9
#09*		Drava	46°12′12″; 17°0′14″	58–71	A	–	10 YR 6/3	8.1	SiL	6.1	0.8	8.4
#10*		Drava	46°12′12″; 17°0′14″	72–102	A	–	10 YR 6/2	8.0	L	1.5	1.3	8.1
#11		Drava	46°14′33″; 16°52′31″	0–30	A	x	10 YR 4/3	7.7	SL	16.5	1.3	4.0
#12		Drava	46°14′9″; 16°52′31″	0–30	A	x	10 YR 5/3	6.5	SiL	13.3	0.5	0.4
#13		Drava	46°12′48″; 16°54′9″	0–30	A	x	10 YR 5/3	7.9	SiL	11.0	0.9	2.5
#14		Drava	46°5′52″; 17°9′14″	0–30	A	x	10 YR 5/3	8.0	SiL	18.7	1.1	2.6
#15		Drava	46°9′25″; 17°98′5″	0–30	A	x	10 YR 5/3	7.9	SiL	18.7	1.9	0.8
#16		Drava	46°11′35″; 17°3′51″	0–30	A	x	10 YR 5/2	7.3	SiL	21.3	1.0	0.5
#17		Drava	46°12′46″; 16°59′45″	0–30	A	x	10 YR 5/3	7.9	SiL	10.3	1.8	8.3
#18	Czech Republic	Vltava	50°7′21″; 14°24′0″	0–10	A	x	10 YR 4/2	6.5	SCL	13.0	0.8	0.2
#19		Vltava	50°7′21″; 14°24′0″	0–10	A	x	10 YR 4/2	6.6	SCL	14.3	0.9	0.3
#20		Vltava	50°7′21″; 14°24′1″	0–10	A	x	10 YR 4/3	6.8	SCL	11.8	0.8	0.2
#21		Vltava	50°7′21″; 14°24′0″	0–10	A	x	10 YR 4/2	6.7	SCL	13.7	0.8	0.2
#22		Vltava	50°7′21″; 14°24′0″	0–10	A	x	10 YR 4/2	6.8	SCL	9.3	0.6	0.2
#23		Labe	50°31′6″; 14°4′39″	0–20	A	–	10 YR 4/3	7.8	L	6.8	0.6	0.2
#24		Labe	50°1′31″; 15°13′40″	0–20	A	x	10 YR 4/3	7.7	SiL	7.5	0.5	0.2
#25		Labe	50°9′55″; 15°5′3″	0–20	G	–	10 YR 5/2	7.5	LS	4.7	1.1	5.9
#26		Labe	50°44′54″; 14°11′12″	0–20	A	x	10 YR 4/3	7.1	L	6.7	0.3	0.1
#27		Morava	48°56′14″; 17°18′30″	0–20	A	x	10 YR 5/3	6.9	SiCL	10.2	0.4	0.1
#28		Morava	48°53′21″; 17°13′25″	0–20	A	x	10 YR 5/3	7.2	SiL	12.3	0.6	0.1
#29		Morava	48°52′57″; 17°11′22″	0–20	G	x	10 YR 5/2	7.4	SiCL	15.6	0.3	0.1
#30		Morava	49°19′51″; 17°21′47″	0–20	A	x	10 YR 5/4	7.2	SiCL	8.6	0.3	0.1
#31		Morava	49°39′23″; 17°13′08″	0–20	A	x	10 YR 5/3	7.4	L	7.1	4.6	0.1
#32		Litavka	49°43′3″; 14°0′50″	0–25	G	x	10 YR 4/2	6.2	SL	56.3	2.7	0.2
#33		Litavka	49°43′3″; 14°0′51″	0–25	G	x	10 YR 3/2	6.4	LS	39.6	1.9	0.2
#34		Litavka	49°43′3″; 14°0′51″	0–25	G	x	10 YR 3/2	6.5	SiL	32.8	1.3	0.1
#35		Litavka	49°43′0″; 14°0′52″	0–25	G	x	10 YR 4/2	6.2	LS	69.5	3.1	0.4
#36		Litavka	49°43′0″; 14°0′52″	0–25	G	x	10 YR 4/3	6.5	CS	11.0	2.4	0.2
#37		Litavka	49°43′0″; 14°0′51″	0–25	G	x	10 YR 3/2	6.5	SL	57.3	2.9	0.4
#38		Litavka	49°43′2″; 14°0′47″	0–25	G	x	10 YR 4/2	5.8	SL	40.7	1.0	0.1
#39		Litavka	49°43′3″; 14°0′50′	0–25	G	x	10 YR 3/2	6.9	LS	52.4	2.5	0.1
#40		Litavka	49°43′5″; 14°0′49″	0–25	G	x	10 YR 3/2	6.6	LS	57.8	2.2	0.2
#41*	Germany	Rhine	49°0′15″; 8°13′8″	0–15	F	x	10 YR 5/3	7.6	SiL	27.6	3.7	27.7
#42*		Rhine	49°0′15″; 8°13′8″	16–41	F	x	10 YR 5/2	7.8	CL	18.2	3.2	23.5
#43*		Danube	48°30′47″; 10°13′9″	0–10	A	x	10 YR 4/3	7.3	SiCL	21.6	1.0	0.2
#44*		Danube	48°30′47″; 10°13′9″	11–38	A	–	10 YR 4/3	7.4	SiCL	20.1	0.7	0.2
#45*		Danube	48°30′47″; 10°13′9″	39–61	A	x	10 YR 4/2	7.2	SiCL	12.6	0.4	0.1

