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ANALYSIS OF CARBON FRACTIONS IN ANTHROPOMORPHIC SOIL MATERIALS, FROM A VIKING AGE TOWN TO RECENT MUNICIPAL WASTE DEPOSITS

Abstract - Traditionally, organic carbon content is expressed as «loss on ignition» (LOI) or as «total organic carbon» (TOC). We present a wet chemical analytical method for organic carbon fractions, which include lipids, fulvic and humic acids, oxydizable humin and inert black carbon. The method has been tested on industrial and urban waste in Northern Germany and on «black earths» from excavations of the Viking age town Kaupang, southeastern Norway. The method is simple (except for the fractionation of lipids), fast, not too costly and can be carried out without special equipment. Our results show that the content of different organic carbon fractions can provide meaningful information for geo-archaeological investigations. Further testing of different types of anthropogenic material is still needed, for determining the significance of the different carbon fractions in archaeological contexts.

Key words - Organic carbon, differentiation, urban waste, black earth, Vikings, Norway, Germany.

Riassunto - *Analisi delle frazioni del carbonio organico in* Anthropomorphic Soil Material *provenienti da una città vichinga e da scarichi municipali recenti.* Il contenuto in C organico è tradizionalmente espresso come «perdita alla combustione» (LOI) o «C organico totale» (TOC). Viene qui presentato un metodo di analisi ad umido per le frazioni del C organico che include lipidi, acidi fulvici ed umici, umina ossidabile e carbonio nero inerte. Il metodo è stato provato su residui industriali ed urbani in Germania settentrionale e su «terre scure» provenienti dalla città vichinga di Kaupang in Norvegia sud-occidentale. Il metodo è semplice (tranne che per il frazionamento dei lipidi), rapido e non troppo dispendioso e può essere applicato senza apparecchiature speciali. I risultati dimostrano che il contenuto in differenti frazioni di carbonio organico può dare informazioni significative per indagini geoarcheologiche. è ancora necessaria la verifica del metodo su altri tipi di materiali di origine antropica per determinare la significatività delle varie frazioni in contesti archeologici.

Parole chiave - Carbonio organico, differenziazione, residui urbani, terre scure, Vichinghi, Norvegia, Germania.

INTRODUCTION

It is generally agreed that plants, living and dead organisms in the soil, and their decomposition products called soil organic matter (SOM) have a major influence on soil formation, weathering and soil properties. In archaeological contexts organic matter may be the remains of bones from humans or domestic animals, food, or household waste such as wood, charcoal, ash, and broken or lost implements, clothing etc. As in natural soils, the anthropogenic organic materials will also undergo change and decomposition after deposition and thus contribute to the development of a soil profile. Some of these soils were classified as «Urbic Anthrosols» (FAO-UNESCO-ISRIC, 1988). However, in a more recent version of this classification system (Deckers *et al.*, 1998; Driessen *et al.*, 2001) urban waste and archaeological soil materials are not considered as proper soil units, but termed *anthropomorphic soil materials*.

In most soil and sediment investigations the organic matter is determined as «loss on ignition» (LOI), or as «total organic carbon» (TOC). These methods do not distinguish the different carbon fractions, nor whether organic carbon is derived from vegetation and/or animal sources. In this paper we present a simple and inexpensive analytical procedure for the determination of organic carbon fractions, which can provide more meaningful information for the interpretation of geo-archaeological investigations.

FRACTIONATION METHODS FOR SOIL ORGANIC MATTER

Since Sprengel (1826) identified «huminsäure» and «humussäure» from alkali extracts, a number of degradative and non-degradative methods have been developed (Kononova, 1966; Schnitzer & Khan, 1978; Stevenson, 1994; Beyer, 1995), for the analysis of soil organic matter (SOM). Soil horizons influenced or formed by ancient civilizations are often rich in anthropogenic charcoal, ash or soot, which contain high amounts of black carbon. Therefore we have adapted a procedure that has been developed by Beyer (1995) and Wu *et al.* (1999), to analyse the anthropomorphic SOM (see Fig. 1). The method has also been used for the characterization of carbonpools in soils (*cf.* Lal *et al.*, 1995) in ongoing projects at our department on greenhouse gas emissions from natural and cultivated soils. One has to keep in mind that the different components which are isolated are «laboratory products» (and the original SOM is chemically modified) but the method has been a standard procedure in many soil investigations, and is so even today. In later years non-destructive methods have been introduced, often in combination with wet chemistry (Stevenson, 1994; Beyer *et al.*, 1996; Kögel-Knabner *et al.*, 2008 [this volume]). However, there are no standardized methods and the technologically elegant methods are expensive and require substantial technical know-how and equipment (Lal *et al.*, 1995).

