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Influence of the mineral matrix on the formation and molecular composition of soil organic matter in a long-term, agricultural experiment

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Abstract. The formation of soil organic matter from grass residues was studied in a 34-year-old pot experiment with grass cultivation on loamy marl using pyrolysis-field ionization mass spectrometry (Py-FIMS). For whole soils, the Py-FI mass spectra indicated clear changes in the molecular-chemical composition during SOM formation from grass residues. In particular, the enrichment of heterocyclic N-containing compounds with time was remarkable.

For organomineral size fractions, even larger differences in the composition of SOM were found. The changes between the 13th and 34th experimental year are partly explained by a net transfer of phenols, lignin monomers und lignin dimers from medium silt to fine silt. Moreover, it is demonstrated that temperature-resolved Py-FIMS enables the determination of the thermal energy required for the evolution of individual compound classes which is a measure of the strength of humic- and organomineral bonds. At lower temperatures (< 400 °C), the enrichment of thermally less stable and/or loosely bound organic matter with cultivation time in clay and fine silt is due to carbohydrates, N-containing compounds, phenols and lignin monomers. Shifts of evolution maxima toward a higher pyrolysis temperature (> 400 °C) in clay, fine silt and medium silt are explained by a higher thermal stability of humic and/or organomineral bonds of lignin dimers, alkylaromatics and lipids, that developed during the last two decades of the experiment.

Introduction

Soil organic matter (SOM) is an important compartment in the global cycles of biogeochemical elements such as C, N and P. However, its chemical structure on a molecular basis is poorly understood (Schlesinger 1991). Progress in understanding SOM chemistry has been achieved by the application of novel analytical methods, e.g. ^{13}C-NMR spectroscopy and applications of analytical pyrolysis, including pyrolysis-mass spectrometry (Py-MS) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The experimental methodology of pyrolysis-field ionization (FI)MS, the uses of mass spectral data, and the results of recent SOM studies have been summarized by Schulten (1987, 1993). Furthermore, Simmleit & Schulten (1989) described the potential of analytical pyrolysis for studies of ecosystem compartments which are linked by the transfer of organic substances. Recently, a comprehensive summary of the results obtained by Py-FIMS in the characterization of forest ecosystems has been given by Hempfling et al. (1991).

To discover biogeochemical processes occurring during SOM formation and soil development, genetic soil horizons were investigated by Schulten et al. (1988) and Zech et al. (1990). Conclusions on the formation of SOM were drawn from comparisons of SOM composition in the vertical sequence of soil horizons. The assignment of differences in SOM composition to the biochemical reactions occurring during its formation is limited because of the translocation of organic substances through the profile, their precipitation in deeper horizons, and the input of fresh root necromass into subsoil. Therefore, it seems appropriate to observe the initial formation of SOM from defined parent materials in humus-free mineral substrates.

The majority of SOM in agricultural soils is strongly associated with the mineral matrix, forming organomineral particles of different size and composition (Turchenek & Oades 1979; Tiessen & Stewart 1983; McKeague et al. 1986; Leinweber & Reuter 1992). In these particle-size fractions, the composition of organic matter has been studied by wet-chemical methods, such as humic substance extractions (Anderson et al. 1974; Catroux & Schnitzer 1987), fractionations of N (Chichester 1969; Schnitzer & Ivarson 1982), amino acids (Christensen & Bech-Andersen 1989) and mono- and polysaccharides (Cheshire et al. 1990). Spectroscopic methods such as ^{13}C-NMR spectroscopy (Oades et al. 1987, 1988; Baldock et al. 1992), and biological methods such as aerobic incubations (Christensen 1987; Lowe & Hinds 1983) have been applied. Observations of organomineral particle-size fractions by differential thermal analyses (DTA), thermogravimetry (TG) and Py-FIMS showed that organic substances of different thermal stability were enriched in distinct particle-size fractions during SOM formation and due to different soil management (Leinweber & Schulten 1992; Leinweber et al. 1992). At present, the chemical structures of these substances and the reasons for their different thermal behaviour are largely unknown.

The objectives of the present study were

- to investigate the changes in SOM composition on a molecular-chemical basis in whole soil samples of initially humus-free loamy marl during 34 years of grass cropping,
- to elucidate the influence of the mineral matrix on the composition of the organic matter, and
- to describe the thermal properties of selected constituents of SOM in particle-size fractions and their changes during 20 years of SOM development.

