



Permanganate-oxidizable soil organic matter in floodplain soils



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ARTICLE INFO

Article history:

Received 15 July 2016

Received in revised form 18 October 2016

Accepted 25 October 2016

Available online xxxx

ABSTRACT

Riverine floodplain soils contain large stocks of soil organic matter (SOM) also in larger depth. Qualitative characterization of SOM, especially in the subsoil horizons of floodplain soils, is scarce. To gain deeper insights into the composition of SOM and the driving parameters of SOM processing, we studied 121 horizons of 18 soil profiles along the Central Elbe River (Germany) by determining permanganate-oxidizable carbon (POXC) and a stability parameter derived from diffuse reflectance infrared (DRIFT) spectroscopy. The absolute and relative amounts of POXC varied between the horizons. While the topsoil horizons contained the largest total contents of POXC (average 923 mg kg⁻¹ soil), the largest relative proportions were detected in subsoil horizons characterized by reducing conditions and water saturation (up to 19% of total organic C), which exceeded those reported for terrestrial soils. The absolute contents of POXC were positively and partially highly significantly correlated with those of total organic, hot-water extractable and microbial-biomass C, confirming its nature as slightly processed and relatively labile fraction of SOM. The correlations were distinctly weaker for the reduced horizons, indicating hampered decomposition. The contents of POXC were also positively correlated with the DRIFT stability parameter, expressing the ratio of aliphatic to aromatic C. Our results suggest the presence of a large fraction of less processed SOM in the subsoils of floodplain soils, originating from inputs of particulate organic matter that was buried and weakly decomposed at water saturation, and partially from charcoal particles, also transported by the river water. The results point to a possible limitation of POXC as an indicator of decomposition to soils lacking an aquic moisture regime.

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1. Introduction

Characterization of soil organic matter (SOM) and its allocation to defined functional pools, based on decomposability of SOM by microorganisms, is still a challenging scientific task. Especially that part of SOM, which is decomposed most easily (“labile”) has gained special attraction, as it is an indicator of soil quality by affecting soil functions (Haynes, 2005). Several approaches have been applied to quantify and partially qualify labile SOM, including for instance particulate OM (POM), separated by density or size, dissolved OM, hot-water extractable OM, dilute-acid-hydrolyzable OM using H₂SO₄, permanganate-oxidizable OM (POXM) and potentially mineralizable OM, obtained in incubation experiments and subsequent determination of evolved CO₂ (Haynes, 2005).

Permanganate-oxidizable OM, determined with 0.02 M KMnO₄ (Weil et al., 2003), has been identified as a relatively labile pool of SOM that is related to small-sized POM (53–250 μm; Culman et al., 2012). Organic matter oxidized by 0.333 M KMnO₄ has been identified

by ¹³C NMR spectroscopy as soil polysaccharides and aromatic compounds (Conteh et al., 1999). The latter may also include lignin with glycol groups, whereas cellulose is not attacked by MnO₄⁻ (Tirol-Padre and Ladha, 2004). Positive correlations have been reported between permanganate-oxidizable C (POXC) and soil-microbial parameters, including microbial biomass and substrate-induced respiration, and particulate organic C (Mirsky et al., 2008; Weil et al., 2003). However, in most studies, in which soils were characterized with respect to POXC, topsoil samples were used, and soils on riverine floodplains were not systematically considered. Only Culman et al. (2012) investigated the profile of a Mollic Ustifluent among others, and Szombathová et al. (2008) studied three profiles of floodplain soils.

The dynamics of SOM in soils on riverine floodplains differ from that in terrestrial soils (Graf-Rosenfellner et al., 2016). The formation and the properties of these soils are characterized by periodical input of previously eroded soil material that includes OM, high net primary production on floodplains and periodical water saturation that induce alternating oxidizing and reducing conditions. These processes and factors may also control the amount and the distribution of labile SOM in floodplain soils. We, therefore, took advantage of 18 profiles of floodplain soils (121 horizons in total) from the Central Elbe River (Germany), which have been thoroughly previously characterized

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(Rinklebe, 2004). The aim of this study was to broaden the understanding of SOM dynamics in floodplain soils by quantifying POXC in entire profiles of floodplain soils, evaluating process-related relationships with other soil parameters and with a stability parameter derived from infrared (IR) spectroscopy.

