Detecting prehistoric fire-based farming using biogeochemical markers

Eckmeier, E

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Abstract

The Holocene fire history of Central Europe has revealed that the charred organic matter found in soils today results basically from anthropogenic burning. The vegetation fires laid since the Early Holocene may well have influenced the properties of soils; the early human impact on the global climate system could also be connected to this prehistoric burning. The present thesis contributes to the investigation of potential effects of prehistoric anthropogenic burning on soils. Information about prehistorical agricultural techniques such as slash-and-burn and their impact on the environment are scarce. We do not know much about the processes that consequently lead to the change of natural environments into human-dominated, open cultural landscapes, as it is indicated by several terrestrial archives and proxy-records from the Neolithic (5500-2200 BC). Advantage was taken of an experimental burning in Forchtenberg (SW-Germany), to determine how much charcoal is produced by slash-and-burn in temperate deciduous forests and if fire affected soil carbon budgets and soil lightness. The charcoal produced by slash-and-burn was slowly incorporated into the soil profile, this was mainly done by earthworms. The aromatic compounds in charcoals are correlated to soil colour, they could be responsible for the dark colour of Chernozems and related soil types. It is not known how much charcoal has been transferred into soils since prehistoric fire-use started, and how high the charcoal loss has been, e.g. by decomposition or erosion. However, after even one fire the mass of potentially available charcoal is relatively high. A literature review was made to elucidate which are the main soil forming factors controlling the pedogenesis of Central European Chernozems. The distribution of Chernozems does not seem to be dependent on natural factors alone, not all the soils possessing Chernozem properties can be steppe soils. Biomass burning, including that for agriculture, might be an important formation factor. It is now an open question as to wether Neolithic settlers did indeed prefer to grow crops where Chernozems occurred or if Neolithic burning formed the chernozemic soils. Biogeochemical markers were used to investigate if Luvic Phaeozems in the Lower Rhine Basin are the natural successors of Early Holocene Chernozems. It was concluded that the investigated dark soils formed as a result of anthropogenic burning during several (pre)historic epochs. A general use of other soil amendments like manure could not be proven. The investigated soils should not be classified as Luvic Phaeozems, they are Luvisols containing a degraded (fossil) anthric horizon. The occurrence of these dark soil horizons documented the transition from a natural to a human-dominated landscape. Additionally, soil charcoals from Southern Switzerland were investigated to obtain further information concerning fire and vegetation history. It was found that the chestnut was present in Southern Switzerland about 1000 years earlier than predicted by the pollen based model of the introduction of the chestnut (Castanea sativa) by the Romans. The application of geochemical methods to detect human impact on soils was problematic for phosphorus and lipid analysis, mainly because not enough control samples were available. Soil charcoal analyses, including 14C dating of microcharcoal, are considered useful tools forreconstructing palaeoenvironments. A main future task would be to consolidate the existing archaeological and palaeoecological data to build an extended model of human impact on the environment in prehistoric societies.

Detecting Prehistoric Fire-based Farming Using Biogeochemical Markers

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Summary

The Holocene fire history of Central Europe has revealed that the charred organic matter found in soils today results basically from anthropogenic burning. The vegetation fires laid since the Early Holocene may well have influenced the properties of soils; the early human impact on the global climate system could also be connected to this prehistoric burning.

The present thesis contributes to the investigation of potential effects of prehistoric anthropogenic burning on soils. Information about prehistorical agricultural techniques such as slash-and-burn and their impact on the environment are scarce. We do not know much about the processes that consequently lead to the change of natural environments into human-dominated, open cultural landscapes, as it is indicated by several terrestrial archives and proxy-records from the Neolithic (5500-2200 BC).

Advantage was taken of an experimental burning in Forchtenberg (SW-Germany), to determine how much charcoal is produced by slash-and-burn in temperate deciduous forests and if fire affected soil carbon budgets and soil lightness. The charcoal produced by slash-and-burn was slowly incorporated into the soil profile, this was mainly done by earthworms. The aromatic compounds in charcoals are correlated to soil colour, they could be responsible for the dark colour of Chernozems and related soil types. It is not known how much charcoal has been transferred into soils since prehistoric fire-use started, and how high the charcoal loss has been, e.g. by decomposition or erosion. However, after even one fire the mass of potentially available charcoal is relatively high.

A literature review was made to elucidate which are the main soil forming factors controlling the pedogenesis of Central European Chernozems. The distribution of Chernozems does not seem to be dependent on natural factors alone, not all the soils possessing Chernozem properties can be steppe soils. Biomass burning, including that for agriculture, might be an important formation factor. It is now an open question as to wether Neolithic settlers did indeed prefer to grow crops where Chernozems occurred or if Neolithic burning formed the chernozemic soils.

Biogeochemical markers were used to investigate if Luvic Phaeozems in the Lower Rhine Basin are the natural successors of Early Holocene Chernozems. It was concluded that the investigated dark soils formed as a result of anthropogenic burning during several (pre)historic epochs. A general use of other soil amendments like manure could not be proven. The investigated soils should not be classified as Luvic Phaeozems, they are Luvisols containing a degraded (fossil) anthric horizon. The occurrence of these dark soil horizons documented the transition from a natural to a human-dominated landscape.

Additionally, soil charcoals from Southern Switzerland were investigated to obtain further information concerning fire and vegetation history. It was found that the chestnut was present in Southern Switzerland about 1000 years earlier than predicted by the pollen based model of the introduction of the chestnut (*Castanea sativa*) by the Romans.

The application of geochemical methods to detect human impact on soils was problematic for phosphorus and lipid analysis, mainly because not enough control samples were available. Soil charcoal analyses, including ^{14}C dating of microcharcoal, are considered useful tools for reconstructing palaeoenvironments.

A main future task would be to consolidate the existing archaeological and palaeoecological data to build an extended model of human impact on the environment in prehistoric societies.

Zusammenfassung

Die holozäne Feuergeschichte Mitteleuropas zeigt, dass die verkohlte organische Substanz, die wir heute in Böden finden, haupsächlich durch anthropogene Brände entstand. Seit dem frühen Holozän veränderte Feuer die Eigenschaften von Böden, und auch ein früher Einfluss des Menschen auf das globale Klimasystem könnte mit anthropogenen Feuern in Zusammenhang stehen.

Die vorliegende Arbeit ist ein Beitrag zur Erforschung möglicher Einflüsse prähistorischer Brandwirtschaft auf Böden. Bislang liegen kaum Informationen über prähistorische Anbautechniken und ihre potentiellen Auswirkungen auf die Umwelt vor. Wir wissen wenig über die Prozesse, die zu dem Wandel von Naturlandschaft zu Kulturlandschaft führten, welcher in terrestrischen Archiven und Proxy-Daten im Verlauf des Neolithikums (5500-2200 v. Chr.) beobachtet werden kann.

Im Rahmen eines Brandexperimentes wurde untersucht, wieviel Holzkohle durch slash-and-burn in einem Mischwald erzeugt wurde und ob Brände die Kohlenstoffgehalte und Helligkeit von Böden verändern. Die produzierte Holzkohle wurde über längere Zeiträume in den Boden eingebracht, hauptsächlich durch Regenwürmer. Die aromatischen Komponenten der Holzkohle korrelieren mit der Bodenhelligkeit, sie können für die dunkle Farbe von Chernozemen und verwandten Bodentypen verantwortlich sein. Unbekannt bleibt die Menge von Holzkohle, die seit dem Beginn prähistorischer Brandwirtschaftsweisen in den Boden gelangte und wie hoch der nachfolgende Verlust war, z.B. durch Abbau oder Erosion. Die Menge potenziell vorhandener Holzkohle nach einem Brand ist allerdings relativ hoch.

Eine Literaturübersicht zur Pedogenese von Chernozemen sollte Auskunft über die verantwortlichen bodenbildenden Faktoren geben. Die Verbreitung der Chernozeme scheint nicht allein von natürlichen Faktoren abhängig zu sein und nicht alle Böden mit den Eigenschaften von Chernozemen haben eine Vergangenheit als Steppenböden. Vegetationsbrände, einschliesslich Brandwirtschaft, könnten ein wichtiger bodenbildender Faktor sein. Es ist jetzt offen, ob die neolithischen Siedler zum Anbau von Kulturpflanzen gezielt die Chernozemgebiete aufsuchten oder ob sie durch den Einsatz von Feuer diese dunklen Böden erst bildeten.

Biogeochemische Marker wurden genutzt um zu untersuchen, ob die Luvic Phaeozems in der Niederrheinischen Bucht die natürlichen Nachfolger der frühholozänen Chernozeme seien. Es konnte nachgewiesen werden, dass diese dunklen Böden durch anthropogene Feuer im Verlauf mehrerer (prä)historischer Epochen gebildet wurden. Ein genereller Einsatz von Felddüngung, z.B. mit Stallmist, konnte nicht festgestellt werden. Die untersuchten Böden sollten nicht als Phaeozems klassifiziert werden, sondern als Luvisols mit einem degradierten (fossilen) anthric horizon.

Weiterhin wurden Holzkohlen aus Böden der Südschweiz untersucht, um Informationen zur Feuer- und Vegetationsgeschichte zu erhalten. Im Gegensatz zum pollenbasierten Modell der Einführung der Kastanie (*Castanea sativa*) durch die Römer erschien diese bereits 1000 Jahre früher als erwartet in der Südschweiz.

Die Anwendung geochemischer Methoden zum Nachweis menschlichen Einflusses auf Böden war problematisch (Phosphat- und Lipidanalyse), im Wesentlichen wegen mangelnder Kontrollproben. Aber die Analyse von Makro- und Mikroholzkohlen konnte als sinnvolles Werkzeug zur Landschaftsrekonstruktion bewertet werden.

Ein weiterführendes Ziel wäre, die existierenden archäologischen und paläoökologischen Daten zusammenzuführen, um ein Modell des prähistorischen menschlichen Einflusses auf die Umwelt zu entwickeln.

Contents

List of Manuscripts

The results of the Forchtenberg slash-and-burn field experiment were published in Manuscripts I, II and IX. Manuscript III summarizes the discussion about Chernozem pedogenesis in Central Europe. Manuscripts IV-VII deal with the investigation of Luvic Phaeozems in the Lower Rhine Basin. Manuscript VIII contains results of soil charcoal analysis as a tool for investigating the fire history of Southern Switzerland.

Manuscript I
Eckmeier, E., Rösch, M., Ehrmann, O., Schmidt, M.W.I., Schier, W. & Gerlach, R. (2007): Conversion of biomass to charcoal and the carbon mass balance from a slash-and-burn experiment in a temperate deciduous forest. *The Holocene* 17: 539-542.

Manuscript II
Eckmeier, E., Gerlach, R., Skjemstad, J.O., Ehrmann, O. & Schmidt, M.W.I. (2007): Only small changes in soil organic carbon and charcoal found one year after experimental slash-and-burn in a temperate deciduous forest. *Biogeosciences* 4: 377-383.

Manuscript III
Eckmeier, E., Gerlach, R., Gehrt, E. & Schmidt, M.W.I. (2007): Pedogenesis of Chernozems in Central Europe - a review. *Geoderma* 139: 288-299.

Manuscript IV
Gerlach, R., Baumewerd-Schmidt, H., van der Borg, K., **Eckmeier, E.** & Schmidt, M.W.I. (2006): Prehistoric alteration of soil in the Lower Rhine Basin, Northwest Germany – archaeological, ^{14}C and geochemical evidence. *Geoderma* 136: 38-50.

Manuscript V
Eckmeier, E., Gerlach, R., Tegtmeier, U. & Schmidt, M.W.I. (in press): Charred organic matter and phosphorus in black soils in the Lower Rhine Basin (Northwest Germany) indicate prehistoric agricultural burning. *British Archaeological Reports*.

Manuscript VI
Eckmeier, E., Wiesenberg, G.L.B. & Schwark, L. (in prep.): Lipid and phosphorus composition in soils - possibly affected by biomass burning in Mesolithic to Neolithic periods?

Manuscript VII
Eckmeier, E., Schmidt, M.W.I., van der Borg, K. & Gerlach, R. (submitted): Chemically isolated microcharcoal can be used for ^{14}C dating when macrocharcoal is absent.

Manuscript VIII
Hajdas, I., Schlumpf, N., Minikus-Stary, N., Hagedorn, F., **Eckmeier, E.,** Schoch, W., Burga, B., Bonani, G., Schmidt, M.W.I. & Cherubini, P. (2007): Radiocarbon ages of soil charcoals from the southern Alps, Ticino, Switzerland. *Nuclear Instruments and Methods in Physics Research* B 259: 398-402.

Manuscript IX
Smernik, R.J., **Eckmeier, E.** & Schmidt, M.W.I. (submitted): Quantitative comparison of solid-state ^{13}C NMR spectra of soil organic matter from an experimental burning site acquired at two field strengths.

Part A
Synopsis

1 Introduction

> *"We now realise that the time-span of human impact on the environment, or at least at regional level, ranges over millennia and not merely the last two centuries of industrialisation"* (Oldfield and Dearing, 2003).

Today, the impact of anthropogenic activity on the environment is a topic of major concerns. The effects of industrialisation, especially the emissions of pollutants and greenhouse gases like CO_2, cause profound changes. Not only since Ruddiman (2003) published his conclusions on early human impact on the climate system, also researchers that investigate the past are involved into the discussion on global change.

Vegetation fires, human land-use, climate variations and ecosystems are closely interconnected (Lavorel et al., 2006). The fire history of Central Europe revealed that mainly anthropogenic fires produced the charred organic matter found in soils and sediments today. Since Early Holocene, burning could have influenced the properties of soils and changed the composition of soil organic matter and the onset of anthropogenic influence on the global climate system could be connected to anthropogenic fires (Carcaillet et al., 2002).

The aim of this geoarchaeological study is to contribute to the investigation of possible effects of anthropogenic burning in Central Europe at a time, when the first settlements were constructed and agriculture emerged. Information about prehistoric agricultural techniques and their potential influences on the environment are scarce. We do not know much about the processes that consequently lead to the change of natural environments to human-dominated, open cultural landscapes that was observed in several archives and proxy records (e.g. Vera, 2000; Kalis et al., 2003).

Biogeochemical markers in soil archives and a literature review were applied to answer the main research questions of this thesis: (i) How much charcoal is produced by slash-and-burn in temperate deciduous forests, and what is its fate in soils? How do fires effect soil carbon budgets and soil lightness? (ii) Are the Chernozems and Phaeozems of Central Europe relics of steppe soils? Or did fire control their pedogenesis? (iii) Are the Phaeozems in the Lower Rhine Basin the natural successors of Early Holocene Chernozems or did they form under anthropogenic influence?

1.1 Geoarchaeology and past environments

"A competent geo-archaeologist should be able to evaluate diverse sources of empirical data, as generated within the archaeological project and as available from external sources, in order to apply the information to construct an integrated model of a geo-environment" (Butzer, 1982).

"Archaeology … is an earth science" (West, 1982).

Geoarchaeology as a research field is not as new as the label it has. In the 19th century earth scientists were often involved in (e.g. Charles Lyell) or even directed (e.g. Jacques Boucher) archaeological excavations to investigate Palaeolithic sites. Since the 1960s, archaeology and prehistory raise questions beyond the sedimentological context of a site, and the main goal of geoarchaeology became the understanding of past human ecosystems. An archaeological site is settled within an environmental matrix and its spatial, economic and social interactions play an important role in understanding the dynamical cultural development. The interrelations between environment and people are therefore important objectives of geoarchaeological research (Butzer, 1982).

In the 1970s, geoarchaeology evolved into an independent discipline that is still in the state of the "classification process" (Rapp and Hill, 1998). Its tasks were determined by Butzer (1973), Rapp et al. (1974) and Renfrew (1976). Shortly, "geoarchaeology implies archaeological research using the methods and concepts of the earth sciences" (Butzer, 1982) and it focuses on the "context in which archaeological remains are found" (Renfrew, 1976). The term geoarchaeology includes several aspects of other research fields, such as archaeometry, soil science, Quaternary geology and geography. It is an interdisciplinary approach to archaeological research questions, and the methods used in geoarchaeology depend on the project aim and the research fields involved (*cf.* Brothwell and Pollard, 2004; Goldberg and Macphail, 2006).

Geoarchaeology not only investigates past environments but also helps to understand present or future processes. To understand the dynamics of environmental systems, it is crucial to know the history of a landscape and how human impacts interact with environmental changes that can be measured via biogeochemical markers and proxy-data. Or, vice versa, to interpret data gathered from terrestrial archives and to understand the processes in the past, the "proxies require rigorous calibration against independent data derived both from present day observations and short term instrumental and documentary time-series" (Oldfield and Dearing, 2003).

1.2 Biomarkers and soil archives

"This makes geochemical prospecting a challenging and complicated endeavour" (Heron, 2004).

Soil properties are a function of five independent factors: parent material, climate, topography, time and organisms (Jenny, 1941). The factor organisms includes also humans, who use a landscape, shape and exploit it. Anthropogenic activity leaves environmental marker substances behind which can be detected in soils after millennia. Environmental markers could be either of biogenic origin (biomarkers) and therefore produced by plants, animals or microorganisms, or of anthropogenic origin (Eganhouse, 1997).

Geochemical methods to detect environmental markers are used to measure the changes in soil inorganic and organic matter caused by human impact; one of the first studies were published by Cook and Heizer (1965). The geochemical changes in soil composition could derive from any kind of activities: decomposed waste products, like food debris, or animal and human remains can be found in settlement areas, while areas used for agricultural purposes could contain traces of manuring or burning. The marker substances that detect anthropogenic activity are diverse and their long-term fate in soils is often unknown (Heron, 2004). The analysis of selected markers, as described in the following, could enable a reconstruction of former topsoil conditions.

The analysis of **phosphorus** (P) or phosphate as a measure of human impact is used in archaeology since Arrhenius (1931). Inputs of P deriving from organic matter remain detectable in soils due to its stability. In acidic conditions, inorganic orthophosphate ions form insoluble associations with Fe and Al, while in alkaline soils they are bond to Ca (Eidt, 1977). Higher than natural background quantities of P were associated with occupation areas (e.g. Barba et al., 1995; Schuldenrein, 1995; Wells et al., 2000), with burials (e.g. Piepenbrink, 1989), or intensive land-use, like manuring, animal husbandry or burning (e.g. Pape, 1970; Eidt, 1977; Leonardi and Miglavacca, 1999; Lehmann et al., 2004; Vitousek et al., 2004). The analysis of P was often criticised, mainly because the extraction methods for quantifying soil P vary widely, making comparisons of data problematical (Bethell and Máté, 1989; Holliday and Gartner, 2007).

Lipids are defined as organic substances being insoluble in water but extractable with organic, non-polar solvents. This group of substances contains various compounds, e.g. *n*-alkanes, fatty acids, alcohols or steroids and polycyclic aromatic hydrocarbons (PAHs; Dinel et al., 1990); lipids found in soils mainly derive from plants and microorganisms (Kögel-Knabner, 2002). Distribution patterns of soil lipid compounds like sterols have been used to identify different sources of organic manure and harvest residues applied to early arable soils (Bethell et al., 1994; Bull et al., 1999; Simpson et al., 1999b; Bull et al., 2002). The distribution of *n*-alkanes could indicate the source of biomass inputs in soils or sediments (e.g. van Bergen et al., 1997) and was used to investigate the environmental history in lake sediments (Schwark et al., 2002; Fisher et al., 2003) or palaeosoils (Xie et al., 2003). Certain lipid compounds, like levoglucosan or PAHs, were applied as biomarkers for burning (Bucheli et al., 2004; Otto et al., 2006).

Charcoal particles (macrocharcoal) in soils and sediments are used to reconstruct past environments and fire-events (Patterson III et al., 1987; Figueiral and Mosbrugger, 2000; Willis and van Andel, 2004), to measure pedological processes (Carcaillet et al., 2006) or to reconstruct the relations between fire and climate (Pierce et al., 2004). The analysis of soil charcoal (pedoanthrocology) is based on the occurrence and distribution of charcoal particles in the soil profile, and it needs an understanding of the taphonomical processes which affect their formation, distribution and sedimentation. However, the fate of charcoal after its production is not yet fully observed, and "[…] it is crucial to improve knowledge on the migration of fragments in natural soils" (Carcaillet, 2001). Charcoal particles on the surface may be photochemically or biogeochemically oxidised (Bird, 1997). Small charcoal particles could be illuviated or mixed into the soil material and transported in the soil profile by soil faunal mixing (Carcaillet, 2001; Topoliantz and Ponge, 2003) or by roots who are attracted by nutrients bound to charcoal surfaces (Zackrisson et al., 1996). In soils, charcoals can break down via freeze-thaw, drought or root growth (Carcaillet and Talon, 1996) or by microbial degradation (Hamer et al., 2004; Hockaday et al., 2006).

Black carbon (microcharcoal) is a geochemical marker for fire-occurrence and could be chemically separated when macrocharcoal is absent (Bird and Cali, 1998; Schmidt and Noack, 2000; Wang et al., 2005). But black carbon represents a continuum of charred material and the acquisition of black carbon data is still troublesome. The measurement of different fractions of black carbon with different methods obtains results that are not directly comparable, a generally accepted definition of black carbon does not yet exist (Bird, 1997; Schmidt et al., 2001; Hammes et al., accepted).

1.3 Anthropogenic fires in temperate deciduous forests

"It is not 'natural' for humans not to burn" (Pyne, 2001).

Palaeobotanical records show that **anthropogenic fires** were more common in past times and that fire might have been deliberately used for various purposes, as shown in Fig. 1. Humans, or maybe even our ancestors, control fire since at least 1.5 million years (Brain and Sillent, 1988) and used burning for hunting, herding or farming in a broad diversity of space and time (e.g. Pyne, 1994).

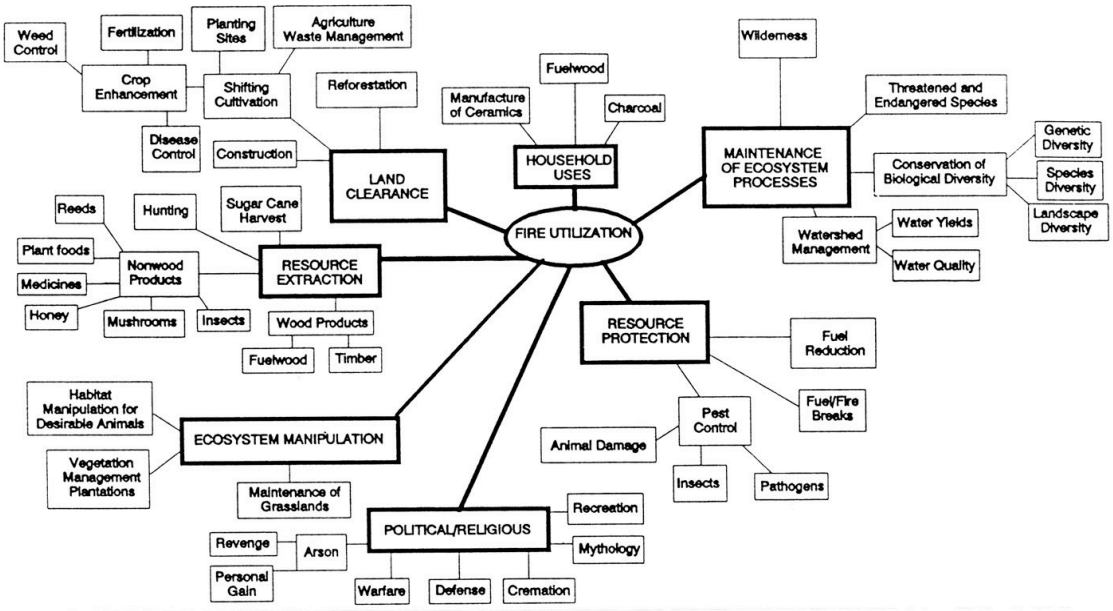

Fig. 1 Fire can be used for a large variety of purposes, including burning for landscape management, agriculture or hunting (Kauffman et al., 1993).

Hunter-gatherers burnt to create open spaces in forests that attract game or to enhance the growth of favoured plant species like oak or hazel (Lewis and Ferguson, 1988; Mason, 2000). Examples of burning for hunting come from pre-European societies in Australia (Pyne, 2001), North America (Lewis and Ferguson, 1988; Woodcock and Wells, 1994; Boyd, 2002), South America (Heckenberger et al., 2003; Huber and Markgraf, 2003) and Africa (Mworia-Maitima, 1997).

In Central European deciduous forests, Holocene fires were rare and they had mainly anthropogenic causes (Tinner et al., 1999; for an overview see Fig. 10). European Mesolithic hunter-and-gatherer communities used fire for shaping the landscape (see above; Mellars, 1976; Simmons and Innes, 1987; Caseldine and Hatton, 1993; Mason, 2000; Bos and Urz, 2003). Haas (1996) and Erny-Rodmann et al. (1997) reported early agricultural burning during late Mesolithic that indicated the transition from foragers to farmers in the Swiss midlands.

First evidence for Neolithic agricultural burning came from Northern Germany and Denmark, where burning accompanied the transition from Mesolithic to Neolithic agricultural techniques and created a cultural landscape since 4000 BC (Iversen, 1941; Kalis and Meurers-Balke, 1998). Clark et al. (1989) reported that farmers in Late to End Neolithic (4400 – 2200 BC) used fire to transform forest to arable land. A shifting cultivation with slash-and-burn was indicated by plant macrofossil, pollen and charcoal data from Lake Constance and the pre-alpine lowlands during the Late Neolithic period (4300-3500 BC; Rösch, 1993; 2000). Neolithic anthropogenic burning was also reported by Carcaillet (1998) for the Northern French Alps. Slash-and-burn, or swidden cultivation, are fire cycles: after burning the vegetation growing on the field, which releases nutrients and kills the weed seeds in the soil, crop grows in the first year. The former vegetation re-enters the field in the second year and the field might be used as feed for livestock or left to grow berries or nuts (Pyne, 2001; Rösch et al., 2002). Charcoal records from the Swiss midlands and alpine regions suggested the burning of forest to gain arable land or meadows not only in Neolithic but also in Bronze and Iron Age (Gobet et al., 2003; Tinner et al., 2005), leading even to a lowering of the timberline in the Alps after 3500 BC (Haas et al., 1998; Carnelli et al., 2004). Fire-fallow silviculture was used until the modern ages, e.g. in the Black Forest to encourage oaks for obtaining tannic acid (Goldammer et al., 1997) or in Southern Switzerland to enhance the cultivation of chestnut trees (Conedera et al., 2004).

Anthropogenic burning had the highest impact on the landscape during Late-Neolithic (3500-2200 BC), when the Central European natural landscape was transformed into a cultural landscape and new regions were colonized using the fertilizing effects of burning. At the same time innovative changes in agricultural technology emerged, such as the transition from Early Neolithic plough-less agriculture to presumably fire-based livestock farming. These changes were connected to a strong human impact visible as colluviation or vegetation changes in nearly all terrestrial archives (Meurers-Balke et al., 1999; Lüning, 2000; Kalis et al., 2003). Vegetation fires, human land-use, climate variations and ecosystems are compounds of an interconnected system (Lavorel et al., 2006).

The onset of anthropogenic influence on the global climate system is still controversially discussed (Ruddiman, 2003; Broecker and Stocker, 2006). Early human impact was possibly connected to anthropogenic fires (Carcaillet et al., 2002; Fig. 2) that are an important factor in the **global carbon cycle**. Biomass burning releases today an estimated 2.5 Pg atmospheric carbon per year (van der Werf et al., 2006) and it produces a substantial amount of potentially stable charcoal carbon.

However, the conversion rate of biomass fuel to charcoal in temperate deciduous forests is still unknown. Field observations and experimental studies are rare and have been conducted mainly in savannah, tropical or boreal forests (cf. Forbes et al., 2006; Preston and Schmidt, 2006).

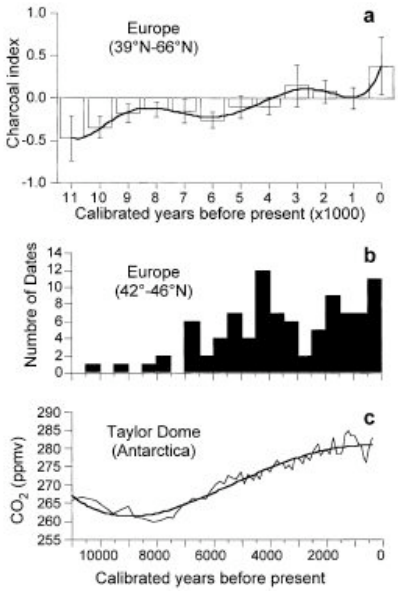

Fig. 2 Biomass burning reconstruction in Europe from the Mediterranean to upper Boreal ecosystems. (a) Charcoal index deduced from stratigraphic time series; error bars correspond to the standard error. (b) Distribution of ^{14}C dates in soil charcoal. (c) CO_2 concentration curve from Indermühle et al. (1999). Figure published in Carcaillet et al. (2002).

Forbes et al. (2006) compiled the available black carbon data and estimated an annual production of 50-270 Tg black carbon, of which more than 80 % goes into soils. Soils were considered carbon reservoirs because black carbon seems to contribute to the slow carbon pools in soils (Prentice et al., 2001; Skjemstad et al., 2004). Contrastingly, black carbon or charcoal is susceptible to microbial degradation (Hamer et al., 2004; Hockaday et al., 2006) and chemical oxidation (Bird et al., 1999; Cohen-Ofri et al., 2006), depending on the chemical recalcitrance of charcoal compounds (Krull et al., 2003) or the physical protection (Brodowski et al., 2006). Still unclear are the processes and amounts of black carbon loss by degradation or burial in terrestrial or marine sediments (Masiello, 2004).

Fires, and therefore also prehistoric burning, could transform the composition and quality of soil organic matter, not only by the production of charred material or black carbon (González-Pérez et al., 2004). These effects may also have implications for pedogenesis, as demonstrated in the following chapter.

1.4 Chernozems as relics of vegetation fires?

The soil type Chernozem was defined as steppe soil, with its pedogenesis dominated by the soil-forming factors of dry continental climate and steppe vegetation (Dokuchaev, 1883; 1889). Dokuchaev's results for the Russian Chernozems were transmitted to Central European Chernozems (e.g. Hohenstein, 1919) and his definition was assumed to be valid for their pedogenesis, too.

The World Reference Base for Soil Resources (FAO/ISRIC/ISSS, 1998) defined Chernozems by their morphological characteristics but was biased by the climo-genetic formation model. Chernozems (Fig. 3) are soils with dark brown mollic or chernic horizons of at least 20 cm, which are rich in organic matter (10 - 16 %), highly saturated with bases and react neutral. Typical features of Chernozems are the formation on mostly aeolian and carbonaceous sediments like loess, the occurrence in continental climate zone under tall-grass vegetation that provides high above-ground

biomass of about 1.0 - 1.5 t ha-1, and an intense bioturbation (FAO/ISRIC/ISSS, 1998; Driessen et al., 2001).

Based on the assumption that Chernozems are steppe soils, a model was developed that explained their conservation and degradation with climatic changes. Chernozems formed under steppe conditions were expected to stay preserved in regions with a balanced or negative water balance. In Central Europe, this would be in geographical regions with a mean annual precipitation of less than 500 mm (Meyer, 1926). Increasing precipitation lead to leaching, the translocation of clay covered with humic material started and Chernozems were transformed into Phaeozems, Luvisols or Albeluvisols (Rau, 1968; Driessen et al., 2001).

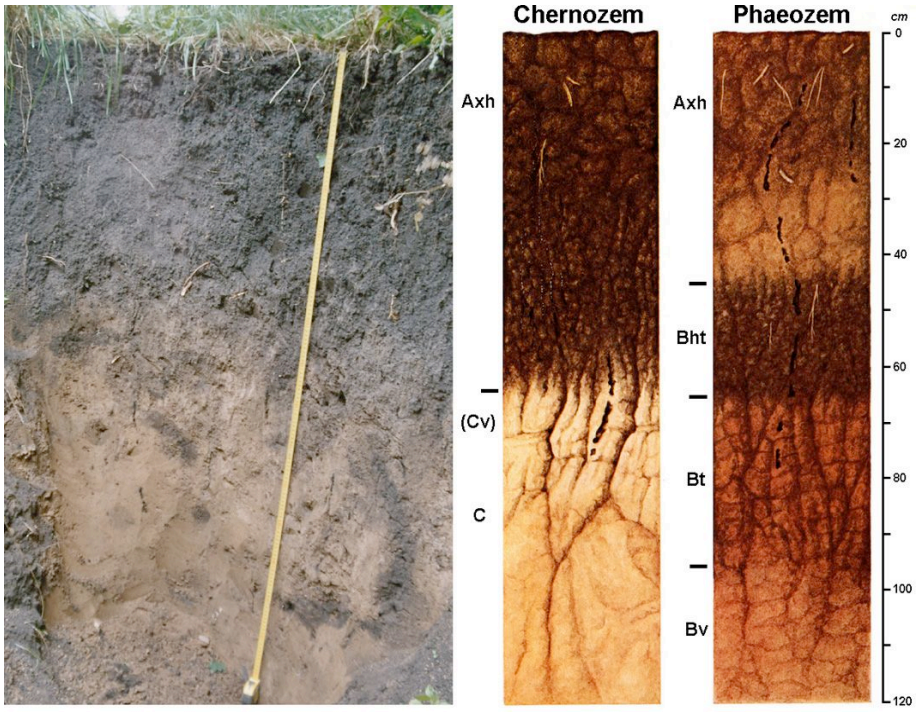

Fig. 3 Chernozem and Phaeozem. Left: Haplic Chernozem, depth of profile approx. 170 cm (Voronezh, Russia); right: idealized soil profiles of a Chernozem (Tschernosem) and a Phaeozem (Tschernosem-Parabraunerde; modified after Mückenhausen, 1985).

However, the formation of Central European Chernozems is under discussion. Continental climate occurred during the Late Glacial but there is no evidence for the presence of Chernozems in Central Europe in the Late Glacial (Rohdenburg and Meyer, 1968; Ikinger, 1996). First evidence for fully developed Chernozems originate from the Early Holocene (Pre-Boreal to Atlantic) when warmer climate and forest vegetation dominated the Central European loess-belt.

Vegetation fire was proposed as a new formation factor in the genesis of Chernozems. As an example, up to 45 % of soil organic carbon in Chernozems of Lower Saxony consisted of black carbon (Schmidt et al., 2002). In North American Chernozems, the proportion reached from 35 % (Skjemstad et al., 2002; Glaser and Amelung, 2003) to 80 % of soil organic carbon (Ponomarenko and Anderson, 2001). Russian Chernozems yielded 17 % black carbon (BPCA-method) up to a depth of 60 cm (Rodionov et al., 2006). The amount of aromatic carbon, a compound of charred organic matter, and the soil colour or lightness correlate (Spielvogel et al., 2004). However, the processes of charcoal incorporation and soil colouring are not yet clearly understood.

2 Objectives

Anthropogenic fires affected the temperate deciduous forests and the soils of Central Europe over millennia. However, not much is known about the taphonomical processes and the fate of charcoal particles in soils, such as conversion rates from biomass to charcoal or charcoal incorporation and transportation into the soil mineral matrix. Burning could influence the soil carbon budgets and the soil colour and would therefore be a pedogenetical factor. The objectives of this part of the study (*Manuscripts I-II*) were:

(i) How much biomass fuel is used and how much charcoal is produced during slash-and-burn in a temperate deciduous forest?
(ii) How are the produced charcoal particles distributed into size fractions?
(iii) Is the carbon mass balance influenced by the fire?
(iv) How much of the produced charcoal do we find in the soil mineral matrix after one year?
(v) Are the total soil organic carbon concentrations affected by the fire?
(vi) Does the soil colour change and does it correlate with the soil charcoal carbon concentrations?

The Luvic Phaeozems investigated in the Lower Rhine Basin were considered predecessors of Chernozems, which should have covered the loess areas under former steppe conditions. However, this assumption conflicts with palaeobotanical evidence from an early reforestation that started in Late Glacial. A review of the literature on pedogenesis of Central European Chernozems (*Manuscript III*) attempted to answer the following questions:

(i) When did Central European Chernozems form?
(ii) Is their formation bound to a certain climate and vegetation?
(iii) Which factors control conservation and degradation of Chernozems?
(iv) Are there unconsidered factors (man and fire) that influence Chernozem formation or their soil properties?

Luvic Phaeozems are characterised by a dark humic subsoil horizon (Bht). In the Lower Rhine Basin, hundreds of anthropogenic pits were connected to these Phaeozem Bht horizons. Small charcoal particles in the dark pit fillings indicated that fire might have played a role in the formation of the dark soil material. Mainly geochemical methods (*Manuscripts IV-VII*) were used to investigate:

(i) Are the Luvic Phaeozems in the Lower Rhine Basin successors of Early Holocene steppe soils or did they form by anthropogenic activity?
(ii) Do we find geochemical traces of anthropogenic activity in the soil, i.e. changes in the soil organic matter composition?
(iii) Could we determine the sources of added organic material?
(iv) When did they form?

3 Summary of material and methods

We investigated two main study subjects and areas (Fig. 4): a slash-and-burn experiment in Forchtenberg (SW-Germany) and Luvic Phaeozem horizons and associated pits in the Lower Rhine Basin. Additionally, we investigated charcoals in soils (Cryptopodzols) in Southern Switzerland (Ticino and Grisons).

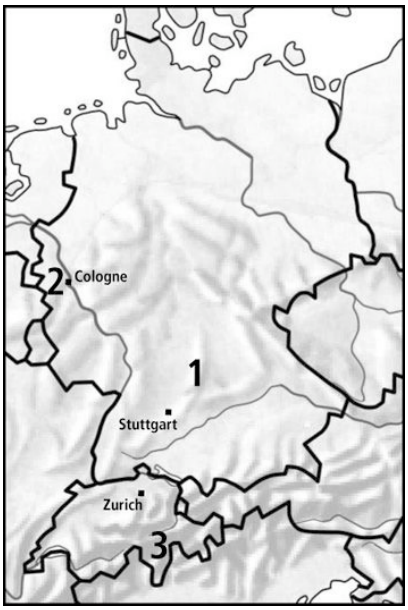

Fig. 4 The study areas. 1: Forchtenberg experimental burning site; 2: Lower Rhine Basin; 3: Soils in Ticino and Grison.

3.1 Experimental field study on prehistoric slash-and-burn

The interdisciplinary field study was designed to mimic Neolithic agricultural slash-and-burn in order to asses the effects on vegetation, crop yields and soil properties (Rösch et al., 2002). The site is located near Forchtenberg (SW-Germany) in a temperate deciduous forest dominated by *Fagus*, *Carpinus* and *Acer*. The site is 3.5 ha in area; it is slightly sloping and exposed to the south (320 m a.s.l.). The mean annual temperature is 8.9 °C and the mean annual precipitation is 849 mm. The soil is a Haplic Luvisol (WRB) with partly stagnic properties.

Before the burning, the trees were cut down within a plot of 30 x 30 m (April 2004) and the trunks and larger branches (diameter > 10 cm) were removed from the site. The small wood pieces were left to dry until an area 11 x 8 m was burnt in October 2004. A pile of burning wood was drawn over the ground with long hooks and was continually fed with wood (Fig. 5). This technique was used so that the grass and herbaceous vegetation could burn completely and to distribute the charcoal and ash as homogeneously as possible.

Tab. 1 Methods used to investigate the conversion of biomass to charcoal; the soil charcoal and carbon concentrations and soil lightness (*Manuscripts I, II*).

Biomass fuel	gravimetrical
Charcoal in litter layer	gravimetrical; collection with vacuum-cleaner; wet-sieving; manual separation of charred and uncharred fraction
Charcoal in soil	mid infrared - Fourier transformed infrared spectroscopy (MIR-DRIFT); ^{13}C nuclear magnetic resonance (NMR)
C, N	Elemental analysis (Elementar Vario EL)
Soil lightness	L* values (Commission Internationale de l'Eclairage, CIE 1976 Standard Observer); photo spectrometer (Dr. Lange spectro-color)

Fig. 5 Impressions from the experimental slash-and-burn in Forchtenberg. (a) Sampling on the burning plot, before burning. (b) The fire starts with incending the wood pile. (c, d) The burning wood is pulled over the plot with hooks. (e) The plot after burning, with ash plume. (f) After six months the crop grows on the burnt plot undisturbed by weeds. Photos: O. Ehrmann, R. Gerlach, E. Eckmeier.

3.2 Luvic Phaeozems in the Lower Rhine Basin

The Phaeozems were investigated taking advantage of gas-pipeline excavations and at archaeological large-scale (0.5 to 5 ha) excavations within the Southern Lower Rhine Basin. The pipeline trench and the excavations were situated on the loess-covered higher and middle terraces, the loamy and sandy lower terrace and the Holocene sandy floodplain of the river Rhine.

Tab. 2 Methods used to investigate the Phaeozem horizons and pit fillings (*Manuscripts IV-VII*).

Macrocharcoal (> 1mm)	Hand-picked from soil; determination of wood species (U. Tegtmeier, Institute of Pre- and Protohistory, University of Cologne).
Microcharcoal (Black carbon)	high-energy UV photo-oxidation & ^{13}C nuclear magnetic resonance (NMR) (CSIRO laboratories, Adelaide, Australia)
Dating	accelerator mass spectrometry (AMS) ^{14}C (Univ. of Kiel and Utrecht); calibration with OxCal v3.5
C, N	Elemental analysis (Elementar Vario EL)
Lipids	Soxhlet-extraction with DCM/MeOH (2/1); GC/MS
Phosphorus	total, organic and inorganic P; Extraction with H_2SO_4; photometrical quantification
Soil lightness	L* values (Commission Internationale de l'Eclairage, CIE 1976 Standard Observer); photo spectrometer (Dr. Lange spectro-color)

Fig. 6 Examples for Phaeozem pits investigated in this study. (a) Phaeozem pit in the sandy Lower Rhine Terrace (Köln-Nord). (b) Phaeozem pit and horizon in the loess covered Middle Rhine Terrace (Frechen). (c, d) Typical slot pit (profile and plane) in the loess covered Middle Rhine Terrace (Pulheim). Photos: (a, b) H. Baumewerd-Schmidt; (c, d) Archbau.

We investigated Phaeozem horizons (Bht horizons) and two types of pits: Phaeozem pits and settlement pits (Fig. 6). The Phaeozem pits were anthropogenic features always connected to the Phaeozem (Bht) horizons. The horizons were distributed as patches (diameter up to 100 m) in surrounding Luvisols. The Phaeozem pits never contained visible artefacts like bones or potsherds, and they could be classified into five morphological units according to their regular shapes. The spatial distribution of horizons and pits was independent of natural factors, e.g. relief or parent material. The slot pits (Schlitzgruben) are well-known in archaeology but of unknown function. They are part of the Phaeozems pits and were also connected to Bht horizons. The settlement pits occurred in clearly defined and archaeologically dated prehistoric settlement areas (on-site features). They contained artefacts, mainly settlement waste as sherds or bones.