(continued on next page)

Table 1 (*continued*)

	Country	River	Coordinates[1]	Sampling depth (cm)	Land use[2]	Mollic horizon[3]	Colour (dry)[4]	pH[5]	Texture[6]	C-450[7] (g kg^{-1})	C-600[8]	IC[9]
#46*		Danube	48°30′47″; 10°13′9″	62–80	A	x	10 YR 5/3	7.6	SiCL	5.8	0.3	0.1
#47*		Danube	48°31′33″; 10°15′57″	0–20	A	x	10 YR 5/3	6.7	SiL	14.5	0.4	0.1
#48*		Danube	48°31′33″; 10°15′57″	21–42	A	x	10 YR 4/3	6.9	SiL	9.2	0.3	0.1
#49*		Danube	48°31′33″; 10°15′57″	43–86	A	x	10 YR 4/3	6.9	SiCL	6.6	0.2	0.1
#50*		Wutach	47°50′32″; 8°28′32″	0–15	G	x	10 YR 5/2	7.8	SL	13.6	2.3	25.2
#51*		Wutach	47°50′32″; 8°28′32″	16–43	G	x	10 YR 5/2	7.9	SL	13.4	2.0	27.0
#52*		Saale	51°57′15″; 11°54′57″	0–15	F	x	10 YR 5/2	6.0	CL	55.8	5.1	1.4
#53*		Saale	51°57′15″; 11°54′57″	16–50	F	x	10 YR 5/2	6.7	CL	45.8	4.0	0.9
#54*		Saale	51°57′15″; 11°54′57″	51–73	F	x	10 YR 5/3	7.6	CL	27.4	2.7	2.3
#55*		Saale	51°57′15″; 11°54′57″	0–18	F	x	10 YR 5/2	7.0	CL	59.8	5.1	0.6
#56*		Saale	51°57′15″; 11°54′57″	19–50	F	x	10 YR 5/2	6.6	CL	52.3	4.0	1.0
#57*		Saale	51°57′15″; 11°54′57″	51–76	F	x	10 YR 5/2	6.7	CL	36.4	2.7	0.3
#58		Wupper	51°4′0″; 6°59′1″	0–10	G	x	10 YR 3/2	6.6	L	52.4	7.4	3.1
#59		Wupper	51°5′4″; 7°0′13″	0–10	G	x	10 YR 3/2	5.7	L	56.2	14.4	7.5
#60		Wupper	51°7′50″; 7°1′35″	0–10	G	x	10 YR 4/2	6.4	SiL	40.8	7.0	2.5
#61		Wupper	51°7′50″; 7°1′35″	11–28	G	x	10 YR 4/2	6.4	L	32.3	7.5	3.4
#62*		Ammer	47°44′13″; 10°58′22″	0–8	G	x	10 YR 4/2	7.3	SiL	44.3	2.9	29.1
#63*		Ammer	47°44′13″; 10°58′22″	9–24	G	x	10 YR 4/2	7.9	SiL	31.3	1.9	24.6
#64*		Ammer	47°44′13″; 10°58′22″	0–7	G	x	10 YR 4/2	7.6	L	28.9	2.3	45.1
#65*		Ammer	47°44′13″; 10°58′22″	8–33	G	x	10 YR 5/2	8.1	L	13.5	1.7	50.0
#66*	Poland	Wisła	53°05′34″; 18°15′31″	0–20	F	x	10 YR 5/2	7.6	SiL	31.5	2.1	8.9
#67*		Wisła	53°05′34″; 18°15′31″	21–40	F	–	10 YR 6/3	7.9	SiL	10.7	1.0	7.1
#68*		Wisła	53°05′34″; 18°15′31″	41–60	F	–	10 YR 6/3	8.0	SiL	8.2	0.8	5.8
#69*		Wisła	53°05′34′; 18°15′31″	61–83	F	–	10 YR 6/2	7.9	SiL	6.6	0.6	3.9
#70*		Wisła	53°05′34″; 18°15′35″	0–40	A	x	2.5 Y 5/2	7.8	SiL	13.8	1.1	4.2
#71*		Wisła	53°05′34″; 18°15′35″	41–60	A	–	2.5 Y 6/3	8.0	SiL	6.8	0.7	3.3
#72*		Wisła	53°05′34″; 18°15′35″	61–80	A	x	2.5 Y 5/3	8.0	SiL	8.5	0.8	4.0
#73*		Wisła	53°05′34″; 18°15′35″	81–100	A	–	2.5 Y 6/3	8.0	SiL	6.5	0.7	3.9
#74*		Wisła	53°05′34″; 18°15′35″	101–110	A	–	2.5 Y 6/3	8.1	SiL	6.4	0.7	4.3
#75*		Wisła	53°05′33″; 18°16′12″	0–33	G	x	10 YR 5/2	7.7	SiL	22.9	1.1	3.8
#76*		Wisła	53°05′33″; 18°16′12″	31–44	G	–	10 YR 6/3	8.0	SiL	9.1	0.8	2.3
#77*		Wisła	53°05′30″; 18°16′27″	0–20	A	x	10 YR 5/2	7.7	SiL	14.1	1.1	1.7
#78*		Wisła	53°05′30″; 18°16′27″	21–40	A	–	10 YR 6/2	7.9	SiL	8.0	0.7	3.3
#79*		Wisła	53°05′53″; 18°15′34″	0–26	A	x	10 YR 5/3	7.1	FSL	12.9	0.6	0.1
#80*		Wisła	53°05′53″; 18°15′34″	27–33	A	x	2.5 Y 5/3	7.4	L	8.8	0.3	0.1
#81*		Wisła	53°05′53″; 18°15′34″	34–76	A	x	2.5 Y 5/2	7.7	SiL	12.1	0.5	0.2
#82		Wisła	53°05′58″; 18°15′31″	0–30	A	x	10 YR 4/2	6.9	L	15.2	0.7	0.1
#83*		Wisła	53°05′58″; 18°15′31″	31–40	A	x	10 YR 5/2	7.4	L	8.4	0.4	0.1
#84*		Wisła	53°05′58″; 18°15′31″	41–50	A	x	10 YR 5/3	7.6	FSL	7.4	0.3	–

(continued on next page)

Table 1 (*continued*)

