



Investigation of vegetation history of buried chernozem soils using near-infrared spectroscopy (NIRS)



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ABSTRACT

The environmental conditions of the evolution of chernozems in Central Europe have not been satisfactory explained. In this paper, seven buried chernozems were investigated using near-infrared spectroscopy (NIRS) in order to get information about the former vegetation cover. Near-infrared (NIR) data were collected from organic matter of recent natural grasslands and forests. The spectra from these two groups of soils were perfectly discriminated by a multivariate statistical analysis. The statistical model was applied on the buried soils. There are four types of vegetation development within the chernozems before the burial. Comparison to other paleoenvironmental proxies shows no major contradiction and confirms the potential of the NIRS as a paleopedological proxy. The identified changes of vegetation are from grassland vegetation to forest vegetation and vice versa. These changes bring new data to the discussion about the pedogenesis of chernozems. According to the radiocarbon dating, buried soils developed and were preserved not only in the Preboreal and the Boreal, but also in later phases of the Holocene.

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1. Introduction

There are many unanswered questions about the environmental conditions of the pedogenesis of chernozems. The first attempt to describe these environmental conditions was made by Dokuchaev (1883), who described chernozem as a typical soil of steppe biomes. This definition has been questioned many times and there were various nuances suggested to this characterization (Gehrt et al., 2002; Eckmeier et al., 2007; Lorz and Saile, 2011; Gerlach and Eckmeier, 2012).

According to the WRB (FAO et al., 2006), a chernozem is a soil with a thick black surface layer that is rich of organic matter. Many chernozems correspond to: calcareous Black Soils and Kalktschernoseme (Germany); chernosols (France); eluviated black soils (Canada); several suborders (especially Udolls) of the mollisols

(United States of America); and chernossolos (Brazil). The parent materials are mostly, but not exclusively, aeolian and re-washed aeolian sediments (loess). They are situated in areas of continental climate with cold winters and hot summers, which are dry at least in the late summer. The terrain of these areas is flat or consists of undulating plains with tall-grass vegetation. A typical profile presents a dark brown or black mollic (or chernic) surface horizon. In many cases, there is a cambic or argic subsurface horizon with secondary carbonates or with a calcic horizon in the subsoil. Chernozems are considered to be very fertile, and most of them around the world are cultivated.

Eckmeier et al. (2007) reported a review of 19 chernozems developed in the Holocene, eleven under steppe, five under forest, and three under forest-steppe. The discrepancy between the traditional definition of chernozem (FAO, ISRIC, ISSS, 2006; Altermann et al., 2005) as a steppe soil and the presence of chernozems in zones which are suitable for the existence of temperate forests (Scheffer and Meyer, 1963, 1965; Rohdenburg and Meyer, 1968; Roeschmann et al., 1982; Schlich, 1981; Ehwald et al.,

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1999) leads to the following question: is vegetation the crucial factor in the pedogenesis of chernozems (Ehwald et al., 1999; Vysloužilová et al., 2014)? Consequently, are chernozems able to persist or even to develop under forest vegetation (Eckmeier et al., 2007)?

Alexandrovskiy (2000) observed in Caucasus that chernozems had degraded into luvisols 3000 years after the forest encroachment. However, a second humus horizon and paleokrotovinas have persisted in former chernozems. In Siberia, Andreeva et al. (2011) used lipid biomarkers for the reconstruction of the vegetation of chernozems. They found in the deeper part of the A horizon a higher nC27/nC31 ratio, indicating that chernozems did not develop exclusively under grass steppe. In this study, our aim is to develop a new proxy in order to produce innovative data about the vegetation that covered chernozems during the Holocene.

Some paleosols of the Holocene buried under colluvium present many similar attributes to chernozems: thick dark humic horizon, carbonated substratum, krotovina, etc. (Dreibrodt et al., 2013; Zádorová et al., 2013). Nevertheless, they may have undergone some sharp post-depositional changes (Gerasimov, 1971), including carbonate leaching or reprecipitation, or organic matter mineralization. For example, there is no calcic horizon in the palaeo-relict chernozem described by Reuter (2000). That is why paleosols do not always fit within the WRB classification which is dedicated to functional soils. Despite some transformations, they can provide evidence about environmental changes in the past. For our study, the key point is the preservation of the soil organic matter (SOM) which contains information about former vegetation.

Until now, the vegetation history of chernozems has been derived from different proxies. The palynological evidence of former vegetation in the chernozem areas is taken from sediments of peats or lakes that are close to these chernozem areas (Havinga, 1972; Svobodová, 1997). There are no data from the soil itself, because biologically active soils do not have the capacity to preserve pollen. The distribution of chernozems in Central Europe has a patchy character (Eckmeier et al., 2007), so it is not possible to attribute specific pollen data to a specific soil type. The palynological evidence does not exclusively reflect the vegetation of chernozems.

In contrast to pollen analysis, malacological, phytolith (Bartoli and Guillet, 1977), and charcoal assemblages can provide information about local vegetation. A number of malacological analyses have been applied in studies of loess series in the Pleistocene (Ložek, 2001; Antoine et al., 2013) and also in a study of colluvium sections in the Holocene (Ložek and Smolíková, 1978). The main proxy is usually a model of the vegetation cover. The results of most malacological studies confirm chernozem as a steppe soil. Studies of phytoliths in chernozems are rare. Studies of buried chernozems in Russia revealed an occurrence of grassland that is followed by steppe-forest vegetation in the Subboreal and Subatlantic (Khokhlova et al., 2001). Barczy et al. (2009) found an assemblage of phytoliths in a buried chernozem which can be interpreted as evidence for steppe vegetation with some isolated tree species. On the other hand, the functional steppe chernozem recently analyzed for a content of phytolith by Petó (2013) shows no trace of any forest vegetation. Pedoanthracological studies of chernozems are rare and come from archeological research near the Linearbandkeramik settlements (Beneš, 2008; Kreuz, 2008; Moskal del Hoyo, 2013). The study of charcoals extracted from the buried soil revealed *Pinus* sp. and *Larix* sp. growing on the Pleistocene chernozems, and the presence of *Quercus* sp., *Ulmus* sp., *Alnus* sp., *Pinus* sp., Betulaceae, and Maloideae on the Holocene chernozems (Vysloužilová et al., 2014).

