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ORIGIN AND COMPOSITION OF ORGANIC MATTER IN PITS FROM THE NEOLITHIC SETTLEMENT AT MURR, BAVARIA

Abstract - The archaeological site in Murr, Upper Bavaria, was settled over the whole Neolithic period between 5500 and 2700 BC. Various pits and a ditch were found in the area, distinct from the surrounding loamy soil by the dark-brown colour of their filling materials. Although numerous artefacts were found, at the present stage of research neither the nature of the filling material nor the function of pits and ditches are well understood. Thus, the organic matter composition of 30 filling layers from 11 Neolithic pits of this settlement was investigated and compared to that of a close-by Luvisol profile and two A horizons from contemporary Phaeozems in southern Germany. The samples were subjected to C and N analysis, soil colour measurements, solid-state ^{13}C CPMAS nuclear magnetic resonance (NMR) spectroscopy, combined fractionation/high-energy ultraviolet (UV) photo-oxidation/ ^{13}C CPMAS NMR spectroscopy, polysaccharide and lignin analysis.

The organic carbon contents are higher in the Neolithic samples than in the Luvisol horizons, but are generally lower than in the A horizons of contemporary phaeozemic soils developed from loess. The Neolithic samples show much higher colour intensity in darkness than the surrounding Luvisol horizons. The organic carbon content of the Neolithic samples can be correlated with the colour lightness value. Solid-state ^{13}C NMR measurements revealed that this correlation is mostly due to their aromatic carbon content, which is considerably higher in the Neolithic samples compared to the contemporary soils. Low polysaccharide contents and no lignin-derived phenols are found in the Neolithic samples. Between 29 and 77% of soil organic carbon survived UV photo-oxidation, mostly present as aromatic structures. Dipolar dephasing NMR spectroscopy indicated a high degree of condensation for the aromatic rings, while scanning electron microscopy showed that the material had a plant-like morphology.

Summarizing, the organic material filling the Neolithic pits shows significant differences in the overall chemical composition compared to the surrounding soil. It represents a highly altered, highly aromatic material, with no evidence for lignin-degradation products, probably deriving from non-soil origin. There is strong evidence that the aromatic carbon is derived from charcoal. The material either originated from soil material that has undergone vegetation fires or from other charred organic material, e.g. residues from cooking or Neolithic fire places.

Key words - Neolithic, pits, Luvisol, Phaeozem, organic matter, Bavaria, Germany.

Riassunto - *Origine e composizione della materia organica proveniente da pozzetti dell'insediamento neolitico di Murr, Baviera.* Il sito archeologico di Murr (Baviera superiore), è stato abitato per tutto il Neolitico, tra 5500 e 2700 a.C. Nell'area sono stati rinvenuti numerosi pozzetti ed un fossato, distinguibili dal circostante suolo limoso per il colore bru-

no scuro del riempimento. Quantunque siano stati rinvenuti numerosi reperti, allo stato attuale delle ricerche né la natura del riempimento né la funzione dei pozzetti e del fossato sono ancora state comprese. Pertanto, la composizione della materia organica di 30 strati di riempimento di 11 pozzetti di questo insediamento è stata analizzata e confrontata con quella di un vicino Luvisol e due orizzonti A di Phaeozems della stessa età della Germania meridionale. Sui campioni sono state effettuate analisi di C ed N, misurazioni del colore, spettroscopia a stato solido CPMAS NMR del ^{13}C , frazionamento/foto-ossidazione UV ad alta energia/spettroscopia ^{13}C CPMAS NMR combinati, analisi dei polisaccaridi e della lignina. Il contenuto in C organico nei campioni neolitici è maggiore che negli orizzonti dei Luvisol, ma in genere minore che negli orizzonti A dei contemporanei Phaeozem sviluppati su loess. I campioni neolitici mostrano una maggiore intensità dei colori scuri rispetto a quella dei vicini Luvisol. Il contenuto in C organico dei campioni neolitici è correlato al colore, e le misure NMR a stato solido di ^{13}C indicano che questa correlazione è dovuta soprattutto al loro contenuto in C aromatico, che è notevolmente superiore rispetto a quello dei suoli contemporanei. Nei campioni neolitici il contenuto in polisaccaridi è basso e non vi sono fenoli derivati dalla lignina. Da 29 a 77% del carbonio organico dei suoli ha resistito all'ossidazione UV, soprattutto come strutture aromatiche. La spettroscopia NMR a sfasamento dipolare ha posto in evidenza un forte grado di condensazione degli anelli aromatici, mentre la microscopia SEM ha mostrato morfologie vegetali.

Riassumendo, il riempimento organico dei pozzetti neolitici mostra differenze significative nella composizione chimica generale rispetto ai circostanti suoli. È costituito da materiale fortemente aromatico molto alterato e senza prodotti di degrado della lignina, di origine probabilmente estranea al suolo. Vi sono forti indizi che il C aromatico derivi da carbone che ebbe origine da materiale pedogenetico coinvolto in incendi di vegetazione oppure da altro materiale organico carbonizzato, ad esempio residui di cottura o focolari neolitici.

Parole chiave - Neolitico, pozzetti, Luvisol, Phaeozem, materia organica, Baviera, Germania.

INTRODUCTION

Much of the present knowledge of ancient times is based on excavated artefacts such as ceramics, art work or jewelry, bone or stone tools, and remains of buildings or graves that are analyzed by classical archaeological means supported by biomolecular techniques. Examples of such biomolecular archaeological investigations include DNA recovery from ancient material (Pääbo *et al.*, 1988; Pääbo, 1989; Poinar, 1998), the analysis of

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pottery surface residues (Oudemans & Boon, 1991), the examination of collagen, proteins and amino acids (Dennison, 1980; Bland *et al.*, 1998), lipids (Evershed, 1990; Gülaçar *et al.*, 1990), sterols (Knights *et al.*, 1983; Evershed & Connolly, 1994) or faecal remains (Frey, 1985). In many cases the archaeological findings are limited to ditches, pits or hills containing a matrix that is admittedly morphologically distinct from the surrounding soil, but accommodates only ancient remains that are degraded or transformed to such an extent to be clearly identified. This is in particular the case if organic material is of interest which has been exposed to microbial reworking and humification.