	Country	River	Coordinates[1]	Sampling depth (cm)	Land use[2]	Mollic horizon[3]	Colour (dry)[4]	pH[5]	Texture[6]	C-450[7] (g kg^{-1})	C-600[8]	IC[9]
#85		Wisła	53°06′02″; 18°15′21″	0–40	A	x	2.5 Y 5/2	7.3	SiL	28.3	1.3	0.2
#86		Wisła	53°06′02″; 18°15′21″	0–14	A	–	2.5 Y 6/1	7.9	SiL	17.3	0.8	0.1
#87		Wisła	53°05′34″; 18°15′09″	0–33	F	x	2.5 Y 5/2	7.5	SiL	26.7	2.1	3.2
#88		Wisła	53°05′33″; 18°15′15″	0–25	W	x	2.5 Y 4/2	7.5	SiL	65.6	4.2	1.8
#89		Wisła	53°05′05″; 18°17′59″	0–25	W	x	2.5 Y 4/1	7.2	SCL	58.5	4.0	0.4
#90		Wisła	53°05′07″; 18°17′58″	0–25	W	x	2.5 Y 4/2	7.6	SiL	37.1	2.3	1.9
#91*	Romania	Aries	46°30′48″; 23′46′42″	0–30	A	x	10 YR 4/2	6.4	SL	20.6	0.7	0.1
#92*		Aries	46°30′48″; 23′46′42″	31–53	A	x	10 YR 4/2	7.1	SL	9.9	0.5	0.1
#93*		Aries	46°29′22″; 23°47′14″	12–24	A	x	10 YR 3/2	8.3	L	24.5	1.9	7.4
#94*		Aries	46°29′22″; 23°47′14″	43–61	A	x	10 YR 3/2	8.3	SL	19.0	2.0	8.1
#95*		Aries	46°34′26″; 23°45′59″	21–31	A	x	10 YR 3/2	7.3	SL	40.3	1.3	0.4
#96*		Aries	46°34′26″; 23°45′59″	38–49	A	–	10 YR 4/2	7.8	SL	15.8	0.5	0.3
#97	Russian Fed.	Devitsa	51°40′31″; 39°2′1″	0–20	NG	x	10 YR 3/2	7.8	L	20.1	1.7	6.3
#98		Kamushki	53°57′29″; 37°29′30″	0–20	NG	x	10 YR 2/1	6.8	CL	85.3	4.7	0.2
#99		Solova	53°57′24″; 37°23′31″	0–20	NG	x	10 YR 3/2	7.6	CL	57.0	3.3	3.2
#100	Serbia	Belica	44°2′44″; 21°13′48″	0–25	A	x	10 YR 5/3	7.1	SL	22.6	1.1	–
#101		Zapadna Morava	43°53′46″; 20°25′3″	0–25	A	x	10 YR 4/2	7.2	SiL	23.6	1.5	0.5
#102		Zapadna Morava	43°53′39″; 20°24′11″	0–25	A	x	10 YR 4/2	7.4	L	15.6	1.2	0.3
#103		Zapadna Morava	43°52′9″; 20°7′24″	0–25	A	x	10 YR 4/2	7.7	SL	24.7	2.3	2.6