Near infrared spectroscopy (NIRS) represents a tool which is able to distinguish the origin of soil organic matter (SOM) according to the type of vegetation, such as grassland or forest (Ertlen, 2009; Ertlen et al., 2010). The qualitative analysis of near infrared spectra shows

the current and the past origin of the SOM. It provides a local signal about the local environment (as with other proxies found in soils). The NIR absorbance spectra measured in soils contain information that comes from the overtones of vibration, from stretching and bending of chemical bonds in the organic materials (Brunet et al., 2007). It is often considered for a fingerprint of the SOM (Palmberg and Nordgren, 1996). Some parts of the SOM have been able to persist in functional chernozems for thousands of years, especially in the deep horizons (Scharpenseel and Pietig, 1970; Guillet, 1979). The NIRS analysis of the SOM mirrors current and past ecosystems.

In this paper, buried soils preserved by later Holocene sediments from the Czech Republic and France are investigated (Fig. 1). The goal of this study is to determine the vegetation cover before the burial or at the moment of the burial, so that the kind of vegetation cover can be reconstructed. For this purpose, buried soils from five areas were sampled and investigated by the NIRS method.

2. Methods

2.1. Analysis of soil organic matter by NIRS

NIRS is used to identify the kind of vegetation that the SOM comes from (Ertlen et al., 2010). This qualitative method is based on comparison of a near infrared spectrum of a sample with an unknown origin with a sample from the reference spectral library. The reference spectral library has been created on basis of samples from topsoil horizons that are covered with well-known vegetation.

2.1.1. Construction of the NIRS reference spectral library

The NIR spectral reference library of chernozems had not existed before, so first it was necessary to set up such a library that would be based on chernozems with well-known vegetation cover. For this purpose, topsoil samples from chernozems or other soils on loess were collected in various forests and grasslands.

The sites of sampling were chosen accordingly to the stability of their vegetation, so that a pure spectrum could be guaranteed. Because the mean residence time (MRT) is very low in the topsoil (often less than 50 years in the 0–5 cm layer), the vegetation is considered as stable if it has not changed for the past 150 years at least (Ertlen et al., 2010). The top 5 cm of the soil contain at least 95% of the SOM which originates from current vegetation.

2.1.2. Spectra acquisition and analysis

Dried and sieved samples from topsoil and buried soils were placed in a rotating cup (diameter 9 cm) and scanned in the wavelength range of 10 000 to 4000 cm⁻¹ with a 2 cm⁻¹ resolution using an FT-IR Frontier Spectrometer (PerkinElmer, USA) with a CaF₂ beam-splitter, an integrating sphere and an InGaAs detector. Each spectrum was measured out of the average of 99 scans of different subsamples on a surface of circa 1 cm². This way of measuring was possible due to the rotating cup. The measured reflectance (R) was transformed into the absorbance (A) using the following equation:

$$A = \log_{10}(1/R)$$

The resulting data matrix with 3001 columns was averaged on 8 cm⁻¹ in order to reduce the data matrix to 751 columns. This reduction has two goals: elimination of some uncertainty and reduction the data matrix to a number that is manageable for the discriminant analysis (Ertlen et al., 2010). The data matrix was standardized by Standard Normal Variate (SNV) function (software Unscrambler 10.3). The standardization provides the subtraction of the average absorbance of the spectra range from all the spectra. This transformation is expected to reduce the influence of the