The present study is focused on the chemical characterization of the organic material from ancient pits and ditches found around a Neolithic settlement, located at Murr, approximately 50 km Northeast of Munich (Germany) that is examined since 1992 (Neumair, 1994). This settlement was dated back to the younger Neolithic period and assigned to the culture of Münchshöfen, an independent alpine gender of the band ceramics. The settlement expands over an area of 30,000 m² and contains several remains of houses, graves, pits and ditches. The shape and size of the building foundations but also excavated bones, ceramic potsherds and stone tools revealed that human activity started around 5500 to 5000 BC at this site with a couple of houses. In the middle Neolithic period (5000 to 4500 BC) during the culture of Münchshöfen (4600 to 4200 BC) this site developed to a larger settlement with approximately 20 houses.

At Murr, all excavated pits and the ditch were filled with several layers of material varying in colour from brownish-black to ochre, morphologically distinct from the surrounding loamy soil. Pits with a long and sharp form were suggested to have been used as post pits for building houses. Small black pieces were discovered within the pits. These pieces were supposed to derive from charred material, probably from charred wood. Other pits were proposed to represent Neolithic waste deposits. Dark coloured spots or layers in some pits are discussed to represent relicts of dark A horizons from Chernozem-like soils. Such Chernozems have developed during the early Holocene along a belt from Siberia to Eastern Europe with isolated occurrences in Germany. In the more humid climate of the Atlanticum, they supposedly underwent decalcification and leaching leading to a change in soil type from Chernozems to Phaeozems or Luvisols (Farruggia *et al.*, 1973). Thiemeyer (1989) investigated the region Friedberger Wetterau near Frankfurt/Main and suggested that the Neolithic people have most probably settled on Chernozem-like soils before a change in soil type took place. In southern Germany relicts of such chernozemic soils are known from the region between Regensburg and Pleinting near the river Danube (Schmidt *et al.*, 1992). This work aims to investigate in detail the nature of the organic carbon infilling the Neolithic pits.

MATERIALS AND METHODS

The archaeological samples were subjected to chemolytic analysis of lignin and polysaccharides, ¹³C nuclear magnetic resonance (NMR) spectroscopy to obtain an overview on their organic matter composition. Dipolar dephasing (DD) experiments, frequently applied to studies on soil organic matter, were applied to selected samples to distinguish between protonated and nonprotonated carbon atoms. A combination of particle-size fractionation, high-energy ultraviolet (UV) photo-oxidation and ¹³C CPMAS NMR spectroscopy was used to further characterize the aromatic carbon (Skjemstad *et al.*, 1996).

Site description and sampling

All Neolithic samples were obtained from pits and a ditch of the Neolithic settlement in Murr, approximately 50 km northeast of Munich in Southern Germany. The site is situated between 450 and 455 m a.s.l. at the top of a small hill and expands over 30,000 m², 200 m in the direction west-east and 150 m in the direction north-south. The area is presently under agricultural use with barley cultivation. The soils are Cambisols and Luvisols (ISSS Working Group Reference Base, 1998), developed from loess, partly showing hydromorphic properties. Before sampling, the plough horizon (40 to 50 cm) was removed in the ancient settlement area. Figure 1 shows the excavated site and a map of the sampled site. Figures 2a and 2b display cross-sections of the sampled pits, sample designations, and the sampling depths. The identification and differentiation of the individual layers was done according to morphological variations, mainly in colour. Sampling was done so that all of the soil material from an individual layer was represented. By means of the artefacts found in them, all sampled pits have been dated to the culture of Münchshöfen (4600 to 4200 BC; Neumair, 1996; Neumair, 1998).

In addition, samples from 7 horizons of a Luvisol profile next to the settlement area, one sample of an Ap horizon from a Haplic Phaeozem from Seeben north of Halle/Sachsen-Anhalt (Schmidt, 1998) and one sample from the A horizon of a Phaeozem (Sontheim near Günzburg), all developed from loess were analyzed (Tab. 1). Soils are classified according to ISSS Working Group Reference Base (1998) Horizons were designated according to FAO (1990).

Soil colour

The degree of darkness was measured with a Minolta CHROMA-METER CR 300 and reported as L*/CIE value according to the CIE L*, a*, b* colour space (CIE, 1978). This system provides a method to visualize colour with the L* axis representing lightness from L* = 0 for absolute black to L* = 100 for absolute white, the a* axis representing redness-greenness from -a* (green) to +a* (red) and the b* axis representing yellowness-blueness from -b* (blue) to +b* (yellow) (Schmid *et al.*, 2001).

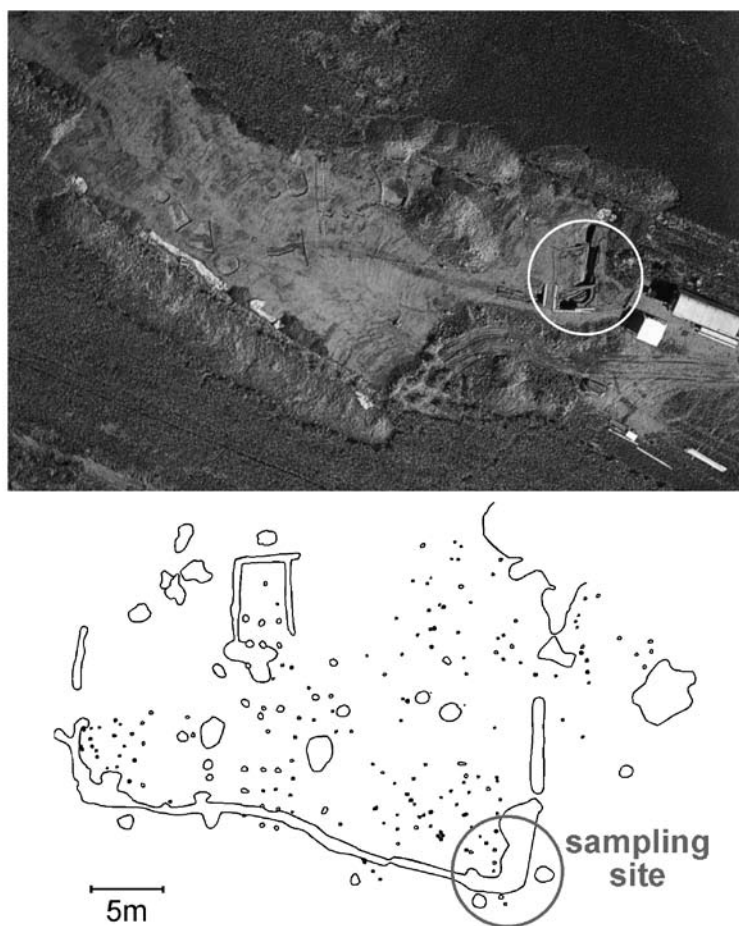


Fig. 1 - Excavated site and map with location of sampling.