#104		Zapadna Morava	43°42′30″; 20°50′10″	0–25	A	x	10 YR 4/2	7.2	CL	20.5	0.8	–
#105		Zapadna Morava	43°41′23″; 20°50′41″	0–25	A	x	10 YR 4/2	7.7	SL	22.4	1.5	0.8
#106		Jadar	44°31′42″; 19°21′17″	0–25	A	–	10 YR 6/3	7.6	LS	14.0	0.8	–
#107		Jadar	44°31′18″; 19°22′43″	0–25	A	–	10 YR 6/4	6.6	LS	15.8	0.3	–
#108		Jadar	44°32′38″; 19°19′30″	0–25	A	–	10 YR 6/4	7.2	SL	17.9	0.6	–
#109		Jadar	44°28′23″; 19°8′38″	0–25	A	x	10 YR 5/3	7.8	L	20.1	1.7	9.4
#110		Raca	44°12′14″; 21°0′29″	0–25	A	x	10 YR 4/2	6.8	SL	23.2	0.8	–
#111		Mlava	44°29′2″; 21°18′49″	0–25	A	–	10 YR 4/2	7.7	CL	23.7	1.2	1.4
#112		Skrapez	44°0′10″; 19°48′46″	0–25	A	x	10 YR 5/2	7.2	CL	42.7	2.3	0.4
#113*	Slovakia	Hron	48°40′1″; 19°8′29″	0–10	A	x	10 YR 4/2	7.1	L	17.8	0.8	–
#114*		Hron	48°40′1″; 19°8′29″	35–45	A	x	10 YR 3/1	7.7	L	16.2	0.6	–
#115*		Turiec	49°0′15″; 18°52′53″	0–10	A	x	10 YR 3/1	7.2	SiL	43.0	3.7	33.1
#116*		Turiec	49°0′15″; 18°52′53″	35–45	A	x	10 YR 4/1	7.9	SL	22.0	2.6	30.5
#117*		Blh	48°22′15″; 20°10′46″	0–10	A	x	10 YR 4/2	5.9	SiL	21.0	1.0	0.1
#118*		Blh	48°22′15″; 20°10′46″	35–45	A	x	10 YR 4/2	6.0	SiCL	19.1	1.0	–
#119*		Váh	48°14′5″; 17°47′28″	0–10	A	x	10 YR 5/2	7.7	CL	24.9	1.2	2.1
#120*		Váh	48°14′5″; 17°47′28″	35–45	A	x	10 YR 5/1	7.7	CL	16.7	1.1	3.6
#121*		Danube	48°2′17″; 17°27′2″	0–10	A	x	10 YR 5/1	8.2	C	15.8	3.0	18.4
#122*		Danube	48°2′17″; 17°27′2″	35–45	A	x	10 YR 4/1	8.3	CL	16.2	4.0	16.8
#123*		Dunaj	47°28′9″; 18°21′22″	0–10	A	x	10 YR 4/1	8.1	CL	19.0	4.1	27.3
#124*		Dunaj	47°28′9″; 18°21′22″	35–45	A	x	10 YR 4/1	8.3	SiC	16.1	3.8	23.4