Materials and methods

Materials

Whole soil samples (< 2 mm particle-size) and organomineral particle-size fractions were investigated from the Rostock long-term pot experiment Hu3 (Reuter 1981). In this experiment, Pleistocene loamy marl was filled in pots and continuously grown with grass. Samples of grass residues (stems and leaves, roots), the loamy marl, and the whole soil of the 2nd, 7th, 13th, 19th, 25th, 29th and 34th experimental years were investigated. These samples (100 g) were dispersed in 250 ml of distilled water and disaggregated using a probe-type ultrasonic disintegrator (USD 20, Emich Ultraschall GmbH Berlin, Germany) for 40 min setting the instrument at $P = 400$ W (1600 J ml^{-1} suspension [with operation/interuption intervals of 10 s]). The soil suspension was separated into sand (2000—63 μm, wet sieving) and clay (< 2 μm), fine silt (2—6.3 μm), medium silt (6.3—20 μm) and coarse silt (20—63 μm) by sedimentation/decantation. The particle-size distribution agreed with the results of the standard pipette method. The mineral composition of the size fractions from the 13th/34th experimental year was as follows: 6/6% quartz, 6/8% feldspars, 55/56% calcite + dolomite, 23/19% three-layer silicates in *clay*; 13/17% quartz, 8/9% feldspars, 58/59% calcite + dolomite, 10/9% three-layer silicates in *fine silt* and 30/32% quartz, 16/15% feldspars, 40/34% calcite + dolomite, 8/11% three-layer silicates in *medium silt* (Leinweber & Reuter 1992). Some other basic characteristics of the samples are given in Table 1.

Analytical methods

Organic C (C_{org}) concentrations were determined by dry combustion after destruction of $CaCO_3$ with 2.6-M HCl. Total nitrogen was determined by the semimicro-Kjeldahl method.

Table 1. Characteristics of *whole soil samples* (Reuter 1991) and *particle-size fractions* (Leinweber & Reuter 1992) from the long-term pot experiment.

Year	Fraction	Weight (% soil d.w.)	C_{org} (%)	N_t (%)	C : N ratio	CEC[1] ($mmol_c$ kg^{-1})
2nd	Whole soil		0.27	0.02	13.5	37
	Clay	18.7	0.49	0.06	8.2	85
	Fine silt	12.2	0.75	0.11	6.8	140
	Medium silt	10.8	0.46	0.04	11.5	31
7th	Whole soil		0.86	0.04	21.5	51
	Clay	18.3	1.18	0.14	8.4	149
	Fine silt	12.3	0.56	0.04	14.6	58
	Medium silt	9.6	n.d.[2]	0.05	n.d.	27
13th	Whole soil		1.01	0.08	12.6	63
	Clay	21.3	1.74	0.26	6.7	199
	Fine silt	10.6	0.61	0.07	8.7	30
	Medium silt	11.0	1.11	0.06	18.5	31
19th	Whole soil		0.96	0.07	13.2	73
	Clay	18.5	2.05	0.25	8.2	249
	Fine silt	13.3	0.80	0.08	10.0	23
	Medium silt	10.8	1.42	0.11	12.9	54
25th	Whole soil		0.98	0.09	10.8	76
34th	Whole soil		0.91	0.12	7.5	96
	Clay	18.9	3.04	0.40	7.4	282
	Fine silt	12.3	1.66	0.15	11.1	100
	Medium silt	10.8	1.94	0.15	12.9	79

[1] Cation exchange capacity.
[2] Not determined.

For Py-FIMS analyses about 5 mg of dried, finely ground soil material were placed in the quartz oven of a Finnigan MAT 731 mass spectrometer with a modified direct introduction system and heated linearly from 50 to 750 °C (Schulten et al. 1987). The extraordinary large samples were chosen to produce strong total ion intensities (TII) for the reproducible and smooth thermograms of selected classes of compounds (see below Figs. 3, 4 and 5). The samples were weighed before and after Py-FIMS. On average, for whole soils and particle-size fractions, between 2% and 7% of volatile matter were observed (Sorge et al. 1993). The mass spectra were recorded electrically by repetitive magnetic scans in the mass range *m/z* 18—1500. The Finnigan MAT data system SS200 enabled the accumulation, integration, and normalization of single spectra and the display of thermograms by plotting the TII versus the pyrolysis temperature. Difference Py mass-spectra were computed from the summed spectra of whole soil samples from different experimental years after normalizing to sample amounts of 1 mg. In addition, thermograms were computed for selected classes of chemical constituents of SOM by adding the intensities of characteristic marker molecules for each substance class (Schnitzer & Schulten 1992; Schulten & Schnitzer 1993a) in each of about 60 single spectra. This was done with the spectra of each of three replicates. The interpretation of mass spectral data was based on studies of the thermal behaviour of polymers with known structure, partly supported by other thermal degradation studies such as thermogravimetry (e.g. Plage et al. 1991), of standard synthetic- and biopolymers (e.g. Schulten & Lattimer 1984; Schulten 1989), on high resolution Py-FIMS (e.g. Hempfling et al. 1988) and on Py-GC/MS with library searches (e.g. Schulten & Schnitzer 1992).