Solid-state ^{13}C NMR spectroscopy

Prior to solid-state ^{13}C NMR analysis, all samples except the Ah horizon of the Phaeozem from Sontheim were treated with hydrofluoric acid (HF) in order to concentrate the organic matter and to remove paramagnetic material (Schmidt *et al.*, 1997).

The solid-state ^{13}C NMR spectra were obtained on a Bruker DSX 200 spectrometer operating at a ^{13}C resonance frequency of 50.3 MHz. The ^{13}C chemical shift scale is referenced to tetramethylsilane (= 0 ppm). For quantification, the spectra were divided into four major chemical shift regions, assignable to alkyl C (0 to 45 ppm), O/N alkyl C (45 to 110 ppm), aromatic C (110 to 160 ppm) and carboxyl/carbonyl C (160 to 220 ppm). The relative carbon distribution was determined by integration of signal intensity in the different chemical shift regions using an integration routine supplied with the instrument software. Details are given in Schmid *et al.* (2001).

Dipolar dephased (DD) NMR spectra were acquired on the Bruker DSX 200 spectrometer by inserting

a delay time (T_{dd}) of 2 - 150 μs without ^1H decoupling between the cross polarization and acquisition portions of the CPMAS pulse sequence. A 180° refocusing pulse was inserted at $\frac{1}{2} T_{dd}$ to assist phasing. During the period when the high-power decoupler is turned off, carbon magnetization becomes influenced (dephased) by strong dipolar interactions between ^{13}C and ^1H spins. Carbons directly bonded to protons are known to dephase much more rapidly than those without attached protons, except if they are subject to rapid molecular motion (methyl or methoxyl groups). Details are given in Schmid *et al.* (2002).

High-energy ultraviolet (UV) photo-oxidation and Scanning Electron Microscopy

The UV photo-oxidation procedure was carried out as described by Skjemstad *et al.* (1996). Scanning electron microscopy (SEM) was carried out on a Cambridge Stereoscan S250 on samples coated with 20 nm of carbon. Elemental characterization was performed using a Link AN1000 energy dispersive X-ray analyzer.

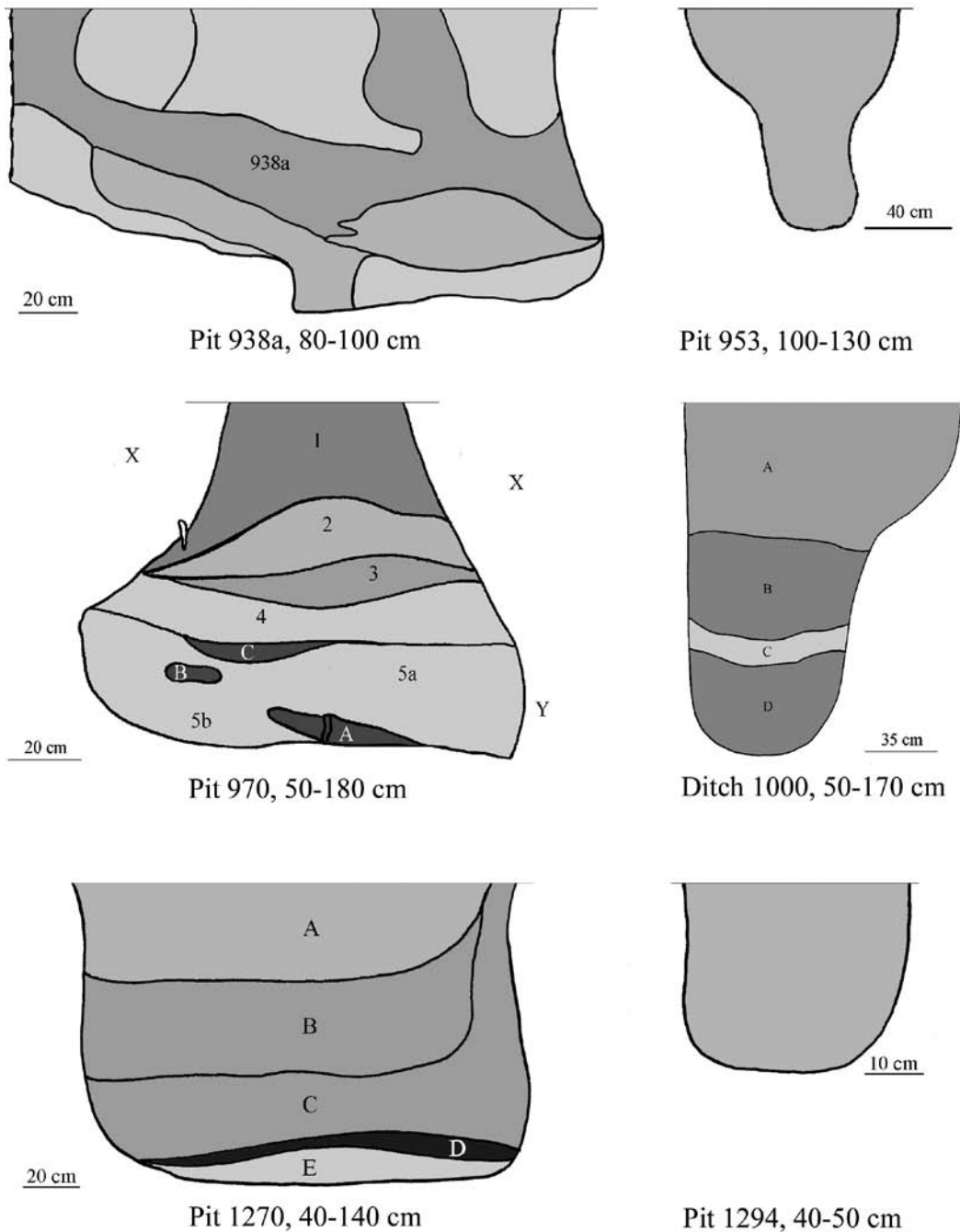


Fig. 2a - Cross-sections of the Neolithic pits in Murr, Bavaria, Germany. Sample differentiation was done according to variations in colour.