[1] all degrees of latitude and longitude refer to N and E, respectively.
[2] A: arable land; F: forest; G: grassland; NG: natural grassland; W: wetland.
[3] 'x': criteria fulfilled; '-': criteria not fulfilled.
[4] Munsell colour.
[5] measured in H_2O.
[6] according to FAO (2006); CL, clay loam; CS, coarse sand; FSL, fine sandy loam; L, loam; LS, loamy sand; SiCL, silty clay loam; SiL, silt loam; SCL, sandy clay loam: SL, sandy loam).
[7] organic carbon combusted at T = 20–450 °C (C-450).
[8] organic carbon combusted at T = 451–600 °C (C-600).
[9] inorganic carbon.

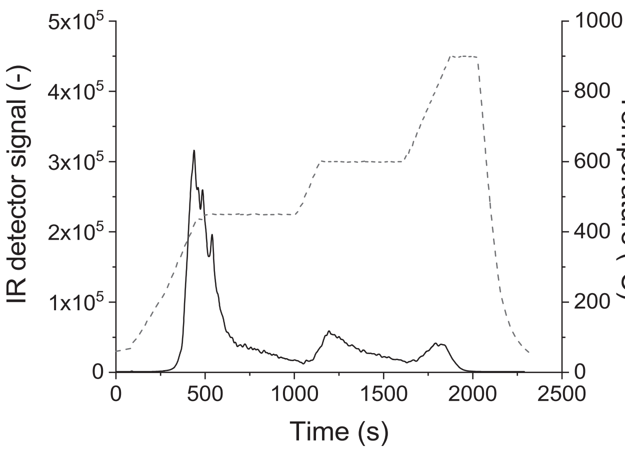

Fig. 1. Example of the thermal-gradient analysis of soil organic matter (sample #47). The solid line represents the signal of the infrared detector for CO_2, the dashed line the temperature. The CO_2 evolved in the first and the second temperature interval represent organic carbon, the CO_2 in the third inorganic carbon.

Noack, 2000). The study of Thiele-Bruhn et al. (2014) showed that SOM in mollic horizons of Chernozems have a similar chemical composition with a BC component that very likely contributes to the dark colour of mollic horizons. Apart from this first morphological result, our chemical analyses additionally pointed to the substantial presence of BC in mollic horizons.

The thermal-gradient method for C quantification generally allowed distinguishing between IC and SOC. Organic C was additionally differentiated, according to the temperature of combustion. The absolute and relative contents of SOC detected in the first interval ($T \leq 450$ °C; C-450) differed among the samples (Table 1). The fraction of C-450 amounted to 79.6 to 98.8% of total SOC for the mollic samples and 81.6 to 97.9% for the non-mollic samples (Tab. S1). Thus, thermolabile material, e.g. SOM rather poorly stabilized by interactions with minerals and mainly assigned to plant fragments in varying states of decomposition (Leinweber et al., 1992; Schulten and Leinweber, 1999), dominated in both types of samples. The C-450 fraction was strongly correlated with the total SOC contents of both mollic and non-mollic samples. The squared Pearson correlation coefficients were 0.994 (mollic) and 0.988 (non-mollic), respectively.