3.3 Soil charcoals from Southern Switzerland

Soil charcoals were collected from three soil profiles that were classified as Cryptopodzols by Blaser et al. (1997). Cryptopodzols typically contain high amounts of relatively stable organic matter. Two soil profiles (C1, C2) were located near Roveredo in the Misox valley (Grisons), and one (C3) near Pura (Ticino).

Pollen-records of lake-sediments indicated that the cultivation of Chestnut (*Castanea sativa*) in the area since the Roman Period (ca. 50 BC) was enhanced by burning the oak-dominated forests (Tinner et al., 1999; Conedera et al., 2004). We dated the soil charcoals with AMS ^{14}C after the wood species was determined to achieve complementary information about the vegetation and fire history of the region.

4 Synthesis

The synthesis summarises the results that can be found in the manuscripts (Part B) and gives a general conclusion.

4.1 Results

4.1.1 Slash-and-burn in temperate deciduous forests and its impact on soil characteristics

We followed the pathway of charcoal particles from production to incorporation into the soil (Fig. 7). It was necessary to cut down a 900 m^2 area of trees to gain enough biomass to burn (11 m^2), half of the wood (trunks and bigger branches) was not used for burning. The slash-and-burn experiment converted about 5 % of the biomass into charcoal and it produced about 5.2 t ha^{-1} of charcoal carbon. Most carbon (91 %) was lost during the burning, as a component of aerosols or gases such as CO_2. About two-thirds of the charcoal particles produced were larger than 2 mm. The distribution of charcoals on the soil surface was very heterogeneous and thus a large number of sample replicates would be necessary to gain quantitative information from charcoal assemblages in the sediment records (*Manuscript I*).

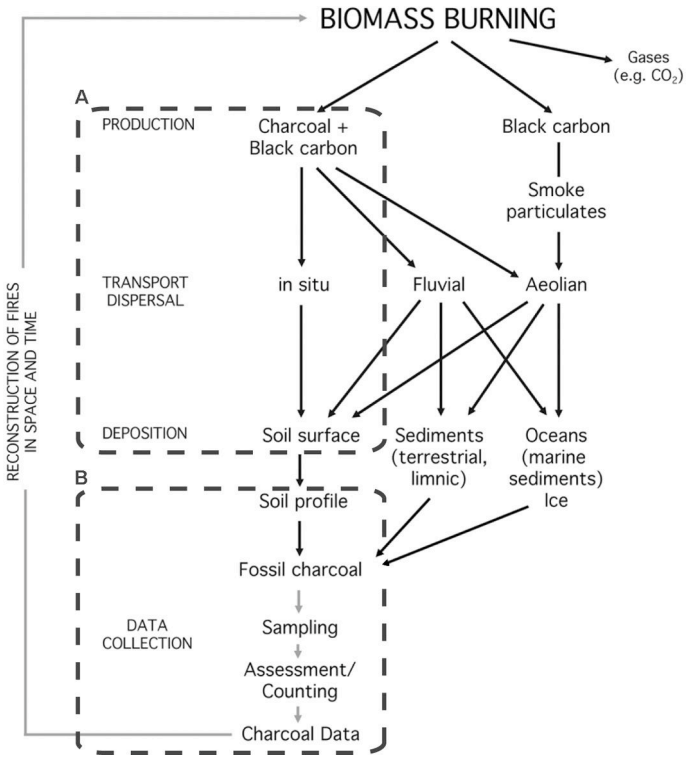

Fig. 7 The production, transportation and deposition of charcoal and black carbon. The dashed rectangles frame the components investigated in this thesis (modified after Graetz and Skjemstad, 2003; Kuhlbusch and Crutzen, 1996).

Only small amounts of the produced charcoal (0.4 g charcoal carbon kg^{-1}) was found in the soil after one year. It was mixed into the soil matrix by soil mixing animals and was transported further down the soil profile as a component of earthworm facies. As a result, soil carbon concentrations did not change significantly. However, the fire affected the soil lightness, it became significantly darker and it correlated with the charcoal carbon concentrations ($r = -0.87^{**}$). The aromatic compounds of the charcoal particles seem to be responsible for darkening the soil material (*Manuscript II*). The changes detected after one year were still small but the process of charcoal incorporation into a soil profile may be very slow.

4.1.2 The pedogenesis of Central European Chernozems

The review of literature on Central European Chernozems and their degraded subtypes since the 1920's (*Manuscript III*) indicated that there is no generally accepted consensus on climate and type of vegetation and thus, the time of pedogenesis (Fig. 8). It revealed that dark humus-rich soils could have different formation histories. The relationship of soil classification to pedogenetic processes is misleading, the occurrence of Chernozems or related soil types does not reflect former climate and vegetation. Continental climate and steppes occurred during the Late Glacial but there is no evidence for the presence of Chernozems in Central Europe. The first evidence for fully developed Chernozems originates from the Early Holocene when warmer climate and forest vegetation dominated the Central European loess belt. A development of Chernozems under forest vegetation is still under discussion, they could have also formed under forest or at least under forest-steppe, as comparisons with Russian soils suggests.

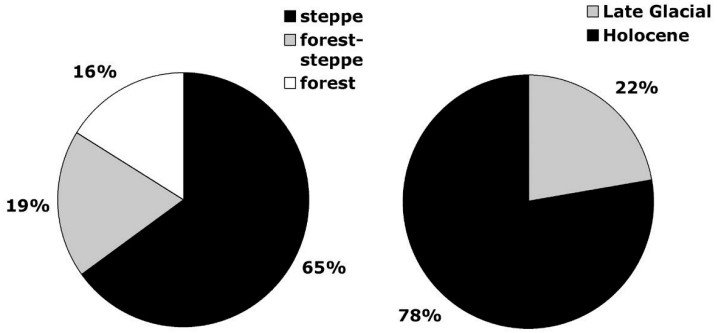

Fig. 8 The results of the literature review on Chernozem pedogenesis in Central Europe revealed that there is no consensus on vegetation-cover and time of formation (percentages from 48 publications).

The factors affecting Chernozem formation and conservation are diverse and their distribution could not be explained by natural factors alone. Biomass burning could form black soils through the input of charred organic matter, which influences the soil lightness (*Manuscript II*). Charcoal is very stable and its presence could explain the relatively high concentrations of organic carbon found in mollic horizons. Small microcharcoal particles could also build the clay-humus-complexes that are typical for Chernozems by bonding to clay minerals. Prehistoric agricultural fires could have produced the charred organic matter found in Chernozems today. The charred material deriving from Chernozems has a wide range of radiocarbon ages. In contrast to Gehrt et al. (2002) we propose that it was not the Early Neolithic settlers that burnt the landscape but rather the End- to Late Neolithic settlers who used biomass burning as an agricultural tool. Palaeobotanic evidence shows that anthropogenic fires were common during this period (Chapter 1.3).

4.1.3 The formation of Luvic Phaeozems in the Lower Rhine Basin

As suggested before, the occurrence of dark fossil soil horizons does not necessarily indicate the former presence of Chernozems and steppe conditions. The characteristics of the Phaeozem horizons investigated in this study suggested a different formation history (*Manuscripts IV-VI*). They were always connected to man-made pits, this was proven by the pit-shapes and the differences in texture between the pit-fillings and the surrounding soils. The differences in wood species composition between the charcoals found in prehistoric settlements and the pit-fillings (Fig. 9), as well as the lack of artefacts in the pits led to the assumption that the dark horizons are archaeological off-site-features.

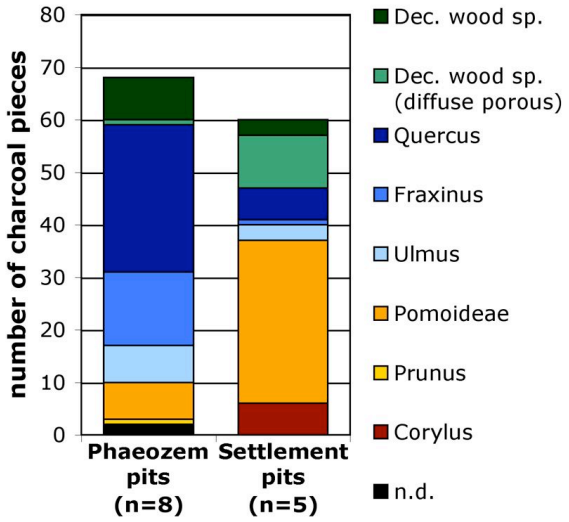

Fig. 9 The number and species of examined charcoal particles (> 1mm) indicated that the settlement pits contain wood species more typical for open forest edges, while the Phaeozem pits contain mainly tree species from closed forest.

The presence of charred organic matter deriving from fires between the Mesolithic and the Middle Ages indicates the burning of deciduous tree species at a time when natural fires were not common in temperate Central Europe (Fig. 10). The faster decomposition of less recalcitrant carbon species led to the relative enrichment of black carbon in the dark soils. Further indicators of burning were the narrow C:N ratios. This could be a result of stable aromatic nitrogen compounds (pyrrols) forming during heating (Gonzáles-Pérez et al., 2003) and the relatively low amount of lipids in the dark soil material. It is still unclear if the unusual distribution of *n*-alkanes, with the predominance of *n*-$C_{16–18}$, is a result of burning. The phosphorus concentrations are generally higher in the Phaeozem pit-fillings but when a selected set of samples with related control samples was examined only half of them contained more phosphorus. The time and the function of the soils that accumulated later in the pits seemed to have influenced the amount of phosphorus.

A re-classification of the investigated soils is difficult, the soil characteristics do not fit the framework of the WRB-FAO. The dark soils resemble anthric horizons (anthropogenic properties) but do not contain enough organic carbon. The carbon content required is 0.6 %, the soils have an average of 0.4 %. Due to the presence of an argic horizon, they could be considered as Luvisols with a fossil degraded anthric horizon.

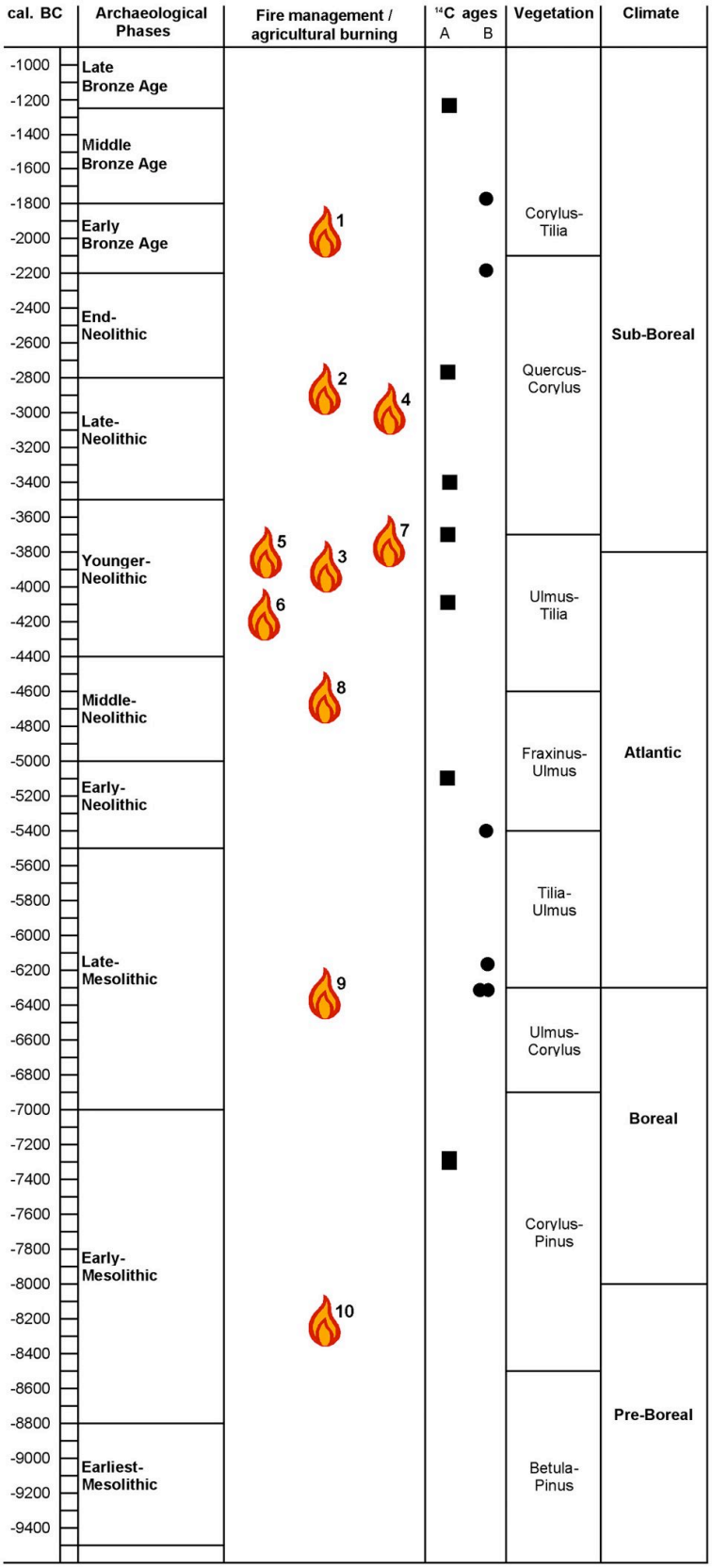

Fig. 10 Time-scale showing archaeological periods, evidence for anthropogenic burning in Central Europe (flames) and the radiocarbon ages of macro- (A) and microcharcoal (B) samples (younger ages are not shown). 1: Gobet et al. (2003); 2: Clark et al. (1989); 3: Rösch (1993); 4: Carnelli et al. (2004); 5, 6: Tinner et al. (2005); 7: Iversen (1941); Kalis and Meurers-Balke (1998); 8: Kerig and Lechterbeck (2004); 9: Haas (1996); Erny-Rodmann et al. (1997); 10: Bos and Urz (2003).

4.1.4 Methodology

Radiocarbon dating of macrocharcoal particles deriving from anatomically identified wood species is commonly used for palaeoecological reconstructions. This approach was used to identify fire-events from soil charcoals in Southern Switzerland (*Manuscript VIII*). The AMS ^{14}C ages suggested a relocation of soil material during the Late Holocene in two of three investigated soil profiles. The undisturbed soil profile contained the oldest charcoal (*Pinus* sp.; 11270-10980 BC) indicating that the fires occurred during the warm and dry Allerød. The presence of two charcoals from chestnut wood aged 1000 – 800 BC and 410 – 200 BC respectively, contrasted to the pollen based model of chestnut trees introduction (*Castanea sativa*) by the Romans around 50 BC. The chestnut came to the Ticino from Northern Italy about 1000 years earlier than expected, either by natural dispersion or through the Celtic Lepontian people.

Not only macrocharcoal, but also chemically isolated microcharcoal material can be used for radiocarbon dating (*Manuscript VII*), although the comparison of ^{14}C AMS ages of micro- and macrocharcoal sample pairs showed that the ages of both charcoal fractions are not comparable. Microcharcoal yielded older ages, presumably because it consists of more stable carbon compounds than macrocharcoal, but the differences did not correlate.

NMR spectroscopy can determine the composition of soil organic matter. Until now it was not known if different instrumental setups would produce comparable results. The spectra of 15 soil samples, taken from the experimental burning plot, were acquired at two different magnetic field strengths, 200 and 400 MHz (*Manuscript IX*). The results obtained from the two different instruments were directly comparable and correlated with the different carbon types.

4.2 Conclusions

The charcoal particles produced during slash-and-burn were incorporated into the soil profile, mainly by earthworms, but also by root growth and other soil-mixing animals. The aromatic compounds in the charcoal material are colouring agents, they could be responsible for the dark colour not only of the investigated soils in the Lower Rhine Basin but also of Chernozems and related soil types. Charcoal is slowly incorporated into the soil matrix. It should be considered that the charcoals we find in Chernozems today are several thousand years old. We do not know how much charcoal was brought into the soils over time and how much was lost through microbial decomposition, by oxidation and by translocation due to erosion. We do know that the mass of potentially available charcoal after one fire is relatively high, it even exceeds the amount of charcoal produced during wildfires in boreal forests.

Soils having the properties of Chernozems could have completely different formation histories. The distribution of Chernozems does not seem to be dependent on natural factors alone, biomass burning for agricultural purposes should be considered an additional soil forming factor. It is now open as to wether the Early Neolithic settlers preferred to grow crops where Chernozems occurred or if prehistoric fire-management, like slash-and-burn, formed soils that have chernozemic properties.

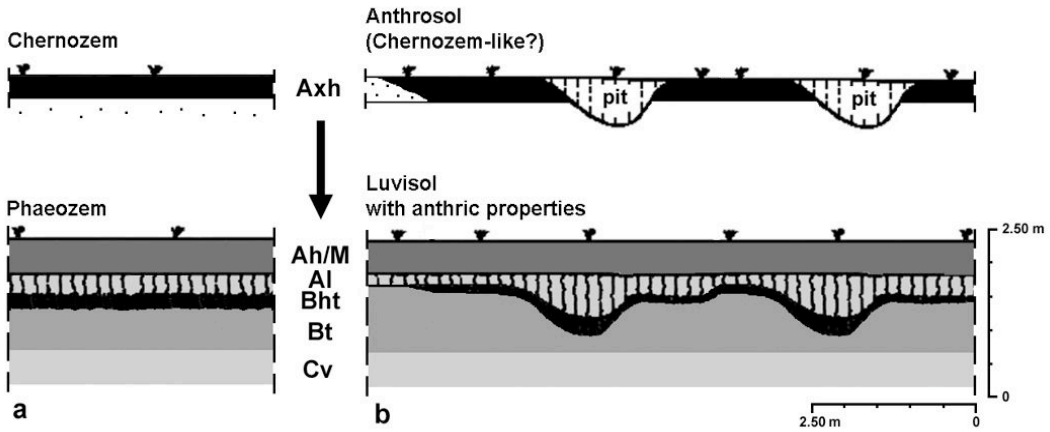

Fig. 11 Proposed formation of dark soils in the Lower Rhine Basin. a: Degradation model from Chernozem to Phaeozem. b: Soil formation as observed in this study. Clay and humus were transported from the topsoil (former Axh horizon and pit fillings) into the recent Bht horizons, which inherit the black colour along the former pit structures. Often a colluvial cover (M horizon) protects the Bht horizons against erosion (modified according to *Manuscript IV*).

The Luvic Phaeozems investigated in this study formed as a result of anthropogenic burning during several (pre)historic epochs, possibly providing the basis for the change to a cultural landscape in the Late-Neolithic. The fires were burnt to clear vegetation before using a field for cropping, or/and to keep grassland open for cattle husbandry or hunting. A general use of other soil amendments like manure could not be proven. The soils are not Luvic Phaeozems, they should be classified as Luvisols with a degraded fossil anthric (anthropogenic) horizon (Fig. 11). The degraded anthric horizon would be a relic of a former topsoil, presumably of an Anthrosol.

In the Lower Rhine Basin, changes in plant composition and increased colluviation during the Late to End Neolithic indicated a transformation from a forested to an open parklandscape (Fig. 12), presumably as a result of a fire-based livestock farming. This development from a natural to a human-dominated landscape could be shown in the investigated dark soils.

Fig. 12 Archaeobotanical records give evidence for a change from natural landscape to a human-dominated cultural landscape in NW-Germany during the Neolithic. Left: Dense deciduous forests dominated by lime (*Tilia*) and elm (*Ulmus*) as they were found by the first settlers (Linienbandkeramik; Early Neolithic 5500-5000 BC). Right: The transformation to open oak (*Quercus*)-dominated forests (End-Neolithic 2800-2200) could be connected to a fire-based animal husbandry since the Younger Neolithic (4400 BC; Meurers-Balke et al. 1999).

One of the aims of the study was to apply geochemical methods to detect human impacts in soil material. This was problematic, mainly because not enough control samples were available and the phosphorus measurement method used needs to be evaluated further. The soil charcoal analysis, including the ^{14}C dating of microcharcoal, can be considered as beneficial tools for reconstructing palaeoenvironments.

4.3 Implications

The results of this study may have implications for:

Soil Science

The pedogenesis of Chernozems in Central Europe is not clear yet because not all dark soils are relics of steppe soils, soil classifications should not be biased by the formation history of that soil. Man and fire could be the factors that account for the formation of black, humus-rich soils. Relatively stable charcoal particles are mixed into the soil profile via bioturbation, the presence of aromatic compounds in the charred organic matter influences the soil colour. In general, the human impact on soils should not be underestimated in future pedological studies.

Archaeology

Soils could be anthropogenic artefacts and therefore archaeological features. Soil features that do not contain visible artefacts should be documented at excavations. Archaeologist should take into account that soils could give new insights into off-site-archaeology and the development of agricultural techniques in prehistorical times.

Geoarchaeology and (palaeo)ecology

Geochemical methods are useful tools for reconstructing not only agricultural systems, but also the environmental history of soil material. It is necessary to apply the methods to a carefully chosen set of samples and to further develop and evaluate the methods that are useful for research. The results from the slash-and-burn experiment could help to interpret charcoal data from sediment archives and past fire events (Carcaillet et al., 2002). The knowledge of prehistoric burning rates would also help to estimate the impact of possible future scenarios. Today, climate change leads to warmer and drier summers, an increase in the amount of wildfires is predicted for temperate regions and deciduous forests (Westerling et al., 2006).

5 Perspectives

Many questions remained unanswered, while others emerged during the investigation, and these questions could be potential topics for further research.

> Why, and which material did the prehistoric farmers burn, which agricultural systems (growing of crops/animal husbandry) dominated in different time periods?
>
> How did the farmers fertilize the soils, by burning or by adding manure or plant material?
>
> What is the long-term fate of charcoal particles in the soil (translocation)? Why do we find old charcoals preserved in soil material (decomposition)?

For future research it could be beneficial to apply methods, which were already used in other contexts or to enhance existing methods. Possible approaches would be to

- determine the amount and species of phytoliths in the archaeological soil material to gain information about the plant species grown on the fields (Boyd, 2002; Parr, 2006);
- isolate sterol-compounds from the lipid fractions to identify the possible sources of manure, or to identify animal husbandry and the species which was bred (Simpson et al., 1999a), and test compound-specific ^{14}C-dating of the soil lipids (Stott et al., 2003; Rethemeyer et al., 2004);
- apply advanced methods of phosphorus analysis in samples from the Late to End Neolithic and the burning experiment, e.g. the Hedley fractionation (Hedley et al., 1982; Lehmann et al., 2004) or ^{31}P spectrometry (Amelung et al., 2001), to investigate the fate of phosphorus after burning (translocation, mineralization);
- search for stable nitrogen compounds formed during heating of soils (pyrrols) with ^{15}N NMR (González-Pérez et al., 2004) to find an explanation for the narrow C:N ratios in the Phaeozem soils;
- investigate the distribution of trace-elements as potential additional markers for burning or manuring (Entwistle et al., 2000; Knudson et al., 2004; Cook et al., 2006);
- measure the magnetic susceptibility to elucidate why Chernozems and Early Neolithic settlement soils have an increased susceptibility (Hanesch and Scholger, 2005), while the soils burnt at the burning experiment and settlement soils from other periods have not (Ch. Hartkopf-Fröder, pers. comm.);

- follow the fate of charcoal particles in soils with long-term field experiments and laboratory experiments in columns, also applying a method for black carbon quantification;
- test if PAHs could also be useful markers for burning events in past times (Bucheli et al., 2004; Lima et al., 2005).

A main future task would be to consolidate the existing archaeological and palaeoecological data derived from geoarchaeology, palaeobotany and geochemistry. Only few estimates of Neolithic land-use, the sizes of arable lands and population densities exist (Gregg, 1988; Zimmermann and Wendt, 2003), and an integrative synopsis would allow to build an extended model of human impact on the environment in prehistoric societies.

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Part B
Manuscripts

Manuscript I

Conversion of biomass to charcoal and the carbon mass balance from a slash-and-burn experiment in a temperate deciduous forest

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Conversion of biomass to charcoal and the carbon mass balance from a slash-and-burn experiment in a temperate deciduous forest

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Abstract: Anthropogenic burning, including slash-and-burn, was deliberately used in (pre)historic Central Europe. Biomass burning has affected the global carbon cycle since, presumably, the early Holocene. The understanding of processes and rates of charcoal formation in temperate deciduous forests is limited, as is the extent of prehistoric human impact on the environment. We took advantage of an experimental burning to simulate Neolithic slash-and-burn, and we quantified the biomass fuel and charcoal produced, determined the resulting distribution of the charcoal size fractions and calculated the carbon mass balance. Two-thirds of the charcoal particles (6.71 t/ha) were larger than 2000 μm and the spatial distribution of charcoal was highly variable (15–90% per m^2). The conversion rate of the biomass fuel to charcoal mass was 4.8%, or 8.1% for the conversion of biomass carbon to charcoal carbon, and 58.4 t C/ha was lost during the fire, presumably as a component of aerosols or gases.

Key words: Slash-and-burn experiment, temperate deciduous forest, charcoal, carbon mass balance, biomass burning.

Introduction

The timing of the onset of anthropogenic influence on the global climate system is still under discussion and is possibly connected to anthropogenic fires (Carcaillet *et al.*, 2002; Ruddiman, 2003). Palaeobotanical records suggest that anthropogenic burning was common in the past and may have been used as a tool for hunting, herding and farming. Anthropogenic fire occurred with high spatial and temporal variation (Pyne, 1994). In temperate central Europe, burning for landscape management and agriculture lasted from the prehistoric Mesolithic until the modern nineteenth century. Most evidence for (pre)historic fire-clearance husbandry comes from alpine regions and the pre-alpine midlands (Clark *et al.*, 1989; Rösch, 1993; Haas, 1996; Erny-Rodmann *et al.*, 1997; Carcaillet, 1998; Tinner *et al.*, 2005), Scandinavia (Iversen, 1941; Kalis and Meurers-Balke, 1998; Hörnberg *et al.*, 2006) and Great Britain (Mason, 2000; Blackford *et al.*, 2006).

The fossil charcoal records, however, do not necessarily reflect former burning and land-use systems. Experimental field studies on slash-and-burn could improve our understanding of the processes involved in anthropogenic burning in temperate deciduous forests. They should include budgets for biomass fuel, charcoal and carbon to infer taphonomical implications such as conversion rates from biomass to charcoal, charcoal size distribution and spatial heterogeneity. But, to the best of

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our knowledge, neither biomass nor charcoal budgets were taken into account in previous slash-and-burn experiments.

We took advantage of a burning experiment in southwest Germany (Forchtenberg) in a deciduous forest. The objectives of our study were: (i) to quantify the biomass fuel and charcoal produced during a typical slash-and-burn event in a temperate deciduous forest, (ii) to determine the distribution of the produced charcoal in size fractions, and (iii) to calculate the carbon mass balance.

Materials and methods

Site description

The experimental slash-and-burn was designed to mimic Neolithic agricultural slash-and-burn in order to asses the effects on vegetation, crop yields and soil properties (Rösch *et al.*, 2002). The site is located near Forchtenberg (SW Germany; 49°16' N, 09°28' E) in a temperate deciduous forest. *Fagus*, *Carpinus* and *Acer* dominate the forest composition and the undergrowth species are characteristic for a woodruff-beech forest (*Galio-Fagetum*). The trees are about 40 years old and the area has been forested for at least two centuries. The site is 3.5 ha in area; it is slightly sloping and exposed to the south (320 m a.s.l.). The mean annual temperature is 8.9°C and the mean annual precipitation is 849 mm. The soil is a Haplic Luvisol (WRB) with partly stagnic properties. Soil moisture was 30 vol.% on the day of burning.

Burning technique

The trees were cut down within a plot of 30 m × 30 m (April 2004), the trunks and larger branches (diameter >10 cm) were removed from the site. The small wood pieces were left to dry until an area 11 m × 8 m was burnt in October 2004. A pile of burning wood was drawn over the ground with long hooks and was continually fed with wood. This technique was used so that the grass and herbaceous vegetation could burn completely and to distribute the charcoal and fertile ash as homogeneously as possible. Similar techniques are known from historical slash-and-burn agriculture in central European mountainous regions; they were described by Schmithenner (1923) and were used in former slash-and-burn experiments (Reynolds, 1977).

Determination of biomass fuel and produced charcoal masses

We determined the amount of dry biomass by (i) weighing the total amount of wood used for burning and measuring its water content, and (ii) collecting the homogeneously distributed grass and herbaceous plants from four different 1 m^2 plots located outside of the burning field and weighing it after drying in an oven at 40°C for three days.

After the burning, the distribution of charcoal particles on the soil surface was visually estimated. We sampled 20 replicates of charcoal and unburnt aboveground biomass using a frame (0.2 m × 0.2 m) and a vacuum cleaner. Each sample was collected in a separate vacuum cleaner bag. Samples were wet-sieved and passed through the mesh sizes 2000 μm, 1000 μm, 500 μm, 250 μm and 125 μm. The material <125 μm, including mineral soil material, was collected and dried. After drying the samples at 40°C for 48 h, they were weighed.

Charcoal particles were separated from the unburnt material for all 20 samples of the fraction >2000 μm and for seven randomly selected samples of the fraction 1000–2000 μm. The charred and uncharred fractions were subsequently weighed. We defined charcoal as black particles completely charred on the surface.

Carbon and nitrogen concentrations and mass balance

Total carbon and nitrogen concentrations were determined for 20 charcoal samples >2000 μm, 20 samples <125 μm and for uncharred biomass samples (beech wood and grass material) by dry combustion via an elemental analyser (Elementar VarioEL). The measured carbon and nitrogen concentrations were used to calculate the carbon and nitrogen mass balance for biomass fuel and resulting charcoal.

Results and discussion

Before the fire, we estimated a woody aboveground biomass of 278 t/ha on the site, a common value for temperate deciduous wood (180–600 t/ha; Schulze *et al.*, 2002). We used 131 t/ha of wood fuel (dry mass) to burn the plot. The moisture content of the wood was 34 vol.%. Grass and herbaceous vegetation comprised a very small proportion of the total fuel mass (Table 1).

This is the first slash-and-burn experiment to record the amount of fuel and the mass of charcoal produced in deciduous forest, and a comparison with data available from natural wildfires is difficult. The amount of fire-consumed biomass varies from ecosystem to ecosystem and fire to fire (Schimmel and Granström, 1996). As examples, burning logging slash (conifer or eucalyptus wood) consumed 140 t/ha, a fire in primary tropical forest 77–228 t/ha (Stocks and Kaufmann, 1997). The amount of wood fuel used during our burning experiment fits well with the above-mentioned amount of burnt logging slash, and it is also in the range of primary tropical forest.

After the fire, the distribution of the remaining biomass on the plot was heterogeneous. The coverage of the area with charcoal after the fire varied between 15 and 90% per m^2. The material remaining on the plot after burning was dominated by fragments larger than 2000 μm (6.71 ± 0.66 t/ha, standard error), compared with the smaller fractions (0.31 ± 0.04 t/ha in 1000–2000 μm), as shown in Figure 1. The amount of charred material reflects the amount of consumed fuel. Natural boreal forest fires in Scandinavia produced 0.235 t/ha of charcoal (Ohlson and Tryterud, 2000) and a high-intensity fire in Siberia generated 0.735 t/ha of airborne charred particles (Clark *et al.*, 1998). A clearing fire in the Amazonian rainforest produced 4.3 t/ha charcoal (Fearnside *et al.*, 2001). Charcoal yields obtained in our burning experiment were larger probably because the burning technique used here involved larger quantities of small-wood fuel and the burning was less intensive than in the wildfires.

The conversion rate was calculated using the total dry biomass and the charcoal mass >2000 μm. We found that 4.8% of the biomass fuel was converted to charcoal, and this is similar to that from fires in other ecosystems. Novakov *et al.* (1997) estimated that generally less than 10% of biomass is converted to charred carbon during wildfires. Wildfires in boreal forest converted 2.0% (Clark *et al.*, 1998) or 2.2% (Lynch *et al.*, 2004) of biomass to charcoal, while an intense crown fire converted 8.0% of fuel to visually identified charcoal (Tinker and Knight, 2000). Slash-and-burn in Amazonian tropical forests converted 1.3–2.9% of fuel carbon to charcoal carbon (Fearnside *et al.*, 2001). The conversion rates differ owing to different burning and sampling conditions; however, the rate of 4.8% measured in our experiment and the rates from Amazonian rainforest and boreal forests are relatively close.

Both organic carbon and nitrogen concentrations increased during the charring of biomass. The average carbon concentration in the wood samples was 463 ± 1.5 g C/kg. Before slashing, the carbon stock of the total woody biomass on the plot was

Table 1 Carbon and nitrogen concentrations (g/kg) and carbon and nitrogen stocks (t/ha) with standard errors in biomass fuel and in post-fire above-ground charcoal and uncharred biomass samples

Material	Particle size (μm)	*n*	Mass (t/ha)	*n*	Carbon		Nitrogen	
					Conc. (g/kg)	Stocks (t/ha)	Conc. (g/kg)	Stocks (t/ha)
Total woody biomass before slashing			278		–	129[a]	–	0.15[a]
Wood fuel			131	2	463 ± 2	61[a]	0.5 ± 0.3	0.07[a]
Grass fuel		4	9.24 ± 0.37	2	437 ± 0	4.04[b]	23.5 ± 0.5	0.22[b]
Charcoal	>2000	20	6.71 ± 0.66	20	775 ± 1	5.20[c]	6.7 ± 0.2	0.04[c]
Uncharred	>2000	20	1.87 ± 0.16		–	0.86[a]	–	0.00[a]
Charcoal	1000–2000	7	0.31 ± 0.04		–	0.24[c]	–	0.00[c]
Uncharred	1000–2000	7	0.10 ± 0.02		–	0.05[a]	–	0.00[a]
Total	500–1000	20	0.66 ± 0.04		–	–	–	–
Total	250–500	20	0.63 ± 0.04		–	–	–	–
Total	125–250	20	0.81 ± 0.08		–	–	–	–
Total	<125	20	0.35[d]	20	144 ± 0	–	5.0 ± 0.2	–

The stocks were calculated using the nitrogen and carbon concentrations and the masses of samples. All size fractions contained charcoal; the fractions >2000 and 1000–2000 μm were visually sorted into charred and uncharred particles.
Averages with standard error.
[a] Calculated with wood C or N concentration.
[b] Calculated with grass C or N concentration.
[c] Calculated with charcoal C or N concentration.
[d] Mass of soil mineral matrix was calculated and substracted from total.
– Not determined.

129 t C/ha. About one-half of the wood material (containing 61 t C/ha) was burnt, together with herbaceous and grass vegetation (4 t C/ha). Nitrogen concentrations in the wood charcoal (6.7 ± 0.2 g N/kg) were larger than in the initial wood (0.5 ± 0.2 g N/kg), showing the preferential enrichment of nitrogen during charring (Almendros *et al.*, 2003). After the fire, 5.2 t C/ha was left in charcoal particles >2000 μm and 0.9 C t/ha in the uncharred debris. Thus, 8.1% of the biomass fuel carbon (wood fuel and grass) was converted to charcoal carbon and 1.3% was left uncharred. We calculated a loss of carbon through aerosols and gases during one fire of 58.4 t C/ha, or 90.6% of the biomass fuel carbon. The calculated mass of emitted CO_2 during the fire was 206 t CO_2/ha, using the emission factor for CO_2 from extratropical forest fires (1569 g CO_2/kg dry fuel burnt) published by Andreae and Merlet (2001).

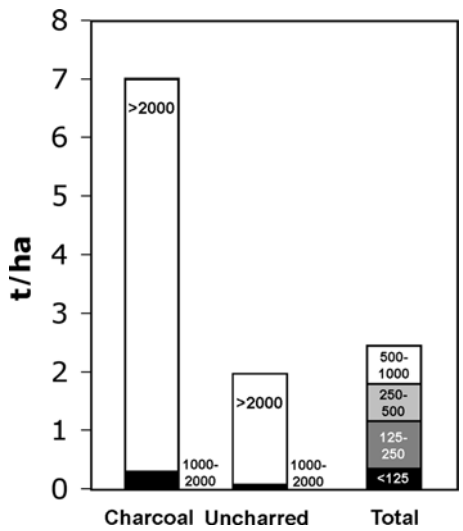

Figure 1 Distribution of litter layer biomass stocks (t/ha) after slash-and-burn in the different size classes (in μm). The fractions >2000 and 1000–2000 μm were visually sorted into charred and uncharred particles

Several limitations to our study should be considered: (i) fires are highly variable. Even our attempts to burn homogeneously led to a heterogeneous distribution of charcoal. The forest at the research area is not a primary forest but a young secondary forest, and the first Neolithic settlers may have encountered denser forests holding more biomass. Nevertheless, we could quantify the amount of biomass fuel and the associated charcoal yield for a fire in a typical deciduous forest. (ii) We assume that in our experiment no large charcoal particles (>500 μm) were carried away by heat exturbations or wind during the burning (Patterson *et al.*, 1987). (iii) The elemental composition of charcoal may differ and depends on the plant tissue from which the charcoal particles are derived and on the charring procedure that occurred.

Conclusions

Experimental slash-and-burn in a temperate deciduous forest converted 4.8% of the forest biomass to charcoal >2000 μm, or 8.1% of the initial biomass fuel carbon to charcoal carbon. During the fire, 58.4 t C/ha was lost as a component of aerosols or gases.

After the burning, the spatial distribution of charcoal was highly variable because the fire, although controlled, did not burn homogeneously. Thus, for representative results, both in the recent and even more in the fossil terrestrial record, a large number of sample replicates is a prerequisite.

The burning produced mainly charcoal particles >2000 μm (6.71 t/ha), which may imply that macrocharcoal would dominate the sedimentary charcoal records. However, before inferring amounts of burnt biomass from the sedimentary charcoal records, one should further investigate the fate of charcoal after its formation, a field where little quantitative information is available.

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Manuscript II

Minor changes in soil organic carbon and charcoal concentrations detected in a temperate deciduous forest a year after an experimental slash-and-burn

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Minor changes in soil organic carbon and charcoal concentrations detected in a temperate deciduous forest a year after an experimental slash-and-burn

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Abstract. Anthropogenic fires affected the temperate deciduous forests of Central Europe over millennia. Biomass burning releases carbon to the atmosphere and produces charcoal, which potentially contributes to the stable soil carbon pools and is an important archive of environmental history. The fate of charcoal in soils of temperate deciduous forests, i.e. the processes of charcoal incorporation and transportation and the effects on soil organic matter are still not clear. We investigated the effects of slash-and-burn at a long-term experimental burning site and determined soil organic carbon and charcoal carbon concentrations as well as the soil lightness of colour (L*) in the topmost soil material (0–1, 1–2.5 and 2.5–5 cm depths) before, immediately after the fire and one year later. The main results are that (i) only a few of the charcoal particles from the forest floor were incorporated into the soil matrix, presumably by soil mixing animals. In the 0–1 cm layer, during one year, the charcoal C concentration increased only by 0.4 g kg^{-1} and the proportion of charcoal C to SOC concentration increased from 2.8 to 3.4%; (ii) the SOC concentrations did not show any significant differences; (iii) soil lightness decreased significantly in the topmost soil layer and correlated well with the concentrations of charcoal C (r=−0.87**) and SOC (r=−0.94**) in the samples from the 0–5 cm layer. We concluded that Holocene biomass burning could have influenced soil charcoal concentrations and soil colour.

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1 Introduction

Palaeobotanical records indicate that anthropogenic fires were common in the past and might have been deliberately used for hunting, herding or farming. Fire-clearance husbandry, or slash-and-burn, was used for landscape management and agriculture from the prehistoric Mesolithic until the modern 19th century and thus may have affected the global carbon cycle during the last 10 000 years (Anderson, 1994; Pyne, 1994; Carcaillet et al., 2002; Tinner et al., 2005).

Anthropogenic burning had the highest impact on the landscape during the Late-Neolithic (3500–2200 BC) when the natural landscape of Central Europe was transformed into a cultural landscape, and new regions were able to be colonized using the fertilizing and clearing effects of burning (W. Schier, personal communication; Lüning, 2000; Kalis et al., 2003). The first evidence for Neolithic agricultural burning came from Northern Germany and Denmark where burning accompanied the transition from Mesolithic to Neolithic agricultural techniques since 4000 BC (Iversen, 1941; Kalis and Meurers-Balke, 1998). Clark et al. (1989) reported that farmers in Late to End Neolithic (4400–2200 BC) used fire to transform forest into arable land. Shifting cultivation with slash-and-burn was proposed by Rösch (1993, 2000) for the pre-alpine lowlands during the Late Neolithic period (4300–3500 BC). Charcoal records from the Swiss midlands and alpine regions suggested that the burning of forest to gain arable land or meadows occurred not only in Neolithic but also in Bronze and Iron Age (Gobet et al., 2003; Tinner et al., 2005). Fire-fallow silviculture has been used until modern times, e.g. in the Black Forest to encourage oaks for tannic acid (Goldammer et al., 1997) or in Southern Switzerland to enhance the cultivation of chestnut trees (Conedera et al., 2004).

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Table 1. Soil properties of the investigated Haplic Luvisol in the Forchtenberg experimental site (data provided by L. Herrmann).

Horizon	Depth	Sand	Silt	Clay	pH	C/N
	cm		$g\,kg^{-1}$		$CaCl_2$	
Ah	0–16	40	810	150	3.9	12
E	16–54	40	800	160	4.0	10
Bt	54–104	20	750	230	4.6	5
Bvt	104–151	20	790	190	5.3	5
Bv	151–179	10	800	190	5.8	5

Biomass burning releases an estimated 2.5 Pg atmospheric carbon per year (van der Werf et al., 2006). Vegetation fires also produce charcoal or black carbon, which are part of a continuum of material generated during incomplete combustion of biomass (Kuhlbusch, 1998). Although recent investigations have shown that microbes can degrade black carbon (Hamer et al., 2004; Hockaday et al., 2006), it still contributes to the slow carbon pools in soils (Skjemstad et al., 2004). Biomass burning could affect the soil carbon stocks, as modelled for the boreal system (Harden et al., 2000) but field observations and experimental studies are rare and have been conducted mainly in savannah, tropical or boreal forests (Forbes et al., 2006). Long-term observations, after burning, have revealed all possible variations: either no changes in soil organic carbon stocks (Roscoe et al., 2000; Dai et al., 2005), a reduction (Bird et al., 2000) or an increase (Ojima et al., 1994). However, the data about soil carbon and charcoal and their dynamics in the soil profile after a fire is limited and to our knowledge no quantitative assessment has been attempted in temperate deciduous forests (Preston and Schmidt, 2006).

The condensed aromatic structure of charcoal or black carbon allows charcoal particles to persist in soils and other sedimentary records over millennial time-scales and makes it possible to reconstruct environmental history and past forestfires (Patterson III et al., 1987; Willis and van Andel, 2004; Wang et al., 2005) or to infer pedological processes (Carcaillet et al., 2006). The interpretation of soil charcoal data needs an understanding of the taphonomical processes that affect charcoal particles but uncertainties still remain related to charcoal transport following a fire or charcoal burial and mixing within a soil profile.