Results and discussion

Development of the molecular-chemical composition of SOM

The organic carbon (C_{org}) and total nitrogen (N_t) concentrations (Table 1) indicate rapid enrichment of SOM during the first 13 experimental years, after which a steady-state level of approximately 0.9—1.0% C_{org} was reached (Reuter 1991). In Fig. 1, difference Py-FI mass spectra are displayed for selected time-periods. The upper spectrum in Fig. 1a shows larger ion intensities over the whole mass range for the 7th (positive relative abundances) compared to the 2nd year. Signals of carbohydrates (*m/z* 82, 84, 96, 110, 112 and 144) are particular intense in the lower, and of alkylaromatics (*m/z* 198, 206, 344, 372 and 386), lipids (*m/z* 228, 280, 294, 352) and lignin dimers (*m/z* 258, 302, 316, 330, 342) in the higher mass range. This indicates the enrichment of particular high molecular weight organic substances in soil during the early stages of SOM formation. In Fig. 1b (spectrum of the 19th year minus spectrum of the 13th year) positive abundance values are observed for signals of carbohydrates, phenols, lignin monomers and lignin dimers. Some negative values (lower spectrum) at *m/z* 113, 197, 258, and between 270 and 350 show that various compounds are detected with lower intensity in the sample from the 19th year. If the spectrum of the 25th year is subtracted from that of the 34th year, negative values are also found for signals of carbohydrates, phenols, lignin monomers, lignin dimers, lipids and alkylaromatics (Fig. 1c). The positive mass signal at *m/z* 186 is assigned to biphenols. Larger ion intensities of some heterocyclic N-containing compounds are indicated by the positive mass signals at *m/z* 67 (pyrrole), *m/z* 81 (methylpyrrole), *m/z* 95 (hydroxypyridine, formylpyrrole or dimethyl-

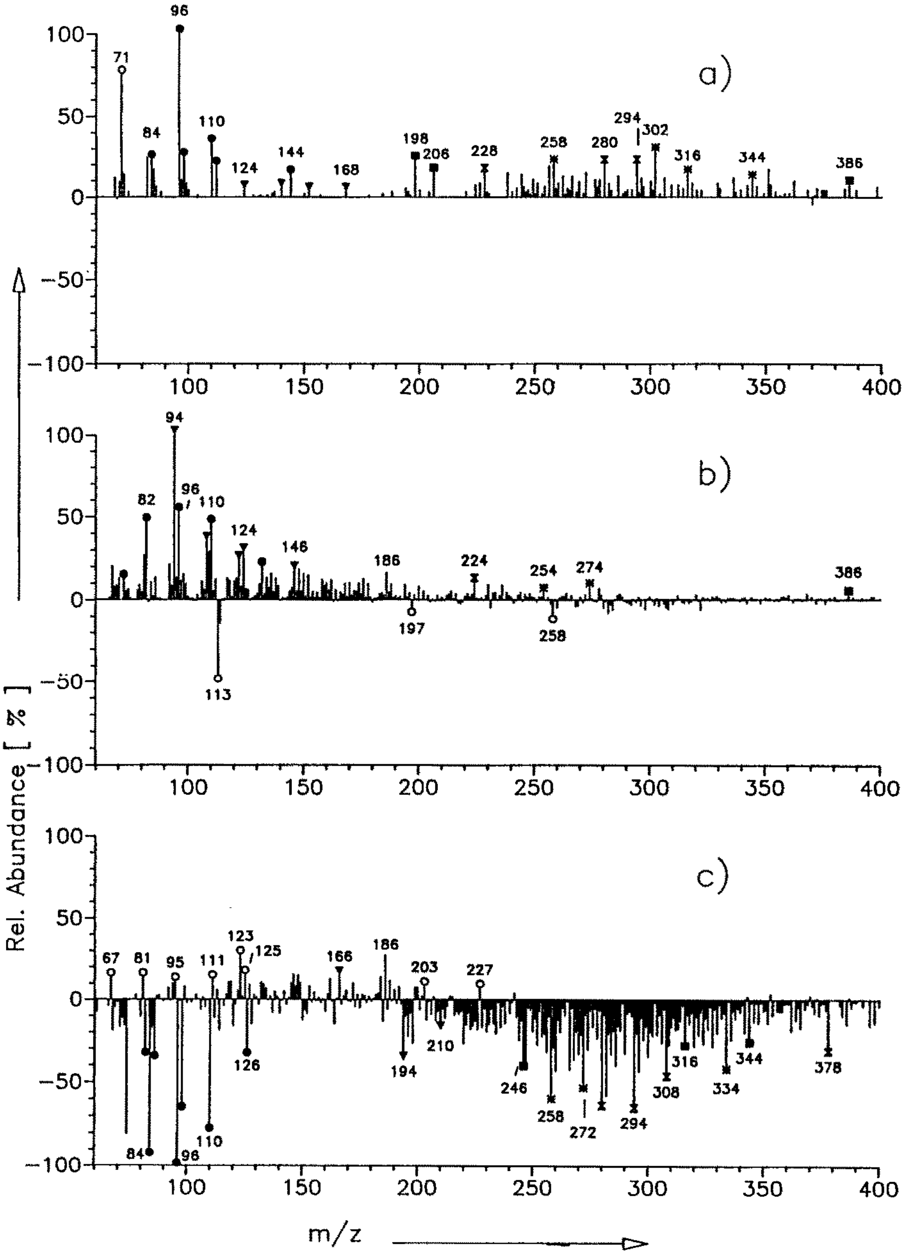

Fig. 1. Difference field-ionization mass spectra of whole soil samples: a) spectrum from 7th year minus spectrum from 2nd year, b) spectrum from 19th year minus spectrum from 13th year and c) spectrum from 34th year minus spectrum from 25th year (●, carbohydrates; O, N-containing compounds; ▽, phenols, lignin monomers; ✳, lignin dimers; ⧗, lipids; ■, alkylaromatics) (Normalization to 1 mg sample).

pyrrole), *m/z* 111, *m/z* 123 (tetramethylpyrrole) and *m/z* 125, 203 and 227 in the upper part of Fig. 1c.