Chemolytic methods (CuO oxidation for lignin and polysaccharide analysis)

The quantitative analysis of polysaccharides was a selective hydrolysis followed by a colorimetric determination of the released monomers after reaction with MBTH (3-methyl-2-benzothiazolinone hydrazone hydrochlorid). Lignin was analyzed with the alkaline

cupric oxide oxidation method in a pressure bomb. The generated lignin derived phenols were cleaned by a C18 column, silylated and subsequently separated and analyzed by gas chromatography with flame ionization detection. Individual compounds were identified by comparison of their retention times with those of commercially available standard compounds compris-

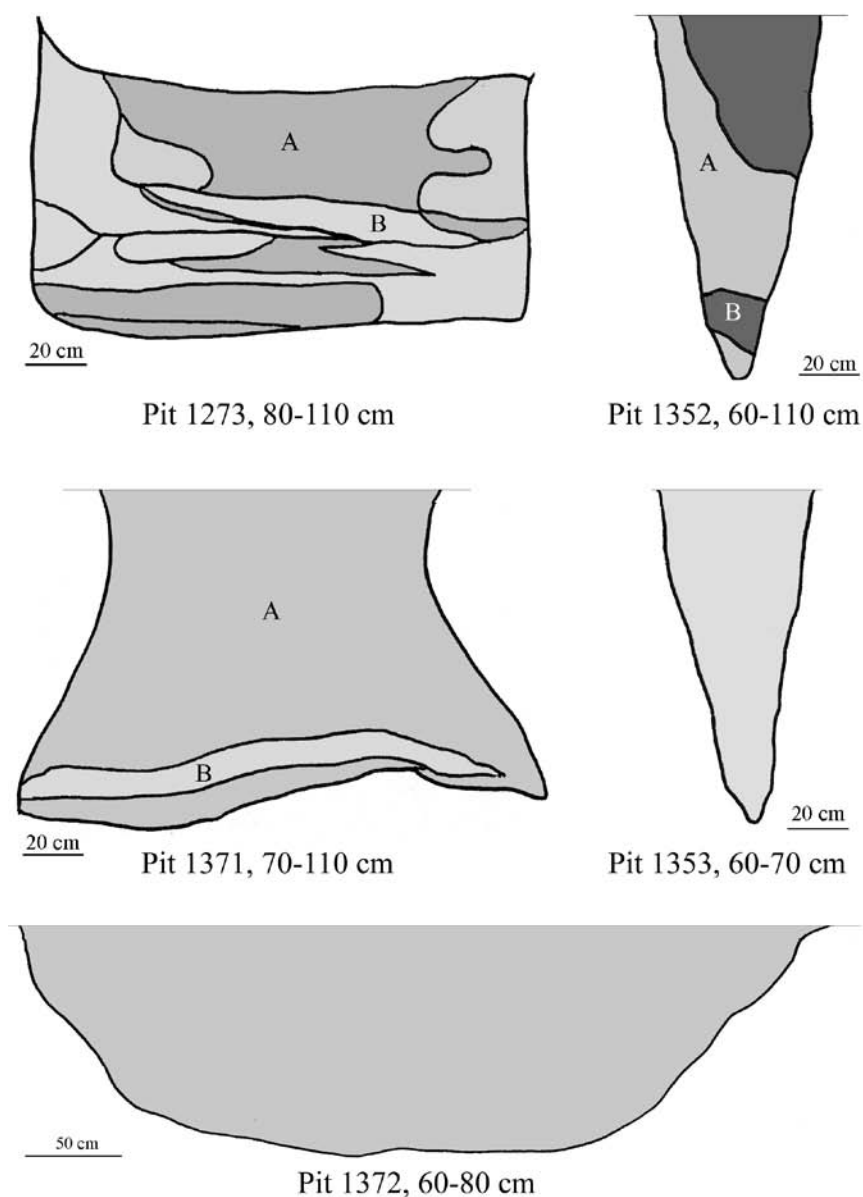


Fig. 2b - Cross-sections of the Neolithic pits in Murr, Bavaria, Germany, with sampling depths. Sample differentiation was done according to variations in colour.

ing vanillin, vanillic acid, syringylaldehyde, syringic acid, acetovanillone, acetosyringone, p-coumaric acid and ferulic acid. A detailed description of both procedures is given by Schmid *et al.* (2001).

RESULTS AND DISCUSSION

Elemental analysis

Inorganic carbon was not detected in any of the Neolithic samples. Organic carbon (OC) varies between 1.4 and 14.8 mg g⁻¹ for most of the archaeological mate-

rial, except for sample pit 1270/D (OC: 41.0 mg g⁻¹). Comparable low OC contents between 2.2 and 2.7 mg g⁻¹ were determined for sample 970/Y and the horizons II SdBv1 and II SdBv2 of the Luvisol profile, located at approximately the same depth. The OC-contents of the remaining horizons of the Luvisol profile next to the settlement area vary between 12.1 and 5.3 mg g⁻¹, which is lower than the values determined for most of the archaeological samples. With OC contents of 23.7 mg g⁻¹ and 59.7 mg g⁻¹, respectively, the A horizons of the contemporary phaeozemic soils located in Seeben and Sontheim, differ clearly from the Neolithic fill-

Tab. 1 - Description of soil samples for comparative purposes.

| Soil | Horizon | Depth (cm) |
|-----------------------------------|---------|------------|
| Luvisol (Murr) | Ap | 0-30 |
| | Eg | 30-60 |
| | Btg | 60-80 |
| | CBwg | 80-105 |
| | CBgw | 105-130 |
| | 2 Bwg 1 | 130-150 |
| | 2 Bwg 2 | 150-172 |
| | 2 Bwg 3 | 172-195 |
| | 2 Bwg 4 | 195-215 |
| Haplic Phaeozem (Seeben) | Ap | 0-20 |
| Phaeozem (Sontheim) | Ap | 30-85 |
| Haplic Chernozem (Bad Lauchstädt) | Ap | 0-20 |
| Haplic Chernozem (Bad Lauchstädt) | | |
| Bare fallow | Ap | 0-20 |

ing matrices. Total nitrogen contents (N_t) vary between 0.3 and 1.5 mg g⁻¹ in the Neolithic material. For most of these samples the C:N ratios, calculated to vary between 9.8 and 14.6 are in the range expected for humified soil organic material. A specific trend is not observed. The N contents of the Luvisol vary between 1.3 and 0.3 mg g⁻¹. They give rise to narrow C:N ratios between 7.0 and 9.0.

