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Chernozem properties of Black Soils in the Baltic region of Germany as revealed by mass-spectrometric fingerprinting of organic matter

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ABSTRACT

Black Soils with dark-coloured, mollic horizons occur in the Baltic region of Germany and their classification as Chernozems was previously discussed. Mollic topsoil horizons are diagnostic for steppe soils. We therefore hypothesized that the molecular characterization of soil organic matter (SOM) by pyrolysis-field ionization-mass spectrometry (Py-FIMS) is suitable to identify similarities between the Black Soils and Chernozems as well as soils from other major soil groups with mollic horizons or otherwise high SOM content. Data were collected from a set of 341 topsoil samples and analysed based on 139 Py-FI mass spectra and thermograms. The OC content in Black Soils reached high values matching those of Haplic Chernozems from Germany and typical steppe climate ecosystems. Arable soil use converted Ah horizons to lighter-coloured Ap horizons that nonetheless had a similar or higher OC content than underlying Ah horizons. Arable soil use led to less stable SOM as indicated by a higher percentage of volatilized organic matter (VM) upon pyrolysis. Furthermore, VM was especially high (21–52%) for redoximorphic soils, whereas it ranged between 5.1 and 15% in the Black Soils, Chernozems and other steppe soils such as Phaeozems or Kastanozems. Assignment of marker signals from Py-FI mass spectra to the compound classes revealed that Black Soils, all Chernozems and other steppe soils had more phenols and N-containing compounds but less sterols and suberin than most of the other soil groups investigated. The percentage of volatilized organic matter (VM) – with low values hinting at SOM stabilization in soil – ranged from 5 to 52%. It was especially high for redoximorphic (21%) and organic soils (52%), whereas it ranged between 5.1 and 15% in the Black Soils, Chernozems and other steppe soils. Principal component analysis unravelled the SOM composition patterns of different soils and showed that the Black Soils clustered together with typical Chernozems, while soils of other units differed. This indicates that sources and especially humification pathways of SOM were different in these soils compared to Black Soils and Chernozems. Notably, this was the case for Colluvic soils (=Colluvic Regosols), redoximorphic soils (e.g. Gleysols, Stagnosols), Luvisols and Phaeozems, although colluviation, influence of ground- or stagnant water, and clay migration were found in several Black Soils as well. Our findings do not support a strong, direct influence of colluviation and perched water on the SOM composition in the mollic horizons of Black Soils. The data also show that the Chernozem-specific SOM formation and clay migration, as in Luvisols and Phaeozems, are temporally discrete processes. The results underline that Chernozem formation in Central Europe is a relic process and is not only due to steppe ecosystem conditions. Rather, it depends on parent substrate properties, especially clay and carbonate content, secondary carbonate input and anthropogenic soil use. These factors preserved or even regraded the relic Chernozems since the Atlantic stage.

1. Introduction

Soils with humus-rich, black-coloured topsoil horizons occur in the near-coastal Baltic region of northeast Germany, i.e. the islands of Fehmarn and Poel (Janetzko and Schmidt, 1996) as well as the Uckermark region (Janetzko and Schmidt, 1996), and southwest of Szczecin (Poland) (Altermann et al., 2005). While these soils have been termed "Tschernosems" by Schucht (1930) and von Bülow (1938) following the genetic German classification system, other authors doubt this classification (Stremme, 1958) or used the provisional term "Black Soils", thus underlining the still open discussion (Albrecht and Kühn, 2011). The term Black Soils is also used in this study. The major property and diagnostic horizon of the Black Soils are the deep, dark, humus-rich, mollic topsoils. These are well-mixed into depth, exceeding today's ploughed layer (about 35 cm), by bioturbation that includes krotovinas in the subsoil. These topsoils developed from carbonaceous marl at

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Fehmarn and Poel (Albrecht and Kühn, 2011; Schimming and Blume, 1993) and from basin silt at Uckermark (Fischer-Zujkov et al., 1999). They often overlie relatively clay-rich and compacted (bulk density > 1.8 kg dm^{-3}) glacial till with stagnating water (Schimming and Blume, 1993). Thus, many of the soil profiles show redoximorphic properties in the subsoil. Moreover, argillic subsoil horizons occasionally show clay coatings from clay covered with humus, indicating soil degradation to Luvic and/or Stagnic Chernozems and Phaeozems (Albrecht and Kühn, 2011; Fischer-Zujkov et al., 1999). This has been reported for Fehmarn and the Uckermark region (Fischer-Zujkov et al., 1999; Schimming and Blume, 1993), whereas illuviation of humus-free clay preceded Chernozem and Phaeozem formation on Poel Island (Albrecht and Kühn, 2011).