The relative quantitative importance of the C-600 fraction differed between the samples, but was similar for both types, 1.2–20.4% (arithmetic mean 7.0%) for the mollic samples, 2.1–18.4% (arithmetic mean 8.7%) for the non-mollic samples (Tab. S1). The C-600 fraction consists of material with a larger thermal stability caused either by stabilizing interactions with soil minerals or by the presence of BC (Kučerik et al., 2018; Kumar et al., 2005; Leifeld, 2007; Schulten and Leinweber, 1999). Interaction with mineral surfaces induces an increase in the temperature, at which thermal decomposition of carbohydrates, lignin monomers and peptides occurs, by up to 70 K (Schulten and Leinweber, 1999). However, based on relative and absolute C-600 quantities alone, it is not possible to distinguish between stabilized SOC and BC in this fraction. The absolute C-600 contents and the total SOC contents of the non-mollic samples were linearly correlated (C-600 = 0.274 + 0.0431 × SOC) with a Pearson r^2 of 0.8. This correlation was distinctly weaker for the mollic samples (C-600 = 0.122 + 0.0676 × SOC, r^2 = 0.47), and the slope was by 57% larger. Apart from a physical property (soil colour), these varying correlations point to qualitative differences in the composition of thermostable SOM between mollic and non-mollic samples. A strong correlation between C-600 contents and total SOC contents points to partitioning, i.e. interaction of a certain SOM fraction with soil minerals. Thus, the poorer correlation for the mollic samples indicates less SOM associated with soil minerals, but being thermostable. This is a further hint on a larger contribution of BC to SOM in mollic samples than in non-mollic samples, as BC tends to less chemical interaction with soil minerals (Rumpel et al., 2006). Accordingly, the C-600 content of the mollic samples tended to be inversely related to the parameters r1395 and r1724 (Fig. 2a, b). This could be expected when SOM in mollic horizons has a stronger contribution from BC than from SOM associated with minerals. Formation of BC by heating reduces the number of carboxyl groups (thus absorption at 1730–1700 cm^{-1}). Less metal-SOM complexation would reduce absorption at 1395 cm^{-1}, as mentioned before. However, the respective data for non-mollic samples (Fig. S1) provided a similar/diffuse impression so that these parameters may not be completely decisive, and thermostable SOM in both types of horizons represented mixtures of BC and SOM-minerals associations. The decrease in absorption intensity at 1724 cm^{-1} may not exclusively be caused by the presence of BC, but additionally by metal complexation of carboxyl groups (Kaiser et al., 1997). Obviously, these effects cannot be differentiated for the non-mollic samples and point to a rather homogeneous mixture of different types of thermostable SOM.

The ratios of SOC and N contents of thermostable SOM in both types of horizons were more meaningful. The SOC:N ratio and the C-600 contents of the mollic samples were significantly linearly correlated (Fig. 2c). Soil OM that is associated with minerals of the clay fraction is characterized by narrow C:N ratios (e.g. Guggenberger et al., 1998; Oades, 1988). Mineral-associated SOM, enriched in N-containing compounds, decomposes thermally at temperatures similar to the C-600 fraction (Schulten and Leinweber, 1999). Based on these findings, thermostable SOM with increasing SOC:N in the mollic horizons must be attributed to larger amounts to BC, than to mineral-associated SOM. Black C in soil is characterized by wide C:N ratios (e.g. Rennert et al., 2018; Rumpel et al., 2006) so that BC contents positively correlate with the SOC:N ratio (e.g. Borchard et al., 2014). There was no significant correlation between SOC:N ratios and the C-600 contents for the non-mollic horizons (Fig. S1), indicating a mixture of materials that is not dominated by BC.