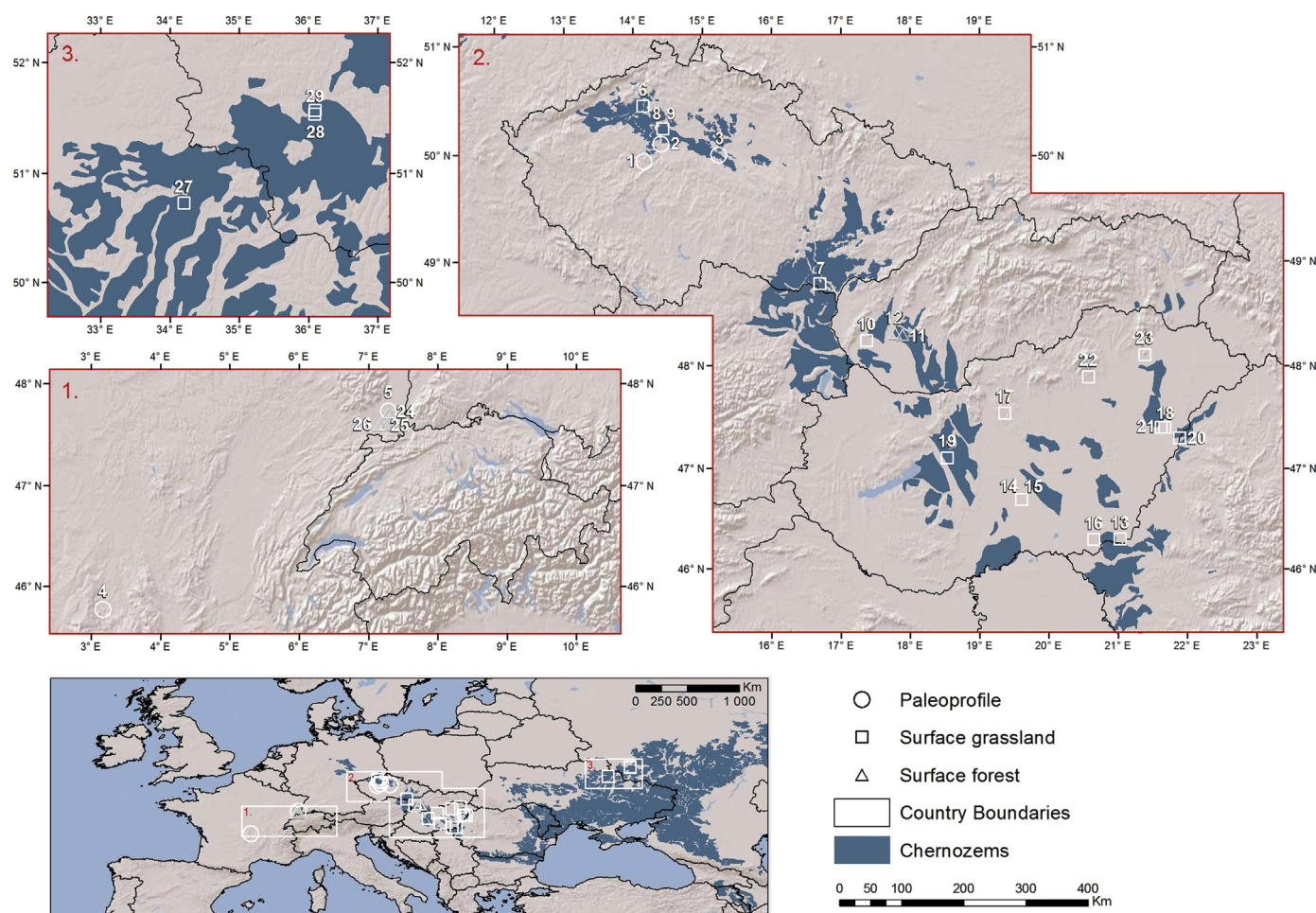


Fig. 1. Locations of the examined sites: 1–5 the studied buried chernozems (1-BRE, 2-BUB, 3-KOL, 4-CPB, 5-MOR); 6–29 surface sites used for the construction of reference library (6-BRO, 7-BUL, 8-KOC, 9-KOR, 10-SEN, 11-BAB, 12-SEN, 13-HUB, 14-HUU, 15-HUUD, 16-HUC, 17-HUM, 18-HUS, 19-HUG, 20-HUP, 21-HUH, 22-HUR, 23-HUT, 24-CAR, 25-HIR, 26-DID, 27-MIK, 28-KUR, 29-STR).

quantity of organic matter and of the heterogeneity of particle size distribution (Barnes et al., 1989; Shenk et al., 2001). The transformation is also useful to highlight the qualitative information contained in the spectra. Afterwards, first derivatives were applied on standardized data matrix in order to extract more useful information (Shenk et al., 2001).

The aim of dealing with spectra is to determine the origin of the SOM (grassland or forest). The multiple discriminant analysis is applied as described by Ertlen et al. (2010) and Viscarra Rossel and Webster (2011). The number of variates plus the number of groups must be less than the number of individuals. That is why the size of data matrix must be reduced. The segment of spectra between $10,000\text{ cm}^{-1}$ and 7304 cm^{-1} was removed because it shows no relevant information. Consequently, a matrix of 447 rows (number of samples) and 415 columns (wavenumber bands) was obtained. This matrix is divided in two sub-matrices: one for the grassland with 312 rows and one for the forest with 135 rows.

In the second step, the discriminant function calculated from the reference library is applied on the unknown spectra collected from buried chernozems. The comparison of values of the unknown data enables an interpretation of the origin of the SOM.

2.2. Sample preparation and analysis

Between 15 and 30 samples of ~50 g were collected at each reference site from the topsoil (0–4 cm). The samples were

taken every 2 m in a steel cylinder. Samples of ~50 g were also taken at every 5 cm depth from each buried soil. The samples were dried in the oven at $40\text{ }^{\circ}\text{C}$ and sieved to pass through a 2 mm mesh.

Particle-size distribution was measured with a laser granulometer (type Beckmann-Coulter LS230). Before the measurement of particles size was made, the samples had been treated by H_2O_2 to destroy the SOM. The samples had been also washed by KCl, distilled water and sodium hexametaphosphate to deflocculate the aggregates without destroying the carbonates.

The organic carbon was measured with the wet oxidation method (Walkey and Black, 1934). The content of carbonate was quantified by measuring the volume of CO_2 lost in the reaction with HCl in a closed atmosphere.

2.3. Radiocarbon dating of the SOM

One or several thin layers (about 5 cm) were collected at several depth within the A horizons in order to measure the radiocarbon age (Fig. 1). In buried soils, the radiocarbon age is the sum of mean residence time (MRT) at the moment of burial and the duration of burial (Guillet, 1979). The MRT of soil organic matter from the sites of Kolín, Bubeneč, Morschwiller-le-Bas, and Bresnice were measured after removal of carbonates from the samples in the Laboratoire de Mesure du Carbone 14, Gif sur Yvette in France. The MRT of the site of Clermont-Ferrand was measured following the

same protocol in the Poznań Radiocarbon Laboratory in Poland. The radiocarbon ages of the SOM were not calibrated because the measured value is an average of various organic components of heterogeneous ages.

3. Regional setting

3.1. Reference library

As chernozems in Central Europe are mostly exploited as agricultural land, it was very difficult to find chernozems covered by stable natural or semi-natural vegetation. The sites fulfilling this characteristic were often found in some nature protected areas. As detailed in Table 1, the convenient sites of grassland vegetation were found in the Czech Republic, Ukraine (Jelenska et al., 2008), Russia (Khitrov et al., 2013; Wiesbauer et al., n.d.) and Hungary (Wiesbauer et al., n.d.; Nagy et al., 2007; Virágh et al., 2008; Horváth, 2010). Chernozems under forest were found in the southeast Czech Republic (SCHKO Pálava, 2006) and Slovakia (Stanová and Valachovič, 2002). The reference library was completed with topsoils from some soils with a mollic horizon (rendzina, calcic cambisols) and with luvisols on loess (Ertlen, 2009; Vyslouchilová et al., 2014).

