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Human activity formed deep, dark topsoils around the Baltic Sea

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ABSTRACT

Previous findings showed that the humus-rich topsoils designated as Chernozems around the Baltic Sea were influenced by the addition of pyrogenic organic matter linked with human activity. For a deeper insight into the human activities, we investigated the isotopic signatures of sulphur ($\delta^{34}S$) and the ^{14}C age from nine soil profiles in order to clarify which kind of organic matter was added to the soils and to estimate the beginning of the Chernozem formation. The study area was expanded by two additional Baltic Chernozem profiles on the island of Fehmarn in which we also analyzed the portions of black carbon (BC) with the benzene polycarboxylic acids (BPCA) method and the SOM composition with the Pyrolysis-field ionization mass spectrometry (Py-FIMS). The compound classes from Py-FIMS and the BC portions were similar to all other Baltic Chernozems and Chernozems from European loess areas and indicated an input of combustion residues to the soils. The $\delta^{34}S$ isotope signature of the SOM in the Axh-horizons (Median: $\delta^{34}S = 11.5‰$) at the island of Poel and Sjaelland indicated an input of seaweed ($\delta^{34}S = 20‰$) or other marine biomass. The AMS^{14}C ages from the humin fraction, i.e. the oldest fraction of SOM, of the Axh-horizons and the settlement history implied that the formation of the Baltic Chernozems started in a time period between the Nordic Bronze Age (3800 to 2800 BP) to the Roman Iron Age (2700 to 2000 BP). In summary, the results provided a strong evidence for an input of combustion residues and marine biomass by anthropogenic activities and we conclude that the formation of the Baltic Chernozems reflects an anthropo-pedogenesis. Therefore, we propose to classify these soils as Anthrosols.

1. Introduction

The kind of pedogenic processes that lead to the regionally restricted formation of deep and humus-rich topsoils in some areas around the Baltic Sea have not yet been clearly identified. These soils were designated as Chernozems due to the similarities in soil organic matter (SOM) composition detected by pyrolysis-field ionization mass spectrometry (Py-FIMS) to typical Chernozems worldwide and dissimilarities to SOM formed under reductive conditions (e.g., Histosols, Gleysols and Stagnosols) (Thiele-Bruhn et al., 2014). Acksel et al. (2016) analyzed large contents of pyrogenic organic matter (black carbon = BC) by the benzene polycarboxylic acids (BPCA) and (Py-FIMS) in the characteristic biogenically mixed Axh-horizons of the Baltic Chernozems at the islands of Poel and Sjaelland and at the peninsula Wagrien (Großenbrode) near the island of Fehmarn (18% BC of C_{org}). Such Chernozems were also found at the island of Fehmarn in the Baltic Sea region (Schimming and Blume, 1993), but SOM sources had not yet been studied. High natural portions of BC with around 40% of BC in SOM is a characteristic property of Chernozems (Glaser and Amelung, 2003; Rodionov et al., 2006; Schmidt et al., 1999), most likely originating from vegetation fires, other combustion residues (Brodowski et al., 2007) and/or paleofire events (Bird and Cali, 1998). Therefore, Acksel et al. (2016) hypothesized that BC-enrichments in the deeper Axh-horizons of Baltic Chernozems resulted from human activities like slash and burn or the disposal of settlement residues, because natural fires were relatively rare in Central Europe in contrast to typical steppe landscapes (Tinner et al., 1999). Furthermore, investigations of charcoal fragments from various soils showed not particularly frequent natural fire events in Europe in the time from 13,000 to 5000 BP (Carcaillet et al., 2002).

The BC content is an important feature of the unusual Axh-horizons, but < 18% BC of C_{org} cannot cause the enrichment of the remaining SOM in the profiles (Acksel et al., 2016). In this context, natural steppe vegetation also is unlikely to be the source of SOM enrichment in the Baltic Chernozems, because pollen analysis from Schmitz (1955) showed that forest was already the dominant natural vegetation during

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the Early Holocene and there are no indications of tall-grass steppe in the southern Baltic region during the Preboreal. In this line Eckmeier et al. (2007) concluded that not all soils classified as Chernozems reflect the typical climate conditions of natural Central European Chernozems or steppe vegetation.