Although these findings point to varying SOM compositions between the mollic and the non-mollic horizons, there was no sharp differentiation between them. This was likely the consequence of the close horizontal or lateral vicinity of the sites from which mollic and non-mollic horizons were taken, as we initially aimed to samples exclusively mollic horizons. Nonetheless, we detected tendencies, rather than strong linear or non-linear relationships between parameters, as illustrated in Fig. 2. We suggest that this was caused by heterogeneity of the soil samples with respect to the mineral parent material and its weathering, climate,

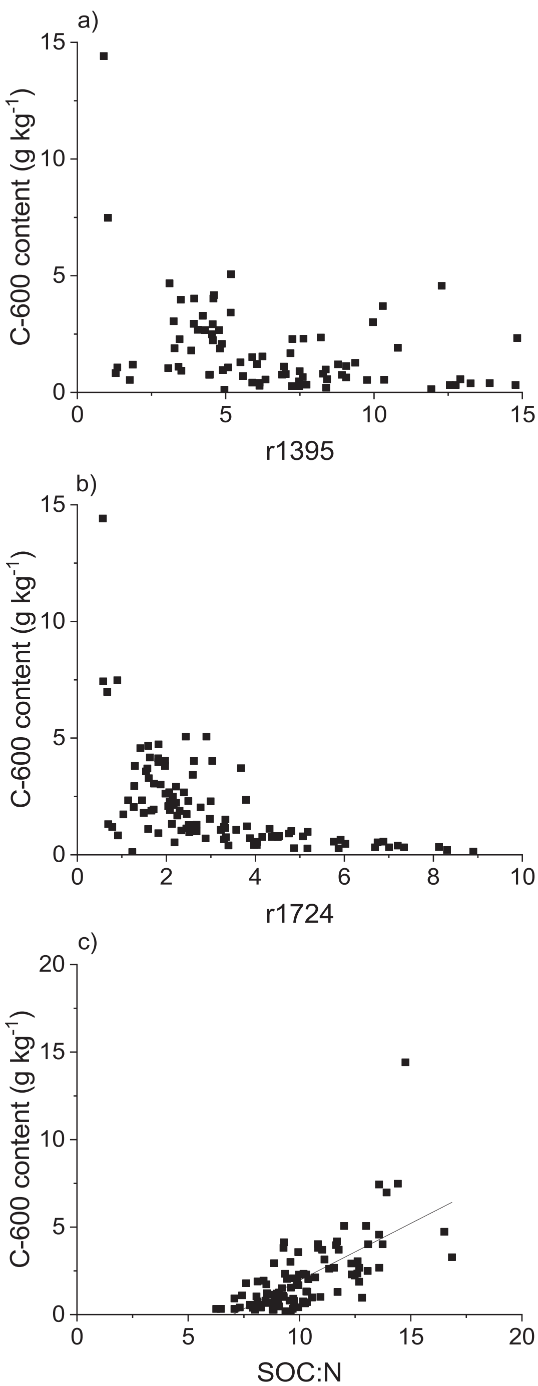

Fig. 2. Ratios derived from diffuse reflectance infrared Fourier transform spectroscopy (a, b) and (c) ratio of soil organic carbon to total nitrogen contents (SOC:N) plotted against the content of thermostable carbon (C-600) of samples of mollic horizons from floodplain soils (C-600 content (g kg^{-1}) = 0.651 × SOC:N − 4.55; R^2 = 0.459, n = 102, $P < 0.05$).

vegetation, recent and historical land use, water budget, fluviatile dynamics, and quantitative, qualitative, spatial and temporal variability of BC inputs.

3.3. *Mollic horizons - even-handedly classified, but differing in composition and formation in floodplain soils?*

The findings reported before point to a variable, but distinct and common contribution of thermostable SOM in mollic horizons of floodplain soils, particularly caused by the presence of BC, similar to that reported for Chernozems that are unaffected by fluviatile dynamics (e.g. Schmidt et al., 1999). This common feature of SOM in mollic horizons of a large variety of central/east European floodplain soils, derived from thermostability and DRIFT spectroscopy has not yet been reported. A contrary aspect of the stability and composition of overall SOM in Fluvisols is the preservation of virtually easily degradable SOM as the consequence of periodic water saturation and thus impeded decomposition (Rennert et al., 2017). However, SOM in mollic horizons, irrespective of the location of the soil relative to a river, is defined by aggregation, pointing to bioturbation, and high 'base' saturation, pointing to at least moderate soil-chemical conditions of SOM decomposition. Apart from the natural water budget and input of BC, which may be both natural and anthropogenic, Łabaz and Kabała (2016) suggested the formation of mollic horizons after drainage and ploughing of histic material, similar to the proposition by Rehfuess (1990). This indicates that a common formation pathway of mollic horizons associated with floodplain soils or with other soils with periodical water saturation is unlikely. Transformation of SOM under periodical water saturation may even prevent the formation of mollic horizons. Thiele-Bruhn et al. (2014) found that the SOM composition of Chernozems and redoximorphic soils such as Stagnosols, Gleysols, and Histosols, as derived from pyrolysis-field ionization-mass spectrometry, showed only a minor overlap.