2. Materials and methods

2.1. Soils

We studied 18 soil profiles of three study areas located on the floodplains along the Central Elbe River, Germany (Rinklebe, 2004). Those study areas served as model regions of common floodplains in temperate Central Europe (Henle et al., 2006). The soils under study were seven Eutric Fluvisols, six Eutric Gleysols, three Mollic Fluvisols and two Dystric Gleysols (FAO, 1988). The 121 horizons of these soils comprised 28 Ah/Aa, 46 Go, 21 Gw, 19 M and seven Gr horizons according to the German soil classification (Ad-hoc Arbeitsgruppe Boden, 2005; Wittmann et al., 1997). The A horizons represented mineral topsoil horizons with a thickness ≥ 2 cm and up to 30% SOM, M horizons were mineral subsoil horizons made up of fluvial, eroded soil material, and G horizons were mineral subsoil horizons affected by ground water (Go: oxidized; Gr: reduced; Gw: without redoximorphic properties). The translation of the German horizon classification into the FAO system (FAO, 2006) is restricted: A Go horizon is a Bl horizon, a Gr is a Br horizon, but there is no equivalent for M and Gw horizons.

All horizons were previously analyzed for organic C (C_{org}), total N, hot-water extractable C (C_{hwe}), microbial-biomass C (C_{mic}), dithionite- and oxalate extractable Fe (Fe_d and Fe_o) and texture (Table 1). Details on the sites, the soils and soil analyses were provided by Rinklebe (2004).

Briefly, the A horizons were more strongly acidified (soil pH measured in 0.01 M $CaCl_2$ ranging from 3.7 to 5.7) than the subsoils up to 1 m depth, where the pH values were up to 6.8. However, the pH of the soil solution in these floodplain soils may vary by up to 2.6 pH units as a consequence of alternating oxidizing and reducing conditions (Rennert et al., 2016). Iron oxides were accumulated in Go horizons. The Gw horizons had the least contents of clay, representing sandy material that contained the least amounts of C_{org} . Typical of floodplain soils, the other subsoil horizons contained partially remarkably large contents of C_{org} , e.g., a Go horizon with 119 g C_{org} kg^{-1} . Also typical of floodplain soils, the C:N ratios were partially very wide (up to 36.2), indicating the presence of charcoal particles (Rinklebe, 2004; Rinklebe et al., 2016). The proportions of C_{hwe} of C_{org} were on average lower than those given by Leinweber et al. (1995) for terrestrial topsoils (3–5%). Szombathová et al. (2008) reported 1.2–2.8% for A horizons and 0.8–1.6% for G horizons. The largest proportions detected in our study for Go (5.6 and 6.69%) and Gw horizons (6.73%) referred to samples with low C_{org} contents (<1.24 g kg^{-1}). It was similar for an outlier among the proportions of C_{mic} of C_{org} for the Gw horizons (8.44% for $C_{org} = 0.43$ g kg^{-1}), but not for the Gr horizons (7.45% for $C_{org} = 5.56$ g kg^{-1}).

2.2. Analysis of POXC and infrared spectroscopy

For this study, POXC was quantified in all 121 soil samples (air-dried, sieved to <2 mm) according to Weil et al. (2003). Briefly, 2.5 g soil (in duplicate) were suspended in 2 ml of a 0.2 M $KMnO_4$ solution (prepared in 1 M $CaCl_2$) and 18 ml de-ionized H_2O , shaken by hand vigorously for 2 s, then shaken horizontally for 2 min at 240 oscillations per minute. The phases were separated by centrifugation, and the remaining MnO_4^- in the supernatant was quantified spectrophotometrically at 550 nm (Varian Cary 50, Darmstadt, Germany).