Various authors reported that different materials such as ashes, turf, organic waste and mineral soil material were used for soil amendment in Norway (Kvamme, 1982; Myhre, 2000; Rønneseth, 1974; Sølvberg, 1976). Humus-rich topsoils of the Jaeren region in SW Norway with high P contents indicate a strong anthropogenic influence in the Viking time, which points to earlier amelioration practices than those forming most Plaggic Anthrosols in Northwest Germany (Schnepel et al., 2014). Davidson and Simpson (1984) reported that such a combination of different materials formed humus-rich up to 75 cm deep topsoils in Orkney (Scotland), and they suggested a wide range of possible inputs from seaweed and sea sand to turfs after the usage for bedding cattle.

Soils, originating from human activities, are classified as Anthrosols with a terric hortic, plaggic, irragric, hydragric or pretic horizon (thickness > 20 cm; IUSS Working Group WRB, 2014). All these soils have similar humus-rich topsoils, despite different climate conditions, soil tillage and application of different types of organic manure. Examples including Anthrosols in Germany (Gerlach et al., 2012, 2006; Lauer et al., 2014; Wiedner et al., 2014), Norway (Schnepel et al., 2014) and Brazil (Glaser et al., 2001, 2000; Liang et al., 2006; Solomon et al., 2007) visually resemble the humus rich topsoils of the Baltic Chernozems. Identifying the sources of added organic matter is a key to understand the formation of these soils.

One possibility to investigate the organic matter source is to measure the stable isotope composition, because the isotope distribution pattern of soils differ in natural systems (Schoenau and Bettany, 1989), mainly affected by vegetation (Freney and Williams, 1983; Krouse, 1989). For example, S isotope ratios in native and cultivated Chernozems (grass: − 2.7‰, Ah: − 1.4‰; wheat straw: − 1.7‰, Ap: − 4‰), Gleysol (grass: − 5.4‰, Ahe: − 7.3‰; persicaria: − 2.1‰, Ap: − 5.2‰) and Luvisol (leaves, grass, moss: + 3.2‰, Ae: + 1.7‰; barley straw: + 2.5‰, Ap: + 1.1‰) in Canada reflected the $\delta^{34}S$ abundance of their predominant vegetation (Schoenau and Bettany, 1989). A long-term field experiment showed a relative enrichment of $\delta^{34}S$ in soils after the application of peat which was explained by the fact that peat was more enriched in $\delta^{34}S$ than other organic materials and was more resistant to decomposition (Kirchmann et al., 1995). This means that the abundance of stable S isotopes in the soil organic material can reveal the source of the organic matter in the Baltic Chernozems.

The mere natural formation of Chernozems in Central Europe was doubted since the late 1990s. Using ^{14}C dating of bulk soil samples (Kleber et al., 2003) determined the main period of Chernozem formation between 6000 and 4200 BP in Central Europe. Recent luminescence datings with 4270 ± 330 supported a termination of Chernozem formation at the same period of time (Kühn et al., 2017). Striking was the occurrence of many Chernozems close to Neolithic settlements (Gehrt, 2005). Complementary, Gerlach and Eckmeier (2012) and Gerlach et al. (2012) found black soils in association to anthropogenic pits in the Rhineland dating to the Neolithic (6400 to 4200 BP). Thus, it has been discussed recently, that the close spatial association of Chernozems with settlements of the Neolithic period may indicate an anthropogenic formation of these soils (Gehrt, 2005; Kleber et al., 2003; Lorz and Saile, 2011). The time period, in which the Baltic Chernozems were formed, is unknown because the AMS ^{14}C ages of 1540 to 1415 BP were determined in bulk soil samples at the island of Poel (Albrecht and Kühn, 2011). Since the bulk samples of mollic horizons are essentially affected by the incorporation of recent organic material into the SOM at 35 to 80 cm, e.g. by bioturbation or rooting (Pessenda et al., 2001; Scharpenseel et al., 1986), it can be assumed that these soils are older than 1540 years BP. One possibility for determining a more precise maximum age is the extraction of the humin fraction in order to remove the recent organic material. AMS ^{14}C datings of soils showed that the humin fraction was older by factor 1.2 to 1.7 than the corresponding age of the bulk SOM (Pessenda et al., 2001; Scharpenseel et al., 1986).