Soil colour

In the Neolithic material, L*/CIE values are between 43.3 (pit 1270/D) and 65.8 (pit 970/5b), with low values corresponding with dark colours and high values corresponding with lighter colours (Torrent & Barron, 1993). For most of the Neolithic samples, except for the sample of pit 1270/D, their OC contents correlate to their lightness (Fig. 3).

This reflects that the black colour generally increases with increasing OC content of the filling layers. A comparable relationship was previously found for non-archaeological soils (Schulze *et al.*, 1993). In those studies it was also shown that soil colour depends not only on the content but also on the composition of the organic matter (Shields *et al.*, 1968; Schulze *et al.*, 1993). This may explain the exceptional behaviour of sample 1270/D and the Ap and Ah horizons of the two Phaeozems, all three having comparable lightness values, but different OC contents. Most of the Neolithic samples have smaller L*/CIE values than soil material surrounding pit 970/X (L*/CIE = 67.3) and 970/Y (L*/CIE = 64.7) and the Luvisol horizons (L*/CIE values between 60.1 and 65.8). This is in accordance with the generally higher OC-content of the Neolithic material. However, the L*/CIE values for the material from ditch 1000/C (= 63.7) and pit 970/4, 5a and 5b (L*/CIE values: 65.3, 64.6 and 65.8) are comparable to those of the

non-archaeological soils, indicating that those samples exhibit similar properties.

Polysaccharide and lignin analyses

Cellulose amounts are solely detected in the top filling layers of pit 970, 1270 and 1273, comprising between 0.7 and 1.6% C of total OC, indicating the presence of partially decomposed plant remains. In the samples in which non-cellulose carbohydrates were identified, their content varies between 4.1 and 10.2% C of OC. Generally, no relationship was found between the contents of carbohydrate C and the signal intensities of O-alkyl C (60 to 110 ppm) in the ¹³C NMR spectra (see below). In addition, the amount of carbohydrates that were determined colorimetrically corresponds to less than one third of the relative intensity observed in the chemical shift region of O-alkyl C of the corresponding solid-state ¹³C NMR spectra.

The yields of cupric oxide oxidation products were too low to be quantified, indicating that lignin, if present at all, is not a major component of the organic matter of the filling matrices.

Solid-state ¹³C nuclear magnetic resonance spectroscopy

¹³C nuclear magnetic resonance (NMR) spectra of selected samples investigated in this study are shown in Figure 4. The relative intensity distribution is listed in Table 2. The alkyl C region (0-45 ppm) of all spectra is dominated by a peak between 30 and 32 ppm, representing alkyl chain carbon, *e.g.* in fatty acids, waxes and resins (Baldock *et al.*, 1992). Signals at 72 and 105 ppm are assigned to the O-alkyl C region (45-110 ppm). In natural soils, these signals are usually assumed to be derived from carbohydrates (Wilson, 1987). A small peak near 56 ppm can be ascribed to methoxyl groups

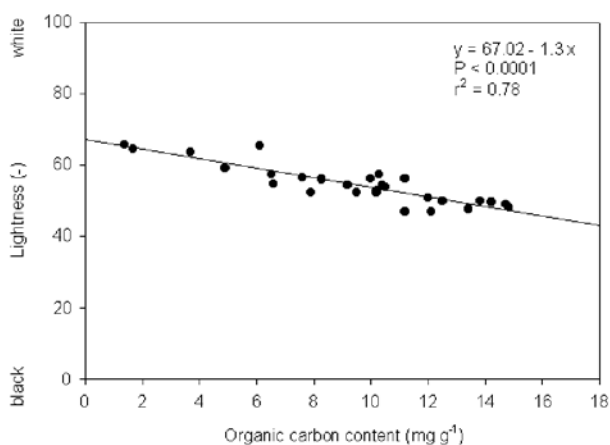


Fig. 3 - Relation between lightness and organic carbon content of all Neolithic samples except for sample 1270/D (n = 28).

or N-substituted alkyl carbon (Preston *et al.*, 1997). The prominent resonance near 130 ppm in the chemical shift region of aryl C (110-160 ppm) may originate from C- or H-substituted aromatic carbon compounds as well as from unsaturated alkyl structures (Knicker & Skjemstad, 2000). The signal between 160 and 185 ppm in the chemical shift region of carbonyl/carboxyl C (160-220 ppm) can be ascribed to carboxyl, amide and ester carbon. Ketone or aldehyde carbon (signal intensity near 200 ppm) could not be identified in the samples.

The most pronounced common property of the organic material of the Neolithic samples is the high content of sp^2 C, most tentatively in aromatic structures. The concentration of those carbons seems to increase with increasing darkness of the sample. In order to spot a possible relationship between those two variables, the darkness of the sample was correlated with the aromatic carbon content (% of bulk soil, Fig. 5). The correlation allows suggesting that the high aromaticity is responsible for the high degree of darkness of the Neolithic material.

Lignin compounds are generally represented by a combination of resonances for methoxyl C (56 ppm), C- α , C- β and C- γ (72 ppm) and phenolic C (145 to 155 ppm) (Preston *et al.*, 1997). Distinct phenolic carbon resonances indicative of lignin or other phenols (*e.g.*, from tannins) can not be identified in the spectra of the Neolithic materials. Thus, phenols can not contribute significantly to the aryl-C signal intensity in the CPMAS ^{13}C NMR spectra, and lignin or other phenols, if present at all, are only a minor component of the organic matter in these materials. This confirms the results from CuO oxidation.

Dipolar dephasing ^{13}C NMR spectroscopy

Samples 1270 B and D were subjected to dipolar dephasing (DD) ^{13}C NMR experiments. Such experiments provide additional structural insight, as a preferential loss