The information about the land use in the past and about the vegetation was acquired from the second military survey, which had been done in the Austrian Empire in Bohemia (1842–1852), Moravia (1836–1840), and Slovakia and Hungary (1819–1869). The second military survey is available on the internet (www.mapy.cz, www.archivportal.arcanum.hu). The sites found in France are documented in the Cadaster survey (1760) and in the Archives of National Forest Office (1860 to present) (Ertlen and Schwartz, 2010). The history of the sites in Russia and in Ukraine was acquired from the literature (Jelenska et al., 2008; Khitrov et al., 2013).

3.2. Buried soil profiles

The locations of the sites of this study are shown in Fig. 1.

3.2.1. Clermont-Ferrand – labeled as CPB (45°46' N, 3°10'E, alt. 352 m)

This site is located in the region called Terres Noires de Limagne (Black Soils of Limagne). In this area, chernozems occur mixed with other types of organic soils (Bornand et al., 1968). Due to the specific climate and lithological conditions, this area is the only one in France where “chernosols” are present according to the French classification (Legros, 2007; Baize and Girard, 2008). The area of

Table 1
Sites used for construction of the NIRS reference library.

Site	Country	Code	Vegetation	Plant species	Soil type	Parent material
Babský les	Slovakia	BAB	Forest	<i>Quercus cerris</i> , <i>Acer campestre</i> , <i>Ulmus laevis</i> , <i>Sorbus torminalis</i> , <i>Carpinus betulus</i> , <i>Cornus mas</i> , <i>Crataegus monogyna</i> , <i>Fraxinus excelsior</i>	Chernozem	Loess
Battonya-Gulya Gyep	Hungary	HUB	Grassland	Rubiaceae, Poaceae, Ranunculaceae, Fabaceae, Apiaceae, Rosaceae	Chernozem	Loess
Brozany	Czech Republic	BRO	Grassland	Poaceae	Chernozem	Loess
Bugac pusztá	Hungary	HUUD	Grassland	Poaceae, Fabaceae, Lamiaceae, Plantaginaceae, Boraginaceae, Convolvulaceae, Asteraceae	Chernozem – arenic hydromorphe	Loess (sandy)
Bugac pusztá – dune	Hungary	HUU	Grassland	Poaceae, Fabaceae, Lamiaceae, Plantaginaceae, Boraginaceae, Convolvulaceae, Asteraceae	Chernozem – arenic	Loess (sandy)
Bulhary	Czech Republic	BUL	Forest	<i>Fraxinus excelsior</i> , <i>Quercus sp.</i> , <i>Acer campestre</i> , <i>Crataegus monogyna</i>	Chernozem	Loess
Czikopuszta	Hungary	HUC	Grassland	Poaceae, Lamiaceae, Rubiaceae, Convolvulaceae	Chernozem	Loess
Gallenhölzchen	France	DID	Forest	<i>Quercus sp.</i> , <i>Fagus sp.</i> , <i>Carpinus sp.</i> , <i>Prunus avium</i> , <i>Acer sp.</i> , <i>Corylus sp.</i> , <i>Ulmus sp.</i> , <i>Hedera</i>	Calcic cambisol	Loess
Dubník	Slovakia	DUB	Forest	<i>Quercus sp.</i> , <i>Cornus mas</i> , <i>Acer campestre</i> , <i>Tilia platyphyllos</i>	Chernozem	Loess
Godolo hills – Szarkabérki valley – steppe	Hungary	HUG	Grassland	<i>Brachypodium pinnatum</i> , <i>Bromus erectus</i> , other Poaceae	Chernozem	Loess
Hajdubágos	Hungary	HUH	Grassland	Poaceae, Apiaceae, Rosaceae, Asteraceae, Fabaceae, Rubiaceae, Joncaeeae	Chernozem	Loess (sandy)
Breiholtz	France	HIR	Forest	<i>Fagus sp.</i> , <i>Quercus sp.</i> , <i>Acer sp.</i>	Calcic cambisol	Loess
Kopeč-rendzine	Czech Republic	KOR	Grassland	Poaceae, <i>Echinops sp.</i> , <i>Achillea millefolium</i> , <i>Melampyrum arvense</i> , <i>Fragaria sp.</i> , <i>Festuca pallens</i>	Rendzine	Loess
Kopeč-chernozem	Czech Republic	KOC	Grassland		Chernozem	Loess
Kursk	Russia	KUR	Grassland	Rubiaceae, Poaceae, Ranunculaceae, Fabaceae, Apiaceae, Rosaceae	Chernozem	Loess
Mezoföld – Belsőbarand-valley	Hungary	HUM	Grassland	<i>Brachypodium pinnatum</i> , other Poaceae, Lamiaceae, Asteraceae, Fabaceae, Rubiaceae, Apiaceae, Apiaceae	Chernozem	Loess
Mikhajlovskaja celina	Ukraine	MIK	Grassland	<i>Stipa sp.</i> , <i>Galium sp.</i> , cf. <i>Padus racemosa</i> , <i>Aguimonia eupatoria</i> , <i>Trifolium sp.</i> , <i>Achillea millefolium</i>	Chernozem	Loess
Poscay	Hungary	HUP	Grassland	Poaceae, Lamiaceae, Apiaceae, Scrophulariaceae, Rubiaceae, Caryophyllaceae, Brassicaceae, Clusiaceae, Fabaceae, Asteraceae, Renonculaceae, Plantaginaceae, Campanulaceae, Liliaceae	Chernozem	Loess
Sarand	Hungary	HUS	Grassland	Poaceae, Lamiaceae, Boraginaceae, Cyperaceae	Chernozem – arenic	Loess (sandy)
Senec	Slovakia	SEN	Forest	<i>Quercus sp.</i> , <i>Acer campestre</i> , <i>Ulmus sp.</i> , <i>Crataegus monogyna</i> , <i>Fraxinus excelsior</i>	Chernozem	Loess
Stoeffelhag	France	CAR	Forest	<i>Fagus sp.</i>	Calcic cambisol	Loess
Streletsk	Russia	STR	Grassland	Poaceae, Compositae, Cruciferae, Rosaceae, Leguminosae, Labiatae, Lamiaceae	Chernozem	Loess
Tard	Hungary	HUR	Grassland	Poaceae – <i>Festuca rupicola</i> , Ranunculales, Plantaginaceae, Lamiaceae, Polygonaceae, Rosaceae, Convolvulaceae	Chernozem – luvic	Loess
Tokaj	Hungary	HUT	Grassland	Poaceae, Iridaceae, Asteraceae, Fabaceae, Santalaceae, Lamiaceae, Dipsacales, Euphorbiaceae, Apiaceae	Calcic cambisol	Loess