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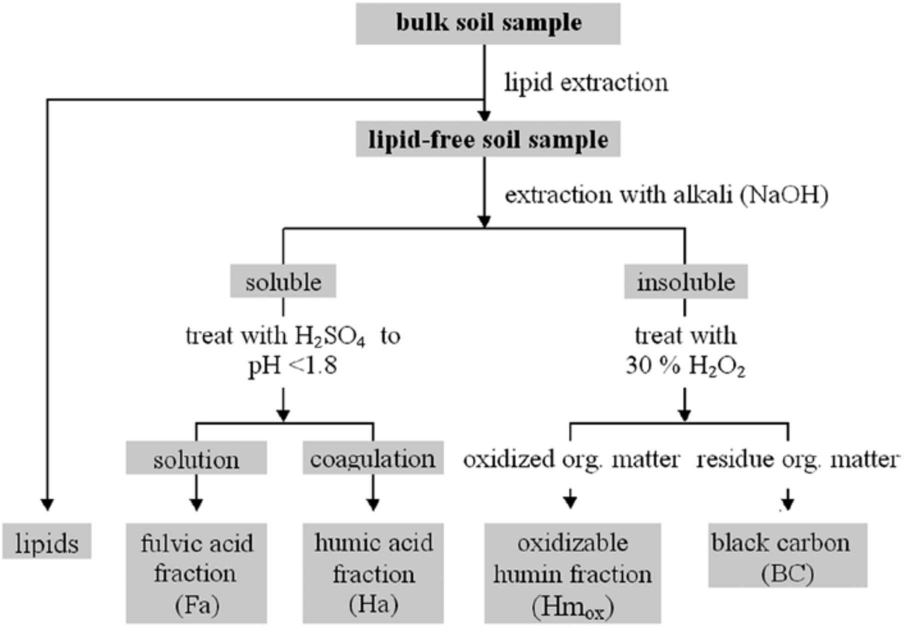

Fig. 1 - Extraction and fractionation of soil organic matter (adapted from Wu *et al.*, 1999).

SAMPLES AND METHODS

Soil profiles of recent municipal waste deposits from northwestern Germany

The method was applied to four soil profiles developed on modern domestic waste deposits. All samples have high pH (range 6.8-7.7 in $CaCl_2$) and 100% base saturation. Selected soil characteristics are summarised in Table 1.

Profile 1a is a *c*. 20 year old waste deposit near Rostock-Warnemunde, consisting of building materials, household waste and various soil materials, with an average thickness of 3.5 m. The site is poorly drained, with reducing conditions, partly due to methane production in the waste, *i.e. reductic* conditions (Driessen *et al*., 2001). The site is covered with nitrophilous ruderal vegetation (Blume & Schleuss, 1997).

Profile 1b is a *c*. 40 year old waste deposit consisting mainly of ashes, organic materials and broken glass and ceramics. The site has long been utilised as garden plots for the town residents of Eckernförde (Blume & Schleuss, 1997). Like site 1a (above) the sub-soils show reductic conditions.

Profile 1c. This is an old (> 50-year) waste deposit that was first used for ash and slag from a gaswork, and later for household waste and occasional dumping of building materials. Also this area was later used as gardens, but is now overgrown with open deciduous woodland (Blume & Schleuss, 1997).

Profile 1d. A modern (< 20 years old) sewage sludge deposit located in a poorly drained area near Kiel, which was treated with lime and iron chloride for nine years up to 1981, to stabilise the sludge. The deposit is approximately 8 m thick and now overgrown with nitrophilous herbs, shrubs and grasses (Blume & Schleuss, 1997). Below *c*. 30 cm depth the profile shows reductic conditions.