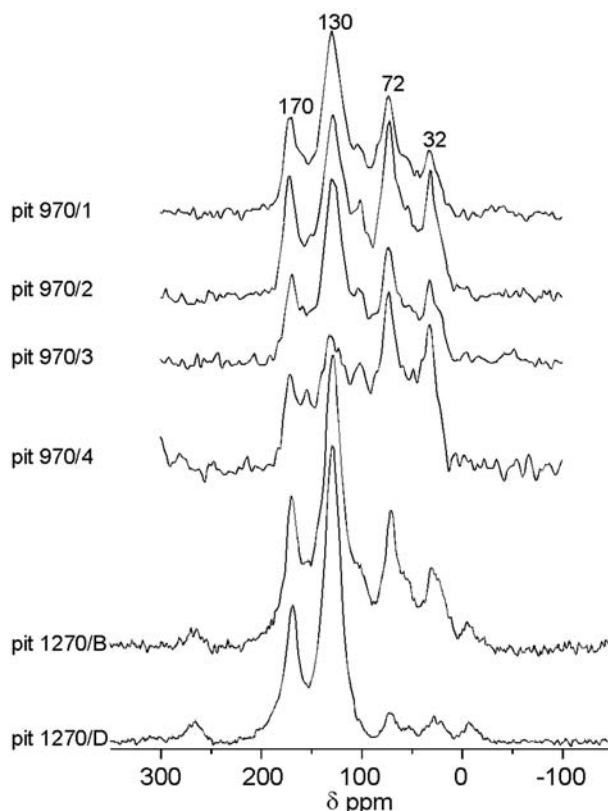


Fig. 4 - CPMAS ^{13}C NMR spectra of selected archaeological soil samples from pit 970 and 1270.

of ^{13}C signal intensity with increasing dephasing time occurs for carbons directly bound to protons, except if they are subject to rapid molecular motion such as in methyl or methoxyl groups. Dipolar interactions are much smaller for carbons without attached hydrogens (Wilson, 1987; Preston *et al.*, 1997). From these experiments the proportion of nonprotonated aromatic carbons can be calculated. The proportion of nonprotonated aromatic carbons accounts for 73 and 67% of the total aromatic carbon in pit 1270 B and D, respectively. Thus, at most, only one-third of the aromatic carbons or an average of two of the six ring carbons is protonated. Skjemstad *et al.* (1999) showed that for soil charcoal materials, only 27% of the carbons in the condensed ring structures were observable with the conventional CP (cross polarization) experiment and a Bloch decay experiment was required to observe all of the carbon nuclei. Here, the carbons are directly excited without prior magnetization of the proton spin system to avoid intensity loss due to inefficient cross polarization from the proton to the carbon spin system (Knicker *et al.*, 1997). If charcoal carbon therefore contributes significantly to the aryl-C region in these spectra, it is likely that, on average, fewer than one carbon per ring is in fact protonated.

Tab. 2 - Intensity distribution in the CPMAS ^{13}C NMR spectra of the Neolithic samples.

| Sample | Depth (cm) | % of total signal intensity | | | |
|--------------|------------|-----------------------------|-------------|------------|---------------------|
| | | Alkyl-C | O/N Alkyl-C | Aromatic-C | Carbonyl/Carboxyl-C |
| Pit 938a | 80-100 | 9 | 23 | 48 | 20 |
| Pit 953 | 100-130 | 12 | 26 | 45 | 17 |
| | | | | | |
| Pit 970/1 | 50-80 | 11 | 35 | 40 | 14 |
| Pit 970/2 | 80-115 | 17 | 38 | 33 | 13 |
| Pit 970/3 | 115-130 | 15 | 35 | 40 | 11 |
| Pit 970/4 | 130-153 | 19 | 43 | 29 | 10 |
| Pit 970/5a | 153-175 | 23 | 43 | 25 | 8 |
| Pit 970/5b | 175-185 | 20 | 44 | 27 | 9 |
| Pit 970/A | 180 | 11 | 24 | 49 | 16 |
| Pit 970/B | 175-180 | 12 | 31 | 41 | 15 |
| Pit 970/C | 160 | 13 | 32 | 41 | 15 |
| Soil 970/X | 50-130 | 26 | 36 | 26 | 13 |
| Soil 970/Y | 153-160 | 19 | 35 | 33 | 12 |
| | | | | | |
| Pit 1270/A | 40-70 | 14 | 32 | 40 | 14 |
| Pit 1270/B | 70-100 | 10 | 26 | 47 | 17 |
| Pit 1270/C | 100-120 | 10 | 23 | 49 | 18 |
| Pit 1270/D | 120-130 | 3 | 8 | 63 | 25 |
| Pit 1270/E | 130-140 | 11 | 25 | 49 | 15 |
| | | | | | |
| Pit 1273/A | 80-90 | 12 | 31 | 41 | 17 |
| Pit 1273/B | 100-110 | 12 | 31 | 42 | 15 |
| Pit 1294 | 40-50 | 12 | 31 | 42 | 15 |
| Pit 1352/A | 60-70 | 14 | 31 | 37 | 19 |
| Pit 1352/B | 90-100 | 12 | 27 | 42 | 18 |
| Pit 1353 | 60-70 | 12 | 28 | 42 | 19 |
| Pit 1371/A | 70-80 | 11 | 29 | 44 | 16 |
| Pit 1371/B | 100-110 | 11 | 32 | 39 | 18 |
| Pit 1372 | 60-80 | 11 | 31 | 41 | 17 |
| | | | | | |
| Ditch 1000/A | 50-90 | 11 | 25 | 47 | 16 |
| Ditch 1000/B | 90-130 | 9 | 18 | 52 | 21 |
| Ditch 1000/C | 130-135 | 14 | 30 | 39 | 17 |
| Ditch 1000/D | 135-170 | 10 | 19 | 51 | 20 |

High-energy ultraviolet (UV) photo-oxidation

The combined fractionation/UV photo-oxidation/ ^{13}C CPMAS NMR technique showed that all investigated Neolithic infilling layers contained high amounts of aryl material resistant to photo-oxidation (Fig. 6). From the

results obtained in the dipolar dephasing experiments, it is evident that the protected carbon has a condensed aromatic structure, and that a significant contribution of charred organic or charcoal carbon to the archaeological samples seems likely.

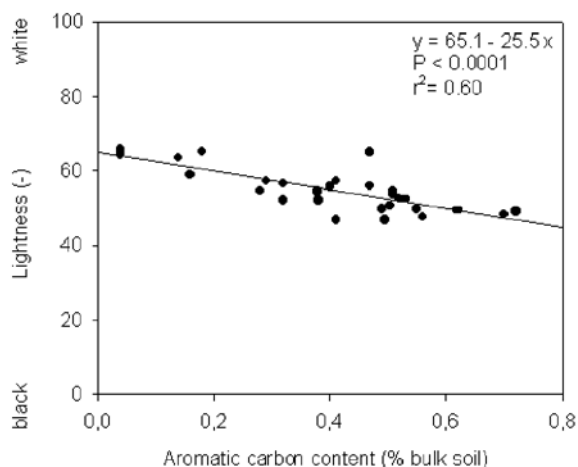


Fig. 5 - Relation between lightness and aromatic carbon content (% of bulk soil) of all Neolithic samples except for sample pit 1270/D (n = 28).