Terres Noires de Limagne is situated considerably distant from the core of the chernozem region in Central and Eastern Europe (Jones et al., 2005). Nevertheless, the local climate is continental and the parent material is stampian marls. The alteration of these lacustrine marls produces a highly carbonated limestone material similar to loess. In the former and in the current French classifications the definition of “chernosols” does not differ from the WRB definition (Baize and Girard, 2008). The series of buried soils in the east of Clermont-Ferrand – Petit Beaulieu were discovered during archeological research of a Bronze Age settlement (1900–1750 BC) (Thirault et al., 2013). The buried A horizon is dark and impregnated by the organic matter to more than 40 cm. It is covered by 130 cm of carbonated colluvium which has been developed as a result of agricultural erosion since the Iron Age at least. The archaeological pits dated from the Bronze Age were dug into the soil and filled with the same dark material. Consequently, it can be considered that the buried soil was already well developed in the Bronze Age. The top 25 cm of buried soil seem to have been probably transformed by the post Bronze Age ploughing, which may explain the lower rate of the organic matter. The C horizon shows the presence of plentiful krotovinas. The distribution of carbonate on the buried soil is difficult to interpret because there is an overlap of the ante- and post-burial processes.

3.2.2. Morschwiller-le-Bas – MOR (47°44'N, 7°17'E, alt. 275 m)

This buried soil was revealed during archeological research of a multicultural settlement. The site has the greatest evidence of the Horgen culture (ca. 3300–2700 BC) in the southern Upper Rhine valley. The beginning of the use of this buried soil probably correspond to the period of the Horgen culture and the use of this soil persisted perhaps the Bronze Age and La Tène periods (Vergnaud et al., in prep.). The dark A horizon is 45 cm thick. It is covered by a 95–110 cm thick layer of colluvium. The parent material of this soil is loess. Nowadays, the site is not situated in an area of chernozems.

3.2.3. Bubeneč – BUB (49°57'N, 14°9'E, alt. 196 m)

The buried soil in Prague-Bubeneč, situated in the heart of the chernozem region of Bohemia (Jones et al., 2005) was revealed during an archeological survey of a prehistoric multicultural settlement. The well structured buried dark A horizon is 55 cm thick and covered by 150 cm of sediments. The undulated surface of the buried soil corresponds to the Early Eneolithic (ca. 4200–3800 BC) (Maříková-Vlčková, unpublished). The C horizon is formed by loess and has some krotovinas.

3.2.4. Kolín – KOL (50°0'N, 15°14'E, alt. 205 m)

The site is situated in the Central Bohemian chernozem region (Jones et al., 2005), on the eastern part of the town of Kolín at the edge of the Elbe river floodplain. The Linearbandkeramik Culture (ca. 5500–4900 BC) settlement was established on this soil. The 70–90 cm thick buried A horizon is covered by 60 cm layer of colluvium. The parent material is loess. The soil was sampled at three spots called KOL1, KOL2, and KOL3. The distance between the spots is approximately 50 m.

3.2.5. Břesnice – BRE (49°56'N, 14°9'E, alt. 291 m)

The site of Břesnice is close to the village of Srbsko in Central Bohemia. This sedimentary sequence of the Holocene is formed of a chernozem described as the Boreal chernozem (Ložek, 1974). The sequence is also covered with two 120 cm thick subsequent layers of sediments. The A horizon of the buried soil has a massive structure that is grown through with pseudomyceliums. There are also many coarse elements and microcharcoals in this A horizon.

The C horizon is formed by reshaped loess. Nowadays, the soil cover of the surroundings is different.

4. Results

4.1. Soil analytical properties

The MRT is low in the topsoil (<100 years). Therefore, the radiocarbon dating of the SOM in topsoils of buried chernozems (Fig. 2) gives an approximation of the exact burial date. The thickness of buried A horizons varies between 40 and 80 cm, which indicates that the soils were probably not truncated. The pH varies between 7.7 and 8.3. The high content of CaCO₃ (>30%) in the profile of Clermont-Ferrand is caused by the content of CaCO₃ in the soil parent material (lacustrine marls). The buried soil of Břesnice is covered by a layer of calcareous swamp sediments that infiltrate to the buried soil with a chernic horizon. The organic C content of this buried chernozem is below or around 1%. The prevailing particle size fraction is silt or sand. The high ratio of the sand fraction does not match with the observation on the field and is probably caused by absence of decarbonization in the applied methodology. The aggregates are bound by carbonates that flocculate and create pseudosands (Vysloužilová et al., 2014). To avoid any confusion, we decided not to present the result of these particle size analyses. The analytical properties of buried soils are summarized in Table 2.

4.2. Reference library

The discriminant analysis of near-infrared spectra distinguishes two groups of soils without overlapping (Fig. 3): topsoils under forest and topsoils under grassland. The discriminant scores have an average of −2.84 for the soils under grassland. The average of discriminant scores of the soils under forest is 6.57. The difference between these two values (i.e. 9.41) is the Mahalanobis distance. This result confirms that the statistical model built from the reference library can be further applied to buried soils in order to recognize the vegetation origin of soil organic matter. This result confirms the potential of the NIRS, which can differentiate soils according to the vegetation origin of the SOM.