Profiles of black earths from excavations at Kaupang, southeastern Norway

Two samples from each of three different soil profiles were analysed (Bukholm, 2001). Five of the six samples have pH (in distilled water) between 5.5 and 5.9. The lowermost sample in profile 2c has a pH of 4.1, due to the strongly reducing conditions in the sub-soil. The two upper profiles have been cultivated for considerably more than 100 years, and have a *c*. 20 cm thick plough layer. The lowermost profile (2c) emerged from the sea approximately 200 years ago but can still occasionally be submerged, and has been cultivated for less than 50 years. Selected characteristics are summarised in Table 2.

Profile 2a was located 1.8 m above the Viking age sea-level. It is characterized by a 40 cm, fairly massive «black earth» below the plough layer. A 2 cm thick charcoal layer lies just above the «sterile» gravelly sand sub-soil.

Profile 2b consists of waste from the Viking age town that was dumped in the harbour, just beyond the shore in approximately 1 m water depth (partly wave-washed). The profile is stratified, with some massive «black earth» layers between sandy gravel with charcoal and two almost pure charcoal layers. Altogether 55 cm of anthropomorphic soil material is described below the plough layer. The underlying sub-soil is massive silty clay with a few pieces of charcoal.

Tab. 1 - Selected characteristics of the soil profiles from deposits of recent municipal waste in northwestern Germany.

Profile	Depth (cm)	TOC (%)	$CaCO_3$ (%)	Clay (%)	C/N (%)	pH	BS (%)
1a-Ah	0-10	6.7	5.9	7	36	7.5	100
C_1	10-50	6.4	5.9	7	36	7.5	100
C_2	50-75	6.5	4.6	6	22	7.3	100
1b-Ah	0-24	9.7	5.4	6	33	7.1	100
C_1	24-36	11.9	11.2	4	58	7.7	100
C_2	36-90	11.5	9.2	5	49	7.5	100
1c-Ah_1	0-12	7.3	1.4	8	27	6.8	100
Ah_2	12-30	5.1	2.2	7	40	7.1	100
C_3	30-53	11.2	3.7	7	58	7.3	100
1d-Ah	0-25	9.2	2.1	8	16	7.1	100
C_1	25-35	9.9	12.1	6	26	7.2	100
C_2	35-175	12.0	2.9	n.d.	6	7.1	87

Tab. 2 - Selected characteristics of soil profiles from excavations at Kaupang, southeastern Norway.

Sample	Horizon	Depth (cm)	TOC (%)	Clay (%)	C/N	pH	BS (%)
2a	I	37-43	3.3	8	10	5.8	90
	II	52-59	1.5	n.d.*	10	5.7	100
2b	I	55-61	4.8	2	30	5.9	88
	II	74-77	9.2	n.d.	27	5.8	85
2c	I	43-48	18.0	n.d.	21	5.5	45
	II	49-53	9.3	21	15	4.1	37

* Not determined.

Profile 2c contains waste materials washed out to deeper water (*c.* 3 m below the Viking age sea-level) by waves and shore currents. Below the plough layer a 20 cm thick layer of sandy foreshore sediments overlies 8 cm of anthropomorphic soil material. The underlying sub-soil is sandy silt, with pronounced oximorphic (Driessen *et al.*, 2001) features.

WET CHEMICAL ANALYSIS OF ORGANIC MATTER

About 15 g sample of soil (< 2 mm) was ground to < 0.1 mm. The content of total organic carbon was determined using a CHN-Analyser (LECO CHN-1000 oven).

The lipid fraction was determined using a soxhlet extractor (Soxhterm 2000 automatic, Gerhardt, Germany). Approximately 10 g of the soil (< 0.1 mm) was extracted with *toluene:ethanol* (ratio 1:2.3) for 3 hours in the soxhlet extractor. After evaporation of the solvent, the residues were dried at 80°C for 2 hours and cooled to room temperature. The content of lipids was determined gravimetrically.