In accord with the difference Py-FI mass spectra, the summed ion intensities of marker molecules of important compound classes in SOM show increased values for nearly all substance classes from the 2nd to the 25th year (Table 2). After 19 experimental years the following range is observed: phenols, lignin monomers > carbohydrates > N-containing compounds, lignin dimers, lipids and alkylaromatics. Alkylaromatics reach a maximum in the 19th year and remain then on a high, relatively constant level, showing the lowest rate of decrease during the final decade of the experiment. Among the N-containing compounds, qualitative changes over time are indicated by decreased relative abundances of nitriles, fluctuating values for amino-N and amides, and increased proportions of heterocyclic N-containing compounds (Schulten et al. 1992). The enrichment of N-heterocycles and immobilization of N_{org} in the final period of the experiment explain the lowered C/N-ratios in Table 1 and indicate a high resistence of these SOM constituents towards microbial decomposition. This is in accord with the finding that N-heterocycles in particular were accumulated in soils subjected to intense management regimes (Schulten & Leinweber 1991; Schulten & Hempfling 1992; Schulten & Leinweber 1993).

Table 2. Whole soil samples: summed ion intensities for the selected classes of compounds in whole soil samples from different years of the pot experiment (units are 10^3 counts/mg sample).

Class of compound	Experimental years					
	2nd	7th	13th	19th	25th	34th
Phenols, lignin monomers	<0.1	<0.1	1.8	5.8	9.5	7.1
Lignin dimers	<0.1	<0.1	1.0	1.0	6.0	2.1
Alkylaromatics	<0.1	<0.1	0.4	2.1	2.0	1.6
Lipids	<0.1	<0.1	0.7	1.0	6.2	2.1
Carbohydrates	<0.1	0.8	2.0	4.5	8.8	5.0
N-containing compounds	<0.1	0.1	1.0	2.6	4.2	3.4

Influence of the mineral matrix

The different development of the C_{org} and N_t concentrations, C/N-ratios and cation exchange capacities (CECs) in size fractions and whole soil samples (Table 1) give an initial indication of the influence of mineral matrix on the amount and the quality of organic substances associated with particle-size fractions. Higher C_{org} and N_t concentrations are observed in clay than in medium silt, fine silt and whole soil. The distribution of C_{org} and N_t in size fractions was possibly influenced by the breakup of coarser-sized carbonate particles and their redistribution to finer fractions (Ducaroir 1990). The larger rates of increase in clay-associated C_{org}, N_t and CEC are explained by the large affinity of clay for newly formed SOM, due to its large specific surface and its negatively charged exchange sites.

In Table 3, the summed ion intensities of marker molecules of selected compound classes (normalized in counts per mg sample weight) are listed for clay, fine- and medium-silt from the 13th and 34th experimental year. For clay, the following sequence is obtained: phenols, lignin monomers > alkylaromatics > N-containing compounds > carbohydrates > lipids > lignin dimers. This is changed in fine silt in-so-far as N-containing compounds and carbohydrates are less abundant in favour of lipids and lignin dimers. In medium-silt, phenols, lignin monomers, carbohydrates and lipids are the predominant contributors to the volatile organics. In the 34th year of this pot experiment, an increase of intensity from clay to medium silt is observed for lipids. The reverse is true for carbohydrates and N-containing compounds.

Table 3. Organo-mineral particle-size fractions: summed ion intensities for the selected classes of compounds in 13th and 34th year of the pot experiment (units are 10^3 counts/mg sample).

Class of compound	Size fractions					
	Clay		Fine silt		Medium silt	
	13th	34th	13th	34th	13th	34th
Phenols, lignin monomers	47.9	86.4	23.2	88.9	75.4	51.5
Lignin dimers	13.2	34.4	16.3	52.7	34.7	49.4
Alkylaromatics	44.0	67.8	21.5	71.9	45.2	47.3
Lipids	19.5	38.1	16.2	58.3	47.0	63.9
Carbohydrates	23.7	52.7	13.9	49.6	48.7	19.2
N-containing compounds	32.3	67.4	11.0	51.6	26.1	23.6

The ion intensities of these compound classes were related to the amounts of volatile organic matter upon pyrolysis (Fig. 2). The resulting relative intensities of SOM constituents appear largely unchanged with time for the clay fraction. Major differences are generally observed for the fine and medium silt fractions. The large values for phenols, lignin monomers, and lignin dimers in medium silt of the 13th year sample are