The above-described observations from field studies are difficult to align with the commonly accepted views on Chernozem formation because parent material, climatic conditions and consequently the natural vegetation in the Baltic region are atypical for Chernozem landscapes. Typical conditions are delineated by the World Reference Base of Soil Resources (WRB) as mostly aeolian and re-washed aeolian sediments (loess) found in regions with a continental steppe climate typically vegetated by tall-grass vegetation (IUSS Working Group WRB, 2006a). The classification of the AC soils in northeast Germany as belonging to Chernozems is therefore controversial. On one hand the climate in the studied soil regions is relatively dry with a mean annual precipitation (MAP) ≤550 mm, as typical for steppe areas around the world (Table 1). On the other hand, the winter temperatures are substantially higher and the summer temperatures are lower than in typical steppe areas. Furthermore, forest apparently dominated during the Preboreal at Poel Island (Albrecht and Kühn, 2011) and no hints of steppe vegetation were found at Fehmarn (Schmitz, 1955). It remains unclear whether steppe or forest vegetation predominated during the early Holocene warming periods in the overall German Chernozem soilscapes (e.g., Eckmeier et al., 2007; Lorz and Saile, 2011). The conclusion has been that the investigated Black Soils are not Chernozems (Stremme, 1958), and that their formation cannot be explained by the genetic theory of Chernozem formation, defining Chernozems as typical zonal soils of the steppe climate and vegetation (Albrecht and Kühn, 2011). It is generally accepted today that German Chernozems are relic soil formations even though they have a morphology similar to recent Chernozems elsewhere (Altermann et al., 2005; Eckmeier et al., 2007; Lorz and Saile, 2011; Zakosek, 1962). German Chernozems developed during the early Holocene warming periods up to the Atlantic stage, when the climate was more continental than today (Albrecht and Kühn, 2011). Recent discussions also point out that Chernozem formation in Central Europe was due not only to the impact of steppe climate and vegetation (Altermann et al., 2005; Eckmeier et al., 2007; Lorz and Saile, 2011). Rather, Chernozem formation and preservation or even the regradation of previously degraded Chernozems is probably closely related to land use by humans. Major activities in this context are the clearing of forests that naturally developed during the Atlantic stage to a steppe-like vegetation, facilitating bioturbation by soil tillage, and adding black carbon (BC) and BC ashes to soil by burning the steppe vegetation (Altermann et al., 2005; Eckmeier et al., 2007; Gerlach et al., 2006). Schmidt et al. (1999) and Rodionov et al. (2006) confirmed this by showing that BC frequently occurs in Chernozem soils. Eckmeier et al. (2007), for example, concluded that bandceramic settlements strikingly coincided with the abundance of Chernozem in Central Europe. Although it is generally accepted that human soil use since the Neolithic period strongly affected the persistence of relic Chernozems, this effect appears to be less dominant than previously assumed. Lorz and Saile (2011) conclusively argued that the distribution of Chernozem and bandceramic settlements cannot be the primary reason for Chernozem formation in Central Europe.

Also, adding secondary carbonate preserved or even regraded Chernozems. For the Black Soils in the Uckermark region, such regradation was attributed to input of secondary carbonate by erosion and calcification from interflow (Fischer-Zujkov et al., 1999). Accepting this as the major reason for Chernozem formation would limit Chernozem soils to land depressions, whereas Black Soils in the Baltic region occur at all positions of the undulating landscape. A further argument for humus accumulation and/or preservation is the influence of high soil moisture from stagnant water and surface-near groundwater (Fischer-Zujkov et al., 1999). This led to Black Soils being termed "Feuchtschwarzerden" (Gleyic/Stagnic Chernozems; Schimming and Blume, 1993) equivalent to soils in the Hildesheimer Boerde, Germany (Bartels et al., 1973). This is supported by the fact that 40% of the Black Soil area at Poel is characterized by the influence of stagnant and groundwater (Albrecht and Kühn, 2011). Correspondingly, Fischer-Zujkov et al. (1999) identified Black Soils along slopes of basins and valleys and associated with redoximorphic fen soils in the Uckermark region.

The diagnostic features of Chernozem and other steppe soils are mollic horizons with an elevated SOM content (IUSS Working Group WRB, 2006a), especially with high molecular weight humic substances, stabilised in organo-mineral associations (Schulten and Leinweber, 2000). The present study therefore hypothesizes that a detailed molecular characterization of SOM by pyrolysis-field ionization-mass spectrometry (Py-FIMS) is especially suited to unravel similarities between the Black Soils from the Baltic region of Germany and soils from other major soil groups with mollic horizons or otherwise high SOM contents. We attempt to answer the following detailed questions:

i. Do Black Soils and Chernozems as well as other steppe soils such as Phaeozems and Kastanozems have a similar and typical SOM composition and
ii. does this SOM composition distinguish them from other soils rich in organic matter a) with similar pedogenesis (Eutric Cambisols, Rendzic Leptosols, Calcaric Regosols), b) completely different soil formation (Podzol-Bh horizons), c) with differently and specifically stabilized SOM (Andosols, Vertisols), or d) with anthropogenic accumulation of organic matter (Plaggic Anthrosols, Colluvic Soils, Technosols)?
iii. Is the influence of high soil moisture (free ground- or stagnant water) relevant for the formation and preservation of Black Soils in the Baltic region so that they have an SOM composition similar to that of strongly water-influenced soils (Stagnosol, Gleysol, Histosol)?
iv. Does long-term agricultural land use degrade or, vice versa, preserve or even regrade Chernozems, specifically their SOM composition (natural vs. arable land)?
v. Methodologically the aim was to investigate whether Py-FIMS analysis of SOM composition can be used to support the subdivision of soil samples, in the present case of steppe soils with mollic soil horizons. To this end, Py-FI mass spectra and thermograms of Black Soils from the islands of Fehmarn and Poel and the Uckermark region were compared with those of other soils using a comprehensive data base and multivariate statistical, principal component analysis.

2. Materials and methods

2.1. Soil samples

Samples were collected from Chernozem soils and other major soil groups (according to WRB; (IUSS Working Group WRB, 2006a)). The selection covers a representative range of Chernozems from different climatic regions and other soils with mollic horizons or otherwise humus accumulation. A total of 341 soil samples were investigated (Table 1). The sample set contained soils with natural steppe vegetation and soils of arable land in use for more than a century. Black Soils from the near-coastal Baltic region of northeast Germany originated from four soil profiles on Fehmarn Island (Großenbrode, Blieschendorf, Sahrensdorf, Petersdorf; Schleswig-Holstein; Schimming and Blume, 1993), five profiles on Poel Island (Vorwerk, Malchow, Niendorfer Hof; Mecklenburg-West Pomerania; Albrecht and Kühn, 2011), and