Humic and fulvic acids were isolated by alkaline extraction. 3.0 g lipid-free soil sample was extracted with 50 ml 0.5 M NaOH under nitrogen atmosphere to hinder oxidation. After shaking for 24 hours the sample was centrifuged to separate the coloured supernatant, which is the fulvic and humic acid fraction (Fa + Ha). The remaining soil was washed with 50 ml 0.1 M sodium sulphate (Na_2SO_4). The solid part (fraction R1) was centrifuged, dried and weighed. The sample R1 contains the oxidisable humin and black carbon. From the supernatant (Fa + Ha fraction), 10 ml of the solution was taken to measure the concentration of organic carbon.

To separate the humic from the fulvic acids, a further 10 ml aliquot of the solution Fa + Ha was transferred to a centrifuge tube, acidified with 2.5 M sulphuric acid (H_2SO_4) to pH 1.8 and allowed to stand (react) for 24 hours at room temperature (25°C). The suspension was centrifuged to separate the soluble fulvic acid (Fa fraction) from the precipitated humic acid (Ha fraction).

The concentration of organic carbon in the solutions Fa and Fa + Ha was determined after evaporation of water by dry combustion. The carbon concentration of Ha solution was calculated from the concentration difference between the fractions Fa + Ha and Fa.

To determine the *oxidizable humin* and *black carbon fractions* 1.0 g of the fraction R1 was weighed in 100 ml tubes and treated with 30% H_2O_2. After 2 hours oxidation at 60°C the suspension was heated to 90°C for 1 hour to evaporate the remaining peroxide.

The solid residue (fraction R2) was centrifuged (as before), dried and weighed. The organic carbon in the fractions R1 and R2 was measured by dry combustion (in a LECO oven).

The carbon in R2 comprises, according to (CPMAS) ^{13}C-NMR-analysis (Wu *et al.*, 1999), polyaromatic hydrocarbons with few functional groups and is therefore called inert or black carbon (BC) (*cf.* Goldberg, 1985; Haumaier & Zech, 1995; Kuhlbusch, 1995).

The content of lipids, Fa, Ha, and BC is calculated as percentages of the total organic carbon content in the original soil sample. The carbon content of the oxidisable humin (Hm_{ox}) is calculated from the difference between the total organic carbon and the sum of organic carbon in the lipids, Fa, Ha, and BC.

RESULTS

Recent municipal waste

The carbon fractionation method was applied to three profiles from recent municipal waste deposits (1a, 1b, 1c) and one from sewage sludge deposit (1d), in northwestern Germany. The results are illustrated in Figure 2.

In contrast to natural soils, the sub-horizons of the investigated deposits contained large amounts of organic matter. The composition of this organic matter is mainly determined by the origin of the parent material, whereas that from the A horizon is to some extent influenced by soil forming processes. In profiles 1a and 1d this is shown by the increase of lipids (the most unstable fraction) with depth.

Viking age black earths

The horizons with the highest TOC in the three profiles (Tab. 2; Fig. 3) were chosen for analysis. Thin section analysis of the moderately drained profiles in the excavation area showed bioturbation, mainly by earthworms (Karen B. Milek, pers. comm., 2003). Thus, some pedogenic alteration has taken place in these > 1000 year old soils.

DISCUSSION

Our samples contain between 1.5 and 18.0% total organic carbon (Tab. 1 and 2). Generally the modern domestic waste has higher carbon contents and higher C/N-ratios than the Viking age black earth. The sewage sludge is most similar to the Viking age town waste materials, although it is difficult to compare the two. We know little about the waste produced by the Viking age town, including the content of household waste versus waste from the industries (carpenters, blacksmiths etc.).

The black earths are generally more acidic and with lower base saturation, compared to the recent domestic waste which contains calcium carbonate (Tab. 1). This probably reflects differences in drainage properties on