Burning has an effect on soil colour; recent work has shown that the content of aromatic carbon, a carbon species which dominates the black carbon structure, correlated significantly with soil lightness (Spielvogel et al., 2004) and that black carbon might be responsible for the dark colour of Chernozem humus horizons (Schmidt et al., 2002). Onethird of the organic matter of fossil dark soil horizons embedded in lighter Haplic Luvisols consisted of black carbon derived from Holocene anthropogenic burning (Gerlach et al., 2006).

In this study, we investigated the influence of slash-and-burn in a temperate deciduous forest on soil organic carbon budgets as part of an experimental burning in Forchtenberg (SW-Germany; Rösch et al., 2002). The same experiment delivered data about the conversion of biomass fuel to charcoal during a slash-and-burn and the amount of charcoal left in the litter layer (Eckmeier et al., 2007).

Our main research questions in this study were: (i) How much of the charcoal produced during one fire (slash-and-burn) do we find in the soil mineral matrix after one year? (ii) Are the total soil organic carbon concentrations affected by the fire? (iii) Does the soil colour change and does it correlate with the soil charcoal carbon and soil organic carbon concentrations?

2 Materials and methods

2.1 Site description and burning technique

The burning took place in October 2004 on a trial site located near Forchtenberg (SW-Germany; 49°16′ N, 09°28′ E) on a slightly sloping (2–4%) and south-exposed plain (320 m a.s.l.). Mean annual temperature is 8.9°C, mean annual precipitation is 849 mm. On the day of burning the average temperature was 18.4°C and the average relative humidity was 71%.

The 3.5 ha area is situated in a temperate deciduous forest dominated by *Fagus*, *Acer* and *Carpinus* (Rösch et al., 2002). The undergrowth species are characteristic for a woodruff-beech forest (*Galio-Fagetum*). The area has been forested for at least two centuries; the trees are about 40 years old. The soil is an acidic Haplic Luvisol (WRB-FAO) with partly stagnic properties (Table 1). We investigated the changes in soil organic carbon and charcoal carbon concentrations of the topsoil material (Ah, 0–16 cm depth), which is followed by an eluviation horizon (E), an argic horizon with hydromorphic features (Bt), a cambic to argic horizon (Bvt) and a cambic horizon (Bv). The parent material is loamy loess over Triassic sandstone. Soil moisture was 30 vol. % on the day of burning.

After the trees were cut on a plot of 30×30 m (April 2004), the trunks and large branches (diameter >10 cm) were removed from the site. The smaller branches were allowed to dry over the summer. In autumn (October 2004) an area of 11×8 m was burnt. The dried wood was collected into a pile off the burning site and a row on the burning site. The wood in the row was ignited and drawn over the ground using long hooks for pulling and permanently supplemented with wood from the pile. This technique was applied to completely burn the grass and herbaceous vegetation and to distribute the charcoal and ash as homogeneously as possible. The temperatures in the soil during the burning were monitored at soil depths of 1, 2, 5 and 10 cm using six temperature

Table 2. Means and standard errors for soil samples taken before the burning (control), immediately after the burning (burnt) and one year after the burning (burnt 1 yr). The values are given for the three depths and the weighted average.

Sample		*n*	L*		SOC		Charcoal C		Charcoal C	Charcoal Mass[1]
	cm			*p*	g kg^{-1}	*p*	g kg^{-1}	*p*	% of SOC	g kg^{-1}
control	0–1	14	49.5±0.5		53.9±1.9		1.5±0.1		2.8	2.0
control	1–2.5	14	51.3±0.4		38.9±1.7		1.1±0.1		2.7	1.4
control	2.5–5	19	52.7±0.4		31.0±1.1		0.8±0.0		2.5	1.0
average[2]	0–5		51.6		37.9		1.0		2.6	1.3
burnt	0–1	17	47.9±0.2	0.124	55.2±1.7	0.925	1.6±0.1	0.802	3.0	2.1
burnt	1–2.5	17	50.3±0.3	0.397	39.5±1.2	0.826	1.1±0.1	0.925	2.8	1.4
burnt	2.5–5	19	52.5±0.3	0.904	29.7±1.1	0.629	0.8±0.1	0.872	2.6	1.0
average[2]	0–5		50.9		37.7		1.1		2.7	1.4
burnt 1 yr	0–1	20	46.3±0.3	0.009	55.2±1.1	0.975	1.9±0.1	0.363	3.4	2.5
burnt 1 yr	1–2.5	20	49.6±0.3	0.167	38.8±1.0	0.432	1.1±0.1	0.730	2.7	1.4
burnt 1 yr	2.5–5	20	53.0±0.2	0.546	26.8±0.7	0.147	0.6 (0.4)[3]±0.0	0.081	2.1	0.7
average[2]	0–5		50.6		36.0		1.0 (0.9)[3]		2.5	1.3

p-values refer to control samples. [1] calculated with average C concentration (775 g kg^{-1}) of charcoal particles in the litter layer (Eckmeier et al., 2007); [2] weighted average; [3] when normalized to the bulk density, the charcoal C concentrations change only in the bottom layer of the burnt 1yr sample set.

loggers. The maximum temperature measured was 72°C at 1 cm depth.

2.2 Soil sampling and analyses

Soil samples were collected in a random sample design in plastic tubes (6×4×15 cm) from the topsoil: 20 samples before burning (control), 20 samples immediately after the burning (burnt) and 20 samples one year after burning (burnt 1yr). They were cut into three depth intervals (0–1, 1–2.5, 2.5–5 cm) and dried at 40°C for 24 h. The aggregates were crushed and coarse material (roots and charcoal particles) >2000 μm was separated by sieving. Sub-samples were ground for carbon analyses.

Total carbon concentrations were determined for all soil samples by dry combustion via an elemental analyzer (Elementar VarioEL). The values for total organic carbon corresponded to the total carbon content because the soil samples did not contain carbonates.

The analysis of charred material in the soil samples was performed using mid infrared - Fourier transformed infrared spectroscopy (MIR-DRIFT; Viscarra Rossel et al., 2006; Janik et al., 2007). Samples were ground and measured directly and the spectra obtained were fitted with the calibration sample set (data collection CSIRO Land and Water, Adelaide). The soil properties were subsequently predicted using partial least-squares (PLS) analysis. For charcoal carbon concentrations the method reached a high correlation of R^2=0.86.

The soil colour was expressed as lightness (L*; Commission Internationale de l'Eclairage, CIE 1976 Standard Observer). The L* values indicate the extinction of light on a scale from L* 0 (absolute black) to L* 100 (absolute white). The soil samples were measured in triplicate using a photo spectrometer (Dr. Lange spectro-color) by observing the diffused reflected light under standardised observation conditions. We used dried and homogenized but not ground samples because grinding the soil material would increase the soil lightness (Torrent and Barrón, 1993).

For micromorphological analysis, undisturbed soil samples were collected with Kubiëna tins (8×6×4 cm). The blocks were air dried, impregnated with Palatal P80-21 polyester resin (BASF) and sliced into 75×55×0.3 mm thin-sections. The sections were described at 12.5–400× magnification under a petrological microscope. Detailed principles and methods used for micromorphological analysis have been described by Stoops (2003).

Data was statistically analysed using the Kolmogorov-Smirnov test for normal distribution. Because the data is not normally distributed, the Wilcoxon test was applied to compare paired samples, and the Spearman correlation (Sigma 2-tailed) to express significant correlations.

3 Results and discussion

3.1 Incorporation of charcoal from the forest floor into the soil mineral matrix

The charcoal carbon (C) concentrations decreased significantly with depth in all sample sets (p=0.000-0.004), as shown in Table 2. Immediately after the burning, 0.1 g kg^{-1} charcoal C had been added into the 0–1 cm layer from the

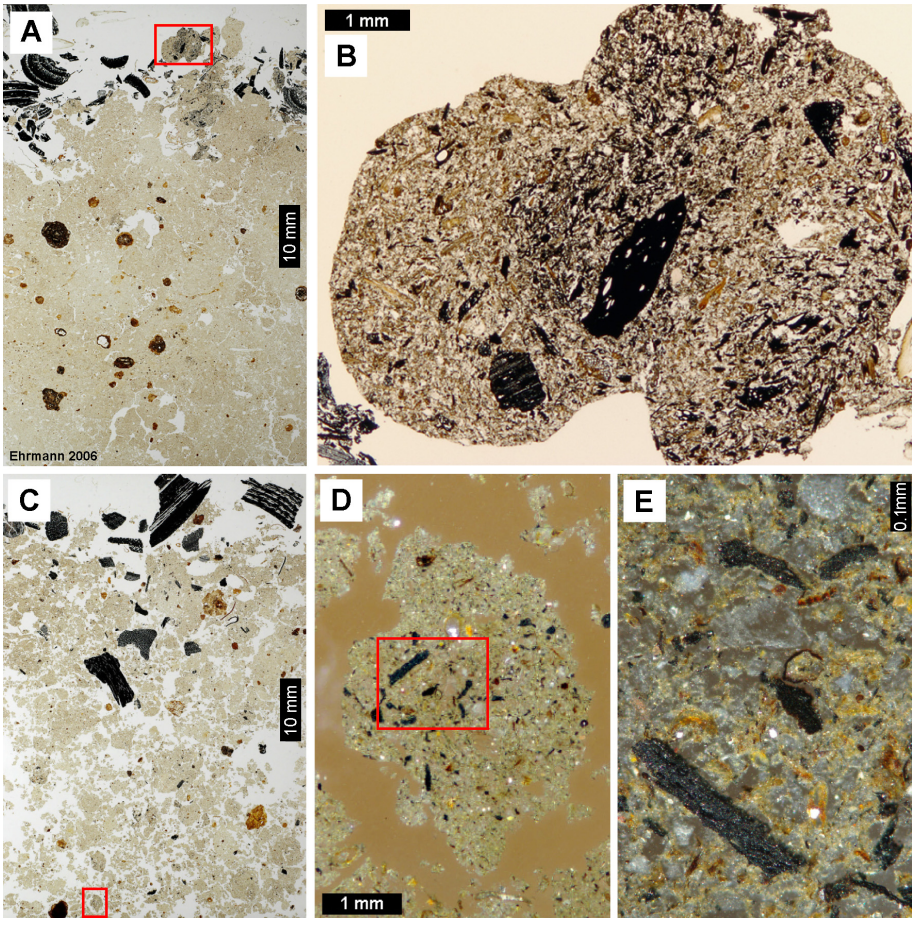

Fig. 1. Thin-sections taken from burnt plots at the Forchtenberg experimental site nearby the plot investigated in this study. **(A)** top 80 mm of a soil (burnt October 2003), showing the situation two years after burning; black charcoal particles lying on the forest floor and earthworm facies containing charcoal; the brown particles in the grey soil matrix are concretions of iron. **(B)** enlargement of the rectangle in (A) (earthworm facies). **(C)** top 80 mm of a soil (burnt October 1998), showing the situation six years after burning; charcoal particles were incorporated into the soil and translocated; **(D–E)** enlargements of the rectangles in the previous figures (earthworm facies), (E) was rotated in 90°; photographs (A–C) were taken using plain polarized light, (D) and (E) using incident light.

charcoal laid upon the surface. One year after the experimental burning, charcoal C concentrations in the 0–1 cm depth had increased by 0.4 g kg^{-1}. On the other hand, the charcoal C concentrations decreased in the 2.5–5 cm depth interval, which gave a constant charcoal C concentration throughout the top 5 cm of the soil profile (weighted average). The control samples contained charcoal, which indicated that charcoal from previous fires laid in the areas surrounding the research field already had already been mixed into the soil material.

The slash-and-burn experiment also provided data on the charcoal budget of slash-and-burn in a temperate deciduous forest. The percentage of the biomass converted to charcoal C is 8.1%, that is 5200 kg ha^{-1} left on the forest floor (Eckmeier et al., 2007). The incorporation of charcoal particles into the soil and their subsequent translocation was observed in thin-sections taken from different burning plots at the same experimental site. Mice had probably mixed charcoal particles lying on the forest floor with the uppermost part of the soil. Figure 1 indicates that earthworms had ingested charcoal particles <2 mm and distributed them in the soil profile. Figure 1a–b shows small charcoal particles incorporated into earthworm faecies lying on the soil surface. In samples taken 6.5 years after the fire (Fig. 1c–e) small charcoal particles in earthworm faecies were concentrated at a depth of 8 cm. Supporting evidence for the translocation of charcoal by soil fauna was provided by Topoliantz and Ponge (2003) and Topoliantz et al. (2006), who reported, for tropical slash-and-burn sites, that earthworms (*Pontoscolex corethrurus*) could ingest small charcoal particles, preferably mixed with humus, and who suggested a rapid incorporation of charcoal into the soil through earthworms. Thus, the increase in charcoal C in the 0–1 cm layer could be explained by mixing the charcoal particles in the litter layer with soil material, and the

decrease in the 2.5–5 cm layer by a translocation of charcoal into soil depths >5 cm. The inclusion of charcoal into soil aggregates would physically protect the charcoal from microbial decomposition (Skjemstad et al., 1996; Baldock and Smernik, 2002; Brodowski et al., 2006), but not from translocation. However, larger particles (>2 mm) were found in soils that nevertheless had resisted decomposition over millennia even in biologically active topsoil horizons (Carcaillet, 2001).

We calculated the charcoal mass from the charcoal C concentration (see Table 2). When normalized to a depth of 0–5 cm, the charcoal mass reached 1300 mg kg^{-1} after one year. Few studies report the masses of soil charcoal and if they do, the masses are often derived from different profile depths. For example, Carnelli et al. (2004) found much less charcoal (up to 19.35 mg kg^{-1}) in an alpine Podzol (10–30 cm depth), or an average of 6.18 mg kg^{-1} in soils below 2400 m a.s.l. Carcaillet and Talon (2001) reported charcoal masses of 102–863 mg kg^{-1} (800–1280 kg ha^{-1}) in soils under temperate *Fagus-Abies* forests. The comparison of charcoal C concentrations to studies that investigated the black carbon content of soils is difficult, in consideration of the methodological differences (Schmidt et al., 2001). Ansley et al. (2006) reported no change in soil black carbon concentrations even after three fires, whereas Czimczik et al. (2003) found that black carbon concentrations in soils could increase after fire by up to 40%. In this study, charcoal C increased by 21% in 0–1 cm depth one year after the fire.

3.2 Influence of burning on soil organic carbon concentrations

Soil organic carbon concentrations decreased with soil depth (p=0.000–0.002) in the three sample sets, with mean values between 53.9±1.9 (control) and 55.2±1.1 (b 1 yr) g kg^{-1} in 0–1 cm, and 31.0±1.1 (control) and 26.8±0.7 (b 1 yr) g kg^{-1} in 2.5–5 cm depth (Table 2). Compared to the control, SOC concentrations did not significantly increase, neither directly after the burning nor after one year. The SOC concentration increased after the fire (1.3 g kg^{-1} in 0–1 cm depth), but at the same time decreased in 2.5–5 cm depth, as did the charcoal C concentration. Only a small proportion of the increased SOC concentration could be contributed to charcoal C (8.7%). The proportion of charcoal C to SOC increased from 2.8% to 3.4% in one year for 0–1 cm, but did not change when normalized to 0–5 cm.

3.3 Changes in soil lightness

The soil was darkest in 0–1 cm depth (Table 2), where it became darker not only directly after the burning but significantly within one year (p=0.009). For all depths and treatments, SOC, charcoal C concentrations and the soil lightness correlated well, the correlation being strongest between SOC concentrations and L* after one year (r=−0.94**). The correlation between soil lightness and charcoal C is exponential (Fig. 2), which can be explained by the fact that the dark charcoal particles cover the surfaces of the mineral particles.

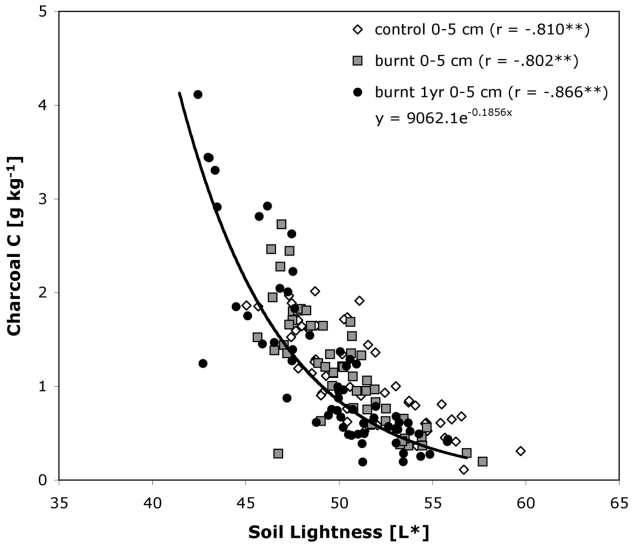

Fig. 2. The values for charcoal C concentration and soil lightness in samples from all investigated soil depths (0–5 cm) show significant and high correlations. The trendline and the equation are given for the sample set burnt 1 yr.

A significant relationship between soil colour and SOC concentrations has been already described by Schulze et al. (1993) and Konen et al. (2003). Spielvogel et al. (2004) observed that the aromatic C is mainly responsible for a dark soil colour, i.e. aryl C and L* correlated significantly (r=−0.87). These results are consistent with observations by Topoliantz et al. (2006), who reported an increase in dark humus material in topsoils after slash-and-burn together with a decrease in visible charcoal in the same material.

4 Conclusions

We investigated the effects of experimental slash-and-burn in a temperate mixed deciduous forest on soil organic and charcoal carbon and soil lightness. The main results of this study are: (i) after one year only a few charcoal particles from the forest floor had been incorporated into the soil matrix by soil mixing animals such as mice and earthworms; the proportion of charcoal C to SOC concentrations increased from 2.8 to 3.4% at 0–1 cm depth. (ii) The SOC concentrations did not show any significant differences. (iii) Soil lightness significantly decreased in the topmost soil layer and correlated with charcoal C (r=−0.87**) and to the SOC concentrations (r=−0.94**) in samples from the 0–5 cm layer.

Our results imply that, one year after the fire, only small changes in soil charcoal carbon concentrations are detectable but a certain amount of charcoal is incorporated into the soil

matrix and, over a longer time-scale, the amount of charcoal carbon stored in soils would increase.

Since little is known about prehistoric slash-and-burn techniques or burning conditions and because recent soil conditions might differ from those of several thousand years ago, implications for prehistoric times should be drawn carefully. Holocene fires in temperate deciduous forests (most were anthropogenic) could have increased soil charcoal storage, which affects pedogenesis and soil colour. Future research should combine the results of the field experiments with archaeological and palaeobotanical evidence to investigate the spatial and chronological dimensions of (pre-)historic slash-and-burn and its effects on soil properties.

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Manuscript III

Pedogenesis of Chernozems in Central Europe - A review

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Pedogenesis of Chernozems in Central Europe — A review

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Abstract

Since Dokuchaev's investigations of Russian Chernozems, Central European Chernozems were established as steppe soils, with their pedogenesis dominated by humus accumulation as a result of dry continental climate and steppe vegetation, with carbonaceous parent material and bioturbation as other prerequisites. The WRB-FAO classification defined Chernozems by their morphological characteristics, but was biased by the climo-genetic formation model. However, the assumption that modern Central European Chernozems are relics of steppe soils conflicts with palaeobotanical evidence from an early reforestation that started in the Late Glacial, and also with pedological studies that dated Chernozem formation to the Early Holocene.

In this review we compile the most important literature on pedogenesis of Central European Chernozems since the 1920s, according to the soil forming factors climate, time, vegetation, relief and man.

Our review demonstrates that there is no consensus on the factors controlling the formation, conservation and degradation of Central European Chernozems in published literature. We found that (1) no absolute time of formation could be stated so far, and that (2) Central European Chernozems formed not only under steppe but also under forest vegetation; (3) the spatial distribution of Chernozems and Phaeozems did not correlate with climate conditions or topographic position, and (4) until now no other factors were considered to be responsible for Chernozem development. Recent studies showed that these unknown factors could include anthropogenic activity and vegetation burning as they could form black soils or strongly affect the composition of soil organic matter.

We concluded that not all soils classified as Chernozems in Central Europe are steppe soils and thus, as they do not necessarily reflect past climate, the classification may be misleading.

Keywords: Chernozem; Phaeozem; Central Europe; Pedogenesis; Literature review

1. Introduction

Since Vassilij V. Dokuchaev's investigations in Russia, Chernozems were defined as steppe soils, with their pedogenesis dominated by the soil-forming factors of dry continental climate and steppe vegetation, with carbonaceous parent material, mainly loess, and bioturbation as other prerequisites (Dokuchaev, 1883, 1889). Dokuchaev's results for the Russian Chernozems were transmitted to Central European Chernozems (e.g. by Hohenstein, 1919) and his definition was assumed to be universally valid for Eastern and Central Europe, although it was deduced from Russian soils.

But a comparison of the results of several studies concerning the formation of Central European Chernozems to Dokuchaev's definition of a Chernozem as a steppe soil showed that there are obvious discrepancies. By definition, Chernozems should be zonal soils, preserved under continental steppe conditions. However, continental climate occurred during the Late Glacial (c. 15000–11500 BP) but there is no evidence for the presence of Chernozems in Central Europe in the Late Glacial (Rohdenburg and Meyer, 1968; Ikinger, 1996). First evidence for fully developed Chernozems originate from the Early

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Holocene (c. 11500–5500 BP; Pre-Boreal to Atlantic) when warmer climate and forest vegetation dominated the Central European loess-belt.

The purpose of this review is to highlight the most important literature on Chernozems in Central Europe published since the 1920s. We did not discuss the Russian Chernozems, because this would exceed the limits of this paper. We also exluded black soils formed with a steady water supply, like Gleyic Chernozems and Gleyic or Stagnic Phaeozems. In this review, we want to discuss the following questions: (1) What is the definition of Chernozems, and (2) where do we find them? (3) When did Central European Chernozems form, and (4) is their formation bound to a certain climate and vegetation? (5) Which factors control conservation and degradation of Chernozems? (6) Are there unconsidered factors that influence Chernozem formation or their soil properties?

We focus on different soil forming factors potentially dominating the pedogenesis of Chernozems in Central Europe, i.e. time, vegetation, climate and, potentially overlooked so far, fire and man. We want to point out that there is no generally accepted consensus on the formation of Chernozems in Central Europe.

2. What is a Chernozem? Definitions and systematics

The World Reference Base for Soil Resources (FAO/ISRIC/ISSS, 1998) defined Chernozems as soils with mollic or chernic horizons of at least 20 cm and with a chrome of ≤2 for substrate finer than sandy loam or ≤3.5 for sandy loam or coarser substrate, respectively. Chernozems should contain concentrations of secondary carbonates starting with in 50 cm of the lower limit of the A horizon but at least within the top 200 cm, they should lack a petrocalcic horizon or secondary gypsum between a depth of 25 and 100 cm, and their diagnostic horizons are no other then argic, vertic or calcic. There should be no uncoated silt and sand grains on the structural ped surfaces. Usually, the dark mollic A horizon is situated on an argic or cambic B horizon. The mollic horizons are rich in organic matter (10–16%), are highly saturated with bases and react neutral. Typical features of Chernozems are the formation on mostly aeolian and carbonaceous sediments like loess, the occurrence in continental climate under tall-grass vegetation that provides high above-ground biomass of about 1.0–1.5 t ha^{-1}, and an intense bioturbation shown by krotovinas (animal burrows) (FAO/ISRIC/ISSS, 1998; Driessen et al., 2001).

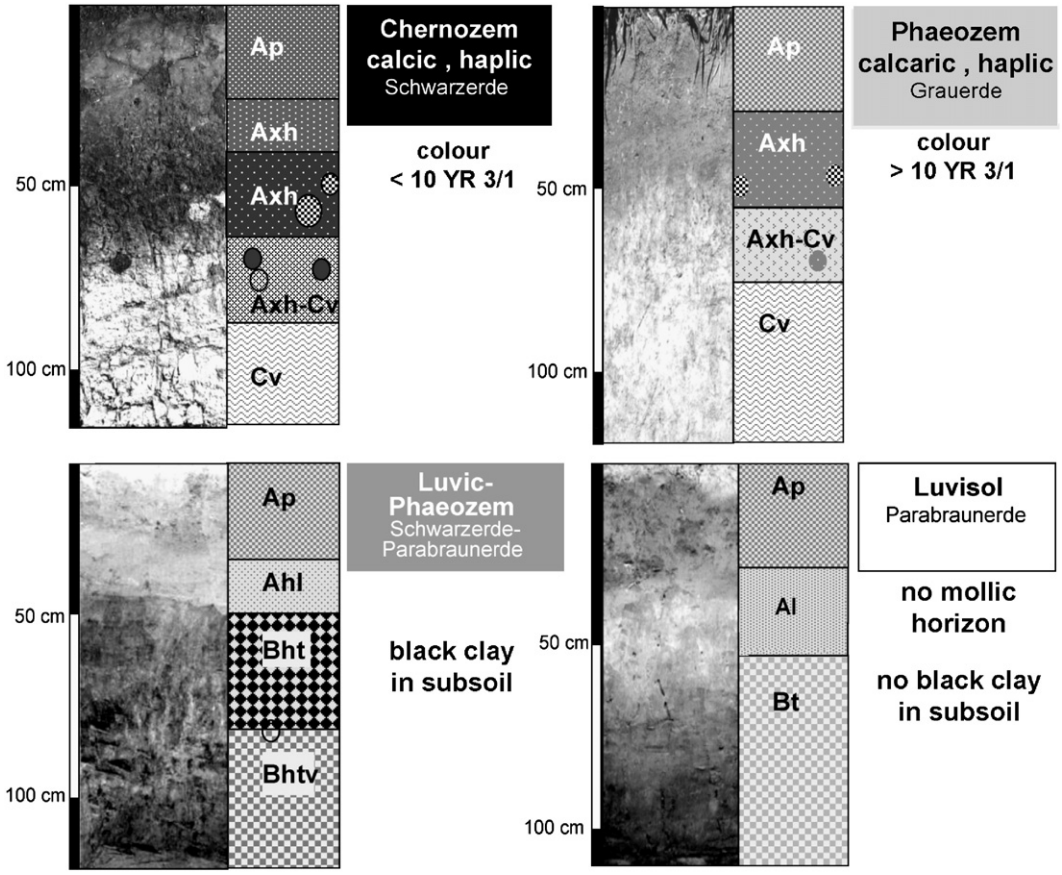

Fig. 1. Central European Chernozems and related soils as described in the German pedological literature. The Chernozem ('Tschernosem') has a dark mollic horizon and could have stagnic or gleyic properties. The latter do not appear in areas with lower water net balance, here secondary carbonates become more frequent. Increasing precipitation and leaching leads to the development of first Haplic, then Cambic and Luvic Chernozems and finally Luvic Phaeozems ('Tschernosem–Parabraunerde'). Some soils have properties that fit to the Chernozem definition, with the exception that their mollic horizon is greyish and not dark brownish to black ('Grauerden'; term is not recognised in the official German classification). These grey soils can contain secondary carbonates (calcic) or can have gleyic or stagnic properties and were assigned to the Phaeozems. Luvisols ('Parabraunerde') develop af ter stronger leachin g and translocation of clay.

Chernozems can develop in to Phaeozems, and the characteristics of Phaeozems resemble those of Chernozems. They have a mollic horizon and a base saturation of at least 50%. They should not contain secondary carbonates up to 100 cm depth and have no diagnostic horizons other than albic, argic, cambic or vertic. Compared to Chernozems, Luvic Phaeozems occur in more humid regions, have higher rates of leaching and therefore lack carbonates. Argic B horizons seem to be relics from stronger leaching and indicate the development towards Luvisols (FAO/ISRIC/ISSS, 1998; Driessen et al., 2001). However, the soil map of the world mentions the subunit Calcaric Phaeozem with more then 2% $CaCO_3$ (FAO-UNESCO, 1981).

The definitions of Chernozems and Phaeozems by FAO-WRB stress their morphology but were biased by the climo-genetical background. This makes it difficult to assign all Central European Chernozem subunits (e.g. for Germany described by Ad-hoc-AG Boden, 2005; see also Altermann et al., 2005) to the FAO-WRB classification. The differences between the soil units described in the German pedological literature are explained in Fig. 1.

Stagnic and Gleyic Phaeozems developed under different conditions than soils in steppe areas (Scheffer and Meyer, 1965). However, the German definition of a 'Schwarzerde' (black earth) subsumes soils with greyish to black (Chroma <3.5, Value ≤ 4) Axh horizons ≥ 40 cm and either with secondary carbonates ('Kalktschernosem') or without ('Tschernosem'). The term 'Tschernosem' includes not only Chernozem or Phaeozem subunits but also Kastanozems, Gleysols and Fluvisols and implies bioturbation as specific formation qualification (Ad-hoc-AG Boden, 2005). Despite these definitions, the terms 'Schwarzerde' and 'Tschernosem' were usually related to the appearance of steppe soil relics in Central Europe, and therefore Chernozems or Phaeozems (Kossowitsch, 1912; Hohenstein, 1919; Wilhelmy, 1950; Altermann and Mania, 1968). Their dark colour was assumed to originate from humic acids coating clay minerals that form stable dark complexes (e.g. Laatsch, 1938; Rochus, 1979; Mückenhausen, 1985a). Kahle et al. (2002) found that Chernozem organic matter accumulates in the clay fractions and seems to be associated with the mineral phase.

3. Where do we find Chernozems and Phaeozems in Europe?

The distribution of Chernozems and Phaeozems in Central Europe is shown in Fig. 2. The Eurasian Chernozem occurs in an area stretching from the Southern Urals to the Ukraine, passing through Moldavia and narrowing in the Danube basin (FAO-UNESCO, 1981; Bronger, 2003). Chernozems were characterized in Romania (Schönhals et al., 1982), Bulgaria (Koinov, 1968), in the Alföld and Banat regions in Hungary

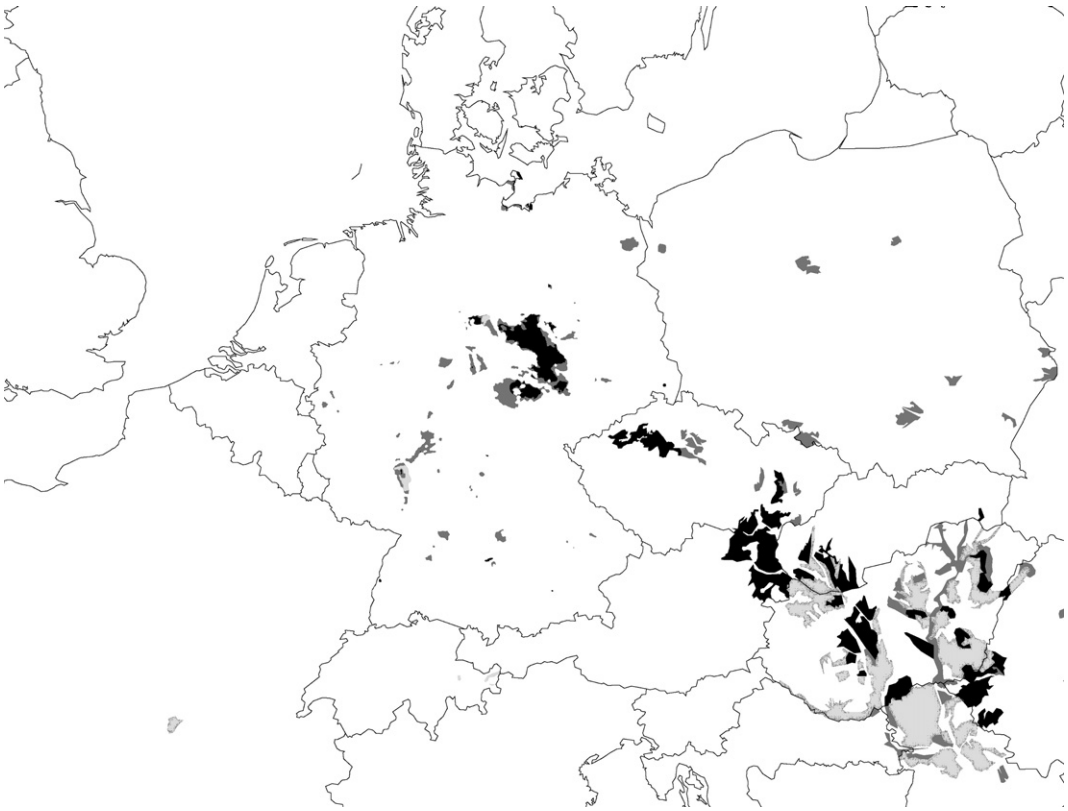

Fig. 2. Distribution of Chernozems and Phaeozems in Central Europe. The map shows the following varieties of Chernozems and Phaeozems: Chernic, Calcic and Vermi-calcic Chernozems (black); Luvic Chernozems, Stagnic, Luvic and Haplic Phaeozems (dark grey); Calcaric, Gleyic and Calcari-fluvic Phaeozems (light grey). Data source: Soil Geographical Data Base of Eurasia at Scale 1:1 000 000 (SGDBE) version 2, http://eusoils.jrc.it/wms/Metadata/Somis_metadata.htm; Bundesanstalt für Geowissenschaften und Rohstoffe, 1995; supplemented by E. Gehrt based on own surveys and information from the different institutes of the German state geological survey.

Table 1
Review of factors determining formation and preservation of Central European Chernozems and Phaeozems

Authors	Soil name		Location	Climate		Vegetation				Time		Man	Fire
	As given by authors	FAO-WRB		Precipitation/ evaporation, temperature	Soil water	Uncertain	Steppe	Forest–steppe	Forest	Late Glacial	Holocene		
Hohenstein (1919)	Schwarzerde (Tschernosem)	Chernozem	Poland	x			x						
(Stremme, 1926, 1936)	Tschernosem	Chernozem	Central Germany	x	x		x				x		
Meyer (1926)	Schwarzerde	Chernozem	Central Europe	x			x						
Schlüter (1929)	Schwarzerde	Chernozem	Central Germany								x	x	
(Laatsch, 1934, 1938, 1957)	Schwarzerde	Chernozem	Central Germany	x			x				x		
Schwarz (1948)	Schwarzerde	Chernozem	Central Germany	x			x				x		
Wilhelmy (1950)	Schwarzerde	Chernozem	Central/Eastern Europe	x			x				x		
Fink (1956)	Tschernosem	Chernozem	Austria	x			x				x		
Harth (1956)	Schwarzerde	Phaeozem	Upper Rhine Valley	x			x				x	x	
Scheffer and Meyer (1958)	Feuchtschwarz–Gleyic erde	Chernozem	Lower Saxony		x				x				
(Zakosek, 1962, 1991)	Rheintal–Tschernosem	Phaeozem	Upper Rhine Valley	x			x			x	x	x	
Hohnvehlmann (1963)	Parabraunerde (Schwarzerde)	Phaeozem	Westphalia	x	x		x				x		
Scheffer and Meyer (1963)	Schwarzerde	Chernozem/ Phaeozem	Lower Saxony	x	x		x		x		x		
Baumann et al. (1964)	Siedlungsschicht	Anthrosol	Saxony									x	
Czerny (1965)	Schwarzerde	Chernozem	Central Germany	x			x				x		
Kopp (1965)	Schwarzerde	Chernozem	Lower Rhine Basin	x			x			x			
Scheffer and Meyer (1965)	Feuchtschwarzerde	Gleyic Chernozem	Lower Saxony		x		– –	– –	– –		x		
Wichtmann (1965)	Schwarzerde	Phaeozem	Westphalia							x			
Meyer (1966)	Feuchtschwarzerde	Gleyic Chernozem	Lower Saxony		x						x		
Altermann and Mania (1968)	Tschernosem	Chernozem	Central Germany	x			x			x	x		
Rau (1968)	Tschernosem	Chernozem	Central Germany	x			x				x		
Roeschmann (1968)	Tschernosem	Phaeozem	Lower Saxony	x	x		x	x		(x)	x		
Rohdenburg and Meyer (1968)	Schwarzerde	Chernozem/ Phaeozem	Germany	x	x				x		x		
Scharpenseel and Pietig (1969)	Fossile Schwarzerde n	Phaeozem	Germany							x			
Altmannsberger (1971)	Tsche rnosem	Chernozem/ Phaeozem	Hesse	x				x					
Bailly (1972)	Schwarzerde	(Gleyic) Chernozem	Lower Saxony	x	x	x	x						
Leser and Maqsud (1975)	Steppenboden	Chernozem	Upper Rhine Valley	x			x			x		x	
Schalich (1981)	Schwarzerde	Phaeozem	Lower Rhine Basin	x			x		x		x		
Bork (1983)	(Feucht) Schwarzerde	(Gle yic) Chernozem	Lower Saxony		x				x		x		
Müller (1982)	Schwarzerde	Chernozem	Central Germany, Upper Rhine Valley	x	x		x	x		x	x		
	Schwarzerde	Phaeozem	Westphalia, Lower Rhine	x				x			x		

(continued on next page)

Table 1 (*continued*)

Authors	Soil name		Location	Climate		Vegetation				Time		Man	Fire
	As given by authors	FAO-WRB		Precipitation/ evaporation, temperature	Soil water	Uncertain	Steppe	Forest–steppe	Forest	Late Glacial	Holocene		
			Basin										
Roeschmann et al. (1982)	Schwarzerde	Chernozem/ Phaeozem	Lower Saxony	x	x				x		x		
Sabel (1982)	Tschernosem	Chernozem/ Phaeozem	Hesse	x	x		– –	– –	– –				
Schönhals et al. (1982)	Brauner Rhe intal–Tschernosem	Phaeozem	Upper Rhine Valley	x			x						
	Donau–Tschernosem	Chernozem/ Phaeozem	Romania	x			x						
Mückenhausen (1985b)	Tschernosem	Chernozem/ Phaeozem	Germany	x			x				x		
Thiemeyer (1989)	Tsche rnosem–Parabraunerde	Phaeozem	Hesse	x	x		x				x		
Thater and Stahr (1991)	Parabr aunerde–Tsche rnosem	Phaeozem	Suebia	x	x			x			x		
Gehrt et al. (1995)	Grauerde	Phaeozem	Lower Saxony			x					x		
Ehwald et al. (1999)	Schwarzerde	Che rnozem	Central Germany	x	x			x			x		
Fischer-Zujkov et al. (1999)	Parabraunerde–Tschernosem	Phaeozem	Uckermark	x	x						x		
(Schmidt et al., 1999, 2002)	Chernozemic soil		Germany	– –	– –		– –	– –	– –	– –	– –		x
(Schmid et al., 2001, 2002)	Archaeological soil		Bavaria									x	x
Scheffer/ Schachtschabel (2002)	Tschernosem (Schwar ze rde)	Chernozem/ Phaeozem	Germany	x			x				x		

Authors (selection) in chronological order. X = yes, – – = no, () = uncertain.

(Szücs, 1963), in the Vojvodina (Neigebauer et al., 1983), in Bohemia and Moravia (Hrasko et al., 1973), in the Pannonian Basin of Eastern Austria (Franz, 1955; Fink, 1956; Blum and Solar, 1986), in the East of Poznan in Poland (Hohenstein, 1919) and in the Central German Dry Area (e.g. Czerny, 1965; Altermann and Mania, 1968).

Phaeozems can be found in different varieties and do not appear in a defined area (FAO-UNESCO, 1981). We could not record all areas covered by the patchy distributed Phaeozems, or their spatial extent had to be exaggerated to show their appearance in Fig. 2. In Germany they occur in loess-covered regions, including Lower Saxony (Scheffer and Meyer, 1963; Bailly, 1972; Roeschmann et al., 1982), Rheingau and Rheinhessen (Hohenstein, 1920; Harth, 1956; Zakosek, 1962; Leser and Maqsud, 1975; Zakosek, 1991), near Stuttgart and Heilbronn (Müller, 1951), Westphalia (Hohnvehlmann, 1963; Wichtmann, 1965), Lower Rhine Basin (Kopp, 1965; Schalich, 1981), Lower Hesse (Haupenthal, 1978), Uckermark (Fischer-Zujkov et al., 1999) and the Wetterau Basin (Altmannsberger, 1971). Phaeozems can be found in the Limagne basin in France (FAO-UNESCO, 1981; ISSS, 1996) and in alpine dry-valleys (Meyer, 1926; Frei, 1980; Blum and Solar, 1986; ISSS, 1996). In warm and dry Swiss alpine valleys, Phaeozems with mollic epipedons occur in altitudes between 600 and 1700 m a.s.l. They usually formed on a mixture of well drained calcareous and silicate parent material, like moraines (Frei, 1980). Soils on the island of Poel (Baltic Sea) were classified as soils with phaeozem-like properties. They have dark mollic A horizons developed on sandy, not on silty loess-like parent material (Albrecht and Kühn, 2003). Similar soils can be found on the island of Fehmarn (Schimming and Blume, 1993) (Table 1).

4. Time — When did Central European Chernozems form?

Late Glacial and Early Holocene were discussed as possible times of Central European Chernozem pedogenesis (Kopp, 1965; Ehwald et al., 1999). Stratigraphical methods and radiocarbon dating were used to determine the age of a soil. But methodological problems, and because the ages vary over time, absolute ages are still not known.

4.1. Stratigraphical and palaeoecological evidence?

The possibility of a formation of Chernozems in the Late Glacial was supported by the occurrence of steppe conditions that were regarded as requirement for their development (Wilhelmy, 1950; Kopp, 1965). Proceeding from west to east, the warmer and more humid climate in the Early Holocene stopped the accumulation of humus material (Kopp, 1965). This view was encouraged by observations of relics of fully developed Chernozem found at archaeological sites related to

the Early Neolithic Period (5500–5000 BC). Thus, Chernozem formation should have been completed before 5500 BC (Schalich, 1981). It was assumed that the first Neolithic settlers (Linienbandkeramik, 5500–5000 BC) found the Central European loess areas covered with Chernozems that provided a basis for the institution of agriculture (Bogucki, 1988; Lüning, 2000).

Black humic horizons under a layer of Laacher See Tephra, the volcanic outburst was dated 12,900 cal. BP, were described by Roeschmann (1968) as remnants of Chernozems formed in the Late Glacial, whereas Rohdenburg and Meyer (1968) denied the existence of fully-developed Late Glacial Chernozems in favour of Calcaric Regosols with less profound humic horizons. Rohdenburg (1978) suggested that a later pedogenesis in the Early Holocene could have affected the substrate under the thin layer of Laacher See Tephra, leading to a misinterpretation of the humic horizons found under the ash layer. Also Altermann and Mania (1968) examined soils buried under Laacher See Tephra and concluded that the formation of Chernozems started in the Younger Dryas. The authors identified the examined horizon as part of an early Chernozem because of high grey humic acid concentrations. Reconsidering the profile descriptions, it could be stated that the fossil A horizon in the profile Weinberg near Schadeleben was only 12 cm thick, did not show any homogeneous humus distribution and had a relatively low carbon content of 3.4 g kg^{-1}. In contrast, the Chernozem described at Salziger See developed in Atlantic. However, the A horizon is still less than 40 cm mighty and it is situated on material with gleyic properties. Still, there are no hints for profound humic horizons under Laacher See Tephra and therefore in Late Glacial (Ikinger, 1996).