From the aryl C content (110 to 145 ppm) of the < 53 μm fraction after UV photo-oxidation, the content of charcoal carbon can be estimated, using the approach of Skjemstad *et al.* (1999). The content of charcoal carbon in the archaeological samples was calculated to be between 1.8 and 28.8 mg C/g soil (Schmid *et al.*, 2002). This corresponds to 23% and almost 70% of the total organic carbon in the fraction < 53 μm used for UV-photooxidation.

Electron micrographs (not shown, see Schmid *et al.*, 2002) show relatively large pieces (5-20 μm) with the characteristic morphology of charcoal. As well, there are evident much more finely divided particles (< 2 μm) with a platy morphology. EDX analysis showed that very few of the particles in these photographs were minerals but were organic in nature. Combining the morphological and chemical nature of these materials, there is little doubt that they are in fact charcoal or highly carbonized materials.

CONCLUSIONS

A number of differences in the quality and quantity of organic matter of most of the Neolithic samples and the studied non-archaeological soils were revealed by chemical analyses. Organic carbon (OC) contents of the Neolithic samples are generally higher than in the surrounding Luvisol horizons, indicating that the infillings contain additional organic material that is not present in the surrounding soil.

As featured by a positive correlation between OC content and darkness this additional OC seems to be responsible for the morphological difference between non-archaeological and Neolithic material at the sampling site of Murr.

The organic matter from almost all of the Neolithic samples consists of material dominated by aromatic structures. A strong correlation between darkness and

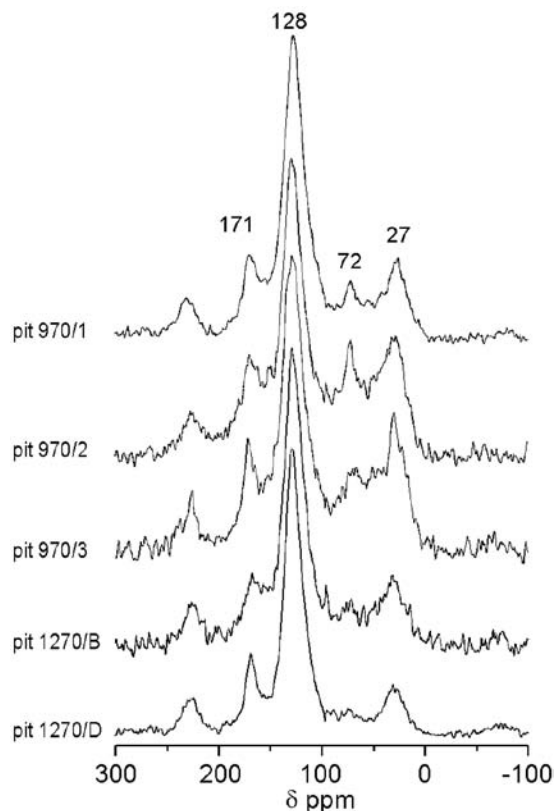


Fig. 6 - CPMAS ^{13}C NMR spectra of archaeological soil samples from pit 970 and 1270 after 2 h of high-energy UV photo-oxidation.

content of sp^2C , most probably in aromatic structures, further indicates that such compounds are responsible for the dark colour of the Neolithic samples. The carbonyl/carboxyl/amide signal of their spectra shifts upfield to 170 ppm which is indicative for the presence of higher amounts of aromatic carboxylic groups. The NMR and CuO oxidation data provided no evidence for the presence of lignin or other phenolic compounds. The contents of polysaccharides are low and do not correspond to the O-alkyl C of the ^{13}C NMR spectra. Dipolar dephasing revealed a high degree of condensation of the aromatic rings. A large proportion of the aromatic carbon was resistant to UV photo-oxidation and particles showed a morphology consistent with finely-divided charcoal. From these results, a large contribution of charred organic or charcoal carbon to the archaeological samples seems most likely. Due to its polyaromatic structure, this type of organic carbon seems to be recalcitrant and thus may survive in the environment over thousands of years (Haumaier & Zech, 1995). At present, we can only speculate about the origin of the charred organic matter. The materials may originate from natural soil organic matter that contained considerable amounts of charcoal formed by vegetation fires (Haumaier & Zech, 1995; Skjemstad

et al., 1996; Schmidt *et al.*, 1999), that filled the pits by topsoil erosion with time. Alternatively, the pits may have been filled artificially with organic matter high in char contents, e.g., as residues from Neolithic fire places, and were subsequently covered with layers of natural soil. The latter could explain the fact that the charcoal contents vary considerably from layer to layer.