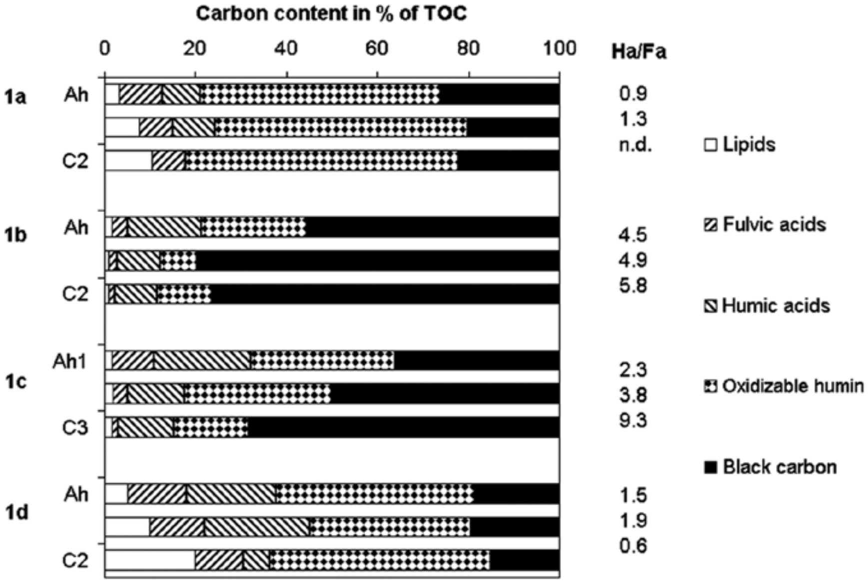

Fig. 2 - Carbon fractions and the ratio of humic to fulvic acids (Ha/Fa) in four soil profiles from northwestern Germany (modified from Blume & Schleuss, 1997).

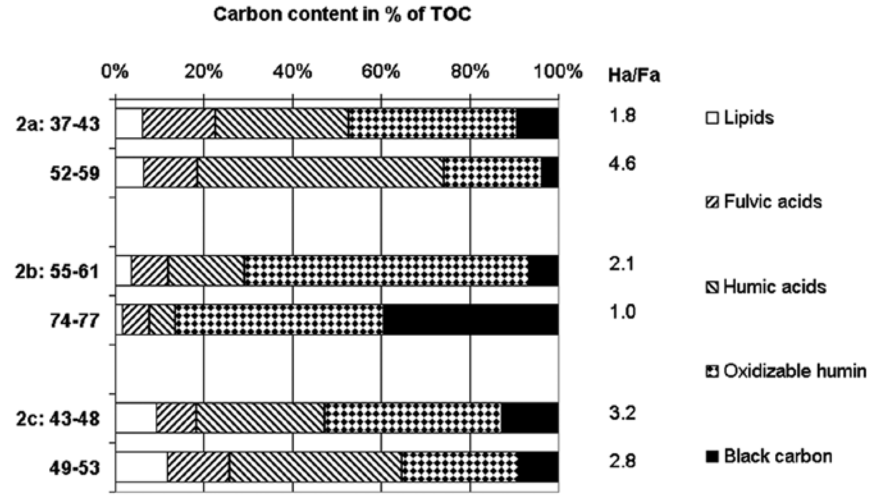

Fig. 3 - Carbon fractions and the ratio of humic to fulvic acids (Ha/Fa) in three soil profiles from Kaupang, southeastern Norway (Bukholm, 2001).

the sites, higher content of the local mineral soil, and long cultivation of the Viking age soils.

Lipids

Soil lipids are normally degradation products of plants and microbial tissues, and dominated by fats, waxes and resins (Stevenson, 1994). In the recent domestic waste the lipid contents are generally less than 10%, with the exception of the C2 horizon in profile 1d which contains more that 20% (Tab. 1). This is most likely due to reducing conditions in the lower horizons of the sewage sludge. Most of the profiles show increasing lipid contents with depth, and this is interpreted as biological degradation and oxidation of lipids in the upper soil horizons (a pedological process). In another investigation from northwestern Germany (Wu *et al.*, 1999), waste from a brown coal mine had a high lipid content. This is in agreement with a study by Rice & MacCarthy (1989) who referred to a solvent-extractable lipid fraction as bitumen.

In natural soils the lipid content rarely exceeds 6% (Beyer, 1995). High lipid contents may thus be used as an indicator for anthropogenic material like sewage sludge and brown coal.