Most authors and textbook knowledge preferred the Early Holocene as time of Chernozem formation (Czerny, 1965; Rau, 1968; Roeschmann et al., 1982; Scheffer/Schachtschabel, 2002), based on the research of Laatsch (1934). He assumed that Chernozems formed in Boreal to Sub-Boreal, mainly in Atlantic (c. 7800–5700 BP). His main argument was that merely more favourable climatic conditions than in Last Glacial would yield enough plant biomass to form the profound mollic horizons, i.e. a warm and moist spring to enhance plant growth alternating with dry hot summers and cold winters when decomposition processes were halted.

4.2. Radiocarbon dating

When using the radiocarbon method, reliable material for dating would be charcoal or wood particles separated from soils. Measuring extracted humic acids does not yield absolute ages, but the apparent mean residence time of soil organic matter, which is a minimum estimate of soil ages. It is not possible to compare these ages to each other or relate them to certain time periods (Geyh, 1983; Scharpenseel and Becker-Heidmann, 1992).

Radiocarbon dating has, since the 1960s, been used to determine the ages of Central European Chernozems and Phaeozems. Scharpenseel and coworkers dated a large number of soil samples (Scharpenseel and Pietig, 1969; Scharpenseel et al., 1996) but until now, a precise date of Chernozem formation could not be confirmed. To determine ages for Chernozems, Scharpenseel and Pietig (1969) dated the soil organic matter (extracted humic acids) of a Chernozem A horizon covered by Laacher See Tephra, which therefore was regarded as being formed in the Late Glacial. A sample taken from material undisturbed by roots was dated 10,580±80 BP (sample 'Michelsberg II'). The authors concluded that the 'Michelsberg II' sample would give an absolute age and that Chernozems could have formed in the Late Glacial, presumably since Bølling (Scharpenseel and Pietig, 1969). On the other hand, Rohdenburg and Meyer (1968) disproved the existence of profound humic horizons in Late Glacial, and the age of the 'Michelsberg II' sample would be the age of a Calcic Regosol, which could represent an initial state of a Chernozem but not yet a fully developed one. Other measured maximum ages of Chernozems and Phaeozems, the oldest ages measured in the deepest part of the soil profiles published by Scharpenseel et al. (1968), covered some thousands of years, from 5550±80 BP (4490-4260 BC) (sample 'Söllingen D') to 2560±60 BP (810-540 BC) (sample 'Wallertheim'). A black soil from Fehmarn (Baltic Sea) dates to the Middle Ages (1850±70 BP or 560-770 AD) (sample Grossenbrode, Ostholsteen A).

Until recently, black soil remnants in Early Neolithic (5500-5000 BC) settlements were classified as remains of Chernozems. However, most data published by Scharpenseel et al. (1996) revealed younger ages of these remnants, most of them related to the period 4500-2200 BC (Younger to End Neolithic). This was supported by AMS ^{14}C ages of charred organic material (black carbon) deriving from different German Chernozems (Schmidt et al., 2002). Unlike single charcoal particles, black carbon data could give mean apparent ages of fire events. The different ages could indicate that Chernozems formed over a longer time period then thought before (Gehrt et al., 2002; Schmidt et al., 2002).

5. Vegetation — Formation under forests or after all still a steppe soil?

Dokuchaev (1883, 1889) concluded that Russian Chernozems formed under continental climate and steppe vegetation. Earlier, it was assumed that they developed under moist and wet conditions like Stagnic or Gleyic Chernozems (WRB-FAO; Bell and McDaniel, 2000). Dokuchaev stated that the soil forming factors interact and that climate would not be the dominating factor (Ehwald, 1984), and steppe vegetation was considered a main prerequisite for the formation of Chernozems (Laatsch, 1934; Driessen et al., 2001). Thus, the recent Chernozems and Phaeozems in Central Europe were regarded as relics of former steppe climate and vegetation (Wilhelmy, 1950).

Palynological evidence set the beginning of reforestation in Central Europe to the end of the Late Glacial (Firbas, 1949). The Central German dry region was covered with extensive forests since approx. 9500 BP (Preboreal) (Lange, 1965; Litt, 1992) and the Pannonian Basin was covered with open forests since Boreal (Havinga, 1972). Therefore, a formation of Central European Chernozems in the Early Holocene would not have occurred under steppe vegetation.

Scheffer and Meyer (1963) warned to draw conclusions from the existence of Chernozems to former climate and vegetation and suggested that they could have formed under forests. Scheffer et al. (1959/60) and Rohdenburg and Meyer (1968) gave evidence for a development of black soils under forests when low precipitation or stagnic conditions stop decalcification. Ehwald et al. (1999) summarized the recent discussion about the formation of Chernozems in the Central German dry area. Here, pollen data suggested that the replacement of the steppe vegetation by birch and pine started in Preboreal and was completed in Atlantic with the appearance of deciduous forests. However, the investigation of fossil mollusc fauna lead Mania and Preuss (1975) to conclude that steppe vegetation was still present in Atlantic. But the mollusc fauna gives evidence only for the local vegetation history, whereas palynological data represents a larger region. Moreover, the molluscs originated from colluvial sediments, and a lack of vegetation to cover soil is a precondition for erosion and subsequent colluviation. The expansion of deciduous forests during Atlantic would be the more convincing scenario (Ehwald et al., 1999).

Ehwald et al. (1999) tried to elucidate the problem of Chernozems formed under forest by comparing Central German soils with Eastern European and Western Siberian soils. In Russia, Typical and Leached Chernozems occur under farmland and open deciduous forests. These soils should correspond to the German Chernozems under farmland. The Russian Grey Forest Soils, covered by dense forests, relate to the Central European Phaeozems and Luvisols. The examination of humic horizons of Chernozems in the steppe region near Kursk seemed to prove the unchanged conservation of Chernozems under open deciduous forests during some thousands of years. This could be an evidence for their genesis under an open forest or a forest–steppe (Ehwald et al., 1999). More examples for Chernozems under open forests were described in Austria (Franz, 1955).

A strong argument for a development of Chernozems under steppe vegetation was the existence of burrows (krotovinas) built by hamsters (*Cricetus*) or ground squirrels (*Citellus*), which live in open landscapes. Their soil-mixing activity was supposed to be essential for the formation of the mollic A horizon. In the Central German dry area only the existence of hamsters could be proved until now, but they probably inhabited the region after agriculture was established (Lange, 1965; Ehwald et al., 1999). More arguments against bioturbation as major soil forming process would be the existence of laminated Chernozems in Lower Saxony (Gehrt et al., 1999) and the results of radiocarbon dating, which showed an increase of age of soil organic matter with increasing soil depth (Scharpenseel et al., 1986).

6. Climate and relief — Conservation and degradation of Chernozems

Based on the assumption that Chernozems are steppe soils, a model was developed concerning conservation and degradation affected by climatic changes (e.g. Rau, 1968 for Central Germany). Chernozems formed under steppe conditions were expected to stay preserved in regions with a balanced or negative water balance. In Central Europe, this would be in geographical regions with a mean annual precipitation of less than 500 mm, as stated by Meyer (1926). With increasing precipitation and leaching, the translocation of clay covered with humic material started and Chernozems were transformed into Phaeozems, Luvisols or Albeluvisols (Rau, 1968; Driessen et al., 2001). This degradation process was also described for Russian soils, where Alexandrovskiy and Chichagova (1998) investigated Luvisols with a fossil humus horizon and explained its formation with a climate change. After a Chernozem developed in Early and Middle Holocene, an increase in precipitation led to humus degradation in Late Holocene. During 2000 to 3500 years the Chernozem was transformed to a Luvisol, which still contains Chernozem material as a second A horizon.

The climo-genetic model was adopted to generate a chronology of Chernozem formation and degradation relating to climate change and archaeological phases. According to that chronology, the formation would have been completed before the Early Neolithic Period (5500–5000 BC), and leaching and degradation would have started with the onset of warmer and more humid Atlantic climate before the Bronze Age (before 2200 BC). Therefore, the Central European Chernozems should have stayed preserved in areas with negative water balance, whereas in other areas they transformed into Luvic Phaeozems or even Haplic Luvisols which do not show traces of their chernozemic past anymore (Scheffer and Meyer, 1963; Schalich, 1981).

Some authors referred to the factors relief and hydrological conditions: Chernozems were assumed to be better preserved under soil water supply that could stop the process of decalcification (Roeschmann, 1968; Thater and Stahr, 1991). On the other hand, black soils affected by high water levels (Gleyic or Stagnic Chernozems; FAO-WRB) could not only be preserved but may even have been formed under wet conditions (Scheffer and Meyer, 1958). Black Chernozem material could also be protected under colluvial sediments, especially when calcareous material stopped the leaching process (Sabel, 1982).

However, the factors affecting the spatial distribution of Chernozems are not well-known yet. Although most authors stressed a change of climate, this factor alone could not explain the present distribution of Chernozems. Stremme (1936) and Bailly (1972) could not correlate precipitation and the distribution of Chernozems, and Sabel (1982) stressed the importance of relief position for Chernozem preservation. Altermann and Fiedler (1975) found that the primary carbon content of the loess parent material is of greater importance to the pedogenesis of Chernozems than microclimate.

In fact, Chernozems often appear in patches but not in extensive covers, with no obvious relation to soil forming factors as climate or relief. Examples were given by Bailly (1972) and Gehrt et al. (1995, 2002) for Lower Saxony, where grey ('Grauerde') and black soils ('Schwarzerde') are distributed in sharply defined neighbouring patches without any differences in parent material, relief position or soil properties (description in Fig. 1). Bailly (1972) investigated Chernozems in Northern Germany and found no direct correlation between their distribution and climate, relief, parent material, hydrology or distribution of forest and farmland. He suggested that still unknown factors influenced the preservation of Chernozems. Kleber et al.

(2003) indicated that the patchy distribution of Chernozems could be explained by prehistoric anthropogenic influence on Chernozem pedogenesis.

7. Man and fire — The missing factors?

7.1. Charred organic matter as colouring agent

Up to now, the dark brown to black colour of Chernozem A horizons was attributed to humic acids that cover clay minerals or are bound between the layers of clay minerals. These resistant clay–humus-complexes remained in the argic subsoil horizons of leached and degraded Chernozems or Phaeozems (Greenland, 1971; Gebhardt, 1971; Rochus, 1979).

In contrast, some black soils seemed to inherit their dark colour from charred organic carbon or black carbon. The term black carbon describes a continuum of charred organic material, and black carbon could be used as a marker for vegetation fire. Up to 45% of the total organic carbon in Chernozems of Lower Saxony consisted of black carbon (Schmidt et al., 2002). In North American Chernozems, the proportion reached from 35% (Skjemstad et al., 2002; Glaser and Amelung, 2003) to 80% of soil organic carbon (Ponomarenko and Anderson, 2001). Russian Chernozems yielded 17% black carbon (BPCA) up to a depth of 60 cm (Rodionov et al., 2006). Black carbon contributes to the highly aromatic and recalcitrant soil organic matter and could be recovered in the chemical fraction defined as humic acids (Haumaier and Zech, 1995; Skjemstad et al., 1996). Schmidt et al. (2002) calculated that one to seven fires would produce 1.7 g black carbon kg^{-1} soil. Gehrt et al. (2002) assessed an annual input of 40 kg black carbon ha^{-1} over 1000 years to reach the proportion of 20% black carbon in the soil organic matter of Chernozems of Lower Saxony.

However, black carbon represents a continuum of charred material, and the acquisition of black carbon data is still troublesome. A generally accepted definition of black carbon does not yet exist. Different analytical protocols are used to measure different fractions of black carbon. These protocols are based on the concept of chemical or thermal oxidation of labile organic matter and subsequent measurement of the relatively inert black carbon. The measurement of different fractions of black carbon with different methods obtains results that are not directly comparable (Bird, 1997; Schmidt et al., 2001).

Despite methodological problems, there is evidence for black soils having been formed as a result of black carbon incorporation in soils through vegetation burning in Australia (Skjemstad et al., 1996, 1997) and Africa (Kuhlbusch et al., 1996) or through the accumulation of hear thashes in Amazonian Brazil (Terra Preta; Glaser et al., 2001). Although the processes of incorporation and colouring are not yet clearly understood, soil colour (lightness) and amount of aromatic carbon, typical for black carbon, correlate (Spielvogel et al., 2004).

Black soil horizons in the Lower Rhine Basin (Northwest Germany) could be relics of anthropogenic fire management. The black soils occurred in patches, were always connected to anthropogenic pits and their soil properties differed very clearly from the surrounding Luvisols. The soil material contained charcoal and black carbon (19-45% of soil organic carbon). The radiocarbon ages from charcoal and black carbon ranged from the Mesolithic period to the Middle Ages, with an emphasis in the Late Neolithic Period 4400–2200 BC) (Gerlach et al., in press). For the Late Neolithic Period, fire management could be supported by pollen records for Northern Europe (Iversen, 1941; Kalis and Meurers-Balke, 1998) and presumably also for the Lake Constance area (Rösch, 1993).

There is evidence that, next to black carbon or charcoal content, magnetic susceptibility of soil material may reflect past fires. Hanesch and Scholger (2005) measured the magnetic susceptibility in different Lower Austrian soils and found that Chernozems have the highest signals of all soil types (77×10^{-8} m^3 kg^{-1}). Bulgarian Chernozems gave similar values of 80×10^{-8} m^3 k g^{-1} in the topsoil and 40×10^{-8} m^3 kg^{-1} in the subsoil, respectively (Jordanova and Jordanova, 1999). The transformation of goethite or ferrihydrite to maghemite takes part during heating (Nørnberg et al., 2004) at temperatures as low as 220 °C (Sidhu, 1988). Zanelli et al. (in press) observed *in-situ* formation of maghemite up to 0.5 m deep in soils affected by forest fires in Southern Switzerland.

Circumstantial evidence suggests that vegetation fire could be a new formation factor in the genesis of black soils. Natural fires emerge rarely in Central European deciduous forests (Tinner et al., 1999). Therefore, vegetation fires ignited by humans may be a source for the black carbon found in Central European Chernozems.

7.2. The influence of human activity

Black soil remnants were of ten found in Neolithic settlement areas. Relics of black soils were preserved as fillings of pits, ditches or postholes and as remains of prehistoric surfaces. These black soils were described as relics of Chernozems, which should have been widespread in the loess-covered areas in Early Neolithic times. Scheffer and Meyer (1963) developed a model for Chernozem formation in Lower Saxony according to their observations on archaeological excavation sites. On some examined sites, e.g. in the Wetterau loess area (Hesse), the black soil horizon in the prehistoric settlement area corresponded to the surrounding Phaeozems (Thiemeyer, 1989). On other sites, as in the Lower Rhine Basin (Schalich, 1981), the black soils clearly differed from the surrounding Haplic Luvisols. In some cases, a mixture of Chernozems and anthropogenic organic material was described (Schwarz, 1948; Meyer, 1966; Grote, 1977).

Geochemical analysis of black soil material from prehistoric settlements and adjacent Phaeozems revealed that their chemical properties and pedogenesis were different. Pit fillings in a Neolithic settlement (Murr; Bavaria) contained high amounts of charred organic material (23–70% of total organic carbon), and the concentrations of charred material correlated with the soil colour. The dark material in the settlement area was a mixture of deposited waste material and soil (Schmid et al., 2001, 2002).

Baumann et al. (1964) analysed black pit fillings and the black surface layer in a Neolithic settlement. The pit fillings consisted of organic material, mainly waste or litter, which was

incorporated into the natural A horizon and was responsible for the dark colour. Furthermore, these black soils were located only in the settlement areas and gave no evidence for a former occurrence of Chernozems.

An evidence for anthropogenic influence on Chernozem formation could be the distribution of 'Grauerden' and 'Schwarzerden' in Lower Saxony. Black and grey soils formed a patchwork with sharp boundaries between the two soil units that were independent of natural causes. Remarkably, Neolithic settlements were mostly situated at the edges of the black soil patches, confirming the idea of black soils as relics of agriculture (Gehrt et al., 2002).

Farming may have different effects on conservation and formation of Chernozems. On the one hand, ploughing could enhance the degradation of humus and therefore Chernozems (Laatsch, 1957). On the other hand, farming was thought to simulate steppe conditions that facilitate the persistence of Chernozems, without regarding the climatic factors (Stremme, 1926). Leser and Maqsud (1975) and Zakosek (1962) suggested that agriculture could even reverse the degradation process, as in Rheinhessen, where Late Glacial Chernozems were leached in the Early Holocene but re-formed after the erosion of the former humic horizon under farmland that seemed to simulate steppe vegetation.

8. Conclusions

This review on the pedogenesis of Central European Chernozems revealed that the processes and factors affecting Chernozem formation and conservation are diverse. Published results often conflict with the definition of Chernozems as steppe soils formed under continental climate.

We found that: (1) No absolute age and time of Chernozem pedogenesis could be stated. Stratigraphical records and radiocarbon data showed that the formation in the Late Glacial, when steppes actually occurred in Central Europe, seems to be unlikely. The radiocarbon data gave Holocene ages spread over about 3700 years, and they gave mean apparent ages of fire events (charred organic matter) or the mean residence times of soil organic matter, but no absolute ages. (2) Chernozems could have formed under forest or at least under forest–steppe. Not the type of vegetation seems to dominate the formation of mollic horizons but soil processes which influence either the presence of bicarbonates or lead to reduced decomposition and therefore accumulation of organic matter. (3) Climate and relief influence Chernozem preservation, but often these factors alone are not sufficient to explain Chernozem distribution and occurrence in certain geographical regions (e.g. Lower Saxony). (4) Man and fire may influence Chernozem properties through agriculture or fire management tools and could be the missing factors that explain the spatial distribution of Chernozems and Phaeozems. Vegetation fire could form black soils or Chernozems that contain high properties of charred organic matter. The black soil material in prehistoric settlements, often interpreted as a proof for Chernozem distribution in the Early Holocene, is usually soil mixed with organic material deriving from anthropogenic activity and does not reflect natural soils.

Concluding, the term Chernozem summarizes different types of black soils that have the same appearance but different formation histories. The FAO-WRB classification of Chernozems and Phaeozems has a pedogenetical background and connects them to steppe soils. From this review, it seems that soils with Chernozem or Phaeozem properties have often been interpreted as witnesses of past climate in Central Europe by their appearance, although dark or black soils could have diverse formation histories. Thus, they do not have to reflect past climate, and the classification may be misleading. This review of Chernozems pedogenesis showed that further investigations are needed to uncover the different formation histories of black soils.

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Manuscript IV

Prehistoric alteration of soil in the Lower Rhine Basin, Northwest Germany – archaeological, ^{14}C and geochemical evidence

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Prehistoric alteration of soil in the Lower Rhine Basin, Northwest Germany—archaeological, ^{14}C and geochemical evidence

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Abstract

In Early Holocene, Chernozems were assumed to have covered the entire loess landscape of the Lower Rhine basin—today mirrored by the distribution of Luvic Phaeozems. These Luvic Phaeozems have characteristic dark brown (Bht) horizons accumulating clay and humus, inherited and translocated from their precursors Chernozem black humic A horizons. We examined Luvic Phaeozems along a 33-km-long and 2.0–2.5-m-deep gas pipeline trench in the Lower Rhine Basin, west of Cologne. Along this transect we discovered clusters of hundreds of regularly shaped pits. These pits were always connected to the Bht horizons of adjacent Luvic Phaeozems. The Luvic Phaeozem horizons and the pits were investigated by combining methods from (geo-) archaeology (geographical distribution within the landscape, shape of the pits, soil texture), geochemistry (content of carbon, nitrogen and black carbon), palaeobotany (species determination of charcoals) and AMS ^{14}C measurements.

We found that the Luvic Phaeozems occurred not only in the loess-covered landscape but also in the sandy Holocene floodplain, and their distribution could not be limited to certain slope positions or parent material. Carbon and nitrogen concentrations in the Luvic Phaeozem horizons and pits were larger than in the surrounding Luvisols, whereas the C/N ratios were small (<10). Material found in the Luvic Phaeozem pits was clearly different from material found in prehistoric settlements. The pits investigated here never contained artifacts, and carbon and nitrogen concentrations and C/N ratios were smaller. We found charcoal particles, and black carbon contributed up to 46% of the total organic carbon. The AMS ^{14}C ages of charcoals and black carbon indicated that fire occurred from Mesolithic (9500–5500 BC) to the Medieval Ages (500–1500 AD), and mainly in the Late-/End Neolithic period (4400–2200 BC). We conclude that (i) the Luvic Phaeozem pits and horizons are man-made, formed during several archaeological epochs between Mesolithic and Middle Ages, (ii) these pits must have been formed outside the actual prehistoric settlements (off-site) and may serve as a novel archaeological feature, (iii) the purpose of these pits at present is not clear and (iv) human activity has altered and ultimately formed the investigated soils of the Lower Rhine basin in prehistoric time.

Keywords: Phaeozems; Black carbon; Prehistoric fire management; ^{14}C; Archaeology; Pedogenesis

1. Introduction

By concept, Chernozems are "zonal" soils, formed under a dry continental climate and vegetation of the mid-

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latitude grasslands on calcareous loess or loess-like sediments (FAO/ISRIC/ISSS, 1998). The pedogenesis of Central European Chernozems (German classification: Schwarzerde/Tschernosem; AG Boden, 1994), especially in Northwest Germany has been studied by soil scientists, palynologists and archaeologists very intensively (Scheffer and Meyer, 1963; Catt, 1989; Ehwald et al., 1999). It is difficult to provide an overview of the discussion, not only because of the multitude of sometimes contradictory hypotheses, but also because different degradation stages of Chernozems have been studied (Ehwald et al., 1999). At the transition to the moister climates of the forest regions, decalcification and clay translocation led to the formation of Luvic Phaeozems with a characteristic dark argic B horizon rich in humus (German classification: Bht horizon). In humid regions, Luvisols were the final products of the soil development (Roeschmann, 1968; Driessen et al., 2001).

In Central Europe, the entire spectrum of this soil development series can be found, from Haplic Chernozems in the Central German dry region to Luvic Phaeozems of the Mainz Basin, Soester and Warburger Boerde, Leine valley, Wetterau and Lower Rhine Basin (Mückenhausen, 1985).

In the Lower Rhine Basin, Kopp (1965) and Schalich (1981) considered Luvic Phaeozems as relicts of former Chernozems which have covered the loess landscape in Early Holocene. Today, these Luvic Phaeozems have characteristic dark brown Bht horizons, which were assumed to be inherited from their Chernozem precursors (Fig. 1a). Although soil maps of the Lower Rhine Basin region do not show Luvic Phaeozems in a separate category, they are included under the term Luvisol with the note: Chernozem relicts or humic horizon (=Bht horizon) present at a depth of a few tens of cm (Kopp, 1965).

In the Lower Rhine Basin, west of Cologne, we followed a gas pipeline, and discovered clusters of hundreds of regularly shaped pits—presumably man-made. These pits were always connected to the Bht horizons of adjacent Luvic Phaeozems, provided that these horizons were not eroded (Fig. 1b). In the present study, we combined complementary methods from (geo-) archaeology (geographical distribution within the landscape, shape of the pits, soil texture), geochemistry (carbon, nitrogen, black carbon), palaeobotany (species determination of charcoals) and AMS ^{14}C measurements to address the following questions:

- Are these Luvic Phaeozem pits natural or man-made?
- Do these Luvic Phaeozems differ from prehistoric settlement soils?
- Are the Luvic Phaeozems and associated pits uniformly distributed in the landscape?
- Which implications do our results have for the pedogenesis (soil forming process and time) of Luvic Phaeozems (and their precursors Chernozems) in the Lower Rhine Basin?

2. Materials and methods

2.1. Study area and sample sites

In the Southern Lower Rhine Basin, west of Cologne, we followed pipeline excavations (Wingas AG Kassel). The trench was 2.0–2.5 m deep and 33 km long, ending at the coordinates 6°45′39″E/51°0′18″N and 6°58′35″E/50°50′35″N (Fig. 2). The entire length of the gas

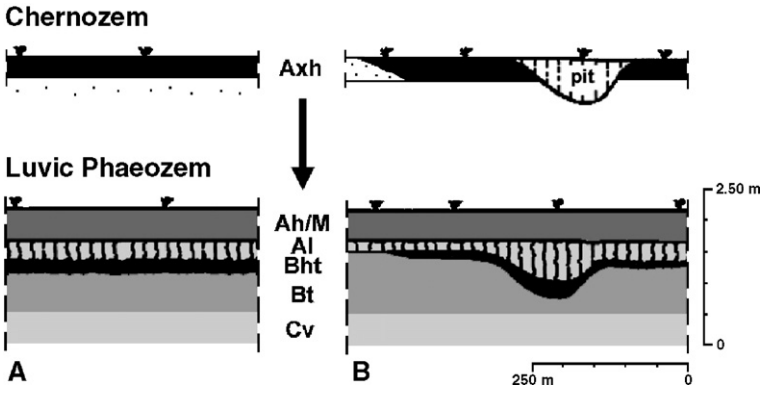

Fig. 1. Soil formation in the Lower Rhine Basin (schematic). (A) Degradation model from Chernozem to Phaeozem, (B) soil formation as observed in this study. Soil formation processes typically transport clay and humus from the topsoil (i.e. a former mollic (Axh) horizon and pit fillings) into the recent argic (Bht) horizons, which inherit the black colour following the former pit structures. Often a colluvial cover (M horizon) protects the underlying horizons against erosion.

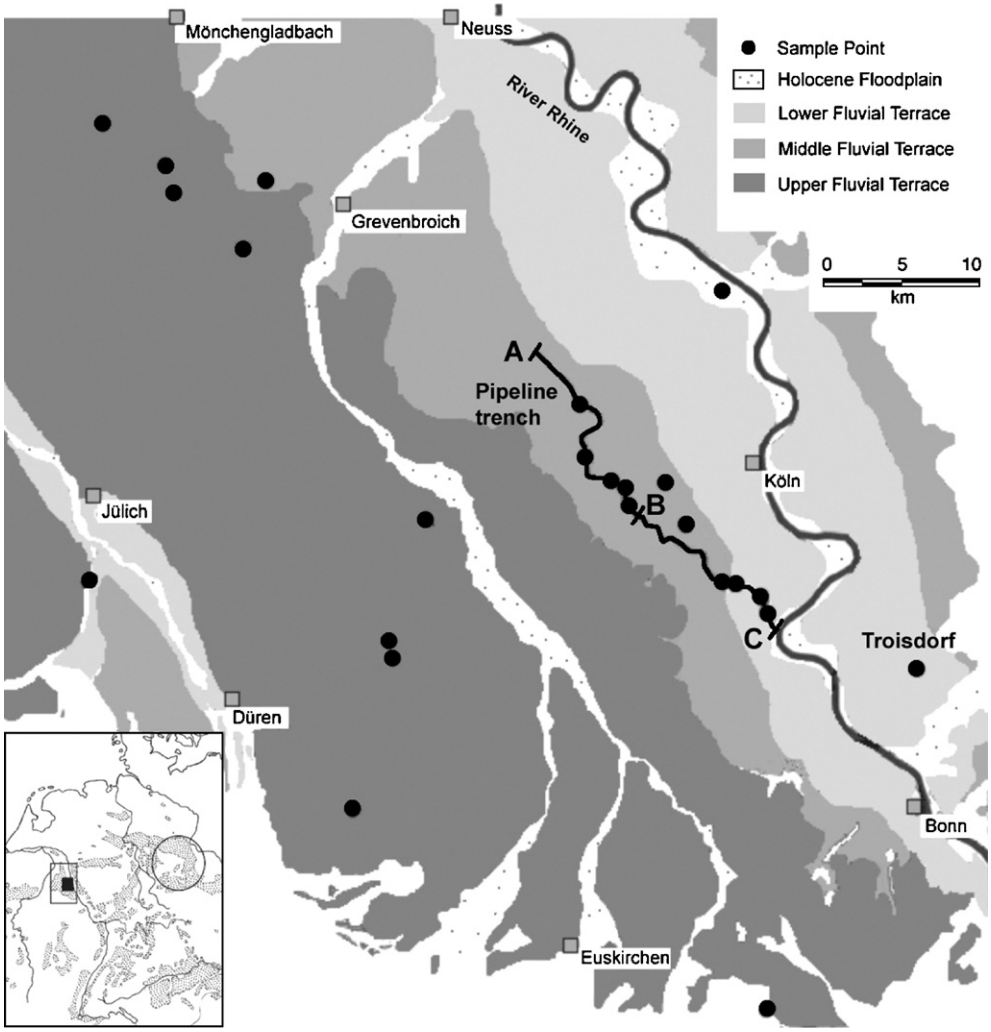

Fig. 2. Study area, including the main geomorphologic units, the pipeline trench (ends indicated with A and C) and locations of soil sampling, and additional sampling plots at archaeological excavations. The inset map shows the distribution of loess in Central Europe, highlighting the Lower Rhine Basin (rectangle), the study area (black square), and the Central German Chernozem region (circle).

pipeline trench was surveyed and 500 pits were discovered, documented and grouped into morphological classes (Fig. 3). The trench crossed the loess-covered higher and middle terraces, the loamy and sandy lower terrace and the Holocene sandy floodplain of the river Rhine. Additionally, we included observations from 15 archaeological large-scale (0.5 to 5 ha) excavations within the region.

Annual precipitation in the study area is 650–700 mm, increasing from the lee of the Eifel mountains (Euskirchen: 550–600 mm) to the West (Jülich 600–650 mm), North (Mönchengladbach 700–750 mm) and East (Cologne/Bonn 700–750 mm) (Minister für Umwelt Raumordnung und Landwirtschaft des Landes Nordrhein-Westfalen, 1989).

2.2. Sample collection and preparation

A total of 71 bulk samples (2 kg each) were taken from soil profiles in the trench and at the excavation sites: six samples from six Bht horizons, 38 samples from 29 black earth pit fillings and, additionally, 14 samples from black prehistoric settlement pit-fillings and five samples from prehistoric settlement floors. Eight samples were taken from the surrounding horizons without humus accumulation (WRB: argic and cambic horizons). After drying at 40 °C the soil aggregates were crushed and coarse material (>2 mm) was removed by dry sieving. Sub samples were ball-milled for carbon and nitrogen analysis.

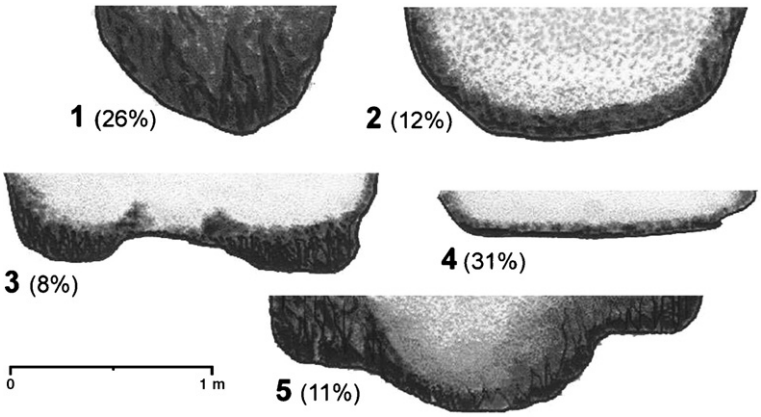

Fig. 3. The five observed types of Luvic Phaeozem pits and their proportions of all 500 observed pits, excluding poorly defined features such as ditches representing 12% of all observed features. (1) Deep v-shaped pits (maximum depth 1.4 m, diameter 0.8–1.0 m). (2) U-shaped pits (maximum depth 1 m, diameter ≤ 1.6 m). (3) Pits with irregular hollows in the base (diameter ≤ 2.8 m). (4) Shallow hollows, potentially heavily eroded type 2 pits. (5) Shallow pits with one hollow in the base (maximum depth 1.5 m, diameter ≤ 2.8 m).

2.3. Soil analyses

The particle-size distribution was examined by wet sieving and gravitational sedimentation (pipette method) according to a standard method (Schlichting et al., 1995), and size classes were selected according to the German classification (AG Boden, 1994; Fig. 7).

Total carbon and nitrogen were determined in duplicates by dry combustion with an elemental analyzer (Elementar Vario EL). The values for total organic carbon corresponded to the total carbon content because the soil samples did not contain calcareous material.

2.4. Charcoal extraction and identification, black carbon quantification, AMS ^{14}C measurements

Macroscopic charcoal pieces were manually selected from bulk soil for radiocarbon dating and identification of wood species (by U. Tegtmeier, Institute of Pre- and Protohistory, Archaeobotanical Laboratories, University of Cologne). Black carbon was measured at CSIRO laboratories, Adelaide, Australia in 11 samples taken from Luvic Phaeozem pits and Bht horizons. Analytical details are reported in Schmidt et al. (1999). Briefly, charred organic carbon was analysed after removal of less stable soil organic matter via high-energy UV photo-oxidation by ^{13}C nuclear magnetic resonance (NMR).

We dated nine charcoal samples and three black carbon samples taken from deeper parts of the Luvic Phaeozem Bht horizons and pits to estimate the approximate age of the soils. The material was washed with deionised water and subsequently dated by accelerator mass spectrometry (Universities of Kiel and Utrecht). The ^{14}C ages were calibrated using the program OxCal v3.5.

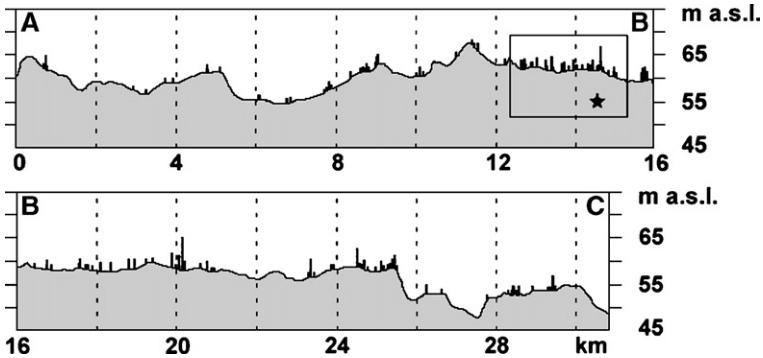

Fig. 4. Cross section showing the loess landscape with typical dry valleys and low hills. The length of the black vertical lines represents the numbers of Phaeozem pits per 50 m. Note the exaggerated relief; actual maximum relief is approximately 25 m. The scale lines on the frame correspond to 2 km. The asterisk marks a known Neolithic settlement area. The rectangle highlights the largest concentration of Luvic Phaeozem pits.

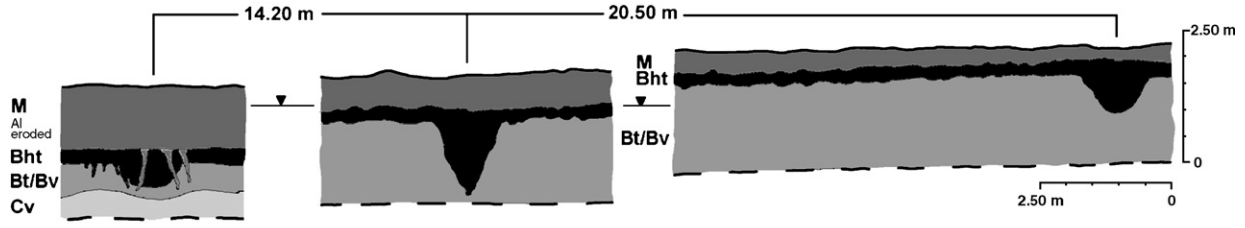

Fig. 5. Typical cross section (ca. 37 m long), as produced by the pipeline trench. The slope dips from right to left, with the thickness of the colluvial cover (M) increasing accordingly. The eluviated horizon (Al) was eroded and not present in this cross section. The Luvic Phaeozem argic horizon (Bht) with humus accumulation and pits are shown in black, followed by the argic horizon without humus accumulation (Bt) or cambic horizon (Bv), respectively, and loess as parent material (Cv). The first pit shows tubular traces of eluviation.

2.5. Geographical information analysis

The entire length (33 km) of the gas pipeline trench was surveyed and 500 pits were documented and classified. Results were expressed as number of pits per 50 m of trench, and were plotted to the relief of the trench (Fig. 4). Geographical information analysis was performed using MapInfo 6.0 software (MapInfo Company, Troy, New York).

3. Results

3.1. Characteristics of Luvic Phaeozems and pits within the pipeline trench and archaeological excavations

For the 240 pits found along the pipeline trench, and another 260 pits that have been documented in archaeological excavations in the Lower Rhine Basin between the years 1999 and 2004 (data not shown here), two observations became clear. First, the Luvic Phaeozem Bht horizons, where clay and humus accumulated, never occurred without pits, filled with material similar to that found in adjacent Bht horizons (Fig. 5). The Bht horizons always followed the floor line of the pits. Second, Luvic Phaeozem pits were always associated with humic Bht horizons of Luvic Phaeozems, but never with the reddish-brown argic horizons of adjacent Luvisols. Thus, the pits must be considered as integral parts of the Luvic Phaeozems. These pits have not been described in the literature so far, and we called them Luvic Phaeozem pits.

When covered with colluvial sediments, the Bht horizons were usually protected from erosion and formed amorphous patches. When the Bht horizons were missing due to erosion, the bottoms of the Luvic Phaeozem pits still were clearly visible in the trench (Fig. 6).

In the 500 described Luvic Phaeozem pits we never found archaeological artefacts, such as pottery or bones —typical for pit fillings found inside prehistoric settlements (in archaeology known as on-site features). From the absence of artefacts and other settlement features, such as post-holes, we concluded that these pits occurred outside the actual settlements (in archaeology called off-site features). The Luvic Phaeozem pits occurred in several distinct shapes, which can be subdivided into five groups (Fig. 3).

Often pits occurred in characteristic clusters with individual pits 1–3 m apart. In the pits we found only few charcoal remains and some reworked gravels. The highest density and greatest number of these Luvic Phaeozem pits occurred close (<1 km) to an established Neolithic settlement (asterisk in Fig. 4).

3.2. Spatial distribution of Luvic Phaeozems and pits

Until now, researchers assumed that in the Rhine region the occurrence of Luvic Phaeozems was limited to loess as parent material and to depressions where a cover of colluvial sediment could protect them from further degradation (Kopp, 1965; Schalich, 1981). However, the results obtained along the pipeline trench showed that Luvic Phaeozems were not limited to loess

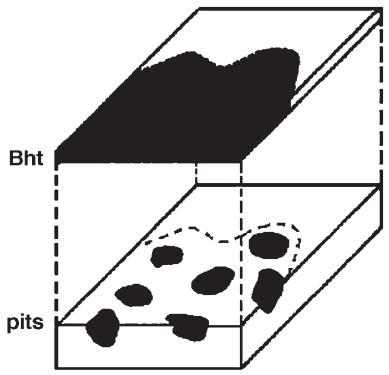

Fig. 6. Luvic Phaeozem (Bht) horizons mostly formed patches. In some cases natural erosion or anthropogenic activity removed the Bht horizon. Then, only the Luvic Phaeozem pits were still visible.

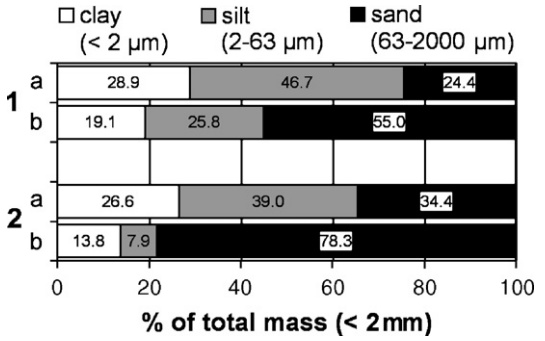

Fig. 7. Particle-size distribution from the location Troisdorf (see Fig. 2) on the lower terrace of the river Rhine. Textures of two pit fillings (a) are compared to the adjacent cambic horizons (b). Size classes according to AG Boden (1994).

as a substrate, but also occurred on loamy and sandy alluvial sediments on the lower terrace of the river Rhine and on the Holocene floodplain (Fig. 2). They appeared in different geomorphologic positions, i.e. in depressions, on slopes as well as on top of hills (Fig. 4). About 80% of the observed Luvic Phaeozems were covered by 20 to 180 cm thick colluvial sediments, but 20% were preserved uncovered. Thus, the preservation of Luvic Phaeozems did not depend on the presence of protecting colluvial cover of sediments, and the occurrence of Phaeozems was independent of substrate, microrelief, microclimate, exposition and slope angle.

3.3. Texture

Particle-size distributions of Luvic Phaeozem pit fillings found within the loess area were similar to the surrounding soil material. Contrasting, pit fillings from the lower Rhine terrace (a in Fig. 7) contained more clay and sand than the surrounding soils (b in Fig. 7), as exemplified for the excavation site at Troisdorf (for site location see Fig. 2). Pits contained more clay (27/29 mass %) and less sand (34/24%) than the adjacent soils (14/19% clay and 78/55% sand). One pit contained a single stone that could not have been fluvially transported.

3.4. Total organic carbon and total nitrogen

The Luvic Phaeozem horizons and pit fillings (Fig. 8) had smaller concentrations for C (arithmetic means: 3.5 g C kg^{-1} for pits and 4.4 g C kg^{-1} for Bht-horizons) and N (arithmetic means: both 0.5 g Nt kg^{-1}) than the materials found within prehistoric settlements, either floors (arithmetic means: 7.6 g C kg^{-1} and 0.6 g N kg^{-1}) or settlement pit fillings (arithmetic means: 5.0 g C kg^{-1}, 0.6 g N kg^{-1}). Resulting C/N ratios are small (arithmetic means: horizons 8, pits 7), although the Bht horizons and pit fillings were supposed to be relicts of humic horizons. Humic Bht horizons of Phaeozems usually have C/N ratios of 10–15 (Gunreben, 1992).

3.5. Identified species of charcoal pieces and black carbon concentration

The identified wood species of the charcoal pieces chosen for radiocarbon dating are shown in Table 1. We found the following species: *Quercus*, *Ulmus*, *Pomoideae* and other unidentified deciduous wood. Large proportions of the soil organic matter taken from the Luvic Phaeozem pits and Bht horizons consisted of

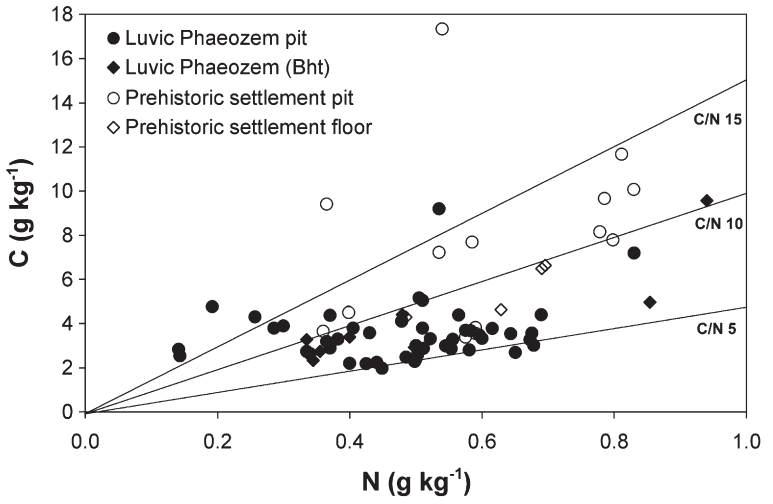

Fig. 8. Total carbon and nitrogen in Luvic Phaeozem horizons and pit fillings (off-site) (black) and in settlement soils (on-site) (white) in the Lower Rhine Basin. The diagonal lines mark C/N ratios 5, 10 and 15.