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REFERENCES

- AG Boden, 1994. Bodenkundliche Kartieranleitung. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.
- Baldock J.A., Oades J.M., Waters A.G., Peng X., Vassallo A.M., Wilson M.A., 1992. Aspects of the chemical structure of soil organic materials as revealed by solid-state ^{13}C NMR spectroscopy. *Bio-geochem.* 16: 1-42.
- Bland H.A., van Bergen P.F., Carter J.F., Evershed R.P., 1998. Early diagenetic transformation of proteins and polysaccharides in archaeological plant remains. In: Stankiewicz B.A., van Bergen P.F. (eds.), Nitrogen-Containing Macromolecules in the Bio- and Geosphere. ACS Symposium Series 707: 113-131. ACS, Washington DC.
- CIE, 1978. Recommendations on uniform colour spaces, colour difference and psychometric colour terms. *Colourimetry*: 2-15.
- Dennison K.J., 1980. Amino acids in archaeological bone. *J. Archaeol. Sci.* 7: 81-86.
- Evershed R.P., 1990. Lipids from samples of skin from seven Dutch bog bodies: preliminary report. *Archaeometry* 32: 139-153.
- Evershed R.P., Connolly R.C., 1994. Post-mortem transformation of sterols in bog body tissues. *J. Archaeol. Sci.* 21: 577-583.
- Farruggia J.-P., Kuper R., Lüning J., Stehli P., 1973. Der Bandkeramische Siedlungsplatz Langweiler 2 Gemeinde Aldenhofen, Kreis Düren. Rheinland-Verlag GmbH in Kommission bei Rudolf Habelt Verlag GmbH, Bonn.
- FAO, 1990. Guidelines for soil description. 3ed., FAO, Rome.
- Frey G.F., 1985. Analysis of fecal material. In: Gilbert R., Mielke J. (eds.), The Analysis of Prehistoric Diets: 127-154. Academic Press, Orlando.
- Gülaçar F.O., Susini A., Klohn M., 1990. Preservation and post-mortem transformations of lipids in samples from a 4000-year-old Nubian mummy. *J. Archaeol. Sci.* 17: 691-705.
- Haumaier L., Zech W., 1995. Black carbon - possible source of highly aromatic components of soil humic acids. *Org. Geochem.* 23: 191-196.
- ISS Working Group Reference Base, 1998. World Reference Base for Soil Resources. Technical Key. World Soil Resources Reports 84, FAO, Rome.
- Knicker H., Fründ R., Lüdemann H.-D., 1997. Characterization of the nitrogen in plant composts and native humic material by natural abundance N-15 CPMAS and solution spectra. In: Nanny M., Minear R.A., Leenheer J.A. (eds.), Nuclear Magnetic Resonance Spectroscopy in Environmental Chemistry: 272-294. Oxford University Press, London.
- Knicker H., Skjemstad J.O., 2000. Nature of organic carbon and nitrogen in physically protected organic matter of some Australian soils as revealed by solid-state ^{13}C and ^{15}N NMR spectroscopy. *Aust. J. Soil Res.* 38: 113-127.
- Knights B.A., Dickson C.A., Dickson J.H., Breeze D.J., 1983. Evidence concerning the Roman military diet at Bearsden, Scotland, in the 2nd century AD. *J. Archaeol. Sci.* 10: 139-152.
- Neumair E., 1996. Murr - eine bedeutende Zentralsiedlung der jungsteinzeitlichen Münchshöfener Kultur. In: Archäologischer Verein im Landkreis Freising e.V. (ed.), Archäologie im Landkreis Freising: 9-89. Freising, Sellier Druck GmbH.
- Neumair E., 1998. Neue Aspekte zum Siedlungswesen der Münchshöfener Kultur anhand von Untersuchungen in Murr, Lkr. Freising. In: Archäologischer Verein im Landkreis Freising e.V. (ed.), Archäologie im Landkreis Freising: 72-88. Freising, Sellier Druck GmbH.
- Oudemans T.F.M., Boon J.J., 1991. Molecular archaeology: Analysis of charred (food) remains from prehistoric pottery by pyrolysis-gas chromatography/mass spectrometry. *J. Anal. Appl. Pyrolysis* 20: 197-227.
- Pääbo S., 1989. Ancient DNA: Extraction, characterisation, molecular cloning, and enzymatic amplification. *Proc. Natl. Acad. Sci. USA* 86: 1939-1943.
- Pääbo S., Higuchi R.G., Wilson A.C., 1988. Mitochondrial DNA sequences from a 7,000-year-old brain. *Nucleic Acids Res.* 16: 9775-9787.
- Poinar H.N., 1998. Preservation of DNA in the fossil record. In: Stankiewicz B.A., van Bergen P.F. (eds.), Nitrogen-Containing Macromolecules in the Bio- and Geosphere. ACS Symposium Series 707: 132-146. ACS, Washington DC.
- Preston C.M., Trofymow J.A., Sayer B.G., Niu J., 1997. ^{13}C nuclear magnetic resonance spectroscopy with cross-polarisation and magic-angle spinning investigation of the proximate-analysis fractions used to assess litter quality in decomposition studies. *Can. J. Bot.* 75: 1601-1613.
- Schmid E.-M., Knicker H., Bäuml R., Kögel-Knabner I., 2001. Chemical composition of the organic matter in Neolithic soil material as revealed by CPMAS ^{13}C NMR spectroscopy, polysaccharide analysis and CuO oxidation. *Soil Sci.* 166: 569-584.
- Schmid E.-M., Skjemstad J.O., Glaser B., Knicker H., Kögel-Knabner I., 2002. Characterization of the aromatic organic carbon in archaeological soils. *Geoderma* 107: 71-91.
- Schmidt F., Böhm A., Hammerl J., Hofmann B., Holzner G., Jochum R., Keller X., Mahler C., Martin W., Petschl A., Prinz R., Schilling B., Spies E.-D., Stimmelmeyer G., Wittmann O., 1992. Die Böden Bayerns - Datenhandbuch für die Böden des Tertiärhügellandes, der Iller-Lech-Platte und des Donautales. Bayerisches Geologisches Landesamt, München.
- Schmidt M.W.I., 1998. Organic matter in natural soils and in soils contaminated by atmospheric organic particles from coal processing industries. Shaker Verlag, Aachen.
- Schmidt M.W.I., Knicker H., Hatcher P.G., Kögel-Knabner I., 1997. Improvement of ^{13}C and ^{15}N CPMAS NMR spectra of bulk soils, particle size fractions and organic material by treatment with 10% hydrofluoric acid. *Eur. J. Soil Sci.* 48: 319-328.
- Schmidt M.W.I., Skjemstad J.O., Gehrt E., Kögel-Knabner I., 1999. Charred organic carbon in German chernozemic soils. *Eur. J. Soil Sci.* 50: 351-365.
- Schulze D.G., Nagel J.L., van Scoyoc G.E., Henderson T.L., Baumgardner M.F., Stott D.E., 1993. Significance of organic matter in determining soil colours. In: Bingham J.M., Ciolcosz E.J. (eds.), Soil Colours: 71-90. Soil Science Society of America, Madison, Wisconsin.
- Shields J.A., Paul E.A., Arnaud R.J.S., Head W.K., 1968. Spectrophotometric measurement of soil colour and its relationship to moisture and organic matter. *Can. J. Soil Sci.* 48: 271-280.
- Skjemstad J.O., Clarke P., Taylor J.A., Oades J.M., McClure S.G., 1996. The chemistry and nature of protected carbon in soil. *Aust. J. Soil Res.* 3: 251-271.
- Skjemstad J.O., Taylor J.A., Smernik R.J., 1999. Estimation of charcoal (char) in soils. *Commun. Soil Sci. Plant Anal.* 2283-2298.
- Thiemeyer H., 1989. Landschaftsgeschichte und bodenkundliche Befunde eines bandkeramischen Siedlungsplatzes bei Bruchentbrücken/Wetterau. *Frankfurter geowissenschaftliche Arbeiten* 10: 31-42.
- Torrent J., Barron V., 1993. Laboratory measurement of soil colour: theory and practice. In: Bingham J.M., Ciolcosz E.J. (eds.), Soil Colour: 21-33. Soil Science Society of America, Madison, Wisconsin.