Humic and fulvic acids

The humic acids have usually higher carbon contents, less oxygen, greater molecular weight and less exchange acidity than fulvic acids (Stevenson, 1994). There are clear differences in Ha/Fa ratios between Podzols (> 60% Fa), «brown earths» (Alfisols), and «black cotton soils» (Vertisols: < 15% Fa) related to the difference in coniferous and deciduous forests and grassland vegetation (Stevenson, 1994: 46). The Ha/Fa ratio may indicate degrees of humification. Fresh vegetation, straw and leaf litter have increasing Ha/Fa ratios of 0.39, 0.70 and 1.42 respectively (Meuser, 1996). The Ha/Fa ratio in soil horizons lies between 2.5 and 3.4, according to Beyer (1995). In comparison to natural soils, the anthropogenic samples from profiles 1a and 1d have relatively lower Ha/Fa ratios, but some horizons from 1b and 1c have extremely high Ha/Fa ratios. The composition of the originally deposited material may have a strong influence on the Ha/Fa ratio. In archaeological contexts, the use of grass and straw from grain crops as fodder, bedding for humans and animals and as building materials, may be reflected in the Ha/Fa ratios. However, we have no clear evidence so far.

In our samples (Fig. 1 and 2), one horizon (in profile 1a) contained no humic acid but otherwise the Ha/Fa ratio varies in a quite wide range between 0.5 and 9.5, implying markedly diverse composition of the original anthropogenic material.

The oxidizable «humin» fraction

This fraction is calculated as a difference (see Methods above). This more resistant carbon fraction is more common in cultivated soils (topsoils) than in forest and grassland soils in Nepal (Yang *et al.*, in press), and the amount in soils and anthropogenic materials may partly be related to the rate of biochemical degradation of organic matter (Frink, 1992, 2001).

Black carbon

The content of black carbon in all the profiles of recent domestic waste deposits (1a, 1b, 1c and 1d) was significantly higher than that observed in natural soils by Yang *et al.* (in press). In natural forest soil in Nepal, the black carbon content lies in the range between 3 and 7% of TOC, whereas in agricultural soils, the BC content is more than 10% of TOC (Yang *et al.*, in press). This may reflect burning during forest clearance, or crop residue burning. In compost, peat and bark mulch the content of black carbon is less than 1% according to Meuser (1996). Black carbon in municipal wastes can be attributed to residuals of burnt wood or coal from households. Black carbon accounted for up to 90% of TOC in samples from flyash and slag from gasworks

(Blume & Schleuss, 1997; Wu *et al.*, 1999). High content of black carbon is a clear indication of anthropogenic origin of the soil material.

In archaeological contexts BC will usually be related to the burning of wood and charcoal, both in households and in industries such as blacksmith work and metal smelting.

CONCLUDING REMARKS

None of the carbon fractions described above are pure substances (*cf.* Schnitzer & Khan, 1978; Stevenson, 1994; Beyer, 1995). There are gradual transitions between all of them. Even in two samples with the same content of one of the fractions, detailed analysis may show that the composition is different, depending on the character of the «parent» material. The oxidation resistant black carbon fraction obtained by our method consists mainly of polyaromatic hydrocarbons with few functional groups (Beyer, 1995; Wu *et al.*, 1999). BC is therefore the chemically and biologically inert part of soil organic matter and has a high residence time in all soils.

Our results further indicate that BC may make up a considerable part of the organic matter in Urbic Anthrosols and anthropomorphic soil materials. Ancient agricultural fields may have high BC contents in the soil, and some forest and grassland soils that have been exposed to fires can also have high BC contents. In general, high contents of BC can be used as an indicator for human manipulation of the environment and the soils.

The lipid contents are usually rather low and this analysis could be excluded, also because it is more time-consuming (and expensive) compared with the other procedures of the whole analysis. However, if one suspects a contribution from, for example, animal sources (human and/or cattle excrements), or the use of brown coal as fuel, one might test the lipid content in a few samples.

The method gives a much more diverse picture of the organic carbon components in all types of soil. However, we still need to test the method on different types of anthropomorphic materials, for interpretation of the significance of the different carbon fractions, by analysing a variety of soils from archaeological excavations.

There is a need to standardise analytical methods for determining the different fractions of organic carbon in all soils (Lal *et al.*, 1995), archaeological soils included, and our method – or a modification of it – is recommended.

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