Table 1
Radiocarbon ages of Chernozems, Luvic Phaeozems and Luvic Phaeozem pits in Germany (calibrated ages calBC/AD; OxCal v3.5)

Ages, calBC/calAD	Material[a]	Identified wood species (charcoals)	Sampling site[b]	Region[c]	Horizon[d]	Data source lab. code
BC						
7530–7200	Charcoal	Deciduous	Köln–Rondorf (lt)	Lower Rhine Basin	LP pit	UtC 11209[e]
7540–7140	Charcoal	n.d.	Köln–Nord (hfl)	Lower Rhine Basin	LP pit	UtC 11208[e]
6230–6090	Black C		Köln–Rondorf (lt)	Lower Rhine Basin	LP pit	UtC 11406 SE 10[e]
5210–5000	Charcoal	Ulmus	Mönchengladbach (ut)	Lower Rhine Basin	LP pit	UtC 11205[e]
4490–4260	SOC		Söllingen D	CDR	AxhSwd	[f]
4460–4250	SOC		Lantershofen	Middle Rhine	Bht	[f]
4230–3990	SOC		Söllingen C	CDR	Axh	[f]
4220–3970	Charcoal	Pomoideae	Pulheim (mt)	Lower Rhine Basin	LP pit	KIA 10696[e]
3890–3640	SOC		Eltville	Rheingau	Bht	[f]
3760–3640	Charcoal	Pomoideae	Kerpen (ut)	Lower Rhine Basin	LP pit	UtC 11203[e]
3700–3380	SOM		Söllingen A	CDR	Axh	[f]
3500–3350	Charcoal	Quercus	Köln–Immendorf (lt)	Lower Rhine Basin	LP pit	KIA 10693[e]
3370–3100	Black C		Seeben/Halle	CDR	Axh	[g]
2890–2670	Charcoal	Quercus	Kerpen (ut)	Lower Rhine Basin	BhtGor	UtC 11201[e]
2880–2630	SOC		Inden	Lower Rhine Basin	Bht	[f]
2880–2620	SOC		Fellbach	Stuttgart	B(h)t	[f]
2880–2620	SOC		Soest II	Westphalia	fAxh/AM	[f]
2860–2470	SOC		Söllingen B	CDR	AxhSwd	[f]
2830–2350	SOC		Hildesheim A	CDR	SwdAxh	[f]
2830–2350	SOC		Soest II	Westphalia	fAxh/AM	[f]
2290–2140	Black C		Köln–Immendorf (lt)	Lower Rhine Basin	LP pit	UtC 11403 SE 69[e]
2200–2030	Black C		Harsum/Hannover	CDR	Axh	[g]
2200–1970	SOC		Muddersheim	Lower Rhine Basin	fBhv	[f]
1880–1690	Black C		Pulheim (mt)	Lower Rhine Basin	LP pit	UtC 11404 SE 70[e]
1525–1430	Black C		Diedenhof/München	South Bavaria	AxhBhv	[g]
1500–1320	Black C		Sossmar/Hannover	CDR	Axh	[g]
1500–1310	SOC		Hildesheim A	CDR	SwdAxh	[f]
1290–1120	Charcoal	Quercus	Pulheim (mt)	Lower Rhine Basin	LP pit	KIA 10697[e]
810–540	SOC		Wallertheim	Rheinhessen	fAxh	[f]
AD						
80–250	SOC		Fehmarn A	Baltic Sea	SwdAxh	[f]
560–770	SOC		Fehmarn B	Baltic Sea	SwdAxh	[f]
675–780	Charcoal	Deciduous	Garzweiler (ut)	Lower Rhine Basin	Bht	UtC 11207[e]
720–940	Black C		Grossenbrode	Baltic Sea	Axh	[g]

Dates were plotted in Fig. 9.
[a] SOC=Soil organic carbon, Black C=Black carbon.
[b] hfl=Holocene floodplain, lt=lower terrace, mt=middle terrace (loess-covered), ut=upper terrace (loess-covered).
[c] CDR=Central dry region of Germany (see Fig. 2).
[d] AG Boden (1994); LP pit=Luvic Phaeozem pit.
[e] This study.
[f] Ages from Scharpenseel et al. (1996) were obtained from the deepest horizons (Bht or Axh) of the analysed soil profiles.
[g] Schmidt et al. (2002).

Table 2
Black carbon concentrations (in g BC kg^{-1} soil) and percentage of black carbon to total organic carbon (TOC) in all analysed bulk soil samples after UV-photooxidation

Lab no. SE	Description	TOC (g kg^{-1})	Black C (g kg^{-1})	Black C (% of TOC)
5	LP pit	4.4	1.7	40
10	LP pit	7.2	2.5	35
16	LP pit	8.2	2.8	34
18	Bht	3.6	1.1	30
25	LP pit	2.3	0.6	25
34	LP pit	2.7	0.5	19
42	Bht	5.9	1.7	29
53	LP pit	5.3	2.2	41
58	LP pit	2.8	0.7	25
59	LP pit	7.5	3.8	46
69	LP pit	3.0	1.0	33
70	LP pit	2.4	0.6	26

black carbon (Table 2), with values between 19% and 46% of total organic carbon (arithmetic mean: 33%).

3.6. Radiocarbon measurements

Charred organic matter is a single–although broadly defined–inert constituent of soils. Soil organic matter, however, comprises a continuum of many constituents, ranging from relatively inert charred particles to microbial biomass turning over in hours to days. Analysis of ^{14}C of an individual charcoal particle may date an individual fire event, whereas measuring mixtures of mechanically separated charcoal particles or bulk soil organic matter may yield mean, apparent ages. Faunal remixing and rejuvenation through biomass input of the soil organic matter can make radiocarbon ages of soil humus difficult to interpret. A closer approximation to the actual soil age can be obtained using deeper and more protected horizons of palaeosoils, buried wood or charcoal (Scharpenseel and Becker-Heidmann, 1992).

In the following, we show results of radiocarbon measurements, transformed into calibrated ages (OxCal v3.5) expressed as years BC or AD (Table 1, Fig. 9). We measured nine charcoal pieces (filled squares) picked manually, and three chemically separated black carbon fractions (filled circles). Those 12 results span a long time period from the Mesolithic (9500–5500 BC), Late/End-Neolithic (4400–2200 BC), Bronze Age (2200–750 BC) to the Middle Ages (500–1500 AD). One charcoal particle dated as Early Neolithic (Linear Pottery Culture; 5500–5000 BC).

Due to the limited number of samples we compared our results with already published results. Black carbon separated from subsurface (Axh) horizons of German chernozemic soils (Schmidt et al., 2002) is displayed as triangles. Scharpenseel et al. (1996) measured radiocarbon concentrations in soil organic matter separated from deeper horizons of chernozemic soils in Germany (diamonds), as they found that in many chernozemic soils radiocarbon ages increased uniformly with depth (Scharpenseel et al., 1968). Despite differences in materials analysed (i.e. charcoal, black carbon, soil organic carbon), radiocarbon ages were complementary and covered a long time period, with a cluster in the Late/End-Neolithic period between 4400 and 2200 BC.

4. Discussion

4.1. Are these Luvic Phaeozem pits natural or man-made?

The shape and presence of Luvic Phaeozem pits were the most obvious evidence for anthropogenic influence.

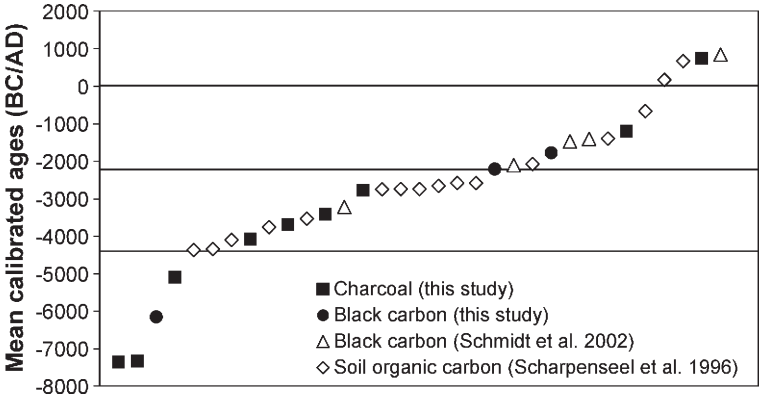

Fig. 9. Radiocarbon ages of charcoal and black carbon taken from Luvic Phaeozem horizons and pit fillings in the Lower Rhine Basin (black symbols), compared to radiocarbon data for black carbon and soil organic matter from different Chernozems and Phaeozems in Germany (white symbols). Details are listed in Table 1.

The Luvic Phaeozem pits on the lower Rhine terrace were filled with material that clearly differed from the surrounding soil, a phenomenon difficult to explain by natural processes. Furthermore, the stone found in one pit is a clear hint for anthropogenic influence. We subdivided the pits into five groups, depending on their shapes (Fig. 3). The pits often have been overlooked during archaeological excavations, or they remained undocumented because they were classified as natural features (weathering structures, tree holes, etc.). Falling trees typically tilt adjacent soil horizons in upright positions (Langohr, 1993), which was never reported in the 240 Luvic Phaeozem pits along the pipeline trench and more than 260 pits investigated between 1999 and 2004 in that region. Although some of these pits might have formed by falling trees or up-rooted tree stumps, the majority of the described pits showed such distinct shapes that we could not find another explanation than that these pits are man-made features.

Elemental analyses for carbon and nitrogen clearly revealed differences between the fillings of the Luvic Phaeozems pits and soil organic matter from adjacent Luvisols and other typical Phaeozems. C/N ratios for Phaeozem Bht horizons typically are in the range of 10 to 15 (Gunreben, 1992). Here, the C/N ratios were surprisingly small (5–10), indicative of bacterial biomass and heavily degraded organic matter containing nitrogen rich material, such as proteins. Soil organic carbon concentrations were low (3.5 g C kg^{-1}), but large fractions of this carbon (19–46%) consisted of black carbon, probably originating from biomass burning. When combined, the last two results show some apparent contradiction and need some further explanation. In the bulk organic matter every fifth to tenth carbon is attached to nitrogen (C/N ratios 5–10), whereas a large fraction of this bulk organic matter was detected as black carbon from charred biomass—typically assumed to be carbon rich (C/N ratios >50). However, the method used here is known to separate not only highly condensed aromatic compounds but also include only slightly thermally altered biomass, i.e. containing functional groups. As an example, charred organic matter produced in the laboratory from peat has more narrow C/N ratios (29), even decreasing with degree of thermal alteration (Almendros et al., 2003). In the char material, nitrogen was present in heteroaromatic structures such as pyrroles, indoles or pyridines with C/N ratios of less than 10. Also black carbon separated from soils using the same method we used here had C/N ratios (14–30) well below 50 (Knicker and Skjemstad, 2000). These observations may explain some of the nitrogen present in the Luvic Phaeozems and pits, but we still cannot explain the small C/N ratios conclusively. It would be promising to find out in which chemical forms the nitrogen survived for millennia, which could help to elucidate the purpose of the pits.

4.2. Do Luvic Phaeozems differ from prehistoric settlement soils?

Black soils found in prehistoric settlement areas were often classified as former Chernozems, and therefore pedogenesis was dated by archaeological evidence. As a clarification, the dark humic soil material found in the Luvic Phaeozem pits should not be confused with the black filling material, e.g. in Neolithic pits and ditches within the actual settlements (on-site), often containing waste material (including excrements, food waste, bone, charred biomass, potsherds) mixed with soil material.

As an example, Baumann et al. (1964) investigated a Linear Pottery Culture settlement near Dresden and concluded that a black soil horizon had formed as an ‘indirect settlement layer’ because of anthropogenic input of organic material into the A horizon within the settlement area. The authors pointed out that the black material should not be equated with Chernozems outside the settlement area. The black soil layer in this Neolithic settlement showed differences from soil A horizons, including higher concentrations of nitrogen and phosphate, larger C/N ratios, different macroscopic features and humus composition. The amounts of humic acids were very high (58–72% humic acids in total carbon).

Geochemical analyses of pit fillings in a Middle to Late Neolithic settlement near Munich (Münchshöfen Kultur, 4600–4200 BC), provided further evidence that pit fillings within prehistoric settlements were not similar to natural soils (Schmid et al., 2001). The black settlement pit fillings differed from A horizons of Phaeozems, when polysaccharide and lignin were analyzed by CPMAS ^{13}C NMR spectroscopy. It was concluded that the black pit fillings could not be interpreted as evidence for the occurrence of Chernozems in the vicinity of the settlement during Middle/Late Neolithic time. Further analyses showed that charred material formed 23–70% of the organic carbon in the pit fillings (Schmid et al., 2002). Again, these black soil remnants that archaeological excavations typically reveal inside prehistoric settlements (on-site) were man-made soils (WRB: Anthrosols) within settlements, and not Chernozems as defined by soil scientists.

4.3. Are the Luvic Phaeozems and associated pits uniformly distributed in the landscape?

As observable in the pipeline trench, Luvic Phaeozems always occurred closely associated with pits and the Bht horizons formed patches with a diameter of up to 100 m. We assume that the relicts preserved today still allow inferring the original distribution of the Bht horizons, although some erosion over time cannot be excluded. The results obtained from the linear trench show that Luvic Phaeozems and pits do not cover the entire landscape but are focused on certain areas. This two-dimensional observation along a transect was supported by large-scale archaeological excavations outside prehistoric settlements (Fig. 2). Once the topsoil was removed, these 0.5–5 ha large excavations showed a typical patchwork of dark coloured Bht horizons and/or pits surrounded by lighter coloured Luvisols.

From these observations we concluded that the Luvic Phaeozems and associated pits probably never covered the entire landscape, even in prehistoric times. If we accept that today's Luvic Phaeozems are relict Chernozems, then also the Chernozems must have formed a patchwork of dark coloured islands, as indicated in Figs. 1 and 5.

A similar patchwork of Chernozem islands has been found in a loess region south of Hannover (Hildesheimer Börde). Satellite images and soil maps showed that the apparently uniform, regional cover of Chernozems is in fact a patchwork of grey (Greyzems) and black soils (Chernozems). Neither relief, parent material nor climate could explain this small-scale distribution and a prehistoric human influence has been postulated (Schmidt et al., 1999, 2002; Gehrt et al., 2002).

4.4. Which implications do our results have for the pedogenesis (process and time) of Luvic Phaeozems (and their precursors Chernozems) in the Lower Rhine Basin?

4.4.1. Agriculture and fire activity as driving factors?

We hypothesise that prehistoric fire-based agriculture may have contributed large amounts of charred organic matter, which could have found its way onto and into the agricultural soils.

There was evidence for fire-based agriculture in the early history of Central Europe. During Pre-Boreal, the forests were dominated by firs, which easily could be ignited by natural causes. However, this is much less the case for the deciduous forests that prevailed during Boreal and Atlantic time. Tinner et al. (1999) estimated that the natural fire frequency in Holocene mixed deciduous forests of the Southern Alps was approximately two fires per year with a total burnt area of 30 ha in a total area of 440 km^2. Studies at Lake Lobsigen showed that these values might be representative for Central Europe as well. Thus, under natural conditions a particular area may therefore burn on average about once every 1400 to 1500 years (W. Tinner, University of Bern, personal communication). These results agreed with estimates for mixed deciduous forest in Southern Switzerland suggesting a mean fire interval of 1800 years (Berli et al., 1994) and of more than 1000 years for similar forest types in Eastern North-America (Aber and Melillo, 1991).

Discussion continues on the distinction between natural and human-caused fires and their frequencies in the temperate deciduous broadleaf forests (Moore, 2000). There is increasing evidence–particularly from the archaeobotanical record–that Mesolithic hunters in Central Europe deliberately used fire as a management tool (Erny-Rodmann et al., 1997; Mason, 2000). For the Lower Rhine Basin loess landscape, re-interpretations of pollen profiles indicated periodic accumulations of charcoal during the Mesolithic period, which could result from fire management by Mesolithic hunters and gatherers (J. Meurers-Balke, University of Cologne, personal communication).

The three charcoal and black carbon ages dating to the Mesolithic originate from pits in the swamp area between the middle and the lower terraces of the river Rhine, which is consistent with the fact that this is a typical environment of Mesolithic hunters and gatherers.

More than half of the radiocarbon ages we compiled for chernozemic soils and from Luvic Phaeozem pits dated to the Late/End-Neolithic time (Fig. 9, Table 1). For this period, archaeobotanical studies (charcoal and/or pollen analyses) showed evidence for extensive and long-term fire-based agriculture both in Southwestern Germany (Rösch, 1993) and Northern Germany to Denmark (Iversen, 1941; Kalis and Meurers-Balke, 1998).

Man-made fires may have peaked during the Late/End-Neolithic but probably were not limited to that period, as shown by radiocarbon ages from the Bronze Age, Roman period and Middle Ages. There may be regional differences in soil formation: Three of the four ages in the last 2000 years derived from chernozemic soils on the island of Fehmarn in the Baltic Sea. Gehrt et al. (2002) calculated that 20% of the organic matter in the Axh horizon of current Chernozems in Lower Saxony consists of charred organic matter. Assuming land use for a period of 1000 years, this would represent

an average annual input of 40 kg BC ha^{-1}. Conversion rates of biomass carbon to black carbon for temperate deciduous forests are still not available. Using data for savannah and temperate coniferous forest, Schmidt et al. (2002) estimated a total of one to seven fires to produce 1.7 g BC kg^{-1} soil, or six to 32 fires to produce 7.6 g BC kg^{-1} soil. Macrocharcoal is rare in the chernozemic soils of Lower Saxony and the Lower Rhine Basin, which may indicate that the black carbon did not originate from charred wood, but from charred herbaceous plants or grass, which easily fall into dust-sized pieces. Charred grass has much smaller C/N ratios (<8) than charred wood and could at least partly explain the small C/N ratios observed in the pits (Knicker et al., 1996).

Circumstantial evidence may come from previously published work. In Australia (Skjemstad et al., 1996) and South America (Glaser et al., 2001) it was shown that fire management practice could form black soils. In Australia, black soils formed in areas regularly burnt by aborigines, whereas adjacent, forested areas had grey soils. In Central Amazonia, fertile black soils (Terra Preta do indio) occurred as small islands (up to 20 ha) surrounded by infertile soils (Ferralsols). The organic carbon of these Terra Preta soils consisted of approximately 20% black carbon from biomass burning, suggesting that they formed as a result of fire-based agriculture. Also in North American chernozemic soils under native grassland black carbon from vegetation fires contributed up to 35% of total organic carbon (Skjemstad et al., 2002; Glaser and Amelung, 2003). Recent work has shown that the content of aromatic carbon, a carbon species which dominates the black carbon structure, correlated significantly with soil lightness (Spielvogel et al., 2004). However, the process of incorporation of black carbon in soils remains unknown, and therefore also the processes that lead to the blackening of soils and the accumulation of deep black horizons remain unclear.

Summarizing, we assume that the Lower Rhine Basin Luvic Phaeozem pits and the associated Luvic Phaeozems originate from human activity, probably including fire-based agriculture, and that man has formed them between the Mesolithic and Middle Ages, clustering in the Neolithic time. However, we never found archaeological artefacts, such as pottery or bones—typical for pit fillings found inside prehistoric settlements (on-site features). From that we conclude that the observed pits must have been formed outside the actual settlements (off-site features). At present the shape does not fit any known pattern of human activity (e.g. storage) and their purpose remains unknown.

4.4.2. Further implications

Our results could have several implications. First, soil formation through fire-based agriculture could explain at least partially how Central European Chernozems, apart from hydromorphic Chernozems, could have formed under a climate too wet and too warm to agree with the current understanding of Central European Chernozems as zonal steppe soil. If the results hold true also for other regions, it may be become necessary to revise conventional wisdom of uniform, natural soil development for many Central European chernozemic soils. Different processes could have affected the formation of these black soils at different times. Some Chernozems may have been formed under typical climate and vegetation, whereas other black soils could have formed through prehistoric or historic agricultural practice. As an example, in the Lower Rhine Basin it seems to have been human activity, probably including fire as a tool, that formed chernozemic soils, with a high activity during Late/End-Neolithic.

Second, archaeologists should differentiate between black pit fillings mixed with soil material often found in archaeological settlements and relict black soils and pits outside settlements, even if both may result from human fire activity. Archaeologists may be able to use relict chernozemic soils as novel archaeological evidence, especially where little other archaeological evidence from off-site areas is available. The localized occurrence of chernozemic relicts with their associated pits might provide new evidence for the type of land use and the extent of prehistoric agricultural lands.

5. Conclusions

In the Lower Rhine Basin, west of Cologne, we discovered clusters of hundreds of regularly shaped pits —presumably man-made. We concluded the following points:

1. These Luvic Phaeozem pits must be of human origin, as indicated by the (i) shape of the pits, (ii) texture contrast between fillings and surrounding soil, (iii) unusually small C/N ratios (5–10), and (iv) residues from biomass burning. The purpose of the pits remained unclear.
2. One implication for archaeology is that the pits never contained visible artefacts, and thus must have been formed outside the actual prehistoric settlements (off-site) and should not be confused with waste-filled pits typically found inside prehistoric settlements (on-site). Thus, off-site pits may serve as a novel archaeological feature, overlooked so far.

3. Luvic Phaeozems and Luvic Phaeozem pits were always closely associated and not uniformly distributed in the landscape, as observations along the linear transect revealed. Luvic Phaeozems and pits were not limited to loess or to depressions with a protecting colluvial cover. The highest density of Luvic Phaeozems occurred close to a known Neolithic settlement.
4. If we accept that man formed these patches of Luvic Phaeozems and adjacent pits, and that these Luvic Phaeozems are relicts of ancient Chernozems then it was human activity which has altered and ultimately formed these Chernozems in prehistoric time. Man must have formed these Luvic Phaeozems pits during several archaeological epochs between Mesolithic and Middle Ages, although dates from the Late-/End Neolithic period were most common, as radiocarbon ages of charcoal and black carbon suggest.

Several questions remain unanswered, including the purpose of these pits, the type of organic matter which survived for millennia in the pits, a conclusive explanation for its small C/N ratios, and finally if this type of prehistoric activity occurred in other regions of Central Europe and has been overlooked so far.

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Manuscript V

Charred organic matter and phosphorus in black soils in the Lower Rhine Basin (Northwest Germany) indicate prehistoric agricultural burning

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Black carbon; phosphorus; archaeology; pedogenesis

Abstract

We investigated the properties of dark soils, namely Luvic Phaeozems in the Lower Rhine Basin (NW-Germany). We discovered clusters of hundreds of regularly shaped pits that were always connected to the Bht horizons of adjacent Luvic Phaeozems. The occurrence of anthropogenic pits in connection with Phaeozems was never reported before, and we called them Phaeozem pits. We conducted archaeobotanical (charcoal analysis) and geochemical (black carbon, carbon, nitrogen and phosphorus concentrations) investigations. We compared soil material from Phaeozem pits with clearly anthropogenic pits: (i) settlement pits, and (ii) slot pits, that can be found outside of prehistoric settlements and do not contain any visible artefacts, but are defined as anthropogenic by their shape.

The main results of our study were: (1) Phaeozem Bht horizons and pits are man-made and archaeological off-site features. (2) Soil properties of the Phaeozem horizons could have been affected by inputs of soil amendments, perhaps to fertilize agricultural fields or gardens. (3) The high proportion of charred organic matter in the dark soil material of Phaeozem horizons and pit fillings results from vegetation fires ignited by man. (4) They were presumably formed in several periods between Mesolithic and the Middle Ages, mainly during Younger to End-Neolithic (4400-2200 BC). We concluded that the Phaeozem horizons could have been formed by agricultural burning, like slash-and-burn, during several (pre)historic epochs.

1. Introduction

Vegetation fire converts living or dead biomass into charred organic matter, or charcoal. Charcoal particles can be found in soils on a global scale and are commonly used to reconstruct Holocene fire history (Figueiral and Mosbrugger 2000; Carcaillet et al. 2002; Carcaillet 1998; Clark and Royall 1996; Patterson et al. 1987). A constituent of charred organic matter is black carbon. The term black carbon describes a continuum of charred material (Goldberg 1985; Hedges et al. 2000). It is resistant to decomposition due to its condensed aromatic structures, although recent studies show that it is susceptible to microbial degradation (Hamer et al. 2004). Black carbon contributes to the stable carbon pools in soils and sediments (Dickens et al. 2004; Schmidt 2004; Skjemstad et al. 1996) and it can be used as a geochemical marker for palaeofire events (Bird and Cali 1998).

In black soils, charred organic matter produced by vegetation fires seemed to supply high organic carbon contents and the dark soil colour. In German Chernozems, which are defined by their very dark brown to black topsoil horizon, black carbon had a proportion of up to 45 % of soil organic matter. As black carbon was found only in black soils, it should be considered being the main colouring agent in these soils (Schmidt et al. 2002). Recent work has shown that the content of aromatic carbon – a carbon species which dominates the black carbon structure - correlated significantly with soil lightness (Spielvogel et al. 2004).

Anthropogenic fire management could form black soils. In Australia, black soils formed in areas regularly burnt by aborigines, whereas adjacent, forested areas had grey soils (Skjemstad et al. 1996). In Central Amazonia, fertile black soils (Terra Preta do indio) occurred as small islands (up to 20 ha) surrounded by infertile soils. The organic carbon of these Terra Preta soils consisted of approximately 20 % black carbon from biomass burning, suggesting that they had been formed as a result of fire-based agriculture (Glaser et al. 2001).

In this study, we investigate the properties of dark soils, namely Luvic Phaeozems in the Lower Rhine Basin (NW-Germany). Phaeozems have characteristic dark brown (Bht) soil horizons that were formed by clay and humus accumulation. Humus was inherited and translocated from the humic material of their precursors Chernozems. The latter were assumed to have covered the entire loess landscape of the Lower Rhine Basin in Early Holocene (Kopp 1965; Schalich 1988). Chernozems are soils which should form under continental climate and steppe vegetation, as it was postulated for Sub-Boreal. After the climate changed to warmer and more humic conditions, Chernozems degraded to Phaeozems (Schalich 1988; Driessen et al. 2001).

We examined Luvic Phaeozems along a 33 km long and 2.0-2.5 m deep gas pipeline trench and at 16 archaeological excavations in the Lower Rhine Basin, west of Cologne. Along this transect we discovered clusters of hundreds of regularly shaped pits. These pits were always connected to the Bht horizons of adjacent Luvic Phaeozems. The occurrence of pits in connection with Phaeozems was never reported before, and we called them Phaeozem pits. We hypothese, that the Luvic Phaeozems in the Lower Rhine Basin could have been formed by vegetation burning. The Phaeozem pits are anthropogenic features, as explained below, although no further visible anthropogenic traces as artefacts or settlement residues were found in the pits or in the surroundings (Gerlach et al. in press).

To uncover the function and history of the dark Phaeozem horizons and the pits in the Lower Rhine Basin, we conducted archaeobotanical (charcoal analysis) and geochemical (black carbon, carbon, nitrogen and phosphorus concentrations) investigations. We compared soil material from Phaeozem pits with clearly anthropogenic pits: (i) settlement pits, i.e. pits in prehistoric settlement areas that contain artefacts or settlement waste (on-site features) and (ii) slot pits, that can be found outside of prehistoric settlements and do not contain any visible artefacts, but are defined as anthropogenic by their shape (off-site features). Additionally, we compared the soil properties of pit fillings to the connecting horizons and surrounding and presumably naturally formed soils.

2. Material and Methods

2.1 Study area and examined types of pits

We followed pipeline excavations (Wingas AG Kassel) in the Southern Lower Rhine Basin, west of Cologne. The trench was 2.0-2.5 m deep and 33 km long, ending at the coordinates 6°45'39"E / 51°0'18"N and 6°58'35"E / 50°50'35"N (indicated in Fig. 1 as A and C).

The entire length of the gas pipeline trench was surveyed and 500 pits were discovered and documented and morphologically classified (Fig. 2). The trench crossed the loess-covered higher and middle terraces, the loamy and sandy lower terrace and the Holocene sandy floodplain of the river Rhine. Additionally, we included observations from 16 archaeological large-scale (0.5 to 5 ha) excavations within the region.

We investigated three different types of pits: (i) 39 Phaeozem pits, (ii) nine settlement pits and (iii) nine slot pits. The Phaeozem pits were always connected to dark brown humic soil horizons, classified as humus and clay accumulation horizons (Bht horizons) of Luvic Phaeozems. The horizons were distributed as patches (diameter up to 100 m) in surrounding reddish light brown Luvisol horizons (Fig. 3 and 4). The Phaeozem pits never contained visible artefacts, as bones or potsherds, and their appearance was never connected to known prehistoric settlements.

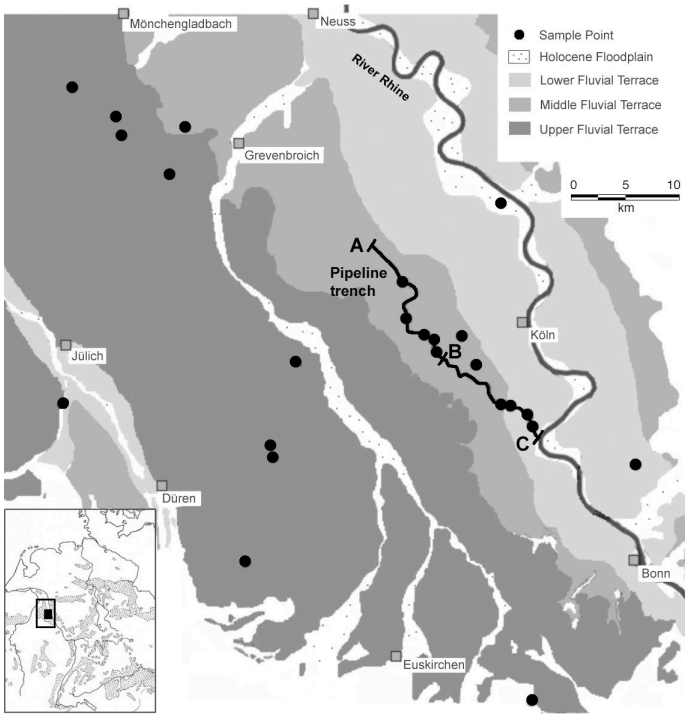

Fig. 1 The large map shows the study area, including the main geomorphologic units, the pipeline trench (ends indicated with A and C) and locations of soil sampling, and additional sampling plots at archaeological excavations. The inset map shows the distribution of loess in Central Europe. Here, we highlighted the Lower Rhine Basin (rectangle) including the study area indicated in the large map (black square).

However, the spatial distribution of horizons and pits was independent of natural factors, e.g. relief or parent material, and the pits investigated on the Holocene sandy floodplain of the river Rhine were filled with material clearly different from the surrounding soils. The pits could be classified into five morphological units (Fig. 2) according to their regular shapes. We concluded that the Phaeozem pits were man-made and archaeological off-site features of still unknown purpose (Baumewerd-Schmidt et al. 2000; Baumewerd-Schmidt et al. 2001; Eckmeier 2002; Gerlach et al. 2006). The pit shapes and the pit fillings differ from pits formed by up-rooting, as falling trees typically tilt adjacent soil horizons in upright positions (Langohr 1993).

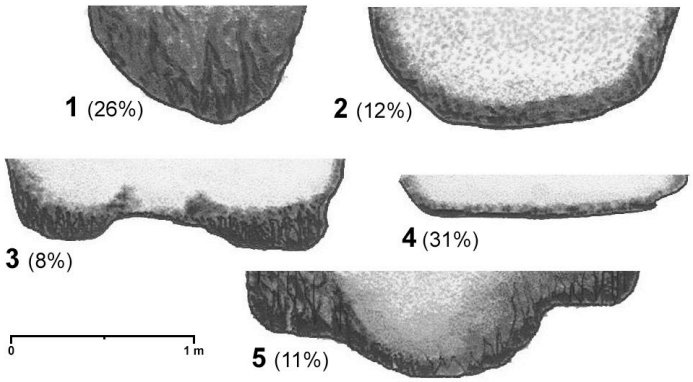

Fig. 2 The five observed types of Luvic Phaeozem pits and their proportions of all 500 observed pits, excluding poorly defined features such as ditches representing 12 % of all observed features. (1) Deep v-shaped pits (maximum depth 1.4 m, diameter 0.8-1.0 m). (2) U-shaped pits (maximum depth 1 m, diameter ≤1.6 m). (3) Pits with irregular hollows in the base (diameter ≤ 2.8 m). (4) Shallow hollows, potentially heavily eroded type 2 pits. (5) Shallow pits with one hollow in the base (maximum depth 1.5 m, diameter ≤ 2.8 m).

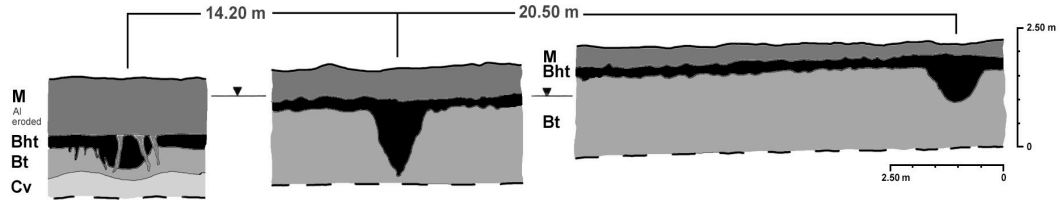

Fig. 3 Typical cross section (c. 37 m long), as produced by the 2.0-2.5 m deep pipeline trench cutting through the loess-covered landscape. The slope dips from left to right, with the thickness of the colluvial cover (M) increasing accordingly. The eluviated horizon (Al) was eroded and not present in this cross section. The Luvic Phaeozem argic horizon (Bht) with humus accumulation and pits are shown in black, followed by the argic horizon without humus accumulation (Bt) or cambic horizon (Bv), respectively, and loess as parent material (Cv). The first pit shows tubular traces of eluviation.

The settlement pits occurred in clearly defined and archaeologically dated prehistoric settlement areas (on-site features). They contained artefacts, mainly settlement waste as sherds or bones.

Not much is known about the function of the slot pits. They were called "Schlitzgruben" (slot pits) or "Schlitzgräbchen" (slot trenches) in the German literature due to their slot-like appearence, up to 5 m deep, 2 m long and narrow (0.2-1 m). They often occur in groups (Struck 1984) near Neolithic settlements (e.g. Langweiler 8, NW-Germany; Boelicke 1988), but do not contain visible artefacts. Buttler and Haberey (1936) and Van de Velde (1973) assumed that they were used for tanning of leather; others interpreted them as animal pitfalls (W. Schier, University of Würzburg, personal communication) or as weaving pits (Gronenborn 1989). We chose these pits because they are clearly anthropogenic and their filling optically resembles the dark soil material in the Phaeozem pits. The slot pits we investigated in the Lower Rhine Basin were also connected to dark brown patchy soil horizons.

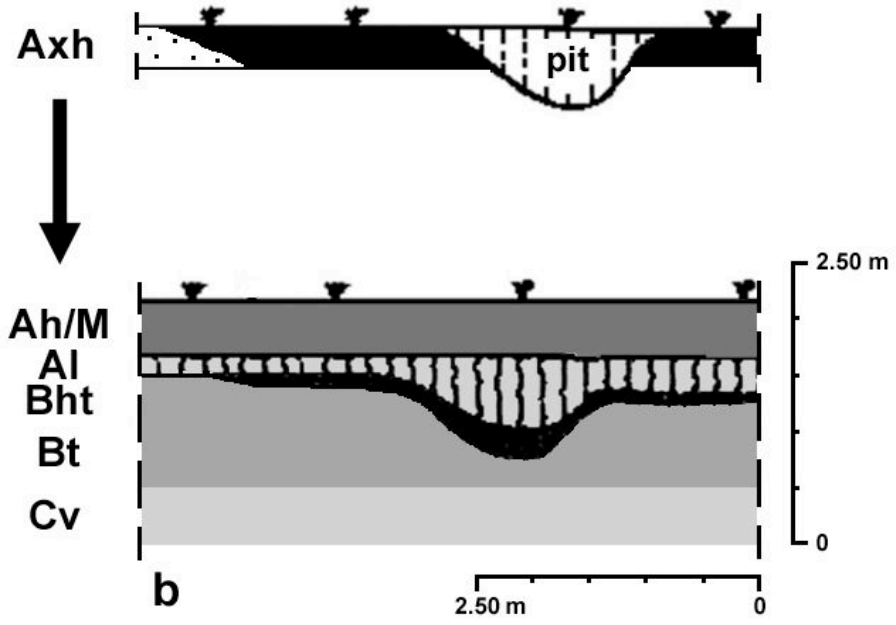

Fig. 4 Soil formation as it might have occurred in the Lower Rhine Basin (schematic). 1a shows the degradation model from Chernozem to Phaeozem, 1b explains soil formation as observed in this study. Soil formation processes typically transport clay and humus from the topsoil (former Axh horizon and pit fillings) into the recent Bht horizons, which inherit the black colour following the former pit structures. Often a colluvial cover (M horizon) protects the Bht horizons against erosion.

2.2 Soil sample collection and analysis

A total of 96 bulk soil samples (2 kg each) were taken from soil profiles in the trench and at the excavation sites: (i) from the Phaeozem pits (43 samples), Phaeozem horizons (seven samples) and surrounding Luvisols (nine samples), (ii) from the settlement pits (15 samples) and settlement soils (five samples), and (iii) from slot pits (12 samples) and surrounding Luvisol horizons (five samples). After drying at 40 °C the soil aggregates were crushed and coarse material (> 2 mm) was removed by dry sieving. Sub-samples were ball-milled for carbon and nitrogen analysis.

Total carbon and nitrogen were determined for all soil samples in duplicates by dry combustion with an elemental analyzer (Elementar Vario EL). The values for total organic carbon corresponded to the total carbon content because the soil samples did not contain bicarbonaceous material.

Phosphorus analysis in soils is used as a marker for human activity. It accumulates in soils as a result of decomposition of organic material and its chemical immobility (Eidt 1977; Arrhenius 1931). We mesured total, inorganic and organic phosphorus concentrations of soil samples in duplicates. Total phosphorus (Pt) was determined photometrically after extraction with sulphuric acid (H_2SO_4) of soils ignited in a muffle furnace. Concentrations of inorganic phosphorus (Pi) were obtained from unignited soil. Organic phosphorus (Po) was calculated by substraction of values for inorganic phosphorus from values for total phosphorus (Klute 1986).

Macrocharcoal pieces (> 1 mm) were manually selected from the bulk soil samples for radiocarbon dating and identification of wood species.

Black carbon was measured at CSIRO laboratories, Adelaide, Australia in 14 samples taken from Phaeozem pits (nine samples), settlement pits (three samples) and slot pits (two samples). Analytical details are reported in Schmidt et al. (1999) and Skjemstad et al. (1997). Briefly, charred organic carbon was analysed by ^{13}C nuclear magnetic resonance (NMR) after removal of less stable soil organic matter by high-energy UV photo-oxidation.

We dated nine charcoal samples and three black carbon samples taken from deeper parts of the Phaeozem horizons and pits to estimate the approximate age of the soil material. Radiocarbon dating of a single charcoal particle may date an individual fire event, whereas mixtures, such as mechanically separated charcoal or black carbon may yield mean, apparent ages. The material was washed with deionised water and subsequently dated by accelerator mass spectrometry (Universities of Kiel and Utrecht). The ^{14}C ages were calibrated using the program OxCal v3.5.

3. Results

3.1 Phosphorus

The pit fillings contained more Pt than the soil surrounding the pits. The settlement pits had the highest concentrations (mean: 649 mg Pt kg^{-1}), followed by the slot pits (mean: 643 mg Pt kg^{-1}) and the Phaeozem pits (mean: 416 mg Pt kg^{-1}).

As Fig. 5 indicates, the amount of organically bound phosphorus (Po) is distributed differently. Here, the settlement soils contained most Po (mean: 169 mg Po kg^{-1}), followed by the slot pits (mean: 127 mg Po kg^{-1}) and settlement pits (mean: 119 mg Po kg^{-1}). The differences between pit fillings and surrounding soils were not as clear as for Pt. The proportion of Po to Pt was lowest in the settlement pits (18 %), and highest in the settlement horizon (53 %). The settlement pit that was connected to the investigated settlement horizon had lower proportions of Po (33 %) in the

upper part of the pit than the horizon, and only 13% of Pt in the lower part of the same pit was Po. The proportions decline because the amount of Pt was much higher in the pit filling (1050 mg kg^{-1}) in the lower part, than in the settlement horizon (361 mg kg^{-1}), while the amount of Po was nearly constant.

Phaeozem horizons contained a higher proportion of Po (32 %) than pit fillings and surrounding soils (both 26 %). The slot pit fillings and the surrounding material have similar concentrations of Po and Pt.

Tab. 1 Arithmetic means (AVE) and standard deviation (SD) for total organic carbon, nitrogen (concentrations in g kg^{-1}), total phosphorus, organic phosphorus (concentrations in mg kg^{-1}) and black carbon (proportion of black carbon to organic carbon) measured for different pit types, horizons and surrounding soils.

Sample type[a]		Corg	N	C/N	Black carbon	Pt	Po	Po
		g kg^{-1}	*g kg^{-1}*		*% of Corg*	*mg kg^{-1}*	*mg kg^{-1}*	*% of Pt*
P pit	AVE	3.53	0.51	7	32	416	107	26
	SD	1.3	0.1	3	9	133	22	
	n=	43	43	43	10	24	24	
P horizon	AVE	4.38	0.53	8	30	396	125	32
	SD	2.5	0.3	1.5	1	116	55	
	n=	7	7	7	2	6	6	
P surr.	AVE	2.10	0.45	5	n.d.	371	96	26
	SD	0.5	0.1	2		110	33	
	n=	9	9)	9		9	9	
V pit	AVE	4.03	0.31	14	36	643	127	20
	SD	0.7	0.1	5	1	75	57	
	n=	12	12	12	2	12	12	
V surr.	AVE	2.54	0.24	11	n.d.	602	114	19
	SD	0.8	0.1	2		95	35	
	n=	5	5	5		5	5	
S pit	AVE	7.35	0.60	13	49	649	119	18
	SD	4.0	0.2	7	13	226	38	
	n=	15	15	15	3	8	8	
S horizon	AVE	4.99	0.60	8	20	316	169	53
	SD	1.6	0.1	2				
	n=	5	5	5	1	1	1	

[a] P pit/horizon/surr. = Phaeozem pit/horizon/surrounding soil; V pit/horizon/surr. = slot pit/horizon/surrounding soil; S pit/horizon = settlement pit/horizon.