The objectives of the present study were (i) to analyze the pyrogenic organic carbon content of further soil profiles in addition to the profiles at the island of Poel and Sjaelland from Acksel et al. (2016) by qualitative and quantitative BC analyses and non-targeted bulk SOM mass spectrometry, (ii) to examine sources of enriched SOM in the Axh-horizons by stable isotope signatures ($\delta^{34}S$), and (iii) to estimate the age of SOM by AMS ^{14}C dating in order to establish the beginning of the Axh-horizon formation for all humus-rich soil profiles in the Baltic Sea area.

2. Material and methods

2.1. Study areas and soil sampling

The Baltic Chernozems are located at the island of Poel in the Wismar bay (54°0′N, 11°26′E), at the island of Fehmarn in the Lübeck bay (54°22′ N, 11°5′ E) and at the island of Sjaelland of Denmark (55°30′ N, 11°49′ E) (Fig. 1). Pyrogenic organic matter so far has been determined only in soils from Poel and Sjaelland (Acksel et al., 2016). Since soils at the island of Fehmarn were classified as Chernozems but not represented in our previous investigation we sampled two Chernozems profiles at the island of Fehmarn at Westermarkelsdorf (F-8) and Gahlendorf (F-9). The purpose was to quantify the BC content by BPCA and analyze the SOM by Py-FIMS and compare these data with the previously investigated Chernozem profiles at the island of Poel (P-1, P-2, P-3, P-4, P-5), Sjaelland (S-7) (Denmark) and the profile in Großenbrode at the peninsula Wagrien near the island of Fehmarn (F-6) (Acksel et al., 2016). From each profile the samples were taken from the top Ah/Ap- (0–35 cm) and the underlying Axh-horizons (26–75 cm). Three samples were taken from each horizon and combined for analyses. The German soil description system (Ad-hoc-AG Boden, 2005) has been used to differentiate the diagnostic mollic horizon of Chernozems according to the WRB (2014) into the upper Ah = humus-enriched and non-tilled, Ap = humus-enriched, periodically tilled arable topsoil horizon, and the underlying Axh = biogenically mixed (bioturbation mostly by earthworms), humus-enriched topsoil horizons that are typical for Chernozems.

2.2. Sample pretreatment and basic soil characteristics

For chemical analyses, the samples were air-dried (60 °C) and sieved < 2 mm. Basic soil characteristics (pH, texture) were determined according to standard procedures (Blume et al., 2011). After ball-milling for 10 min, finely ground subsamples were used for determinations of total C-, N- and S-contents (VARIO EL analyzer; Elementar Analysensysteme GmbH, Hanau, Germany). The humin fraction was separated by extracting 25 g soil of the Axh-horizons with 500 ml 0.1 M NaOH, shaking overnight, centrifuging at 1560 g for 15 min and freeze-drying (Khan and Sowden, 1971). Soil color of < 2 mm-samples was determined using a Konica Minolta CR410 chromameter (28,217 Bremen, Germany). The applied measurement technology and system (L*a*b) for the determination of the soil color were described in detail, e.g. by Acksel et al. (2016).

2.3. Quantification of benzene polycarboxylic acids (BPCAs)

The BC content was quantified by the $BPCA_S$ method after (Glaser et al., 1998), which was modified by (Brodowski et al., 2005) and (Kappenberg et al., 2016). This method previously has been applied to the profiles of the Baltic Chernozems at Poel, Sjaelland and Großenbrode of Acksel et al. (2016).