4.3. Application of the model to buried soils

The results of discriminant canonic function are shown in Fig. 4. The relationship between the relative depth (i.e. 0 = top of the palaeosol) and the canonical discriminant function is represented for each buried soil by a separate curve. In general, the MRT of functional soils increases in proportion with the depth. The SOM found at depth of the profile is considered as very old. The MRT reaches to 6000 years at 1 m depth, but it is young in the topsoil (<100 years) (Scharpenseel et al., 1986; Vysloužilová et al., 2014). These facts must be taken in consideration in examinations of buried soils. The signature of the SOM in the topsoil of buried soils corresponds to vegetation that was present at the moment of burial. At the bottom of a buried soil, the signature of the SOM matches with the mixture of the old SOM and of the more recent SOM. A change of scores of the discriminant function in a profile indicates a change of vegetation.

The results demonstrate clearly that sites KOL 1, KOL 2, KOL 3, and MOR have a forest signature in the topsoil. They retain this signature in the entire profile. On the other hand, the CPB has a grassland signature in the whole profile. The BRE has a grassland signature in most of the profile, but it shows a slight development to forest in the upper part. The BUB shows a clear development from the forest signature at the basis of the profile to the grassland signature at the topsoil.

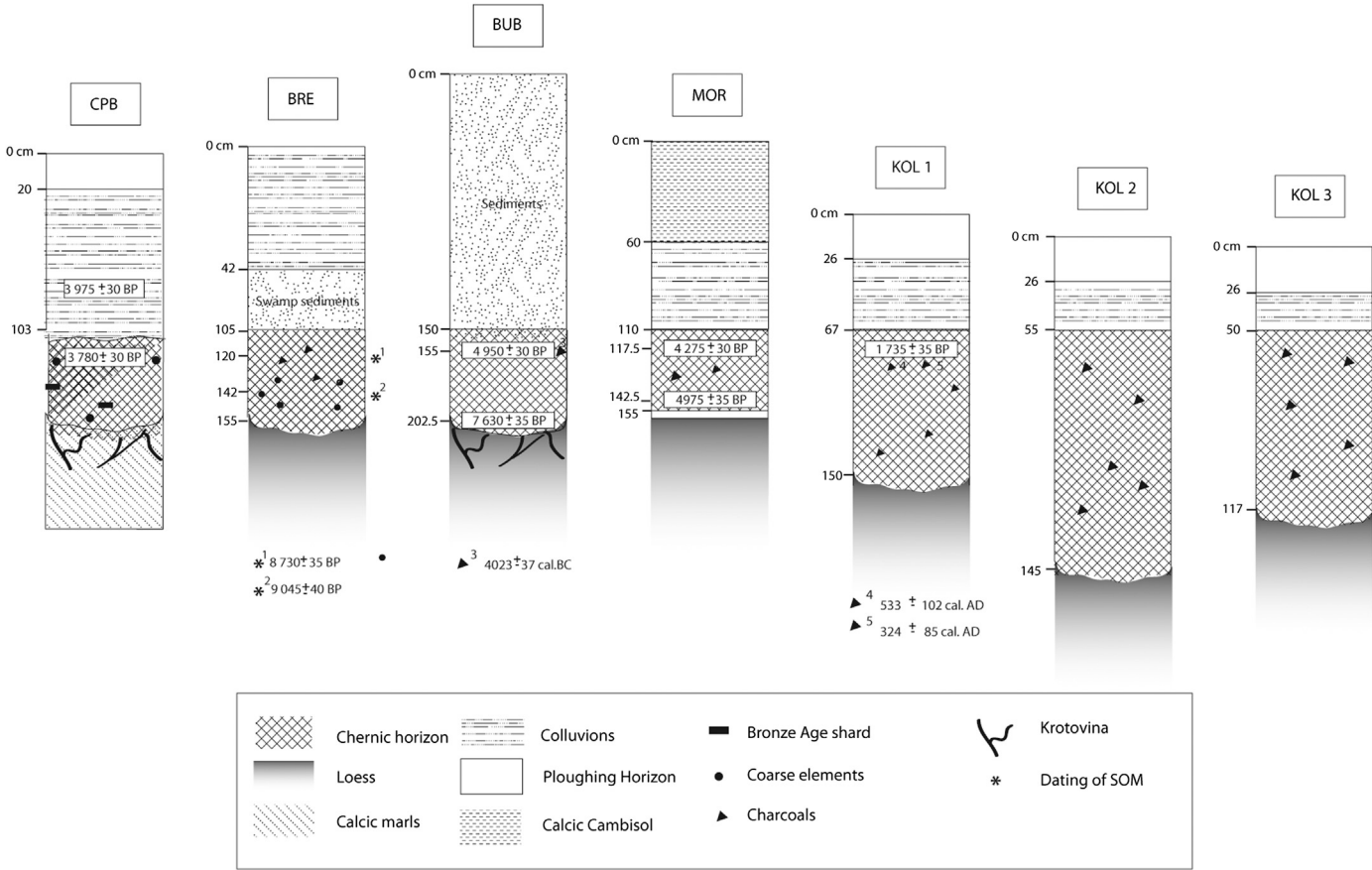


Fig. 2. Stratigraphy of the profiles including the studied buried chernozems. Laboratory numbers of radiocarbon dates of soil organic matter (SOM): CPB- Poz46306, Poz46305; MOR- SacA32353, SacA32347; BRE SacA 32352, SacA32351; BUB- SacA 32348, SacA 32349; KOL1-SacA 25551. Laboratory numbers of radiocarbon dates of charcoals: BUB-SacA 32350, KOL1-SacA 29630, SacA 29631. The radiocarbon dates of the SOM are not calibrated.

Table 2
Analytical properties of paleosols.