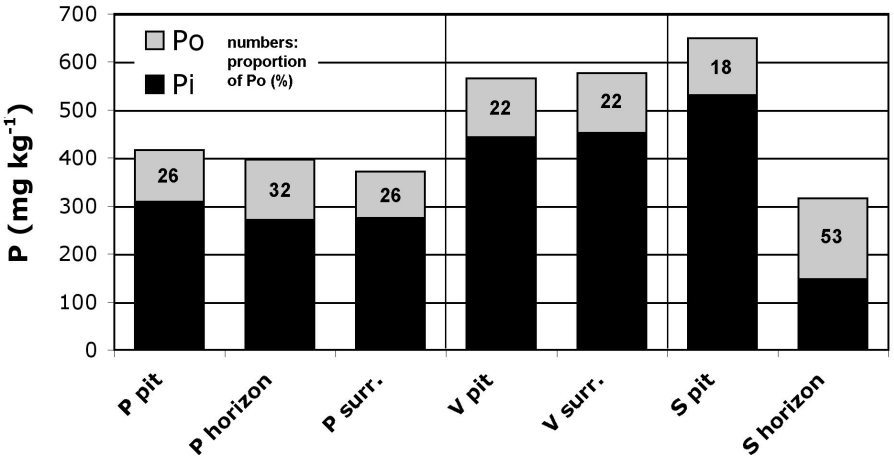

Fig. 5 Average means of concentrations of inorganic (Pi) and organic (Po) phosphorus (in mg kg^{-1}) and proportion of Po of total phosphorus (%) in Phaeozem pits (P pit), connected horizons and in surrounding soils; in slot pits (V pit) and surrounding soils; in settlement pits (s pit) and in one settlement horizon.

3.2 Nitrogen, organic carbon and C/N ratio

The Phaeozem pit fillings had smaller concentrations of nitrogen (mean: 0.51 g Nt kg^{-1}) than the settlement pits (mean: 0.60 g N kg^{-1}). The values for the slot pits were lowest (mean: 0.31 g N kg^{-1}). The concentrations of total organic carbon (Corg) were higher in the pit fillings than in the surrounding soils, as shown in Fig. 6 and Table 1. The Phaeozem pits contained less Corg (mean: 3.53 g kg^{-1}) than the materials found in slot pits (mean: 4.03 g kg^{-1}) and in settlement pits (mean: 7.36 g kg^{-1}).

Resulting C/N ratios were small for Phaeozem pits (mean: 7), due to the relatively high nitrogen concentrations, although the Phaeozem horizons and pit fillings were supposed to be relics of humic horizons. Humic horizons (such as Bht) of Phaeozems usually have C/N ratios of 10-15 (Gunreben 1992).

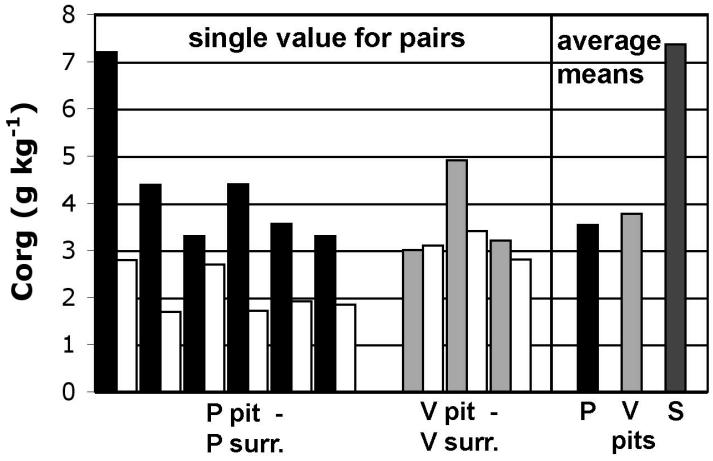

Fig. 6 Concentrations of total organic carbon (Corg, in g kg^{-1}) for pairs of Phaeozem pits (p pit) or slot pits (V pit) and surrounding soils, compared to the average means of all examined Phaeozem pits, slot pits and settlement pits (S pits).

3.3 Charcoal and black carbon

Charcoal pieces were distributed homogeneously in the soil material. We found 128 identifiable charcoals (> 1 mm) in 13 pits, 54 pieces in seven Phaeozem pits, 14 pieces in one slot pit and 60 pieces in five settlement pits (see Table 2). As the amount and the masses of charcoal per soil sample were too small, we could not calculate the concentration of charcoal in the soil. Following wood species could be identified: Pomoideae (pomaceous fruit trees), Quercus (oak), Fraxinus (ash), Ulmus (elm), Corylus (hazel), Prunus (stone fruit trees) and not further indentifiable deciduous wood species.

Black carbon was found in all examined samples, with proportions between 19 to 57 % of total organic carbon. The highest yields were measured in the settlement pits (mean: 49 %), followed by the slot pits (mean: 36 %) and the Phaeozem pits (mean: 32 %). The concentration of black carbon correlated highly with Corg (r^2 = 0.91), as indicated in fig. 7. Table 3 lists the concentrations of all analysed black carbon samples.

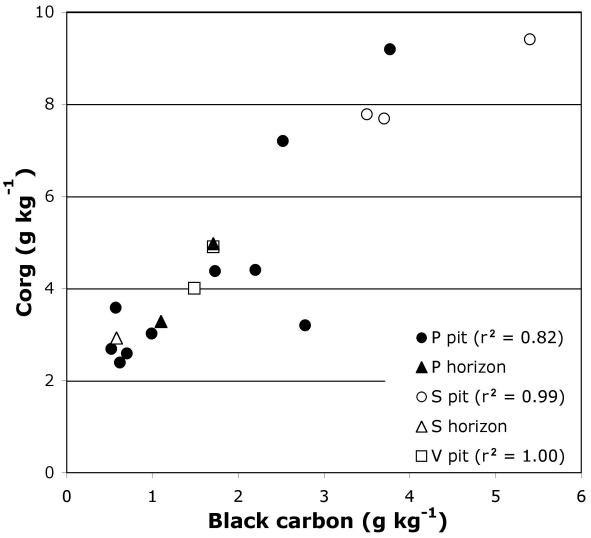

Fig. 7 Concentrations and correlations of total organic carbon (Corg) and black carbon in g kg^{-1} in all examined samples (P =Phaeozem, S = settlement, V = slot).

Tab. 2 Wood species and number of identified macrocharcoal particles in different pit types.

Wood species in number of pits[a]	P pit 7	V pit 1	S pit 5	total 13
Corylus (hazel)	0	0	6	6
Prunus (stone fruit trees)	1	0	0	1
Pomoideae (pomaceous fruit tree)	7	0	31	38
Ulmus (elm)	7	0	3	10
Fraxinus (ash)	0	14	1	15
Quercus (oak)	28	0	6	34
Deciduoud wood species (diffuse porous)	1	0	10	11
Deciduous wood species	8	0	3	11
not determinable	2	0	0	2
total	54	14	60	128

[a] P pit = Phaeozem pit; V pit = slot pit; S pit = settlement pit.

Tab. 3 Black carbon concentrations (in g BC kg^{-1} soil), proportion of black carbon to organic carbon (Corg) in all analysed bulk soil samples after UV-photooxidation.

Lab-Nr. SE	Description[a]	Corg *g kg^{-1}*	Black C *g kg^{-1}*	Black C *% of Corg*
5	P pit	4.4	1.7	40
10	P pit	7.2	2.5	35
16	P pit	8.2	2.8	34
25	P pit	2.3	0.6	25
34	P pit	2.7	0.5	19
53	P pit	4.4	2.2	50
58	P pit	2.6	0.7	25
59	P pit	8.3	3.8	46
69	P pit	3.0	1.0	33
70	P pit	2.4	0.6	26
18	P horizon	3.6	1.1	30
42	P horizon	5.9	1.7	29
77	V pit	4.9	1.7	35
88	V pit	4.0	1.5	37
17	S pit	7.2	3.0	41
19	S pit	9.4	5.4	57
23	S pit	7.7	3.7	48
57	S pit	7.8	3.5	45
71	S horizon	2.9	0.6	20

[a] P pit/horizon = Phaeozem pit/horizon; V pit = slot pit; S pit/horizon = settlement pit/horizon.

3.4 AMS ^{14}C ages

Nine charcoal pieces picked manually, and three chemically separated black carbon fractions were measured. Those twelve results span a long time period from the Mesolithic (9500-5500 BC), Early Neolithic (Linear Pottery Culture; 5500-5000 BC), Younger to End-Neolithic (4400-2200 BC), Bronze Age (2200-750 BC) to the Middle Ages (500-1500 AD). The results of AMS ^{14}C measurements were transformed into calibrated ages (OxCal v3.5) and expressed as years BC or AD. Details are given in Table 4.

Tab. 4 Radiocarbon ages of charcoal and black carbon in Phaeozem horizons and pits (calibrated ages calBC/AD; OxCal v3.5).

Ages calBC/ calAD	Archaeo-logical period[a]	Material[b]	Identified wood species (charcoals) [c]	Sampling site[d]	Description[e]	Lab. code
BC						
7530-7200	Mesolithic	Charcoal	Deciduous	Köln-Rondorf (lt)	P pit	UtC 11209
7540-7140	Mesolithic	Charcoal	n.d.	Köln-Nord (hfl)	P pit	UtC 11208
6230-6090	Mesolithic	Black C		Köln-Rondorf (lt)	P pit	UtC 11406 SE10
5210-5000	Early N	Charcoal	Ulmus	Mönchengladbach (ut)	P pit	UtC 11205
4220-3970	Younger N	Charcoal	Pomoidae	Pulheim (mt)	P pit	KIA 10696
3760-3640	Younger N	Charcoal	Pomoidae	Kerpen (ut)	P pit	UtC 11203
3500-3350	Late N	Charcoal	Quercus	Köln-Immendorf (lt)	P pit	KIA 10693
2890-2670	End N	Charcoal	Quercus	Kerpen (ut)	P horizon	UtC 11201
2290-2140	Early BA	Black C		Köln-Immendorf (lt)	P pit	UtC 11403 SE69
1880-1690	Older BA	Black C		Pulheim (mt)	P pit	UtC 11404 SE70
1290-1120	Younger BA	Charcoal	Quercus	Pulheim (mt)	P pit	KIA 10697
AD						
675-780	Middle Ages	Charcoal	Deciduous	Garzweiler (ut)	P horizon	UtC 11207

[a] N = Neolithic, BA = Bronze Age. [b] Black C = Black carbon. [c] n.d. = not derminable. [d] hfl = Holocene floodplain, lt = lower terrace, mt = middle terrace (loess-covered), ut = upper terrace (loess-covered). [e] P pit/horizon = Phaeozem pit/horizon.

4. Discussion

4.1 Variations of human activity reflected in different pit types

To examine human activity we measured the amount of phosphorus accumulated in the different soils. The Pt distribution showed an addition of organic material in the investigated Phaeozem and settlement pits, and it could be an indicator for phosphorus coming from bone material, as it could be bound to calcium.

Geochemical investigations of Neolithic settlement pit fillings showed that they consist of a mixture of mineral soil matrix and organic material, i.e. settlement waste. Main characteristics of prehistoric settlement pit fillings are higher concentrations of nitrogen and phosphate, larger C/N ratios and different humus composition (Baumann et al. 1964). Further evidence that pit fillings within prehistoric settlements were not similar to natural soils was provided by geochemical analyses of pit fillings in a Middle to Late Neolithic settlement near Munich (Münchshöfen culture, 4600-4200 BC) (Schmid et al. 2001). The black settlement pit fillings differed from A horizons of Phaeozems, when polysaccharide and lignin were analyzed by CPMAS ^{13}C

NMR spectroscopy, and charred material formed 23-70 % of the organic carbon in the pit fillings (Schmid et al. 2002).

The main source for Po is plant biomass and manure or fecal material. We expected the highest proportions in the settlement pits, as they could be used as deposits for kitchen residues. Surprisingly, the proportion of Po was low in the settlement pits, but highest in the settlement horizon (53 %). The higher Pt values for the Phaeozem samples could indicate a higher content of organic soil amendment in general. Nevertheless, the higher value for Phaeozem horizons (32 %) pointed to a higher input of Po limited to the area of dark horizons, e.g. by fertilizing with livestock manure or kitchen residues. When looking at single sample pairs, the picture became more heterogeneously. Although the amount of Pt in Phaeozem horizons and pits was in the same range, the values for Po were distributed differently.

The slot pits and surrounding horizons did not show any differences. The Pt and Po values for the slot pits were similar to the settlement pits, which could mean that the soil material has comparable characteristics. On the other hand, the Corg and N concentrations of soil material in slot pits were much lower, in the range of Phaeozem pits. All examined pit types showed human influence by accumulation of organic material in contrast to the surrounding soil, although the composition of the material filled into the pits seemed to be different.

4.2 Prehistoric fire management as source of charred organic matter

All examined pit fillings and connecting horizons contained black carbon and black carbon concentrations correlated highly with Corg. About one-third of the organic carbon consisted of charred material. Macroscopic charcoal particles were also present in all pit types, most was found in settlement pits. Settlement pits were usually filled with mixtures from soil material and organic waste or residues of hearth fires, which contributed to the high Corg and black carbon values.

The spatial distribution of the Phaeozem pits indicated that they were not connected to any known settlement activities. However, the charred material accumulated in these pits must derive from vegetation burnings. The Holocene temperate deciduous forests cannot be easily ignited by natural causes (Tinner et al. 1999). Under natural conditions a particular area may therefore burn on average about once every 1400-1500 years (W. Tinner, University of Bern, pers. com.). Estimates for mixed deciduous forest in Southern Switzerland suggest a mean fire interval of 1800 years (Berli et al. 1994), and for similar forest types in Eastern North-America of more than 1000 years (Aber and Melillo 1991). Nevertheless, the distinction of natural and human-caused fires in the archaeobotanical records is still under discussion (Brown 1997; Moore 2000), and several parameters, as charcoal influx, fungi and plant succession should be considered (e.g. Erny-Rodmann et al. 1997).

Burning practices for different landscape management purposes seemed to be commonly used in the Holocene. Mesolithic hunters in Central Europe may have used fire as a management tool (Mason 2000; Erny-Rodmann et al. 1997; Zvelebil 1994). The three charcoal and black carbon ages dating to the Mesolithic originate from Phaeozem pits in the swamp area between the middle and the lower terraces of the river Rhine, which is consistent with the fact that this is a typical environment of Mesolithic hunters and gatherers (Gerlach et al. 2006).

There is no evidence for burning during the Early Neolithic (Lüning 2000). Nevertheless, one charcoal dated to the period of the Linear Pottery Culture (5500-5000 BC). Four samples from twelve dated to the Younger to End-Neolithic. In this epoch burning was presumably established as part of agricultural processes both in

Southern and Northern Germany. Evidence for extensive and long-term fire-based agriculture comes from the Lake Constance area (Rösch 1993) and Northern Germany to Denmark, the "landnam" period (Kalis and Meurers-Balke 1998; Iversen 1941), where fire was used to help introducing agriculture on soils with low nutritional value.

Three obtained radiocarbon ages date to the Bronze Age, one to Early (2200-1900 BC), to Older (1900-1200 BC) and to Younger (1200-700 BC) Bronze Age, respectively. An example for Bronze Age fire management is the use of burning to clear forest and establish meadows for livestock pasture in the sub-alpine region of the Upper Engadin (Switzerland) since c.1950 BC (Gobet et al. 2003).

Macrocharcoal was rare in the investigated soil material, which may indicate that the black carbon did originate from charred herbaceous plants or grass, which easily fall into dust-sized pieces. Charred grass has much smaller C/N ratios (< 8) than charred wood (Knicker et al. 1996), and burning could form stable aromatic and hetrocyclic nitrogen containing structures (Almendros et al. 2003), which could be an explanation for the small C/N ratios observed in the Phaeozem pits. Gehrt et al. (2002) calculated that an average annual input of 40 kg BC ha^{-1} for a period of 1000 years is needed to achieve a proportion of 20 % of the organic matter in a topsoil.

The charred organic matter we found in the Phaeozem horizons and pits was most likely formed in several epochs from Mesolithic to the Middle Ages, with an emphasis in Younger to End-Neolithic (4400-2200 BC). Black carbon was presumably produced by either fire management practices, as performed by Mesolithic hunter and gatherers, or by agricultural fires like slash-and-burn. Subsequently, it could have been stored in the humic topsoils of the predecessors of the present Phaeozems and could have acted as a colouring agent. Later, it possibly could have been translocated downwards, accumulated and could be preserved in the Bht horizons, as described in Fig. 4.

5. Conclusions

The investigation of dark soil horizons and adjacent pits of Luvic Phaeozems in the Lower Rhine Basin and the comparison with man-made slot pits and pits in prehistoric settlements led to the following main results: (1) Phaeozem Bht horizons and pits are man-made and archaeological off-site features, as shown by their shape, spatial distribution and by the differences between the Phaeozem soil material and the material surrounding these features. (2) Soil properties of the Phaeozem horizons could have been affected by inputs of soil amendments, like livestock manure or kitchen residues, perhaps to fertilize agricultural fields or gardens. (3) The high proportion of charred organic matter in the dark soil material of Phaeozem horizons and pit fillings, as they were not situated in prehistoric settlement areas and temperate deciduous forests burn very rarely, results from vegetation burnings ignited by man. (4) They were presumably formed in several periods between Mesolithic and the Middle Ages, mainly during Younger to End-Neolithic (4400-2200 BC), as indicated by the AMS ^{14}C ages (Gerlach et al. 2006).

We concluded that the Phaeozem horizons could have been formed by fire management practices during several epochs. Especially agricultural burning, like slash-and-burn, could have created the patchy dark soils, as their properties could also hint to organic fertilizing. We could not uncover the function of the Phaeozem pits so far, we speculate that the function was related to agricultural practices. Also the reason for the unusual morphology of the slot pits remains unknown, as the pit filling

material showed influence of burning and human activity but did not reveal any characterizing chemical or physical soil properties.

However, a number of open questions remain. The process of incorporation of black carbon in soils is still unknown, and therefore the processes that lead to the blackening of soils stay uncertain, too. Also scarce are numbers of conversion ratios of biomass carbon to black carbon, ratios for temperate deciduous forests are not available at all. By investigating both archaeological excavations and experimental burning in field trials as performed in Forchtenberg (SW-Germany; Rösch et al. 2002) the input and fate, as degradation, of charred organic carbon in soils after agricultural burning shall be further examined.

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Manuscript VI

Lipid and phosphorus composition in soils - possibly affected by biomass burning in Mesolithic to Neolithic periods?

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Archaeological Science, environmental marker, human impact

1. Introduction

Anthropogenic activity can modify the composition of soil organic matter. These changes in soil organic matter composition are part of the archaeological record, and could be derived from any kind of human activities: decomposed waste products or animal and human remains are found in settlement areas, while areas used for agricultural purposes could show traces of manuring. Especially the identification of soils formerly used for cropping and animal husbandry via geochemical methods could contribute to the archaeological discussion of changing cultural landscapes and economic developments since the first farmers started agriculture at about 5500 BC. Until now, information about agricultural techniques like fertilizing is scarce (Bakels, 1997). A disadvantage of using geochemical markers is that the marker substances showing an anthropogenic activity are diverse, and that their fate in soils in the long-term is often unknown (Heron, 2004).

The analysis of phosphorus (P) is used in archaeology since Arrhenius (1931) to detect human impact. Higher than natural background quantities of P were associated with occupation areas (Barba et al., 1995; Schuldenrein, 1995; Wells et al., 2000), with burials (Piepenbrink, 1989), or intensive land-use (Pape, 1970; Eidt, 1977; Leonardi and Miglavacca, 1999; Lehmann et al., 2004; Vitousek et al., 2004). The P analysis was often criticised, mainly because the extraction methods for quantifying soil P vary widely, and it was proposed to measure total P, or organic and inorganic P respectively (Bethell and Máté, 1989; Holliday and Gartner, 2007).

More recently, lipid analysis became an application to detect human input on palaeoenvironments. The distribution patterns of lipid compounds like *n*-alkanes may indicate the sources of biomass inputs in soils or sediments (e.g. van Bergen et al., 1997). Therefore, lipid analysis could detect vegetation or land use changes, e.g. to identify the use of grass turfs to build the Orkney plaggen soils (Bull et al., 1999) or to follow the environmental history in lake sediments (Schwark et al., 2002; Fisher et al., 2003) and in a sequence of palaeosoils (Xie et al., 2003). A variety of lipid patterns and componds are diagnostic for different organic materials used for manuring and soil management practises (Pepe and Dizabo, 1989; Bethell et al., 1994; Evershed et al., 1997; Simpson et al., 1998; Bull et al., 1999).

In this study, we applied phosphorus and lipid analyses to soil material from pit fillings in the Lower Rhine Basin. The pits and connected dark sub-soil horizons were affected by burning since Mesolithic, and we attempted to gain further information about the activities and processes that affected these soils.

2. Material and methods

Soil samples were collected in the Southern Lower Rhine Basin from a gas pipeline trench and from 16 archaeological large-scale (0.5 to 5 ha) excavations within the region. We investigated different types of prehistoric pits: (i) Phaeozem pits and (ii) settlement pits. Control samples were taken from the soil material next to the pits. The Phaeozem pits were always connected to dark brown humic soil horizons, classified as humus and clay accumulation horizons (Bht horizons) of Luvic Phaeozems. The horizons were distributed as patches in surrounding Luvisols. The Phaeozem pits, which also include the deep (up to 5 m) and narrow (0.1-2 m) slot pits, never contained visible artefacts, as bones or potsherds, and their appearance was not connected to known prehistoric settlements. The pits have regular shapes, they are archaeological off-site features of still unknown purpose (Gerlach et al., 2006). The settlement pits were sampled in clearly defined and archaeologically dated prehistoric

settlement areas. They contained artefacts, mainly settlement waste like pot-sherds or bones.

Phosphorus was measured as total, inorganic and organic phosphorus concentrations of soil samples in duplicates. Total phosphorus (P_{tot}) was determined photometrically after extraction with sulphuric acid (H_2SO_4) of soils ignited in a muffle furnace. Concentrations of inorganic phosphorus (P_{in}) were obtained from unignited soil. Organic phosphorus (P_{org}) was calculated by subtraction of values for inorganic phosphorus from values for total phosphorus (Kuo, 1996).

For lipid extraction, soil samples (100 - 120 g) were extracted via a Soxhlet-extractor for 24 h using dichloromethane/methanol (2/1; v/v). The obtained total lipid extract (TLE) was separated into two fractions by elution on a KOH-SiO_2 column: (i) a neutral fraction and (ii) an acid fraction, containing mainly fatty acids. The neutral lipids were subsequently separated using the medium-pressure liquid chromatography separation scheme (MPLC) described by Radke et al. (1980) into the following fractions: (i) aliphatic hydrocarbons, (ii) aromatic hydrocarbons, (iii) low polarity hetero-compounds. TLEs were derivatised by heating aliquots with added N_2O-bis(trimethylsilyl)trifluroacetamide (BSTFA) prior to GC-MS measurements. Deuteriated standards (d_{50}-tetracosane and d_{10}-pyrene) were added to the fractions for quantification. Identification of compounds was performed on an Agilent 6890N gas chromatograph with a diphenyldimethylpolysiloxan-coated (0.33 µm) silica capillary column (50 m x 0.2 mm; J&W DB5), coupled to an Agilent 5973 mass spectrometer. The initial temperature was held at 70°C for three minutes after injection, then ramped to 140°C at 10°C per minute, followed by a temperature increase of 3°C per min. until 320°C and held constant at 320°C for 30 minutes.

3. Results and Discussion

3.1 Phosphorus

Inorganic P (P_{in}) occurs as mineral or is bound to clay minerals or Fe/Al oxyhydroxides. In acidic soils, inorganic orthophosphate ions form insoluble associations with Fe and Al, in calcareous soils it is associated with Ca (Bethell and Máté, 1989; Sims and Pierzynski, 2005). The investigated soils are slightly acidic (pH 5.5-6.5), and rich in clay. The conditions for a preservation of P through mineral fixation are therefore given.

Half of the investigated pit fillings contained more total P (P_{tot}) than the soil surrounding the pits. The pit filling in sample set 1 contains nearly twice as much P_{tot} than the control sample. The opposite distribution was found in sample set 14, where the P_{tot} concentrations in the pit were nearly half of the P concentration in the control sample. The concentrations of organic P (P_{org}) are mostly lower in the pit fillings, as is the percentage of P_{org} in P_{tot}.

The main source for P_{org} is non-mineralized organic matter, and between 30 and 65 % of P_{tot} could be P_{org}. Most common P_{org} compounds are inositol phosphates, phospholipids, or nucleic acids (Sims and Pierzynski, 2005). Fresh organic amendments contain mainly P_{org}, in contrast to industrial P fertilizers. But these amendments are mineralized relatively fast, so that an elevated concentration of Pin is considered typical for soil used for agriculture (Eidt, 1977; Schuldenrein, 1995; Leonardi and Miglavacca, 1999). On the other hand, stable P_{org} compounds like inositol polyphosphates deriving mainly from crop seeds would increase the proportion of P_{org} (Ottaway, 1984). Here, also the values for P_{in} were higher in only half of the pit fillings. The dark horizons in sample sets 1 and 3 have lower P_{tot}

concentrations than the pit fillings and control samples, but higher concentrations of P_{org}, indicating an input of fresh organic material at the higher parts of the profile.

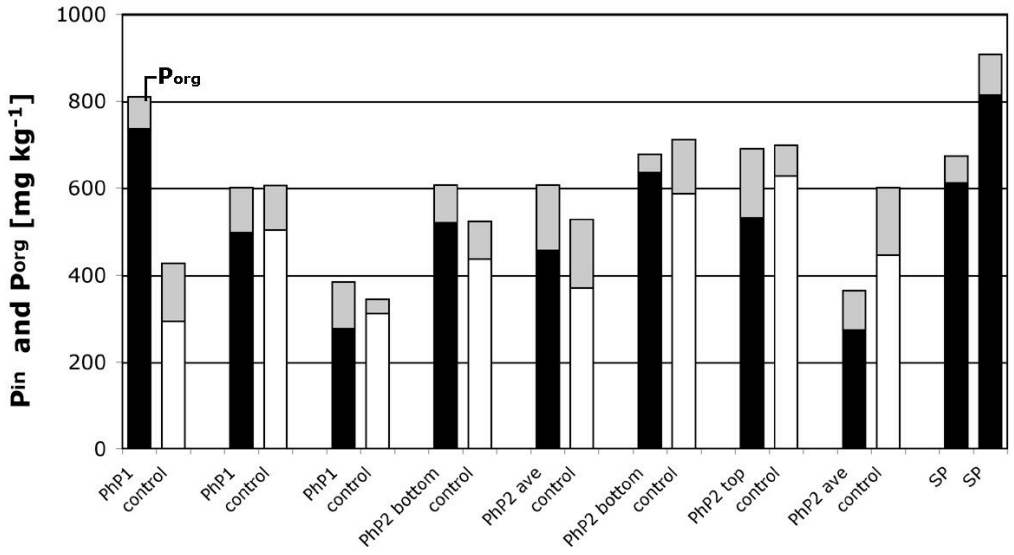


Fig. 1 The concentrations of inorganic (P_{in}, black and white) and organic phosphorus (P_{org}, grey) in all investigated samples (PhP1 = Phaeozem pit, excl. slot pits, PhP2 = Phaeozem slot pit, SP = settlement pit).

Tab. 1 Description of all investigated pits, and results of lipid and phosphorus analysis.

Pit set	Age[1)]	SE no.	Pit type[2)]	SOC *g kg^{-1}*	TLE *g kg^{-1}*	TLE *% of SOC*	P_{tot} *mg kg^{-1}*	P_{in} *mg kg^{-1}*	P_{org} *mg kg^{-1}*	P_{org} *% of P_{tot}*
1	Mesolithic[a)]	10	PhP1	7.2	0.17	2.3	810	736	74	9
		42	Ph horizon	5.0	0.10	1.9	395	253	142	36
		43	Control	2.8	0.13	4.6	426	293	133	31
3	Mesolithic/	84	PhP1	3.3	0.16	4.7	600	497	103	17
	Early	85	Ph horizon	4.4	0.16	3.6	535	368	168	31
	Neolithic[b)]	83	Control	2.7	0.18	6.7	605	503	102	17
6	Neolithic[b)]	47	PhP1	3.7	0.11	3.1	384	276	108	28
		52	Control	1.7	0.06	3.4	343	311	33	9
9	Early	74	PhP2 bottom	3.0	0.14	4.8	606	520	86	14
	Neolithic[b)]	72	Control	3.1	0.10	3.1	523	436	87	17
10	Early	76	PhP2 top	4.3	0.40	9.3	533	391	142	27
	Neolithic[a)]	77	PhP2 bottom	4.9	0.18	3.7	679	523	156	23
		75	Control	3.4	0.47	13.9	527	370	157	30
11	Mesolithic[a)]	88	PhP2 bottom	4.0	0.13	3.3	678	635	42	6
		86	Control	1.7	0.15	8.6	712	587	125	18
12	Mesolithic[b)]	89	PhP2 top	4.3	0.08	1.9	689	532	158	23
		87	Control	1.7	0.08	4.9	698	628	70	10
14	Neolithic[b)]	105	PhP2 top	1.6	0.14	9.0	203	196	7	3
		106	PhP2 middle	1.3	0.08	5.8	236	178	58	25
		108	PhP2 middle	1.2	0.39	32.3	372	284	88	24
		109	PhP2 bottom	1.8	0.10	5.3	646	435	211	33
		114	Control	1.3	0.15	11.6	600	446	154	26
15	Early Neol.[a)]	19	SP	9.4	0.18	1.9	908	814	93	10
16	Early Neol.[b)]	20	SP	1.7	0.13	7.5	673	612	61	9

[1)]Age determined by [a)] ^{14}C AMS or [b)] archaeological context. [2)]PhP1 = Phaeozem pit, excl. slot pits, PhP2 = Phaeozem slot pit.

The measurement of P in the dark soil material gave an ambiguous picture of anthropogenic activity. The accumulation of P in half of the pit fillings indicated a different function or treatment of the area surrounding these pits. In Mesolithic or Early Neolithic manure was not used (Bakels, 1997), but organic residues from camp sites or settlements could have increased the amount of organic matter. However, it is possible that only intensive organic manuring increases soil P levels, as in plaggen soils (Pape, 1970). Areas which were less intensively used may not have increased P levels. When investigating the soil properties of a former Roman agricultural occupation area now covered with forest, Dupouey et al. (2002) found high P levels within the house and enclosure area and slightly elevated concentrations in the near agricultural terraces, but not in the remote terraces.

3.2 Lipids

The proportion of total lipids at total soil organic carbon was in most cases ($p = 0.128$) lower in the dark pit fillings than in the surrounding Luvisols. The proportions do not show any relation to the pit type, the highest (13.1 %) and the lowest proportions (1.9 %) were found in a slot pit filling. The lower proportion of lipids in the pit fillings might indicate an advanced degradation of organic matter, e.g. by heating. In charred soil surface samples, Otto et al. (2006) found less extractable lipids than in charred subsurface soil material, probably because of an exposure of the material to higher temperatures. Contrastingly, burning could also increase the abundance of lipids by releasing organic plant material, which is subsequently translocated into the soil (DeBano et al., 1970).

Most sample sets, with the exception of sets 10-12, displayed a particular high abundance of short-chain and even carbon-numbered *n*-alkanes. The distribution of alkanes is dominated by *n*-C_{16} - C_{18}. *n*-C_{2o} and *n*-C_{22} are highly abundant in sample set 6 and in the settlement pits. Sample sets 10-12 contain high amounts of odd carbon numbered *n*-alkanes (*n*-C_{17} and *n*-C_{19}). The highest detectable *n*-alkane in all samples was *n*-C_{31}; *n*-C_{29} and *n*-C_{31} were relatively higher abundant than *n*-C_{21-28} and *n*-C_{30}. The sample set 14 showed that the pattern of *n*-alkanes in a pit is comparable; here, the predominance of even-numbered *n*-alkanes in not as clear as in the other samples.

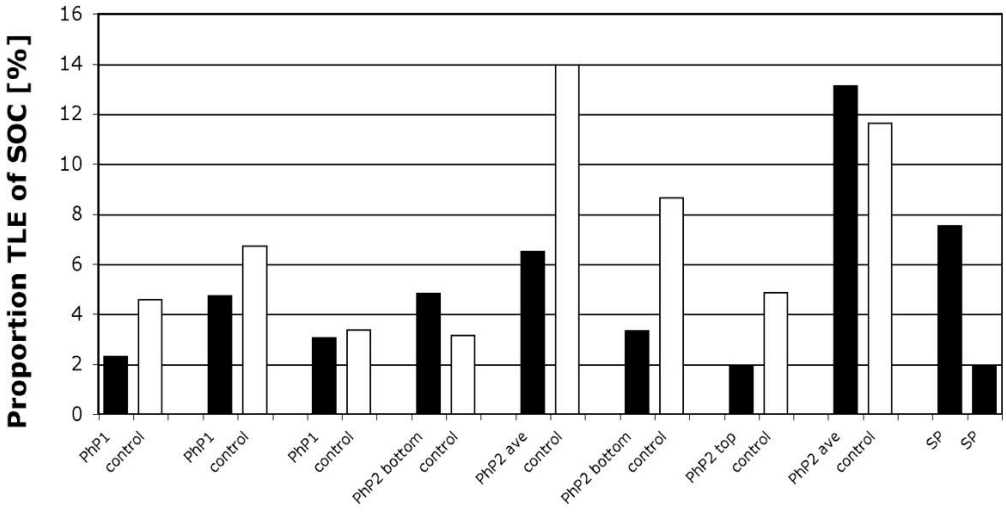


Fig. 2 The proportion of the total lipid extract (TLE) at soil organic carbon (SOC) given in percent for all investigated samples (PhP1 = Phaeozem pit, excl. slot pits, PhP2 = Phaeozem slot pit, SP = settlement pit).

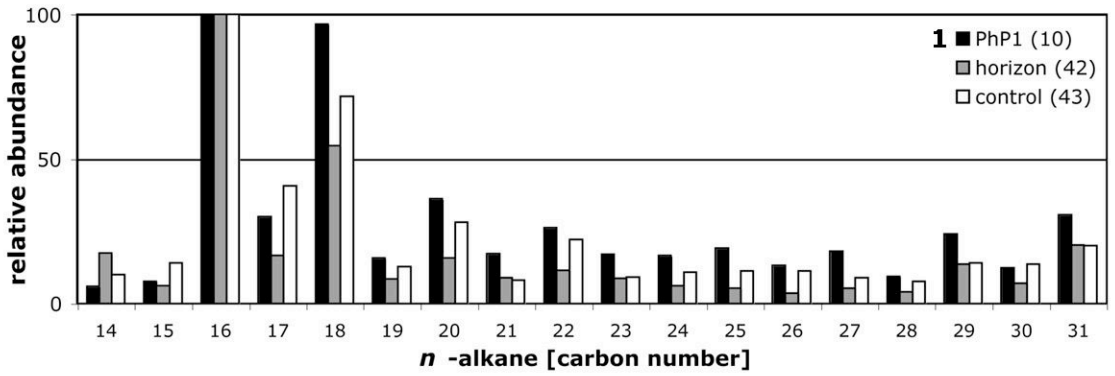
The incorporation of higher plant biomass usually leads to long-chain *n*-alkanes with a relative enrichment of odd carbon-numbered homologues. The elevated amount of *n*-C_{31} alkanes might indicate the input of grass or crops, while the *n*-C_{29} alkane would derive from woody biomass (van Bergen et al., 1997). The even-over-odd distribution of *n*-alkanes that was found also in the control samples could result of a still unknown process of plant material decomposition, maybe by a reduction of corresponding *n*-fatty acids (Welte and Ebhardt, 1968). An even-over-odd predominance of *n*-alkane compounds, including *n*-C_{16} - C_{18} alkanes, was reported by Love et al. (2005) from products deriving from diverse marine and freshwater microalgae and bacteria species. Xie et al. (2003) found maximum peaks at *n*-C_{16} or *n*-C_{18} in palaeosoils, but with an odd-over-even predominance above *n*-C_{22}.

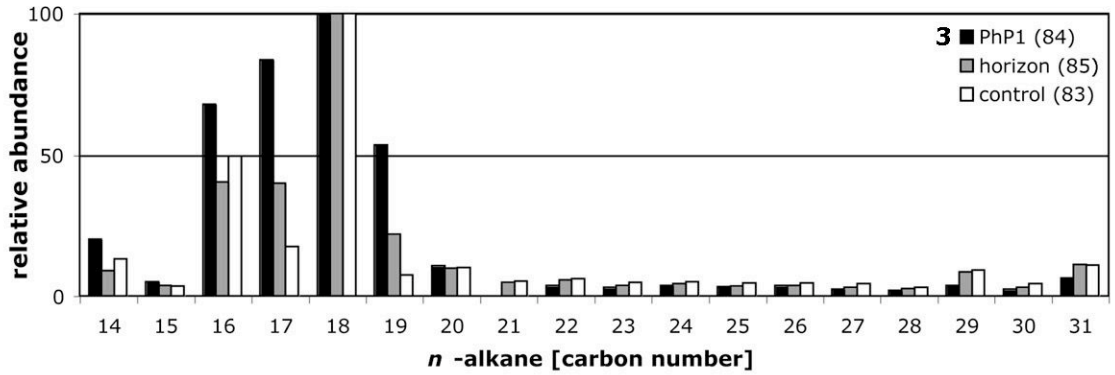
4. Conclusions

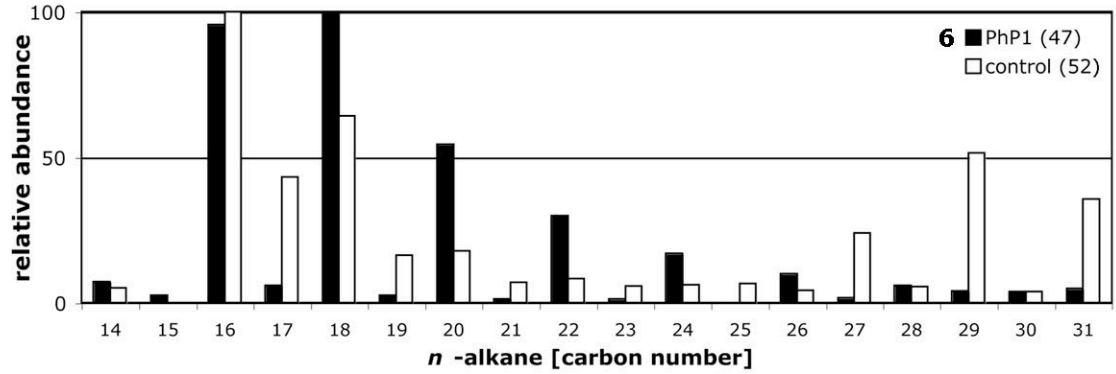
The analyses of phosphorus and lipid distributions in soils altered by Mesolithic to Neolithic burning showed that: (i) the P concentrations are higher in the pit fillings, but only in half of the sample sets; (ii) the amount of total lipids was reduced in the pit fillings; (iii) the samples showed a high abundance of short-chain and even carbon-numbered *n*-alkanes, dominated by *n*-$C_{16\text{-}18}$, with relatively high amounts of *n*-C_{31} and *n*-C_{29}.

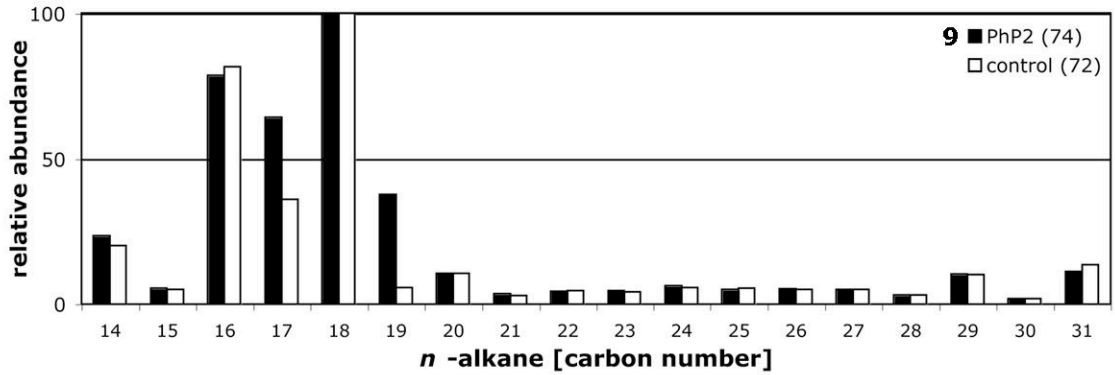
Changes in soil organic matter composition are not necessarily detectable after a time period of up to 9000 yrs, the reasons could be decomposition or translocation of material. Either organic material was added only at some sites, or the amount was very small, suggesting that the comparable shapes of the pits do not indicate a comparable function of the pits or sites.

The distribution of lipids could not be explained yet. Further analysis should test if the distribution of *n*-alkanes is a result of burning, if it derived from microorganisms or if the sampled soil material was even contaminated, e.g. with plasticisers.


1 PhP1 (10)
horizon (42)
control (43)
relative abundance
100
50
0
14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
n -alkane [carbon number]


3 PhP1 (84)
horizon (85)
control (83)
relative abundance
100
50
0
14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
n -alkane [carbon number]


6 PhP1 (47)
control (52)
relative abundance
100
50
0
14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
n -alkane [carbon number]


9 PhP2 (74)
control (72)
relative abundance
100
50
0
14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
n -alkane [carbon number]

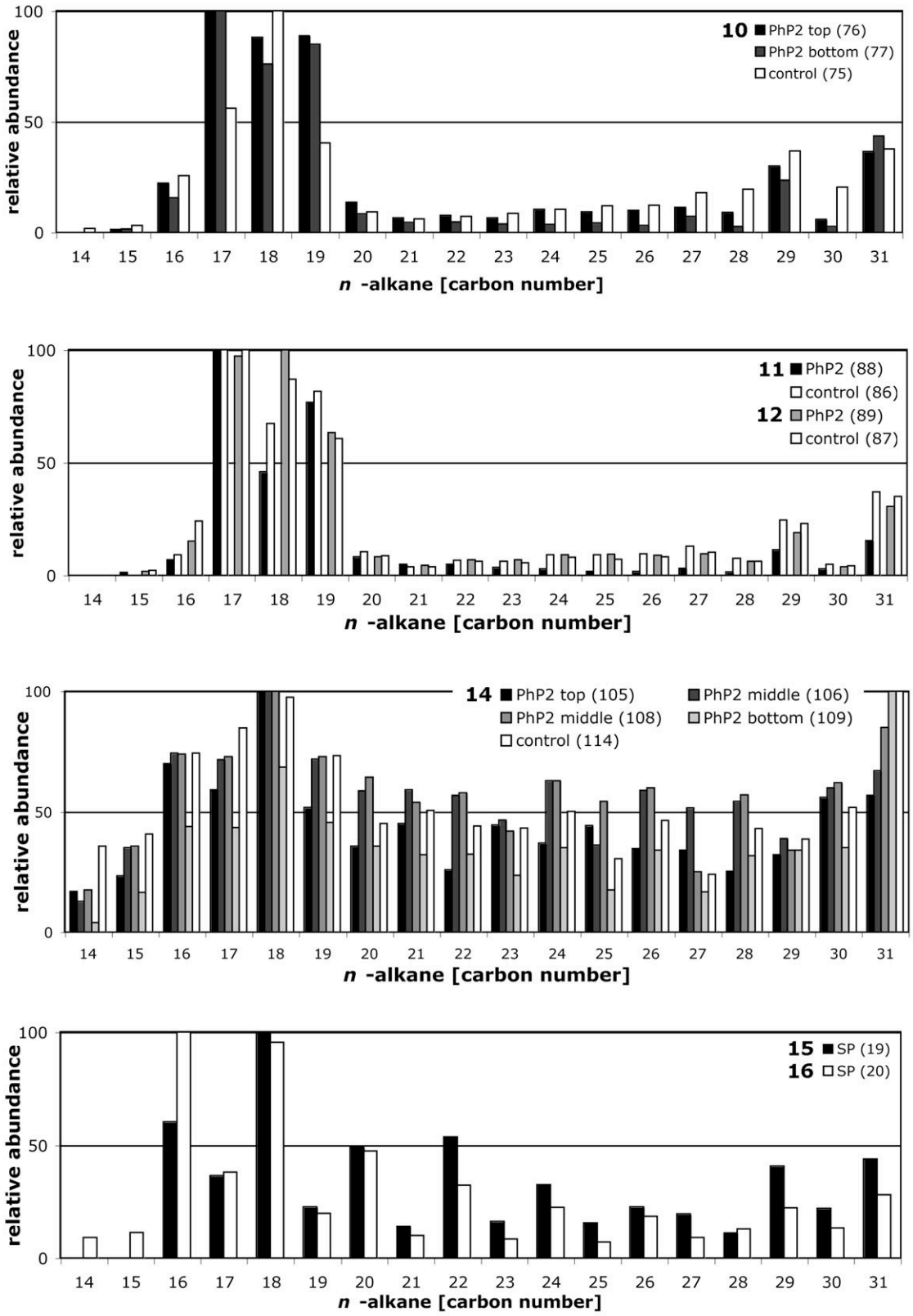


Fig. 3 The relative abundance of *n*-alkanes in all investigated sample sets (PhP1 = Phaeozem pit, excl. slot pits, PhP2 = Phaeozem slot pit, SP = settlement pit).