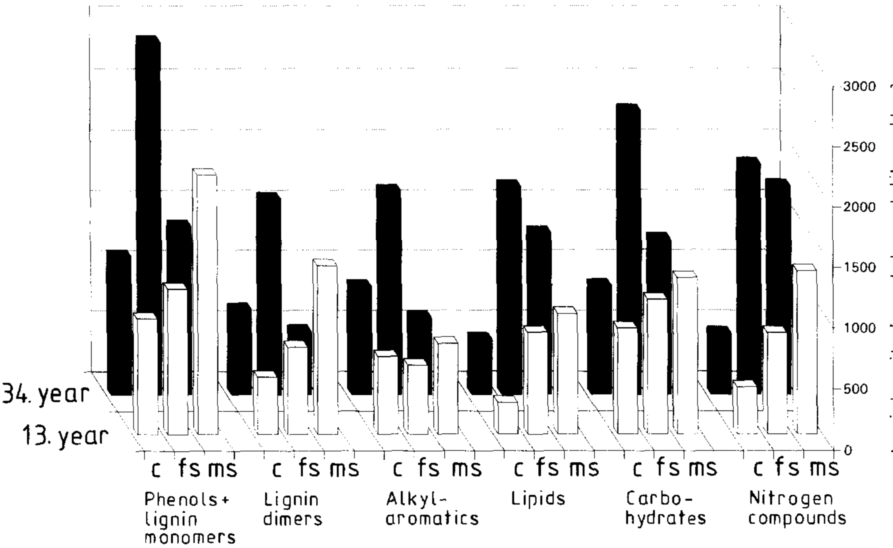

Fig. 2. Quantitative comparison of selected compound classes of SOM in different particle-size fractions of the 13th and the 34th experimental year (*c*: clay, <2 µm; *fs*: fine-silt, 2—6.3 µm; *ms*: medium-silt, 6.3—20 µm).

absent in the 34th experimental year. After this period of time, these substances are highly abundant in fine silt. In this fraction, an enrichment in alkylaromatics and lipids is also observed.

A comparison of the data in Tables 2 and 3 indicates, in general, even stronger differences in the molecular-chemical composition between size fractions than between whole soil samples from the different experimental years. The tendency of increased ion intensities of carbohydrates and N-containing compounds in passing from medium silt to clay was also observed in two treatments of the 108-year-old 'Eternal Rye Cultivation' experiment at Halle, Germany (Schulten & Leinweber 1991). Moreover, this observation is in line with the results of wet chemical determinations of N-containing compounds (Schnitzer & Ivarson 1982; Christensen & Bech-Andersen 1989) and carbohydrates in size fractions (Cheshire et al. 1989). Thus, it is suggested that particle size is possibly of greater influence for the retention of these SOM constituents than soil age or management.

The present study enables the assignment of particular enrichments of organic matter in fine silt to specific compound classes of SOM. As an example, the relative abundances of SOM compounds in Fig. 2 indicate a net transfer of phenols, lignin monomers and lignin dimers from medium silt toward fine silt between the 13th and the 34th year of the experiment.

Thus, the decomposition, transfer to, and stabilization in fine silt and clay are larger than the subsequent delivery of organic substances from primary sources to medium silt. For carbohydrates, this pathway of decomposition of plant tissue from coarser-sized and subsequent transfer to finer-sized fractions was also suggested by Turchenek & Oades (1979), based on extensive particle-size and density fractionations and monosaccharide analyses. The larger amounts of alkylaromatics, lipids and carbohydrates in fine silt of the 34th year can not by explained by decomposed organic matter from medium silt, but indicate additional input of these substances from other sources, e.g. from soil organisms or root exudates or necromass. This is in agreement with a model for the oxidative decomposition of plant materials, proposed by Baldock et al. (1992) on the basis of CP/MAS ^{13}C NMR spectroscopy. The large redistributions between medium and fine silt (Fig. 2) confirm the importance of noncolloidal size fractions for SOM turnover. This was also found in the four other fertilization treatments of this pot experiment (Leinweber & Reuter 1992).

Thermal evolution of selected classes of SOM compounds

The thermal evolution of carbohydrates and N-containing compounds (Fig. 3), of phenols, lignin monomers and lignin dimers (Fig. 4), and of alkylaromatics and lipids (Fig. 5) is illustrated for Py-FIMS of particle-size fractions of the 13th and 34th experimental year. In general, the sequences of summed ion intensities for these compound classes, plotted versus the pyrolysis temperature, result in characteristic curves of either gaussian-like or bimodal shape. A clear shift of thermal evolution toward higher pyrolysis temperatures is observed from medium silt to clay. The thermal release of pyrolysis products assigned to carbohydrates reaches a first maximum between 330 and 380 °C. This is followed by a second maximum at 520—580 °C. The thermal evolution curves of N-containing compounds are similar to those of carbohydrates, although maxima are registered at somewhat higher temperatures (see Fig. 3a, b). Phenols and monomeric lignin subunits reach maxima of their thermal evolution at 360—400 °C and at 540—600 °C. The peak temperatures dropped from 560 °C and 430 °C in clay to 530 °C and 410 °C in fine silt and 400 °C in medium silt (13th year, Fig. 4a). A similar shift is also observed in the sample from the 34th experimental year (Fig. 4b). Lignin dimers are characterized by evolution maxima at 20—40 K higher temperatures, in comparison to phenols and lignin monomers. In addition, no low-temperature pyrolysis is observed for lignin dimers in the clay and fine-silt fractions. The temperature profiles for lipids and alkylarmatics (Fig. 5) are