Site	Horizon	Depth (cm)	pH (H ₂ O)	% CaCO ₃	% C _{org}
CPB	IIA	130	7.9	32.3	0.4
	IIA	140	8.2	30.3	0.7
	IIA	150	8.0	28.1	0.5
	IIA	160	8.0	31.0	1.1
	IIA	167.5	8.0	36.0	0.5
	C	200	8.1	34.9	0.2
MOR	IIA	105	7.7	1.0	0.3
	IIA	120	7.7	1.0	0.3
	IIC	165	8.1	25.3	0.1
BRE	IIA	112.5	7.8	66.6	0.5
	IIA	127.5	7.9	37.3	0.8
	C	177.5	7.9	37.9	0.7
BUB	IIA	152.5	7.8	1.8	1.0
	IIA	157.5	7.9	1.0	1.4
KOL1	IIA	175	8.0	1.0	0.7
	IIA	95	8.4	1.4	0.6
	IIA	120	8.1	1.1	0.4
	IIA	140	8.3	1.2	0.4
KOL2	C	165	8.2	1.2	0.4
	IIA	65	8.2	6.5	0.6
	IIA	85	8.1	1.3	0.7
	IIA	115	7.9	1.0	0.9
KOL3	C	155	7.8	1.0	0.3
	IIA	60	8.3	0.8	0.9
	IIA	85	8.2	1.3	1.0
	IIA	105	8.1	0.6	0.6
	C	120	8.1	0.7	0.2

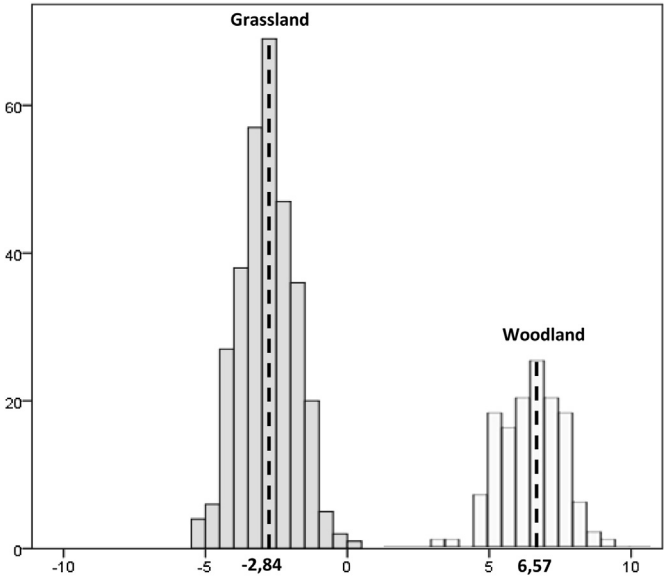


Fig. 3. Histogram of canonical scores for soils under grassland and forest. The range of canonical scores for grassland varies between -5.30 and 0.26; the mean value is -2.84. The range of canonical scores for forests varies between 3.44 and 9.36; the mean value is 6.57.

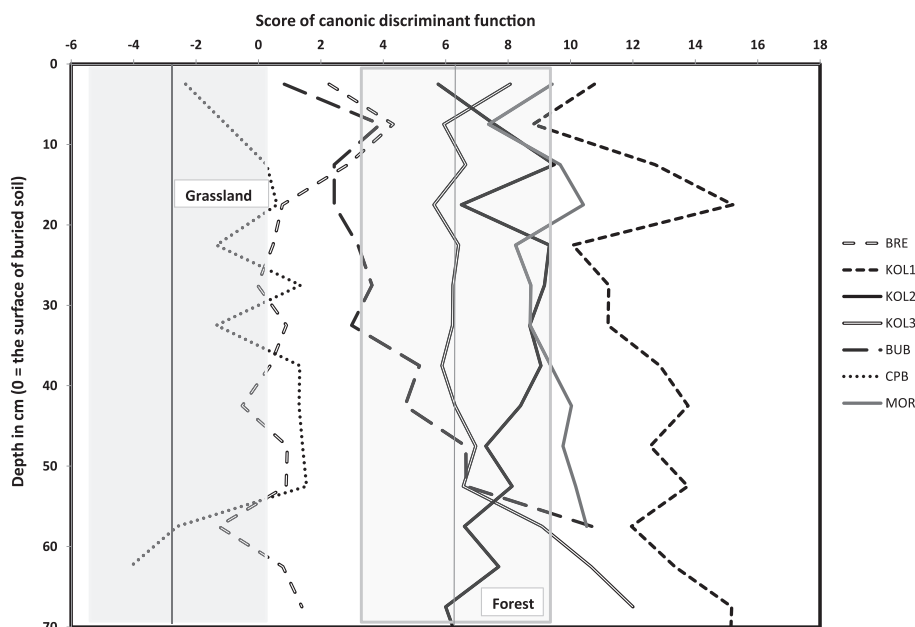


Fig. 4. Relation of scores of the canonic discriminant function and of the depth of the buried soil – 0 represents the surface of buried chernozems. The ranges of canonical scores corresponding to the groups of vegetation (–5.30 and 0.26 for grassland; 3.44 and 9.36 for forests) are represented by the grey background.

5. Discussion

5.1. Relevance of the reference library

The results of the discriminant analysis of the constructed reference library are in accordance with the previous NIR qualitative studies (Ertlen et al., 2010). After first derivatives had been applied on a very heterogeneous soil reference library, a Mahalanobis distance of 12.2 existed between grassland soils and forest soils (Ertlen et al., 2010). However, the homogeneous reference library, composed from soils developed on loess, shows a slightly lower Mahalanobis distance. This could be explained by the high content of CaCO_3 that influences spectra immensely (Lagacherie et al., 2008) and reduces proportionally the influence of the SOM. Contra Ertlen et al. (2010), there was no increase in Mahalanobis distance after application of the second derivatives (not presented).

From the point of view of the ecosystems, the reference library is still limited. The reference library cannot provide any distinction between different kinds of forest and different kinds of grassland. In particular, the distinction is not possible between natural vegetation of steppe, grassland, or even cultivated fields. The definition of intermediate ecosystems such as steppe forest remains indefinite in the reference library. However these facts put limits to the paleo-environmental reconstruction, as the difference of steppe or other types of grassland and forest is obvious. The NIRS has a capacity to bring key information about environmental conditions of the pedogenesis of paleosols.