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Manuscript VII

Chemically isolated microcharcoal can be used for ^{14}C dating when macrocharcoal is absent

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Research Report
submitted

Keywords
macrocharcoal; microcharcoal; ^{14}C-AMS

Abstract

Dating macroscopic charcoal particles from soils and sediments with ^{14}C AMS is commonly used to reconstruct past environments. We dated seven pairs of macro- and microcharcoal samples isolated manually and by UV-photo-oxidation, respectively. The results showed that macro- and microcharcoal had similar ^{14}C ages although chemically separated microcharcoal yielded more conservative ^{14}C dates. Thus, dating chemically separated microcharcoal could substitute dating macrocharcoal.

1. Introduction

Soil organic matter (SOM) has been radiocarbon dated as bulk material or in different physically or chemically separated fractions since the 1960s (Scharpenseel et al., 1996). But SOM consists of a conglomerate of organic materials with different turnover times, and therefore in different stages of decomposition (Scharpenseel and Becker-Heidmann, 1992). Different fractions of soil organic matter should yield different radiocarbon ages, and the most stable carbon component must not be the oldest (Krull et al., 2006). A closer approximation to the actual soil age can be obtained using charcoal particles separated from the soil material (Scharpenseel and Becker-Heidmann, 1992). As examples, Pessenda et al. (2001) showed that the ^{14}C ages of SOM were always significantly younger than the ages of the humin fractions, but the ages of the humin fractions agreed well with macrocharcoal ages. Kristiansen et al. (2003) ^{14}C-dated chemical SOM fractions and reported different age-patterns. In one sample the difference between charcoal and humic acid ages reached nearly 2000 years.

Charcoal carbon is highly resistant to decomposition due to its condensed aromatic structures, although recent studies show that it is prone to microbial degradation (Hamer et al., 2004), and that it changes its chemical and physical structure during decomposition in oxic environments like soils (Cohen-Ofri et al., 2006). The heterogeneous structure of charcoal effects its susceptibility to oxidation, so that charcoal consists of different age groups (Krull et al., 2006).

Radiocarbon dating of macroscopically visible charcoal particles (macrocharcoal) in sediments or soils is commonly used to reconstruct past environmental processes and archaeological developments (e.g. Patterson III et al., 1987; Figueiral and Mosbrugger, 2000; Carcaillet et al., 2002). Non-visible microcharcoal can be chemically separated from the more labile soil organic matter, e.g. by high-energy UV photo-oxidation that was found to isolate the stable and older carbon components. Resulting microcharcoal samples can be dated with ^{14}C AMS (Skjemstad et al., 1993; Skjemstad et al., 1999). Dating of chemically isolated microcharcoal might provide information if macroscopic charcoal is absent in the sedimentary or soil record. To elucidate if the dating of chemically isolated microcharcoal could substitute the dating of macrocharcoal particles, we compared ^{14}C ages of macrocharcoal particles to the ages of microcharcoal, both charcoal fractions separated from the same soil sample.

2. Material and Methods

Soil samples (c. 0.5 kg) were taken from humic fossil soil horizons of Phaeozem-like soils in the Lower Rhine Basin (NW-Germany). The humic horizons were always connected with man-made pits filled with dark soil material that contained macrocharcoals (Gerlach et al., 2006).

The macrocharcoal particles (> 1 mm) were distributed homogeneously in the soil material; all visible particles were manually selected from the bulk soil samples for radiocarbon dating and identification of wood species. They derived from deciduous wood species, like *Quercus* (oak) or *Ulmus* (elm). Microcharcoal was isolated from the less stable total soil organic matter via high-energy UV photo-oxidation and identification of charcoal carbon by ^{13}C NMR (Skjemstad et al., 1993; Skjemstad et al., 1999). About one-third of the soil organic matter consisted of charred organic matter.

We dated seven macrocharcoal samples and seven microcharcoal samples. The material was washed with deionised water, treated according to the laboratory protocols and subsequently dated by accelerator mass spectrometry (Universities of Kiel and Utrecht). The ^{14}C ages were transformed into calibrated ages (cal BP; 1σ-probability) using the program OxCal v3.5.

3. Results and Discussion

The AMS radiocarbon ages of macro- and microcharcoal ranged between 12800 - 12450 cal BP to 3240 - 3070 cal BP; the macrocharcoals yielded ages from 3240 – 3070 to 7130 - 7010 cal BP, the microcharcoals from 12800 - 12450 to 3830 - 3640 cal BP (Table 1). Most microcharcoal samples (six of seven) were older than the macrocharcoals, although the differences were not significant ($p = 0.128$) and the ages of macro- and microcharcoal did not correlate ($r = 0.46$). While the five younger sample pairs yielded relatively similar ages ($r = 0.90^*$), the two oldest sample sets showed larger differences between the macro- and the microcharcoal ages (Figure 1).

Tab. 1 Radiocarbon ages given in calibrated years before present (cal BP; 1σ-probability) of macrocharcoal particles (> 1mm) and microcharcoal chemically separated from labile soil organic matter by UV photo-oxidation, both fractions deriving from the same soil samples.

Sample name	Analysed material	$\delta^{13}C$	^{14}C years	^{14}C ages
		‰	*BP*	*cal BP*
SE 70	Macrocharcoal			3070 - 3240
SE 69	Macrocharcoal			5300 - 5450
SE 58	Macrocharcoal	-26.6	4920±60	5590 - 5710
SE 17	Macrocharcoal	-24.9	6158±50	6950 - 7100
SE 57	Macrocharcoal	-28.1	6180±60	6990 - 7210
SE 23	Macrocharcoal	-24.7	6210±50	7010 - 7130
SE 19	Macrocharcoal	-25.9	6212±44	7020 - 7130
SE 70	Microcharcoal	-25.1	3454±35	3830 - 3640
SE 69	Microcharcoal	-25.5	3797±34	4240 - 4090
SE 58	Microcharcoal	-29.9	10460±90	12800 - 12450
SE 17	Microcharcoal	-25.1	6300±80	7320 - 7030
SE 57	Microcharcoal	-26.9	6760±80	7680 - 7510
SE 23	Microcharcoal	-27.7	8690±80	9860 - 9540
SE 19	Microcharcoal	-24.5	6260±80	7270 - 7020

The age of a macrocharcoal does not date a fire-event, but the death of the charred plant. This inbuilt age, i.e. the time-delay between death and charring could be several centuries, e.g. between 30 and 610 years in coastal temperate rainforest of British Columbia Canada. The radiocarbon ages of wood charcoal would over-estimate the date of burning and thus would give the maximum ages of fire-event (Gavin, 2001). Dating of a pool of macrocharcoal gives a mean age of charcoal assemblages, which would be a representative age of the burning event. However,

Gavin et al. (2003) reported that one radiocarbon date per site was sufficient to identify the time since the last fire.

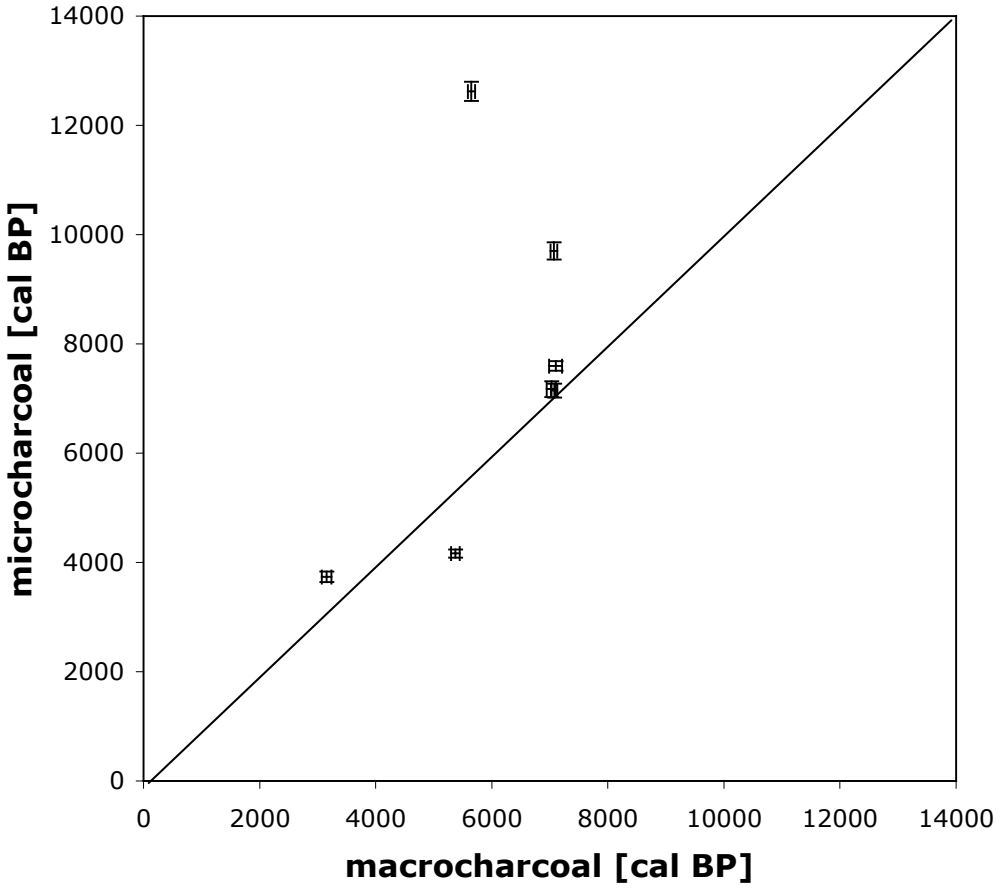

Fig. 1 Radiocarbon ages (cal BP; 1σ-probability) of macrocharcoal particles (> 1mm) and microcharcoal chemically separated from labile soil organic matter by UV photo-oxidation. The line shows the equal age distribution.

Charcoal consists of various chemical compounds and is very heterogeneous. The resistance against biological or chemical decomposition is determined by the combustion conditions and depends on the elemental composition or chemical recalcitrance of the charcoal components. Organo-mineral associations seem to stabilize carbon only over decadal time-scales (Krull et al., 2006). Older charcoal, compared to recently charred material, has a different elemental composition, indicating the degradation of charcoal over time. Cohen-Ofri et al. (2006) used a variety of spectroscopic analyses to show that the graphitic component of charcoal oxidises into material resembling humic acids. They confirm the findings of Bird et al. (2002) who described degraded internal structures of fossil charcoal. Products of charcoal carbon decomposition - condensed aromatic rings - were identified in dissolved organic matter of charcoal leachates and soil pore water (Hockaday et al., 2006). Presumably the more labile compounds degrade over time, and more stable carbon moieties would be preferentially enriched. Black carbon consists mainly of recalcitrant aromatic carbon structures, and therefore should yield older ages. Schmidt et al. (2002) reported that in three of four dated samples black carbon yielded older ages than the total SOC.

The differences between the ages of macro- and microcharcoal, especially in the two oldest sample sets, could be explained by (1) a homogenisation of charred material in the microcharcoal fraction. The microcharcoal sample may comprise mean ages of different biomass samples, while a single macrocharcoal would date a single event in time; and (2) the microcharcoal fraction might consist of more stable components than macrocharcoal, i.e. the compounds which are more resistant against degradation and therefore of older age.

4. Conclusions

We determined the ^{14}C AMS ages of seven pairs of macro- and microcharcoal taken from the same soil samples and found that the microcharcoal fraction yields older ages than single macrocharcoal pieces. We concluded that in soil and sediments (1) microcharcoal consists of more stable components than macrocharcoal and thus yields more conservative ^{14}C dates, and (2) chemically separated microcharcoal can be used for dating when macrocharcoal is absent. But microcharcoal would give a mean age of organic material and the ages of the older, more stable, compounds. As a result, the ages of both fractions are not comparable because different carbon compounds are examined.

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Manuscript VIII

Radiocarbon ages of soil charcoals from the southern Alps, Ticino, Switzerland

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^{14}C AMS, charcoal, soils, *C. sativa*

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Abstract

Radiocarbon dating of macroscopic charcoal is a useful tool for paleoclimatic and paleoecologic reconstructions. Here we present results of ^{14}C dating of charcoals found in charcoal-rich soils of Ticino and the Misox Valley (southern Switzerland) which indicate that the Late Glacial and early Holocene fires coincided with warm phases in the North Atlantic region and low lake levels in the Central Europe. Late Holocene charcoals found in these soils document an earlier than believed presence of sweet chestnut (*Castanea sativa* Mill.) in southern Switzerland. Sweet chestnut trees play a key role in Mediterranean woodlands, and for longer than two millennia have been used as a food source. Based on palynological evidence it is commonly believed that in southern Switzerland *C. sativa* was first introduced 2000 years ago by the Romans, who cultivated it for wood and fruit production. Our results indicate that this tree species was present on the southern slopes of the Alps ~1500 years earlier than previously assumed, and therefore was likely introduced independently from cultivation by the Romans.

PACS: 91.80.+d; 92.70.G+

Keywords: AMS ^{14}C dating; Charcoal; *Castanea sativa*; Paleo fires; Misox Switzerland

1. Introduction

The genus *Castanea* has been present in the northern hemisphere for the last 80 Ma with the maximum of its extension during the tertiary when the mild, moist climate favoured its growth and expansion. Cooling that occurred sometime between 5 and 1.8 Ma and the following Quaternary glaciations led to the extinction of chestnut at high latitudes and finally to its retreat to the glacial refuges in southern and central Italy, and the Balkans [1]. Spatial distribution of the locations, into which chestnut retreated during the last glacial maximum (LGM), has been exclusively based on pollen reconstructions and correlation with ^{14}C dated records. Krebs et al. [2] summarized the data on distribution of *Castanea sativa* in Europe and North Africa showing more frequent glacial refuge areas and possibly earlier post-glacial presence of chestnut in some of the regions. Despite being an extremely powerful tool for paleo-reconstructions, pollen analyses have limitations, which in the case of *C. sativa* appear to add to the controversy. Drawing maps of the past vegetation distribution is inconclusive if the pollen of a specific taxon are not frequent or not present at all. In addition, pollen of *C. sativa* is difficult to identify precisely because it is morphologically

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very similar to other pollen of *Lotus, Hypericum, Sedum* [3,4]. Macrofossils can be helpful in resolving problems with pollen strata, especially where fragments of charcoal are present. Wood-anatomical analyses of macroscopic charcoal fragments (>2 mm) provide additional information about the presence of trees in the region. Moreover, well characterised charcoal macro remains can be used as a material for radiocarbon dating. In many cases dating of single pieces of macroscopic charcoals, which weigh as little as a few milligrams, is possible using the AMS technique. Such analyses had been successfully applied in archaeology and, more recently, have been used in studies of paleo fires as well as environmental reconstructions (for a review see [5]).

Recently, Willis and van Andel [6] published a compilation of radiocarbon ages (^{14}C ages between 16 and 40 ka BP) of full-glacial age charcoal macrofossils found in 40 archaeological locations of central and eastern Europe. This collection of 151 radiocarbon ages, which was obtained on identified charcoals of various tree species, calls into question the previous picture of steppe-tundra vegetation covering land between the Alps and the Scandinavian Ice Sheet.

Based on the pollen data of the Alpine regions it is believed that *C. sativa* was reintroduced into this region by humans but the arrival path and timing remain controversial. Most previous pollen studies concluded that the Romans introduced *C. sativa* [1,7–9]. However, we believe that an earlier post-glacial expansion of the chestnut tree may have been obscured in pollen spectra. The direct ^{14}C dating of charcoal found in soil and sediments has a great potential for resolving the paleoecology of *C. sativa* in the southern Alps region.

1.1. Study site

Charcoal macrofossils were collected from three soil profiles sampled at two locations near Pura (Ticino) and Roveredo, in the Misox valley (Grisons), in southern Switzerland. The climate is temperate with a mean annual temperature of 12 °C (January, 1 °C; July, 22 °C) and a mean annual precipitation of 1800 mm, which is characteristic of the southern Alpine region. Forest fires are common during dry winters with mean monthly precipitation of 60 mm or less. Heavy rains occur during the rest of the year with a maximum monthly precipitation of 200 mm during the summer. The deciduous forest at the lower elevations (below 1000 m above sea level) is dominated by chestnut (*C. sativa* Mill.) accompanied by oak (*Quercus petraea*, *Q. pubescens*), birch (*Betula pendula*), beech (*Fagus sylvatica*) and to lesser extend elm (*Alnus glutinosa*), ash (*Fraxinus excelsior*), and linden (*Tilia cordata*). Between 1000 and 1400 m the beech (*F. sylvatica*) tree dominates and coniferous forest, whereas Norway spruce (*Picea abies*) and silver fir (*Abies alba*) prevails at elevations higher than 1400 m.

1.2. Soil profiles

Two soil profiles at Roveredo were sampled: Pian d'Arf at 515 m (46°22′51″N, 9°13′25″E) and Prebonella at 1000 m (46°22′50″N, 9°13′57″E). The profile sampled at Pura, is located west from Locarno at 650 m (Pura, 45°98′50″N, 8°86′24″E). These three profiles were studied by Blaser et al. [10] who classified them as cryptopodzolic soils. They contain a thick blackish-brown mineral horizon of exceptionally stable soil organic matter. Soils at the sites dominated by chestnut forest in southern Switzerland usually have extremely high soil organic matter (SOM) stocks (the highest found in Switzerland) of approximately 177 tC ha^{-1} [4]. This feature is explained as the result of a unique combination of mild/wet climate, Fe–/Al– rich acidic bedrock (gneiss) and the presence of high amounts of phenols and tannins in the litter layer, which is characteristic for the chestnut forest [10]. A high content of black carbon (BC), which is formed by incomplete combustion, was also found in our profiles [11] but not in control profiles with low C content, which implies that this form of carbon might have contributed significantly to the high SOM.

1.3. Charcoals

Six charcoal-rich soil profiles were sampled to reconstruct fire frequencies and the impact of burning on the vegetation in Ticino and Misox Valley, Switzerland [11]. Charcoal was extracted from each soil horizon by floating/washing technique then dried and weighted to estimate charcoal content. More than 500 pieces of charcoal (pieces larger than 2 mm) were analysed under the microscope using wood identification techniques in order to determine the botanical species or genus of charred wood [12].

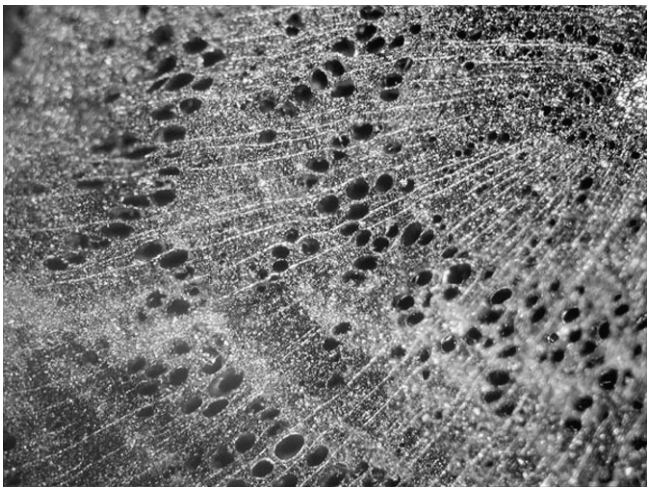

Fig. 1. Microphotograph (50×) of the oldest chestnut charcoal piece found in Swiss soils (ETH-28464, 1640–1420 BC). The wood-anatomical structure is ring-porous, with pores in radial dendritic groups, and homogeneous uniseriate rays, which is characteristic for charcoal derived from the burning of a chestnut tree (*Castanea sativa* Mill.).

Differentiation between deciduous and coniferous trees is straightforward because of the uniform distribution of cells within the annual layer of coniferous trees. However, identification of botanical species requires well-preserved charcoals. Particularly relevant for our study was the identification of charcoal that derived from *C. sativa*. Structure of this wood shows similarities to that of oak (*Quercus* sp.) so that sufficiently large pieces are required for identification. The wood of chestnut is ring-porous, with pores in radial dendritic groups, and homogeneous uniseriate rays (Fig. 1). These are rather narrow (1–2 cells wide) in contrast to the typical 30 cell-wide rays of oak wood.

Fourteen identified charcoal samples were selected from three soil profiles as material for AMS ^{14}C dating. These included silver fir (*Abies alba*) ($n = 4$), pine (*Pinus* sp.) ($n = 2$), diffuse-porous broadleaf species ($n = 2$), chestnut (*C. sativa*) ($n = 5$) and one piece not identified at the species level, described as either oak (*Quercus* sp.) or chestnut (*C. sativa*). The problems with the identification of this one piece of charcoal were caused by small size of the sample (approximately 2 mm in diameter) which does not allow for observation of structure of dendritic rays (thin or thick), because the fragment may derive from a piece of wood between two rays.

1.4. Radiocarbon dating

Charcoal samples were cleaned using the modified acid–alkali–acid (AAA) procedure [13] in order to remove possible contamination with carbonates and humic acids. This involved longer treatment (12–24 h) with the first acid (0.5 M HCl, 60 °C) that removes carbonates. The dry sample i.e. ca. 2–4 mg of clean charcoal was weighed, placed in the pre-cooked Vycor tube together with pre-cooked CuO (oxidizing agent) and silver, which removes gases (SO_2) that might hamper conversion of CO_2 to graphite. The evacuated tube was then sealed and left for 2 h in 950 °C to combust. The purified CO_2 was mixed with H_2 and heated to 625 °C to reduce to graphite over the cobalt catalyst [13]. The $^{14}C/^{12}C$ ratio was then measured for each graphite sample. Measurements were corrected for blank values and isotopic fractionation [14]. Conventional radiocarbon ages (Table 1) were calculated following the convention of Stuiver and Polach [15] and calibrated using OxCal program [16].

2. Results and discussion

In both profiles from Roveredo (Profile C1 and C2) inversions in the ^{14}C chronology indicate reworking and replacement of the material (Table 1 and Fig. 2). Erosion processes, freeze and thaw cycles, bioturbation, and uprooting can lead to transport of charcoal in soil profile [17]. These two 'disturbed' profiles represent late Holocene deposits whereas the third profile from Pura C3, which is the oldest of all, is free of such disruption (Fig. 2). The Late

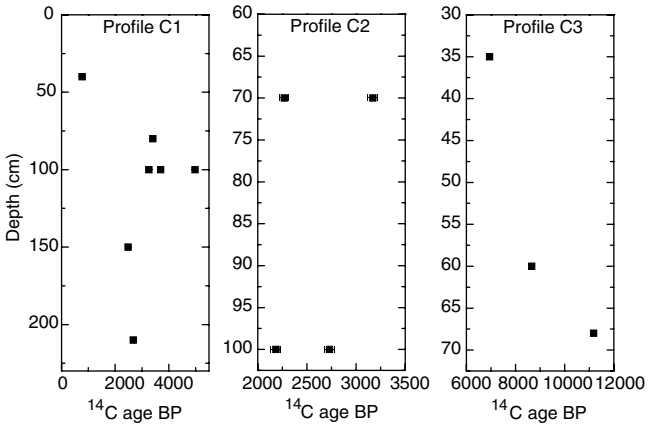

Fig. 2. Radiocarbon ages of identified charcoal samples found in soil profiles plotted versus depth scale.

Table 1
AMS ^{14}C ages of charcoal samples from three soil profiles: C1 (Pian d'Arf), C2 (Prebonella) and C3 (Pura), Ticino, Switzerland

Lab number ETH	Profile	Depth (cm)	Tree species BP	^{14}C age $\pm 1\sigma$	Calibrated ages
28466	C1	40	*Castanea sativa*	770 ± 45	1170–1300 AD
28457	C1	80	*Abies alba*	3405 ± 50	1880–1530 BC
28464	C1	100	*Castanea sativa*	3255 ± 50	1640–1420 BC
28465	C1	100	Diff. porous broad leaf	4980 ± 55	3950–3650 BC
28456	C1	100	*Abies alba*	3695 ± 50	2280–1940 BC
28463	C1	150	*Castanea sativa*	2480 ± 50	780–410 BC
28462	C1	210	Diff. porous broad leaf	2675 ± 50	930–780 BC
28459	C2	70	*Abies alba*	3170 ±50	1540–1310 BC
28468	C2	70	*Castanea sativa*	2270 ± 45	410–200 BC
28467	C2	100	*Castanea sativa*	2730 ± 50	1000–800 BC
28458	C2	100	*Abies alba*	2185 ± 50	390–100 BC
28469	C3	35	*Quercus*[a] *(Castanea sativa)*	6945 ± 70	5990–5710 BC
28460	C3	60	*Pinus* sp.	8660 ± 65	7940–7570 BC
28461	C3	68	*Pinus* sp.	11180 ± 75	11270–10980 BC

Calibrated ages (2σ ranges, 95% confidence level) were obtained using OxCal v3.10 calibration program [16] (INTCAL04 data set [26]) are expressed in BC/AD.

[a] Because of the small sample size, exact identification of this sample was impossible.

Glacial/Early Holocene radiocarbon ages of charcoal provide direct dating of forest fires. It had been shown previously that annual fire frequencies before 4.5 ka BP remained on low level and corresponded to the natural level of fire frequencies in this region [18]. Moreover, pollen and charcoal analysis of sediments from Lago di Origlio and Lago di Muzzano (Ticino), which are located close to our studied soil profiles, have shown that charcoal minima coincide with cold and wet climate periods [18]. The remarkable old ages of charcoal from profile of Pura C3 coincide with the warm periods of late Alleröd (ETH-28461; 11 180 ± 75 BP) and the early Holocene (ETH-28460; 8660 ± 65 BP). The later age falls in the Preboreal low lake level period (11 050–10 300 cal BP), which has been recognized in Holocene sediments of central European lakes [19]. This is also in agreement with the oldest ^{14}C ages (B–6228, 8663 ± 45 BP and B–6229, 8782 ± 35 BP) of *Larix* tree trunks transported by Riedgletscher (Central Alps, west of Ticino) which were found at the elevation of 2060 m [20] thus indicating that the early Holocene fires in Ticino coincided with the glacial recession in the central Alps. The ^{14}C ages of charcoals of oak/chestnut (6945 ± 70 BP) and deciduous tree (4980 ± 50 BP), coincide with low lake level phases documented in the Swiss and French Jura [19], and other Swiss and Austrian lakes [21]. Such climatic conditions resulted in high density of the Early Neolithic lake dwelling villages (Cortaillod-Pfyn culture) [19]. Interestingly, there are no matching data from the Alpine tree-line reconstructions published to date which show glacial recession between 6000 and 5500 cal BP [20]. Following the wet and cold period between 5600 and 5300 cal BP [22] the lake levels were very low in the Jura and Alpine region and lakeside dwelling villages of the Middle Neolithic had grown dense. For this reason the observed increase of charcoals in lake sediments of Lago di Origlio and Lago di Muzzano, which were interpreted as an anthropogenic impact on the forest [18], should rather be viewed as a mixed signal of anthropogenic and natural induced fires. Similarly, the ages of soil charcoals obtained in our study are most frequent between ca. 4250 and 3250 cal BP and 2950 and 2050 cal BP (Fig. 3) and the origin of the fires in this time period can be due to natural and/or anthropogenic factors.

Pollen and charcoal studies suggest that in contrast to the early and mid Holocene, there is a clear evidence in vegetation development that sometime after 2000 BP fires were of anthropogenic origin [18]. Our late Holocene record does not provide evidence that the fires were more frequent after 2000 cal BP. Perhaps the location of our soil profile in chestnut dominated forests can explain the results. As shown by a 'jump' in concentration of chestnut pollen at ~2000 BP this fire resistant tree [23] became the dominating species in the southern Alps forest. Paradoxically, these significant pollen changes at 2000 BP created a common believe that have obscured the real history of the postglacial re-colonisation of the southern slopes of the Alps. For this reason our radiocarbon dating of chestnut charcoal

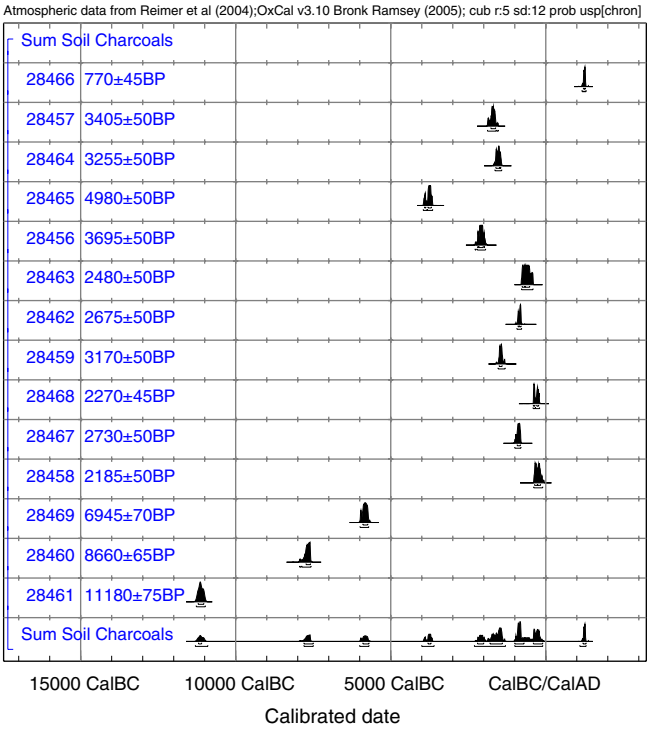

Fig. 3. Combined probability distribution of charcoal ages from all three Ticino soil profiles.

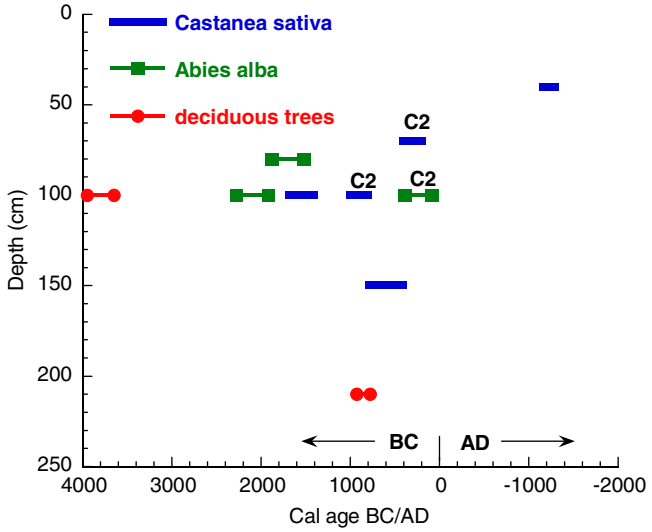

Fig. 4. Calibrated radiocarbon ages (BC/AD) (2σ ranges, 95% confidence level) of charcoal found in two soil profiles of Misox: Pian d'Arf and Prebonella (labelled C1 and C2, respectively see Table 1) shown on the common depth scale. With one exception, the ^{14}C ages of chestnut indicate its presence in southern Switzerland prior to Roman times.

provides interesting new evidence. According to the pollen based model of chestnut arrival the *C. sativa* charcoals found in the Alps should be 2000 years old or younger Surprisingly, our data contain only one age of chestnut charcoal that falls into the expected calibrated age interval and all the other calibrated ages are older than 200 BC (Fig. 4 and Table 1). These findings are challenging the

common believe based on pollen analysis of lake sediments that the Romans have introduced the chestnut into the studied region and more generally in the Alps (northern Italy) [7,9]. Previous studies showed pollen and macrofossils of chestnut in bronze age settlements (1200–750 BC) in Switzerland [24], pointing to an earlier introduction of chestnut, which was attributed to contacts with Mediterranean populations (e.g. trade with the Etruscans). Moreover, recent research on chestnut glacial refugia and Holocene cultivation [2,25] questions a direct link between Romans and the expansion of the chestnut tree. The radiocarbon ages of chestnut charcoals presented here date back to 1690–1410 BC and provide the first unambiguous evidence for an earlier presence of sweet chestnut in southern Switzerland. It is still an open question whether *C. sativa* arrived through natural dispersal or was introduced through pre-Roman cultures such as the ancient Celtic populations identified by the ancient Greek and Roman authors as Lepontians, who occupied territories of the present Canton Ticino during the whole first millennium BC.

3. Conclusions

Results of radiocarbon analyses performed on macroscopic charcoal found in three charcoal-rich soil profiles from Ticino and Misox Valley (Switzerland) show the great potential for paleo studies. The main advantage of using ^{14}C dating as a tool is the ability to directly date the climate proxy, in this case macroscopic charcoals. Four ^{14}C ages were obtained on charcoals, which presumably originated from natural fires that occurred in the southern Alps during dry and warm periods of the Late Glacial and early-mid Holocene. The two groups of late Holocene ages (Bronze Age and Iron Age) might reflect a combination of anthropogenic and natural impact on the forest fire frequencies. The presented radiocarbon ages of *C. sativa* charcoal are older than 2000 years and provide the first clear evidence of a pre-Roman presence of the chestnut in the Southern Alps.

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Manuscript IX

Quantitative comparison of solid-state ^{13}C NMR spectra of soil organic matter from an experimental burning site acquired at two field strengths

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Abstract

Solid-state ^{13}C cross polarization (CP) NMR spectra were acquired for fifteen soil organic matter samples on two different spectrometers (200 MHz and 400 MHz). Distributions of broad functional group classes – carboxyl, aryl, O-alkyl and alkyl – were determined by integration across broad chemical shift regions. The distributions derived from the two spectrometers were closely correlated (r^2 0.77-0.93). Only slight biases were identified – carboxyl C contents were on average 8% lower and alkyl C contents 5% higher for spectra acquired on the 400 MHz spectrometer. These results indicate that valid ^{13}C CP spectra can be acquired at field strengths up to 400 MHz, and that spectra acquired at different field strengths can be directly comparable.

1. Introduction

The main use of NMR spectroscopy in the analysis of soil organic matter (SOM) is to determine the relative proportions of broad functional group classes, for example, alkyl, O-alkyl, aryl and carboxyl. This is achieved by integration across broad chemical shift regions, but the reliability of this approach is affected by (i) spinning sidebands, which can transfer signal from one C type into regions assigned to other C types, (ii) different sensitivities of different C types to cross polarization (CP), and (iii) interference by paramagnetic species. These quantitation issues have been discussed at length, including in a number of recent reviews (Cook, 2004; Preston, 1996; Preston, 2001). A number of techniques have been developed to both improve quantitation (Cook et al., 1996; Mao et al., 2002; Mao et al., 2000; Skjemstad et al., 1994; Smernik and Oades, 2003) and to better gauge quantitation problems (Keeler and Maciel, 2003; Smernik and Oades, 2000a; Smernik and Oades, 2000b). Numerous recommendations have been made as to the "ideal" set-up for analyzing SOM (Conte et al., 2004; Dria et al., 2002; Mao et al., 2000), but no consensus has yet been reached. However, as discussed by Preston (2001), much of this discussion is moot, because most soil scientists have very limited access to NMR spectrometers, and often lack the resources to implement sophisticated techniques. So even if a consensus could be reached on the ideal field strength, MAS rate and pulse sequence, the present situation in which almost all SOM studies use a simple CP sequence and utilize whatever spectrometer is available to them regardless of field strength, would likely prevail. In these circumstance, the key question becomes: "how comparable are ^{13}C CP NMR spectra acquired on different spectrometers?".

Very few direct comparisons of SOM spectra acquired at different fields have been published. Fründ and Lüdemann (1994) reported that ^{13}C CP spectra of 19 soils and 5 humic extracts acquired on a 300 MHz spectrometer at a MAS rate of 15 kHz contained substantially less carboxyl and aryl signal than those acquired on a 100 MHz spectrometer at a MAS rate of 4 kHz. Mao et al. (2002) also concluded that the ^{13}C CP NMR spectra of two humic acids acquired at different field strength were substantially different. On the other hand, Dria et al. (2002) reported very similar distributions of C types in spectra of three SOM samples acquired on 100 MHz and 300 MHz spectrometers. In a previous study, we reported that ^{13}C CP NMR spectra acquired on 200 MHz and 400 MHz spectrometers differed very little, with just a slightly higher proportion of carboxyl and aromatic C detected at the lower field (Smernik, 2005). In that study, as well as comparing CP spectra acquired at different fields, we also compared spectra acquired with different MAS rates, spectra acquired using direct polarization (DP), and gauged the effect of field strength on key relaxation rates. In this paper, we confine the comparison to ^{13}C CP NMR spectra, but analyze a larger range of fifteen SOM samples.

2. Materials and methods

2.1. Collection and description of soil samples

The samples were collected from an experimental burning site located in SW-Germany (Forchtenberg slash-and-burn experiment). The 3.5 ha site is situated in a temperate deciduous forest; the soil is a slightly acidic Haplic Luvisol with partly stagnic properties (Rösch et al., 2002). The investigated trial plot (11 x 8 m) was burnt in October 2004; small wood pieces were collected in a row and ignited, and the pile of burning wood was drawn over the ground (Rösch et al., 2002).

Soil samples were collected before burning, immediately after burning and one year after burning. For each treatment, a total of five samples were analyzed (one 0-1 cm, two each of 0-2.5 cm and 2.5-5cm). The samples were dried at 40°C for 24 h, the aggregates were crushed and coarse material (roots and charcoal particles) >2 mm was removed by sieving. The organic carbon content of the soil, which did not contain carbonate, was determined by dry combustion (Leco furnace). The nitrogen content of the soil was determined by elemental analysis (Elementar VarioEL). Charcoal carbon concentrations were measured using mid infrared - Fourier transformed infrared spectroscopy (MIR-DRIFT) (Janik et al., in press). Prior to NMR spectroscopy, the soils were treated with 2% HF to remove Fe and concentrate the organic carbon (Skjemstad et al., 1994).

2.2. NMR spectroscopy

Two spectrometers were used, a Varian Unity 200 spectrometer (henceforth referred to as "the 200 MHz spectrometer") and a Varian Unity INOVA 400 spectrometer (henceforth referred to as "the 400 MHz spectrometer").

All solid-state ^{13}C NMR spectra were acquired with magic angle spinning (MAS) and high-power ^{1}H decoupling. Spectra acquired on the 200 MHz spectrometer were acquired at a ^{13}C frequency of 50.3 MHz and with a MAS rate of 5 kHz, whilst those acquired on the 400 MHz spectrometer were acquired at a ^{13}C frequency of 100.6 MHz and a MAS rate of 7 kHz. A Doty Scientific high-speed MAS probe was used on the 200 MHz spectrometer and a Doty Scientific supersonic MAS probe was used on the 400 MHz spectrometer. Both probes use 7 mm diameter cylindrical zirconia rotors and Kel-F end-caps. Free induction decays were acquired with a sweep width of 40 kHz on the 200 MHz spectrometer and 50 kHz on the 400 MHz spectrometer. A total of 1216 data points were collected for all spectra, representing an acquisition time of 15 ms on the 200MHz spectrometer and 12 ms on the 400 MHz spectrometer. All spectra were zero-filled to 8192 data points and processed with a 50-Hz Lorentzian line broadening and a 0.010-s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm.

Spectra were acquired on the 200 MHz spectrometer using a standard cross polarization (CP) pulse sequence, and on the 400 MHz using a ramped-amplitude cross polarization (CP-ramp) pulse sequence, in which the ^{1}H spin lock power was varied linearly during the contact time. The "width" of the ramp, which controls the maximum and minimum power levels, was optimized for one of the samples, and this value was used for all of the other samples. CP-ramp was not available on the 200 MHz spectrometer. Spectra represent the accumulation of 4000 scans and were acquired using a 1-ms contact time and a 1-s recycle delay.

3. Results and discussion

The ^{13}C cross polarization (CP) spectra of the fifteen soils acquired on the 200 MHz and 400 MHz spectrometers are shown in Figs 1-3. All of the spectra are superficially similar, as been noted previously for the ^{13}C CP spectra of soil organic matter in general (Mahieu et al., 1999). Close inspection does reveal some differences, for example, samples 5 (Fig. 1) and 7 (Fig. 2) contain more than average signal in the alkyl (0-45 ppm) region, whilst samples 3 (Fig. 1) and 12 (Fig. 3) contain more than average signal in the aryl (110-165 ppm) region.

The soils were sampled from the same field in a slash-and-burn experiment. They vary considerably in C and N content, and also charcoal content, as detailed in Table 1. These differences, as well as the differences in the spectra (Figs. 1-3), reflect variations in the amount and nature of organic matter with soil depth and the effects of burning.

Tab. 1 Some properties of the 15 soil samples analyzed in this study.