The soil samples were characterized by diffuse reflectance infrared (DRIFT) spectroscopy using the external DRIFT accessory of a LUMOS IR microscope (Bruker, Ettlingen, Germany). Briefly, 75 mg pestled soil material was diluted with 75 mg KBr, and 200 spectra per sample were collected at a resolution of 4 cm^{-1} in the spectral range from 4000 to 500 cm^{-1} (background spectra recorded with KBr). The spectra were converted to Kubelka-Munk units using the OPUS 7.2 software (Bruker). Mirzaeitalarposhti et al. (2016) suggested the ratio of the intensity at 2930 cm^{-1} and the sum of the intensities at 2930, 1159 (both aliphatic C), 1620 and 1520 cm^{-1} (both aromatic C) as a measure of the stability of SOM that was closely positively correlated with the amounts of hot-water extractable and microbial-biomass C and N of A horizons. The ratio was multiplied with 100 and designated as rP2930 in the following. Spectra of samples with C_{org} contents <1 g kg^{-1} were excluded from the evaluation because of the poor resolution of absorption bands of aliphatic C.

3. Results and discussion

Table 2 indicates larger contents of POXC in topsoils than in subsoil horizons, where the total contents of POXC were partially as low as <10 mg kg^{-1} soil. The POXC contents were in the same order of magnitude like those reported by Culman et al. (2012) for 1379 samples from 53 sites in the US. The larger contents in A horizons may result from continual input of fresh biomass, representing SOM that is partially not yet stabilized. We interpret the large contents detected in Gr horizons as the result of inhibited decomposition of SOM owing to the lack of O_2 induced by high groundwater tables in these reduced horizons. Low soil-microbial biomass is a feature of soils with long flooding periods (Rinklebe and Langer, 2006, 2010). The other subsoil horizons showed smaller contents of POXC, but with large ranges, possibly because of variable input of SOM by flooding and sedimentation.

The proportion of C_{org} oxidized by 0.333 M $KMnO_4$ has been found to be 15–30% in several studies (Haynes, 2005), and particularly up to 10.8% in A horizons of floodplain soils (Szombathová et al., 2008). The proportions detected in this study (Table 2) were smaller (A and M horizons) or within this interval (G horizons). The latter indicates the particular oxidizability of SOM in subsoils of floodplain soils because smaller proportions should be expected by treatment with a dilute 0.02 M $KMnO_4$ solution used in this study (Weil et al., 2003). This may be caused by the origin of SOM in these horizons from sediments delivered during periodical flooding, which contain free and occluded POM (Graf-Rosenfellner et al., 2016) that is partially susceptible to oxidation

Table 1
Selected soil biological and soil chemical parameters of 121 horizons from 18 floodplain soil profiles of the Central Elbe River (Germany). Data taken from Rinklebe (2004). C_{org} : organic C; C:N: ratio of C_{org} to total N; C_{hwe} : hot-water extractable C; C_{mic} : microbial-biomass C; Fe_d : dithionite-extractable Fe; Fe_o : oxalate-extractable Fe.

Horizon	C_{org}			C:N			C_{hwe}			C_{mic}			clay			Fe_d			Fe_o		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
	(g kg^{-1} soil)			–			(% of C_{org})						(%)			(g kg^{-1} soil)					
Ah/Aa	62.8	22.2	129	12.5	9.2	11.4	2.59	0.62	5.30	0.71	0.08	2.12	26.8	11.0	48.0	14.1	2.77	23.0	9.23	1.89	18.2
M	10.5	3.3	23.7	9.3	8.2	12.3	1.47	0.26	2.38	0.72	0.30	1.24	22.3	6.0	34.0	11.9	7.48	18.9	6.03	3.04	10.5
Go	18.1	0.5	119	11.9	6.2	36.2	1.31	0.11	6.69	0.65	0.04	3.20	24.2	1.0	46.0	13.0	1.28	34.2	8.50	0.87	38.2
Gw	3.0	0.4	9.7	13.1	7.1	24.3	2.64	0.16	6.73	1.72	0.24	8.44	3.75	1.0	14.0	2.91	0.35	8.50	1.10	0.04	4.33
Gr	17.1	0.8	39.0	11.1	8.6	12.3	1.18	0.21	2.97	2.37	0.12	7.45	23.1	1.0	39.0	7.01	0.31	12.2	5.25	0.03	10.3

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