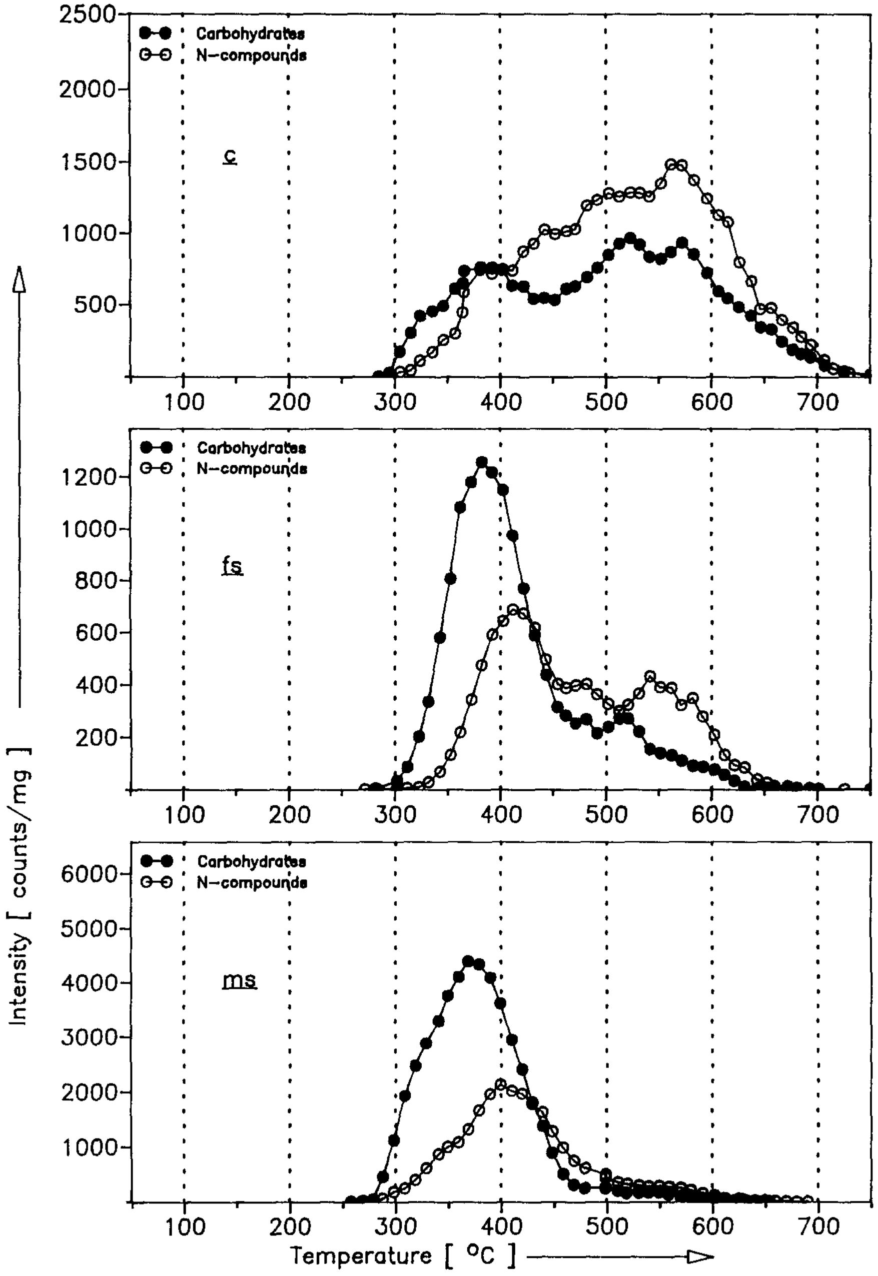

Fig. 3a. Temperature profiles for carbohydrates and N-containing compounds of SOM in different particle-size fractions clay (*c*), fine silt (*fs*) and medium silt (*ms*) from the 13th experimental year (Normalization to 1 mg sample).