5.2. Interpretation of the model applied to buried soils

The curves of dependence of discriminant analysis and depth of soil (Fig. 4) show the vegetation dynamics in buried soils. Scores recorded at the topsoil of buried soils specify the vegetation before the burial. The evolution of the scores in profiles has to be interpreted as dynamics of vegetation. The data indicate different types of vegetation dynamics in chernozems. Three sites represent a stable type of vegetation: grassland (CPB) or forest (KOL, MOR). The curves, which show a tendency from one group to

the other one, represent changes of vegetation during pedogenesis (BUB, BRE).

There are two possibilities of interpretation of intermediate values of scores that are classed between the two groups: the SOM can originate from a forest-steppe like vegetation; or the SOM represents a mixture of the SOM coming from the grassland and forest. Some stable intermediate vegetation (forest-steppe) would show this intermediate value along the whole profile. In the second case, the values of scores must show an evolution, as a consequence of the variation of the MRT with depth. At the top of the buried soil, the composition of the SOM is influenced by the vegetation present just before the burial. In the lower part of A horizon, the replacement of SOM is slow, and the scores reflect the more ancient vegetation. In the second case, a clear evolution of the scores with the depth can be observed. Consequently, the BUB profile suggests an evolution from forest to grassland and the BRE profile from forest to grassland.

5.3. Relevance of NIRS as a paleopedological proxy

A similarity of results by comparison of the results of the NIRS analysis to the other proxies available from the examined sites can be observed. The burial of the paleosol of BRE was dated by radiocarbon at about 8700 BP (Fig. 2) in the Boreal (9700–8000 BP). The Boreal is characterized by a dry climate and is considered to be suitable for the existence of steppe and for pedogenesis in Central Europe (Lorz and Saile, 2011). Based on stratigraphic and malacological studies, Ložek (1974) described the vegetation of this soil as chernozem flower steppe with a progressive expansion of pure thermophilous forest in the upper part. The results of the NIRS analysis confirm this scenario: the SOM at the bottom of the profile originates from grassland, and at the top of the profile the signature changes to forest. Abundant charcoals were also found in the upper part of this buried chernozem. The presence of these charcoals confirms the existence of trees.

The three studied chernozems of the KOL1, KOL2, and KOL3 are interpreted as forest soils by NIRS. The NIRS results are supported by a pedoanthracological study of the soil profiles (Vysloužilová

et al., 2014). This study shows the occurrence of various deciduous tree species with prevailing *Quercus* sp. charcoals. In the CPB, the paleosol buried in the Sub-Boreal were characterized as grassland soil. The palynological study of catchments where the profile is situated shows a predominance of forest vegetation in the Atlantic and Sub-Boreal. Nevertheless, it was claimed that approximately 20% of the catchment area was covered by Poaceae, ruderals, and cereals (Macaire et al., 2010). The palynological data are difficult to connect with a patch of a specific soil type. There is a possibility that this examined chernozem was found in a grassland patch within this catchment. The presence of fertile soil probably attracted the Bronze Age settlers. The question about the nature of grassland cannot be answered yet.

For the other sites, there are no other data of paleovegetation that would come directly from the studied profiles. Among these three sites, the NIRS analysis method has worked well for the sites of the BRE and KOL, and shows no major contradiction for the CPB site. These results confirm the potential of NIRS as a paleopedological proxy. Thus, it was further applied to other paleosols (BUB, MOR).

5.4. Evolution of vegetation in other examined soils

The chernozem of the BUB was buried at about 4950 BP according to the dating of the SOM of the topsoil. The second dating of charcoal from the top of the soil is younger and does not match with the burial date. The charcoal could have been of an intrusive nature or the soil profile could have been partly truncated before burial. The NIRS signature shows an evolution from forest to open vegetation. Anthropogenic influence could have caused this change. This site is situated in the core of Bohemia which is known to have been densely populated since the Neolithic (Pavlu and Zápotocká, 2007).

The analysis of paleosol of the MOR buried around 4975 BP shows the presence of forest vegetation in the whole period of functioning of the soil. This dating is confirmed through the presence of archaeological features from the Middle Neolithic (Vergnaud et al., in prep.). The forest clearance of the Neolithic settlers might have been too short (few decades) to be registered in the score values. The forest signature is confirmed by existence of many charcoals in this buried soil.

Radiocarbon data from the KOL1 show that the formation of colluvium is not connected to Neolithic cultivation. The formation of colluvium can be of later, historical origin. Considerable erosion rates were recorded in the Middle Ages and as a consequence of modern (since 1950s) agriculture practice in the Czech Republic (Zádorová et al., 2013). The stability of values of the scores in the profile indicated that the forest had been stable for a very long time in this area, perhaps from the Neolithic to the deforestation in the beginning of the Middle Ages. The chernozem soil remains despite this long period of forest vegetation.

6. Conclusion

In the Holocene, chernozem-like soils developed even in climatic areas in which they do not exist today. Their preservation is mostly connected with colluviation in the early stages of the agricultural exploitation of the soil.

Compared to other available proxies, the results of the NIRS analysis are coherent with the other paleoecological evidence. It is confirmed that qualitative NIRS is a valid alternative and a complementary tool for the paleoenvironmental reconstruction of paleosols.

The NIRS analysis shows that the vegetation cover on chernozems could be forest or open grassland. These results bring new data to the discussion about the pedogenesis of chernozems. They

also correspond to the statement that chernozems are not exclusively found under steppe or grassland vegetation (Eckmeier et al., 2007). It is quite clear that some chernozems or relict features of chernozems have existed under forest for thousands of years (Alexandrovskiy, 2000). It is still unclear if some chernozems could have developed under forest from the beginning of their existence. If they actually could have developed this way, the characteristics of the forest remain uncertain. Further NIRS study could bring more information about the kind of forest that covered the buried palaeosols (Ertlen, 2009).

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