Nonetheless, our study indicates that BC may be a common feature of SOM in mollic horizons of floodplain soils, making sure that the requirements regarding colour and SOC content are fulfilled. This is very similar to mollic/chernic horizons not affected by fluviatile dynamics, but formed from aeolian sediments, particularly loess deposits. However, the difference to mollic horizons in soil developed from non-fluvial materials is that in Fluvisols mollic horizons have not necessarily formed in situ, as the BC-containing material may have been deposited during flooding. The BC in this material may have originated from natural vegetation fires, which may have occurred throughout the entire Holocene, or from anthropogenic BC produced after industrialization.

Tockner and Stanford (2002) assumed that floodplains are the most anthropogenically changed ecosystems in Europe. Apart from the possible anthropogenic influence and spatial variability of its formation, it may be variable whether mollic horizons of floodplain soils are recently forming or constitute a relic of former environmental conditions. Furthermore, it may be variable, whether formation/preservation of these mollic horizons is a degradative (e.g. decomposition of former histic material; Łabaz and Kabała, 2016) or a constructive process, i.e. formation of stable, mollic SOM in situ, affected by Ca-containing groundwater (Kohl et al., 1954).

As the BC-containing SOM found in mollic horizons of floodplain soils might have formed onsite or offsite, i.e. in upstream soils, eroded and subsequently deposited on downstream sites, the question arises whether the diagnostic 'mollic horizon' in this pedogenetic environment is properly described by the WRB classification. When the mollic horizon consists of deposited sediment, the term 'mollic material' seems more appropriate. In addition, by transferring the 'mollic' (and accordingly the 'umbric') attribute from the set of diagnostic horizons into the set of diagnostic materials within the WRB system, the partial overlapping that presently exists among mollic, chernic, hortic, and some other SOM-rich surface horizons would be alleviated. Accordingly, keying out the WRB reference soil groups would be easier.

4. Conclusions

Based on the results obtained with the methods applied, we detected rather similar SOM compositions in mollic horizons of floodplain soils. Although properties such as relative and absolute contents of thermolabile and thermostable SOC varied among the mollic samples, they had the distinct presence of presumably BC in common. This was the most pronounced difference to adjacent non-mollic horizons, the thermostable SOM of which was a more homogeneous mixture of mineral-associated SOM and BC. Thus, we can rather affirm our initial research question, whether SOM in mollic horizons of floodplain soils has a common feature. The presence of BC affects SOM stabilization, as BC decomposes slower than fresh plant litter. However, the presence of BC is not directly reflected in the diagnostic WRB criteria (e.g. by a certain BC content), but indirectly, by colour. Although the chemical properties of SOM and the formation of mollic horizons as such are yet not fully understood, utilizing more special and process-based parameters rather than macroscopic structure, SOC content and colour could be an approach to differentiate surface horizons in the WRB classification that are characterized by SOM properties, such as mollic, umbric, hortic, and plaggic horizons.

Mollic horizons of floodplain soils very likely form by a variety of processes that have a spatial dimension, considering the formation of SOM in situ or ex situ. However, classification is based on similar morphological and chemical properties, which do not necessarily reflect common processes of formation and development. Consequently, apart from field, sedimentary and morphological studies and similar to SOM in mollic horizons never affected by fluviatile dynamics, sophisticated chemical analyses of SOM in mollic horizons of floodplain soils are demanded. These analyses may provide a more detailed understanding of the chemical properties and potentially the variable formation pathways of mollic horizons in floodplain soils. Nonetheless, the combination of rather easily applicable and inexpensive methods, i.e. thermal-gradient SOC quantification and DRIFT spectroscopy, provided a qualitative approximation of the contribution of BC to SOM, and thus a common feature of SOM in mollic floodplain soils.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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