Sample	Treatment	Depth	Organic Carbon	Nitrogen	Charcoal Carbon	Charcoal Carbon
		cm	——————*g kg^{-1}*——————			*% of SOC*
1	control	0-1	55.7	4.5	1.6	2.9
2	burnt	0-1	60.5	4.6	2.4	4.0
3	burnt 1yr	0-1	24.9	3.9	3.4	13.8
4	control	0-2.5	33.3	2.5	1.0	3.0
5	control	2.5-5	21.4	1.6	0.5	2.4
6	control	0-2.5	44.8	3.2	1.2	2.8
7	control	2.5-5	27.5	1.9	0.7	2.6
8	burnt	0-2.5	50.4	4.7	1.7	3.3
9	burnt	2.5-5	35.5	3.2	1.2	3.1
10	burnt	0-2.5	45.3	3.7	1.6	3.5
11	burnt	2.5-5	30.0	2.6	0.9	2.8
12	burnt 1yr	0-2.5	53.8	3.3	2.8	5.1
13	burnt 1yr	2.5-5	39.5	2.3	0.8	2.0
14	burnt 1yr	0-2.5	50.2	3.9	2.1	4.2
15	burnt 1yr	2.5-5	30.9	2.7	1.0	3.3

Control = samples taken before burning; burnt = samples taken directly after burning; burnt 1yr = samples taken one year after burning.

We (and other researchers in this area) are ultimately interested in using solid-state ^{13}C NMR spectroscopy to understand the effect of management on the nature of soil organic matter. However, the purpose of this paper is not to report the results for this particular set of samples, but rather to gauge the extent to which the subtle differences in organic C chemistry that are evident in the ^{13}C CP spectra are reproducible on different spectrometers. Therefore the two most important features to note about the spectra presented in Figs. 1-3 are that there are differences between the samples and that in every instance corresponding spectra acquired on the 200 MHz and 400 MHz spectrometers appear very similar.

Differences between spectra acquired on the 200 MHz and 400 MHz spectrometers were quantified by integrating the spectra over broad chemical shift regions that are assigned to different broad chemical environments. We used a set of four integral regions – 185-165 ppm (carboxyl C), 165-110 ppm (aryl C), 110-45 ppm (O-alkyl C) and 45-0 ppm (alkyl C). Signal in spinning sidebands (SSBs) for the

carboxyl and aryl resonances was corrected for in the usual way (Schmidt et al., 1999), i.e. by adding twice the integrated signal of the low-field SSB to the integrated signal for the central band, and subtracting this signal from the region where the corresponding high-field SSB falls (Tables 2 and 3).

Tab. 2 Assignment of chemical shift regions for spectra acquired on the 200 MHz spectrometer.

Region	**Assignment**
A: 285 - 265 ppm	Carboxyl SSB
B: 265 - 245 ppm	Aryl SSB
C: 245 - 210 ppm	Aryl SSB
D: 185 - 165 ppm	Carboxyl CB
E: 165 - 110 ppm	Aryl CB
F: 110 - 45 ppm	O-alkyl + carboxyl SSB + aryl SSB
G: 45 - 0 ppm	Aliphatic + aryl SSB
Carbon type	**Combination of regions**
Carboxyl	D + 2 _ A
Aryl	E+ 2 _ B + 2 _ C
O-alkyl	F – A - B
Alkyl	G - C

CB – centre band; SSB spinning sideband

Tab. 3 Assignment of chemical shift regions for spectra acquired on the 400 MHz spectrometer.

Region	**Assignment**
A: 255 - 235 ppm	Carboxyl SSB
B: 235 - 185 ppm	Aryl SSB
C: 185 - 165 ppm	Carboxyl CB
D: 165 - 110 ppm	Aryl CB
E: 110 - 45 ppm	O-alkyl+ carboxyl SSB + aryl SSB
F: 45 - 0 ppm	Alkyl
Carbon type	**Combination of regions**
Carboxyl	C + 2 _ A
Aryl	D+ 2 _ B
O-alkyl	E – A - B
Alkyl	F

CB – centre band; SSB spinning sideband

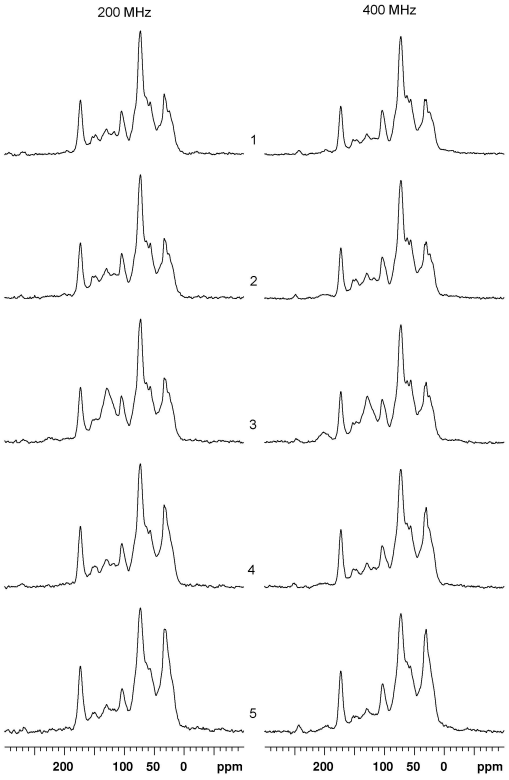

Fig. 1 Solid-state ^{13}C CP NMR spectra of soil samples 1-5.

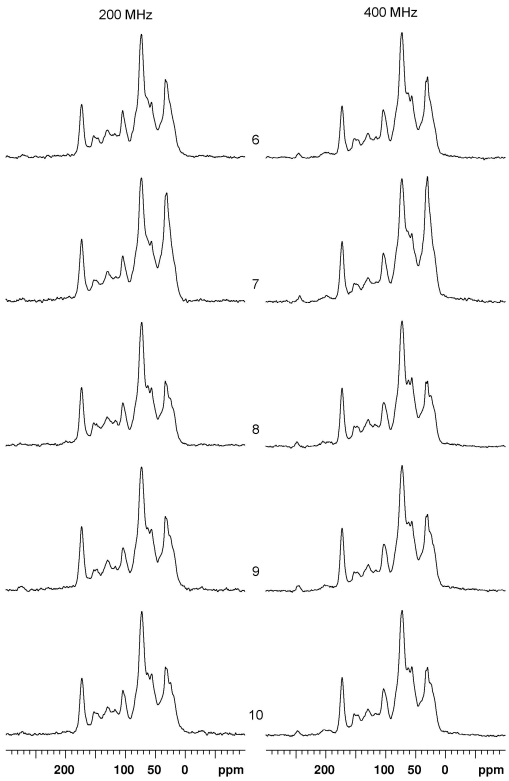

Fig. 2 Solid-state ^{13}C CP NMR spectra of soil samples 6-10.

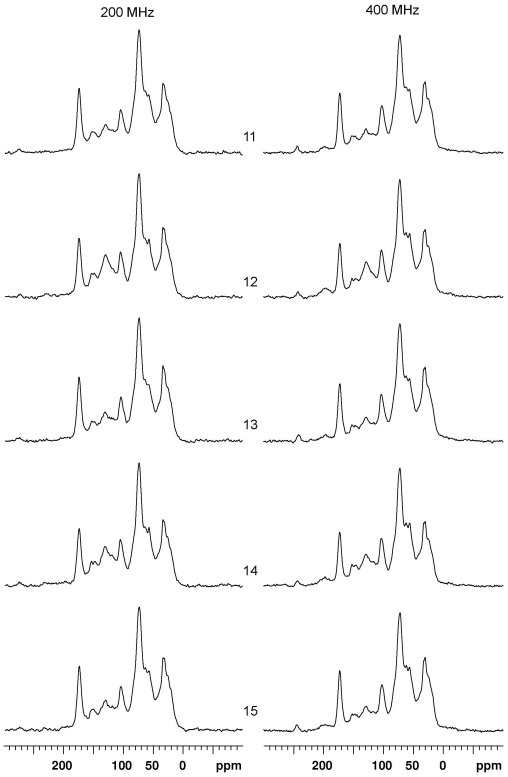

Fig. 3 Solid-state ^{13}C CP NMR spectra of soil samples 11-15.

Spinning sideband correction was complicated by the fact that the ratio of MAS rate to field strength was different for the two spectrometers. Therefore the position and sizes of the SSBs differed. A MAS rate of 5 kHz was used on the 200 MHz spectrometer, resulting in the appearance of SSBs 100 ppm from the central band, whereas a MAS rate of 7 kHz was used on the 400 MHz spectrometer, resulting in the appearance of SSBs 70 ppm from the central band. The choice of MAS rate was governed by a number of factors. Clearly it is desirable to spin samples as rapidly as possible in order to decrease the size of SSBs and prevent overlap of SSBs with other resonances. However, rapid spinning may decrease cross polarization efficiency, resulting not only in lower sensitivity, but more importantly in poorer quantitation, as some ^{13}C nuclei, including those without directly attached protons, are more affected (Frund and Lüdemann, 1994; Mao et al., 2002; Smernik, 2005). Finally, there were hardware restrictions that prevented us spinning faster than 7 kHz on the 400 MHz spectrometer. We believe that the treatment of SSB corrections described in Tables 2 and 3 enable the best possible comparison between spectral distributions on the two spectrometers in the circumstances. However, this treatment is not perfect for a number of reasons including:

(i) in some cases the chemical shift ranges assigned to the central band and sidebands do not differ by exactly 70 ppm for the 400 MHz spectra (Table 3).

(ii) it is clear from the 200 MHz spectra in Figs 1-3 that there is some signal in the region 185-220 ppm (usually assigned to C in ketones and aldehydes). This signal overlaps with, and is assigned to, the SSB of the aryl signal in the spectra acquired on the 400 MHz spectrometer (Table 3), whereas it is not measured at all in the spectra acquired on the 200 MHz spectrometer. This results in a positive bias in signal assigned to aryl C for the spectra acquired on the 400 MHz spectrometer.

(iii) the corrections assume equal intensities of high-field and low-field SSBs, which is not always justified (Newman et al., 1987). This source of error is potentially larger for the spectra acquired on the 400 MHz spectrometer, since the SSBs are larger.

We could have run the spectra under conditions that gave rise to SSBs of equivalent size and spacing (e.g. by using a MAS rate of 3.5 kHz on the 200 MHz spectrometer). However, the point of this exercise was to not to acquire the most comparable spectra, but rather to choose optimal acquisition conditions for each spectrometer independently and then compare the spectra. This addresses the circumstances of most soils researchers who are very restricted in the choice of NMR spectrometer that they have access to, and face the inevitability of comparing their spectra against published spectra that have been acquired at different fields and MAS rates.

Figure 4 shows that the relative amounts of the four C types, determined by integration of the spectra acquired on the two spectrometers, are very similar.

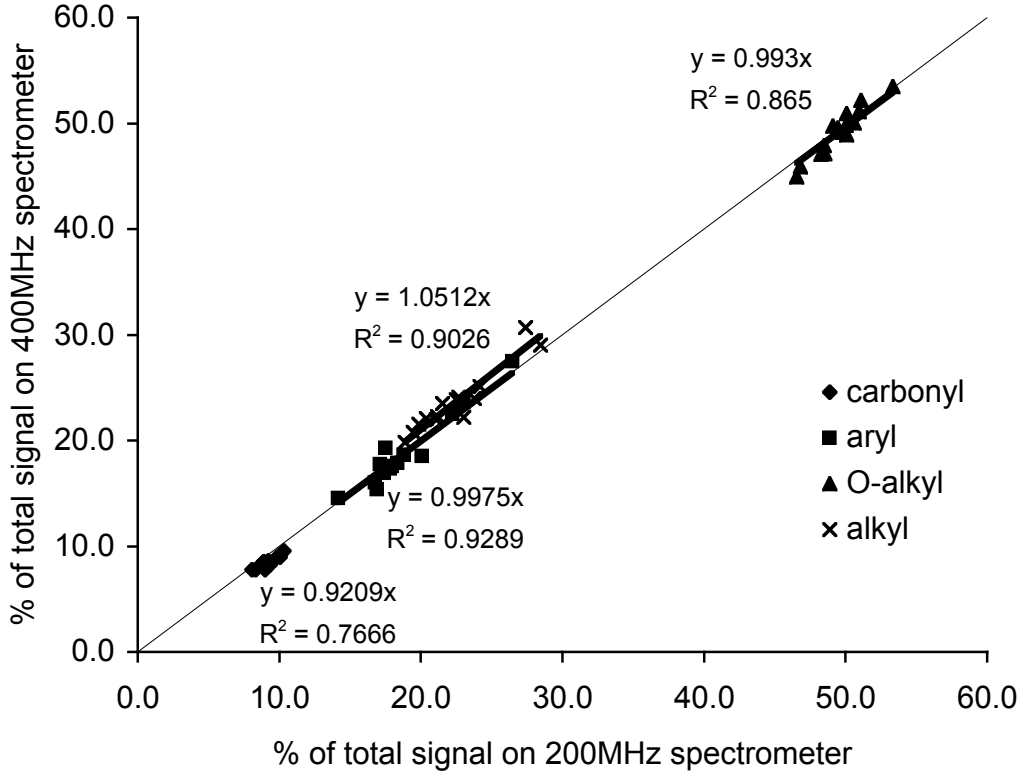

Fig. 4 Comparison of percentage signal assigned to different C types derived from spectra acquired on the two spectrometers. A 1:1 line is included to aid comparison.

Correlations between corresponding values are strongest for aryl C (r^2 = 0.93), followed by alkyl C (r^2 = 0.90), O-alkyl C (r^2 = 0.87) and carboxyl C (r^2 = 0.77), reflecting the order of decreasing variation of these parameters (i.e. the proportion of aryl C varied the most between samples and the proportion of carboxyl C content varied the least). The strength of the correlations is consistent with estimated uncertainty in each measurement of around ±2% (Baldock and Smernik, 2002; Smernik et al., 2006). There is no apparent bias for aryl or O-alkyl C, as the slopes of the correlation curves are within 1% of the 1:1 line. On the other hand, a slight bias is apparent for carboxyl C, the values of which were on average 8% lower when determined on the 400 MHz spectrometer. There is also a slight bias apparent for alkyl C, the values of which were on average 5% higher when determined on the 400 MHz spectrometer.

The negative bias against carboxyl C at the higher field (and more crucially higher MAS rate) is consistent with previous findings by ourselves (Smernik, 2005) and others (Frund and Lüdemann, 1994; Mao et al., 2002). However, in these previous studies, there was also a bias against aryl C, which we do not see here. This may be due to our treatment of SSBs. As discussed above, the small amount of signal in the region 185-210 ppm due to ketone and aldehyde C is disregarded in the integration scheme of the spectra acquired on the 200 MHz spectrometer, but falls within the aryl SSB, and hence is counted as aryl C in the integration scheme of the spectra acquired on the 400 MHz spectrometer. This may cancel out the expected negative bias for aryl C at the higher field. The negative bias against carboxyl C must be counteracted by a relative increase in signal elsewhere. We see this in the alkyl C region, but not in the O-alkyl region. This may be a further effect of the inflated aryl

SSB intensity, since this signal is subtracted from the region assigned to O-alkyl C in the in the integration scheme of the spectra acquired on the 400 MHz spectrometer.

4. Conclusions

These results provide some reassurance as to the validity of the large number of SOM studies that utilize ^{13}C CP NMR characterization. Firstly, the strong correlations between distributions of C types derived from ^{13}C CP NMR spectra acquired on two different NMR spectrometers ensure that differences between the soils identified in the NMR spectra are independent of which spectrometer the spectra were acquired on. This is the most important point for most SOM studies. Secondly, the correlations lie close to the 1:1 line, i.e. the actual distributions are fairly independent of the spectrometer, notwithstanding the slight biases in carbonyl C (on average 8% lower on 400 MHz spectrometer) and alkyl C (on average 5% higher on 400 MHz spectrometer). This means that comparisons between distributions of C types derived from spectra acquired on these two spectrometers would only be affected by fairly small biases. By extension, provided sample preparation and acquisition conditions are appropriate, there is no reason why SOM samples should not be characterized using field strengths up to 400 MHz. However, it should also be remembered that all ^{13}C CP spectra of SOM are subject to potential biases associated with remote protonation, highly mobile domains and paramagnetic relaxation. In other words, the differences between ^{13}C CP spectra acquired on different spectrometers are likely to be smaller than differences between ^{13}C CP spectra and ^{13}C DP (direct polarization) spectra. It remains, as ever, prudent to gauge the potential for quantitation problems by spin counting (Keeler and Maciel, 2003; Smernik and Oades, 2000a; Smernik and Oades, 2000b) and to implement less sensitive or more sophisticated techniques (Mao et al., 2002; Mao et al., 2000; Smernik and Oades, 2000a; Smernik and Oades, 2000b; Smernik and Oades, 2003) to obtain better quantitation when required.

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Part C
Appendix

Tab. 1 Characteristics and analysis data of investigated Phaeozem soil samples (PhP1 = Phaeozem pits; PhP2 = Phaeozem slot pits; SP = Settlement pits).

Pit set	SE no	Location	Archaeological site number	Sample type	Clay	Silt	Sand	pH
					mass%			
1	SE 10	Köln-Rondorf	99.013.43-7	PhP1	41	41	18	6.0
	SE 42	Köln-Rondorf	99.013.43 (5)	P horizon	35	41	24	6.6
	SE 43	Köln-Rondorf	99.013.43 (6)	control (Bt)	35	39	27	6.4
2	SE 5	Pulheim-Brauweiler	NW 1999/1103/11-7	PhP1	19	71	10	6.3
	SE 4	Pulheim-Brauweiler	NW 1999/1103/15 (4)	P horizon	20	75	4	6.4
	SE 3	Pulheim-Brauweiler	NW 1999/1103/15 (5)	control (Bt)	22	70	8	6.4
3	SE 84	Pulheim B59n	NW 2003/1002/261	PhP1	24	74	2	5.8
	SE 85	Pulheim B59n	NW 2003/1002/261	P horizon	21	77	2	5.6
	SE 83	Pulheim B59n	NW 2003/1002/261	control (Bt)	21	77	2	6.0
4	SE 53	Troisdorf	OV 2001/1012/44-12 (1)	PhP1	27	39	34	6.6
	SE 54	Troisdorf	OV 2001/1012/44-12 (2)	control (Bt)	14	8	78	6.6
5	SE 55	Troisdorf	OV 2001/1012/45-12 (1)	PhP1	29	47	24	6.7
	SE 56	Troisdorf	OV 2001/1012/45-12 (2)	control (Bt)	19	26	55	6.6
6	SE 47	Jüchen	NI 2001/1017/10-10	PhP1	21	77	2	6.6
	SE 48	Jüchen	NI 2001/1017/10-11	PhP1	20	78	2	6.4
	SE 49	Jüchen	NI 2001/1017/10-12	PhP1	20	78	2	6.5
	SE 51	Jüchen	NI 2001/1017/10-14	PhP1	18	79	2	6.5
	SE 46	Jüchen	NI 2001/1017/10-9	control (Bt)	21	77	2	6.5
	SE 50	Jüchen	NI 2001/1017/10-13	control (Bt)	19	79	2	6.6
	SE 52	Jüchen	NI 2001/1017/10-15	control (Bt)	18	80	2	6.7
7	SE 116	Dürwiss	NW 2005/1016/ 183 -15	PhP1 (35 cm)	18	81	2	6.5
	SE 117	Dürwiss	NW 2005/1016/ 183 -16	PhP1 (15 cm)	14	84	2	6.7
	SE 119	Dürwiss	NW 2005/1016/ 183 -18	control (20)	22	77	1	6.8
	SE 115	Dürwiss	NW 2005/1016/ 183 -14	control (55)	20	78	1	6.6
	SE 118	Dürwiss	NW 2005/1016/ 183 -17	control (60)	21	78	1	6.9
8	SE 151	Titz	NW 2005/1018/61	PhP1 (10)	21	78	1	5.9
	SE 152	Titz	NW 2005/1018/61	control (10)	20	79	1	5.9
9	SE 73	Pulheim B59n	NW 2003/1002/35-21	PhP2 top	0	75	2	5.8
	SE 74	Pulheim B59n	NW 2003/1002/35-22	PhP2 bottom	0	75	1	5.6
	SE 72	Pulheim B59n	NW 2003/1002/35-20	control (Bt)	0	78	2	5.7
10	SE 76	Pulheim B59n	NW 2003/1002/35-24	PhP2 top	22	76	2	5.9
	SE 77	Pulheim B59n	NW 2003/1002/35-25	PhP2 bottom	27	72	2	5.6
	SE 75	Pulheim B59n	NW 2003/1002/35-23	control (Bt)	23	75	2	5.6
11	SE 88	Pulheim B59n	NW 2003/1002/268-26	PhP2 bottom	22	74	4	6.0
	SE 86	Pulheim B59n	NW 2003/1002/268-26	control (Bt)	20	79	1	5.9
12	SE 89	Pulheim B59n	NW 2003/1002/268-26	PhP2 top	25	74	2	n.d.
	SE 87	Pulheim B59n	NW 2003/1002/268-26	control (Bt)	22	77	1	6.0
13	SE 92	Pulheim B59n	NW 2003/1002/321-21	PhP2 middle	25	74	2	5.8
	SE 93	Pulheim B59n	NW 2003/1002/321-21	PhP2 top	24	74	2	5.9
	SE 94	Pulheim B59n	NW 2003/1002/321-21	PhP2 bottom	34	64	2	5.6
	SE 91	Pulheim B59n	NW 2003/1002/321-21	control (Bt)	26	73	2	5.9
14	SE 105	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	PhP2 (10)	16	84	1	6.6
	SE 106	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	PhP2 (40)	16	83	1	6.7
	SE 107	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	PhP2 (65)	20	79	1	6.7
	SE 108	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	PhP2 (90)	21	79	1	6.7
	SE 109	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	PhP2 (125)	25	74	1	6.7
	SE 110	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	control (Bbv 145)	18	81	1	6.7
	SE 111	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	control (Bt 20)	22	78	0	6.6
	SE 112	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	control (Bvt 55)	19	81	0	6.7
	SE 113	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	control (Bbtv 80)	17	82	1	6.8
	SE 114	Grevenbroich-Neurath	OV 2004/1013 /524 - 19	control (Bbv 100)	19	79	1	6.7
15	SE 19	Mönchengladbach-Wanlo	NI 91/266/108-11	SP	13	81	6	6.6
16	SE 20	Mönchengladbach-Wanlo	NI 91/266/109-10	SP	14	80	6	6.5

Pit set	SE no	Sample type	Colour L^*	SOC $g\ kg^{-1}$	N $g\ kg^{-1}$	C:N	BC %SOC	P_{tot}	P_{in}	P_{org}	TLE %SOC
								$mg\ kg^{-1}$			
1	SE 10	PhP1	43.2	7.20	0.83	9	35	810	736	74	2.3
	SE 42	P horizon	50.2	4.97	0.85	6	34	395	253	142	1.9
	SE 43	control (Bt)	52.2	2.79	0.71	4	n.d.	426	293	133	4.6
2	SE 5	PhP1	53.6	4.38	0.37	12	39	554	437	118	n.d.
	SE 4	P horizon	56.0	2.33	0.35	7	progr.	415	339	76	n.d.
	SE 3	control (Bt)	56.7	1.69	0.30	6	n.d.	337	259	78	n.d.
3	SE 84	PhP1	50.2	3.30	0.38	9	n.d.	600	497	103	4.7
	SE 85	P horizon	50.5	4.40	0.48	9	n.d.	535	368	168	3.6
	SE 83	control (Bt)	50.3	2.70	0.31	9	n.d.	605	503	102	6.7
4	SE 53	PhP1	49.9	4.40	0.69	6	50	357	237	120	n.d.
	SE 54	control (Bt)	43.5	1.71	0.40	4	n.d.	248	158	89	n.d.
5	SE 55	PhP1	49.6	3.56	0.68	5	n.d.	362	281	81	n.d.
	SE 56	control (Bt)	48.4	1.92	0.48	4	n.d.	245	135	110	n.d.
6	SE 47	PhP1	48.2	3.68	0.58	6	n.d.	384	276	108	3.1
	SE 48	PhP1	49.5	3.32	0.52	6	n.d.	420	340	81	n.d.
	SE 49	PhP1	55.7	3.28	0.56	6	n.d.	356	212	144	n.d.
	SE 51	PhP1	54.6	2.88	0.51	6	n.d.	337	248	89	n.d.
	SE 46	control (Bt)	55.7	2.01	0.44	5	n.d.	331	238	93	n.d.
	SE 50	control (Bt)	50.3	1.83	0.43	4	n.d.	359	278	82	n.d.
	SE 52	control (Bt)	52.5	1.69	0.38	4	n.d.	343	311	33	3.4
7	SE 116	PhP1 (35 cm)	48.9	3.60	0.38	9	n.d.	n.d.	n.d.	n.d.	n.d.
	SE 117	PhP1 (15 cm)	52.6	3.55	0.35	10	n.d.	n.d.	n.d.	n.d.	n.d.
	SE 119	control (20)	53.0	2.05	0.29	7	n.d.	n.d.	n.d.	n.d.	n.d.
	SE 115	control (55)	54.5	1.40	0.225	6	n.d.	n.d.	n.d.	n.d.	n.d.
	SE 118	control (60)	54.6	1.35	0.24	6	n.d.	n.d.	n.d.	n.d.	n.d.
8	SE 151	PhP1 (10)	46.3	3.60	0.42	9	n.d.	n.d.	n.d.	n.d.	n.d.
	SE 152	control (10)	49.8	2.10	0.30	7	n.d.	n.d.	n.d.	n.d.	n.d.
9	SE 73	PhP2 top	45.2	5.40	0.49	11	n.d.	553	431	122	n.d.
	SE 74	PhP2 bottom	49.3	3.00	0.39	8	n.d.	606	520	86	4.8
	SE 72	control (Bt)	51.4	3.10	0.38	8	n.d.	523	436	87	3.2
10	SE 76	PhP2 top	47.6	4.30	0.22	19	n.d.	533	391	142	9.3
	SE 77	PhP2 bottom	46.1	4.90	0.24	20	35	679	523	156	3.7
	SE 75	control (Bt)	50.3	3.40	0.25	13	n.d.	527	370	157	14.0
11	SE 88	PhP2 bottom	46.6	4.00	0.26	15	37	678	635	42	3.3
	SE 86	control (Bt)	53.2	1.70	0.16	11	n.d.	712	587	125	8.6
12	SE 89	PhP2 top	46.7	4.30	0.22	20	n.d.	689	532	158	1.9
	SE 87	control (Bt)	53.6	1.70	0.12	14	n.d.	698	628	70	4.9
13	SE 92	PhP2 middle	50.8	3.20	0.20	16	n.d.	771	495	276	n.d.
	SE 93	PhP2 top	48.6	3.60	0.36	10	n.d.	573	447	126	n.d.
	SE 94	PhP2 bottom	44.2	4.80	0.44	11	n.d.	725	633	93	n.d.
	SE 91	control (Bt)	52.5	2.80	0.27	10	n.d.	549	420	128	n.d.
14	SE 105	PhP2 (10)	59.3	1.60	0.18	9	n.d.	203	196	7	9.0
	SE 106	PhP2 (40)	57.4	1.30	< 0.1		n.d.	236	178	58	5.8
	SE 107	PhP2 (65)	56.6	1.80	0.16	11	n.d.	412	212	200	n.d.
	SE 108	PhP2 (90)	56.2	1.20	< 0.1		n.d.	372	284	88	32.4
	SE 109	PhP2 (125)	55.1	1.80	0.24	8	n.d.	646	435	211	5.3
	SE 110	control (Bbv 145)	56.7	1.10	0.17	7	n.d.	700	485	215	n.d.
	SE 111	control (Bt 20)	55.6	1.70	0.18	10	n.d.	406	262	144	n.d.
	SE 112	control (Bvt 55)	57.2	1.20	0.13	9	n.d.	542	450	92	n.d.
	SE 113	control (Bbtv 80)	57.5	1.80	0.11	16	n.d.	515	433	82	n.d.
	SE 114	control (Bbv 100)	56.4	1.30	0.14	9	n.d.	600	446	154	11.6
15	SE 19	SP	43.2	9.41	0.37	26	57	908	814	93	1.9
16	SE 20	SP	35.5	17.33	0.54	32	n.d.	673	612	61	7.5

Tab. 2 Data of investigated burning experiment soil samples (0-1 cm; 0-2.5 cm marked *).

FO no	Description	BD $g\ cm^{-3}$	Colour L^*	SOC $g\ kg^{-1}$	N $g\ kg^{-1}$	C:N	Char $g\ kg^{-1}$	Char %SOC
23*	control	0.6	50.9	41.6	3.2	12.8	1.3	3.3
24*	control	0.1	47.2	80.4	6.0	13.4	3.1	2.6
25*	control	0.1	45.0	90.9	6.8	13.4	2.0	2.2
26	control	0.5	47.7	55.6	4.5	12.3	1.6	2.9
27*	control	0.5	48.9	53.6	4.4	12.1	2.1	4.0
28*	control	0.5	51.5	46.4	3.6	12.7	2.0	4.3
29	control	0.6	47.5	58.4	4.4	13.3	1.9	3.2
30	control	0.3	48.7	67.3	4.6	14.7	2.0	3.0
31	control	0.5	47.8	49.4	3.9	12.6	1.7	3.4
32	control	0.9	47.4	50.8	4.0	12.6	1.5	3.0
33	control	0.4	50.4	57.2	3.9	14.8	1.7	3.0
34	control	1.3	54.1	29.4	2.2	13.4	0.8	2.7
35	control	0.5	52.0	48.8	3.4	14.2	1.4	2.8
36	control	0.4	50.3	49.9	3.5	14.4	1.7	3.4
37	control	1.4	56.6	24.5	1.9	13.2	0.7	2.8
38	control	0.7	51.6	56.6	4.2	13.6	1.4	2.5
39	control	0.6	48.5	62.6	4.8	13.2	1.1	1.8
40	control	0.2	45.0	71.3	5.9	12.1	1.9	2.6
41	control	0.5	45.7	72.6	5.2	14.1	1.9	2.6
43	burnt	0.7	46.9	52.7	4.1	12.8	2.7	5.2
44	burnt	0.5	47.5	49.3	4.0	12.4	1.8	3.7
45	burnt	1.0	49.6	31.4	2.8	11.4	1.0	3.2
46	burnt	0.4	47.8	53.5	4.4	12.3	1.8	3.4
47	burnt	0.5	46.5	43.6	3.6	12.0	1.9	4.5
48	burnt	0.7	50.2	36.3	2.9	12.4	1.2	3.3
50	burnt	0.8	48.5	56.0	4.2	13.4	1.6	2.9
51	burnt	0.7	48.0	53.4	4.0	13.5	1.8	3.4
52	burnt	0.5	46.4	63.2	4.9	13.0	2.5	3.9
53	burnt	0.5	50.8	33.2	2.6	12.8	0.8	2.3
54	burnt	0.5	46.6	71.0	5.1	13.9	1.4	1.9
55	burnt	0.3	45.6	85.2	5.9	14.5	1.5	1.8
56*	burnt	0.3	48.1	76.6	5.7	13.5	1.8	3.1
57	burnt	0.4	51.0	54.8	4.7	11.7	1.0	1.7
58	burnt	0.5	46.8	58.4	4.8	12.3	0.3	0.5
59*	burnt	0.3	50.1	50.2	4.0	12.6	1.7	3.7
60	burnt	0.6	47.3	69.9	5.0	13.9	1.7	2.4
61	burnt	0.4	46.9	64.6	25.5	2.5	2.3	3.5
62	burnt	0.5	47.4	61.0	4.6	13.3	2.4	4.0
83	burnt 1 yr	1.1	47.5	56.1	3.6	15.5	2.2	4.0
84	burnt 1 yr	0.5	42.7	65.4	4.0	16.4	1.2	1.9
85	burnt 1 yr	1.2	47.2	45.6	3.3	13.8	0.9	1.9
86	burnt 1 yr	0.2	42.5	62.8	3.4	18.5	4.1	6.5
87	burnt 1 yr	0.9	49.6	35.7	2.7	13.2	0.8	2.1
88	burnt 1 yr	1.6	45.1	48.0	3.8	12.7	1.8	3.6
89	burnt 1 yr	0.7	45.7	59.4	4.2	14.2	2.8	4.7
90	burnt 1 yr	0.6	45.9	51.3	3.5	14.9	1.5	2.8
91	burnt 1 yr	0.7	43.4	58.6	4.2	13.9	3.3	5.6
92	burnt 1 yr	0.3	50.0	36.8	2.4	15.3	0.9	2.4
93	burnt 1 yr	0.6	46.8	59.9	4.3	13.9	2.0	3.4
94	burnt 1 yr	0.5	44.5	67.5	4.3	15.6	1.9	2.7
95	burnt 1 yr	1.2	47.5	52.4	3.8	13.7	1.4	2.7
96	burnt 1 yr	0.7	46.5	59.8	4.3	14.1	1.5	2.5
97	burnt 1 yr	0.9	50.1	48.9	3.6	13.6	0.7	1.4
98	burnt 1 yr	0.6	47.6	58.4	4.3	13.7	1.8	3.1
99	burnt 1 yr	0.6	43.0	59.2	3.9	15.3	3.4	5.8
100	burnt 1 yr	0.5	46.2	70.9	5.0	14.3	2.9	4.1
101	burnt 1 yr	1.1	47.5	44.6	3.5	12.7	1.3	2.9
102	burnt 1 yr	0.9	47.3	62.9	4.1	15.3	2.0	3.2

Tab. 3 Data of investigated burning experiment soil samples (1-2.5 cm).

FO no	Description	BD $g\ cm^{-3}$	Colour L^*	SOC $g\ kg^{-1}$	N $g\ kg^{-1}$	C:N	Char $g\ kg^{-1}$	Char %SOC
23	control	-	-	-	-	-	-	-
24	control	-	-	-	-	-	-	-
25	control	-	-	-	-	-	-	-
26	control	0.3	48.8	44.9	3.9	11.5	1.6	3.7
27	control	-	-	-	-	-	-	-
28	control	-	-	-	-	-	-	-
29	control	0.7	48.0	49.4	3.9	12.8	1.6	3.3
30	control	0.8	51.1	44.7	3.4	13.3	1.9	4.3
31	control	0.6	48.8	38.7	3.2	12.1	1.3	3.3
32	control	0.8	47.8	50.5	3.9	12.9	1.2	2.4
33	control	0.8	53.0	50.5	3.5	14.5	1.0	2.0
34	control	1.0	54.7	23.2	1.6	14.4	0.6	2.6
35	control	1.0	53.7	33.1	2.5	13.4	0.8	2.5
36	control	0.5	53.8	29.3	2.1	13.7	0.8	2.9
37	control	1.1	56.7	9.9	0.8	12.3	0.1	1.1
38	control	0.7	54.7	29.2	2.4	12.3	0.5	1.8
39	control	0.4	49.3	53.3	4.4	12.2	1.1	2.1
40	control	0.6	50.4	38.9	3.3	11.9	0.6	1.6
41	control	0.6	47.3	48.8	4.0	12.3	2.0	4.0
43	burnt	0.9	54.7	21.0	1.8	11.9	0.6	2.7
44	burnt	0.7	49.7	39.2	3.4	11.7	1.1	2.9
45	burnt	0.7	51.8	40.0	3.3	12.3	0.6	1.5
46	burnt	0.7	51.2	35.8	3.2	11.2	1.3	3.7
47	burnt	0.4	47.1	44.2	3.5	12.5	1.4	3.3
48	burnt	0.7	50.8	33.7	2.7	12.7	1.1	3.3
50	burnt	0.7	49.7	38.5	3.2	12.1	1.1	3.0
51	burnt	0.7	49.3	36.3	3.2	11.4	1.2	3.3
52	burnt	0.7	48.3	44.1	3.5	12.5	1.8	4.1
53	burnt	0.8	53.3	21.9	1.8	12.1	0.4	1.7
54	burnt	0.8	52.0	35.6	2.8	12.7	0.8	2.3
55	burnt	0.4	49.0	55.5	4.0	13.9	0.6	1.1
56	burnt	-	-	-	-	-	-	-
57	burnt	0.8	53.5	30.1	3.4	8.9	0.4	1.5
58	burnt	0.6	47.5	54.3	4.4	12.4	1.7	3.1
59	burnt	-	-	-	-	-	-	-
60	burnt	0.6	47.2	52.5	4.0	13.2	1.4	2.6
61	burnt	0.8	50.7	39.7	17.8	2.2	1.5	3.9
62	burnt	0.8	49.2	48.5	3.8	12.7	1.6	3.4
83	burnt 1 yr	0.9	50.0	39.5	2.9	13.8	0.9	2.4
84	burnt 1 yr	0.4	47.5	44.0	3.1	14.0	2.6	6.0
85	burnt 1 yr	0.8	50.5	30.9	2.2	14.1	0.5	1.6
86	burnt 1 yr	0.3	43.0	55.7	3.5	16.1	3.4	6.2
87	burnt 1 yr	0.8	51.3	26.5	2.1	12.4	0.5	1.9
88	burnt 1 yr	0.8	50.2	31.3	2.7	11.5	0.6	1.8
89	burnt 1 yr	0.8	50.9	35.0	2.5	13.7	1.2	3.5
90	burnt 1 yr	0.9	50.7	32.2	2.5	12.7	0.5	1.5
91	burnt 1 yr	0.6	50.2	34.7	2.8	12.5	1.0	2.8
92	burnt 1 yr	0.5	50.6	33.3	2.2	14.8	1.3	3.9
93	burnt 1 yr	0.5	53.2	26.3	2.0	13.3	0.6	2.3
94	burnt 1 yr	0.8	48.8	45.7	3.5	13.1	0.6	1.3
95	burnt 1 yr	0.8	51.3	40.6	2.9	13.9	0.6	1.5
96	burnt 1 yr	0.8	51.2	42.6	3.4	12.6	0.4	0.9
97	burnt 1 yr	0.9	51.0	35.2	2.9	12.3	0.5	1.4
98	burnt 1 yr	0.8	49.4	43.5	3.4	12.6	0.7	1.6
99	burnt 1 yr	0.3	43.5	56.9	4.0	14.3	2.9	5.1
100	burnt 1 yr	0.9	48.4	50.7	3.9	12.9	1.5	3.0
101	burnt 1 yr	0.9	50.7	30.6	2.7	11.3	0.8	2.5
102	burnt 1 yr	1.0	49.9	40.1	3.1	12.9	0.7	1.8

Tab. 4 Data of investigated burning experiment soil samples (2.5-5 cm).

FO no	Description	BD $g\ cm^{-3}$	Colour L^*	SOC $g\ kg^{-1}$	N $g\ kg^{-1}$	C:N	Char $g\ kg^{-1}$	Char %SOC
23	control	1.1	55.4	22.3	1.8	12.1	0.6	2.7
24	control	0.8	51.4	41.4	3.5	11.7	0.5	1.3
25	control	0.3	48.4	55.1	4.5	12.2	1.6	2.9
26	control	0.5	50.6	33.2	3.1	10.7	1.0	3.0
27	control	0.7	51.2	35.8	3.1	11.7	0.9	2.5
28	control	1.1	52.5	33.2	2.8	11.8	0.9	2.8
29	control	0.8	52.1	28.8	2.2	13.2	0.6	2.0
30	control	0.6	50.2	35.0	2.7	12.7	1.3	3.8
31	control	0.5	49.1	33.0	2.7	12.3	0.9	2.8
32	control	0.9	49.0	40.2	3.2	12.5	0.9	2.2
33	control	0.9	55.5	31.2	2.3	13.4	0.8	2.6
34	control	0.9	56.3	18.3	1.3	14.3	0.4	2.2
35	control	1.0	55.7	23.0	1.8	12.8	0.5	2.0
36	control	0.5	54.6	21.3	1.5	14.4	0.6	2.8
37	control	0.9	59.7	14.9	1.1	13.2	0.3	2.1
38	control	1.0	56.0	22.7	1.7	13.2	0.6	2.8
39	control	0.7	50.4	42.3	3.8	11.0	0.8	1.8
40	control	0.6	54.2	23.4	2.1	11.0	0.4	1.5
41	control	0.9	48.7	33.7	2.8	11.9	1.3	3.7
43	burnt	0.9	57.7	14.6	1.1	13.8	0.2	1.3
44	burnt	0.9	51.7	32.7	2.8	11.6	0.6	1.8
45	burnt	0.8	53.7	21.9	2.0	10.9	0.4	1.7
46	burnt	0.5	53.5	22.8	2.2	10.3	0.7	2.9
47	burnt	0.8	48.9	36.7	3.1	11.7	1.2	3.4
48	burnt	0.9	51.5	30.5	2.4	12.5	0.8	2.5
50	burnt	0.5	51.9	29.0	2.4	12.0	1.0	3.3
51	burnt	0.7	51.5	30.6	2.8	11.1	1.0	3.1
52	burnt	0.7	49.5	38.2	3.2	12.1	1.3	3.5
53	burnt	1.0	54.4	17.4	1.4	12.5	0.5	2.6
54	burnt	1.4	54.5	20.3	1.7	11.9	0.4	1.8
55	burnt	0.6	52.5	32.8	2.4	13.9	0.6	1.9
56	burnt	0.6	50.6	50.3	4.1	12.2	1.7	3.3
57	burnt	0.8	56.9	15.5	5.4	2.9	0.3	1.9
58	burnt	0.7	50.7	38.7	3.3	11.7	1.4	3.5
59	burnt	0.8	52.5	30.8	2.5	12.4	0.8	2.5
60	burnt	0.8	51.5	34.9	2.8	12.5	1.1	3.0
61	burnt	0.6	53.4	25.8	28.6	0.9	0.4	1.6
62	burnt	0.8	50.2	41.6	3.4	12.2	1.2	2.9
83	burnt 1 yr	1.0	53.1	31.7	2.1	14.7	0.7	2.1
84	burnt 1 yr	0.8	51.9	29.3	2.2	13.1	0.7	2.3
85	burnt 1 yr	1.1	53.5	23.0	1.9	11.8	0.3	1.2
86	burnt 1 yr	0.6	49.9	36.8	2.9	12.7	1.0	2.7
87	burnt 1 yr	0.5	54.4	21.2	1.5	13.9	0.3	1.2
88	burnt 1 yr	1.1	53.4	22.9	2.1	11.0	0.2	0.9
89	burnt 1 yr	0.9	53.7	20.5	1.8	11.6	0.6	3.0
90	burnt 1 yr	0.8	53.1	23.2	1.9	12.3	0.4	1.7
91	burnt 1 yr	0.9	54.3	22.1	2.0	11.1	0.5	2.2
92	burnt 1 yr	0.8	52.0	30.3	2.1	14.4	0.8	2.6
93	burnt 1 yr	0.7	55.8	20.6	1.6	13.0	0.4	2.0
94	burnt 1 yr	0.9	51.3	30.1	2.2	13.9	0.2	0.6
95	burnt 1 yr	0.9	53.2	25.7	2.0	12.7	0.5	2.1
96	burnt 1 yr	1.0	55.8	23.7	2.1	11.5	0.4	1.8
97	burnt 1 yr	1.0	54.9	20.9	1.8	11.5	0.3	1.3
98	burnt 1 yr	0.9	52.7	28.0	2.4	11.8	0.6	2.0
99	burnt 1 yr	0.7	50.4	40.8	3.1	13.1	1.2	3.0
100	burnt 1 yr	0.9	50.1	36.4	3.2	11.5	1.4	3.8
101	burnt 1 yr	1.2	53.8	21.9	2.1	10.7	0.5	2.4
102	burnt 1 yr	1.0	53.0	25.8	2.1	12.3	0.5	2.1

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