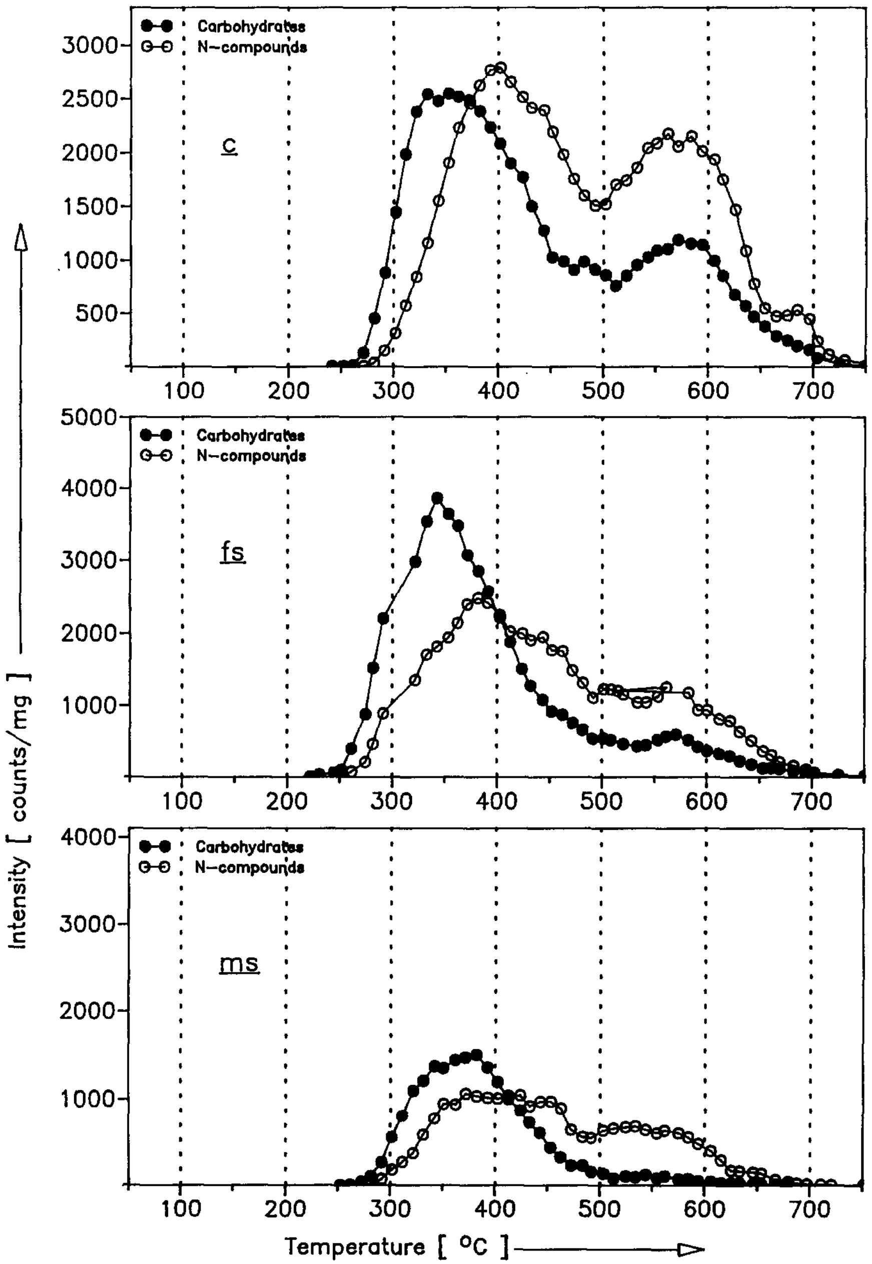

Fig. 3b. Temperature profiles for carbohydrates and N-containing compounds of SOM in different particle-size fractions *c*, *fs* and *ms* from the 34th experimental year (see Fig. 3a).

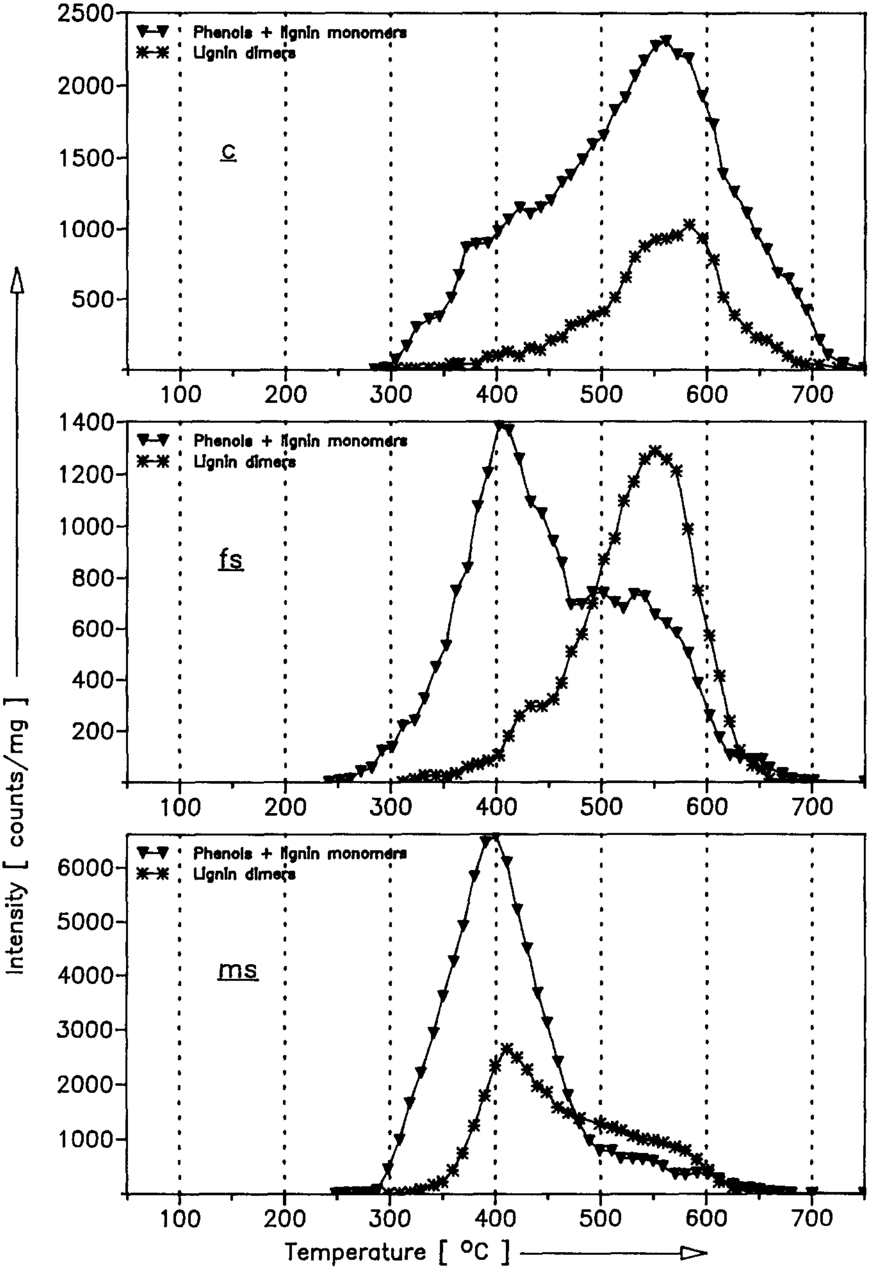

Fig. 4a. Temperature profiles for phenols, lignin monomers and lignin dimers of SOM in different particle-size fractions *c*, *fs* and *ms* from the 13th experimental year (see Fig. 3a).

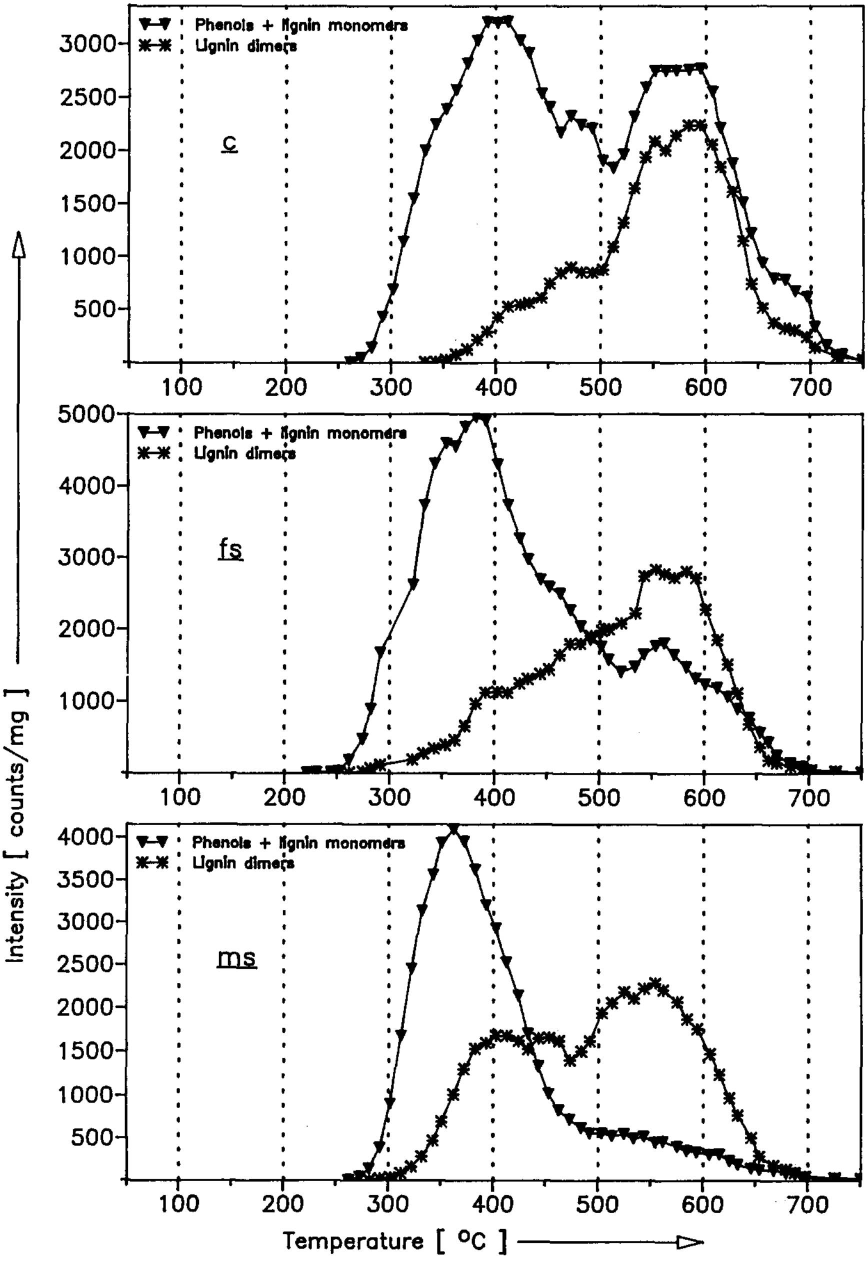

Fig. 4b. Temperature profiles for phenols, lignin monomers and lignin dimers of SOM in different particle-size fractions *c, fs* and *ms* from the 34th experimental year (see Fig. 3a).

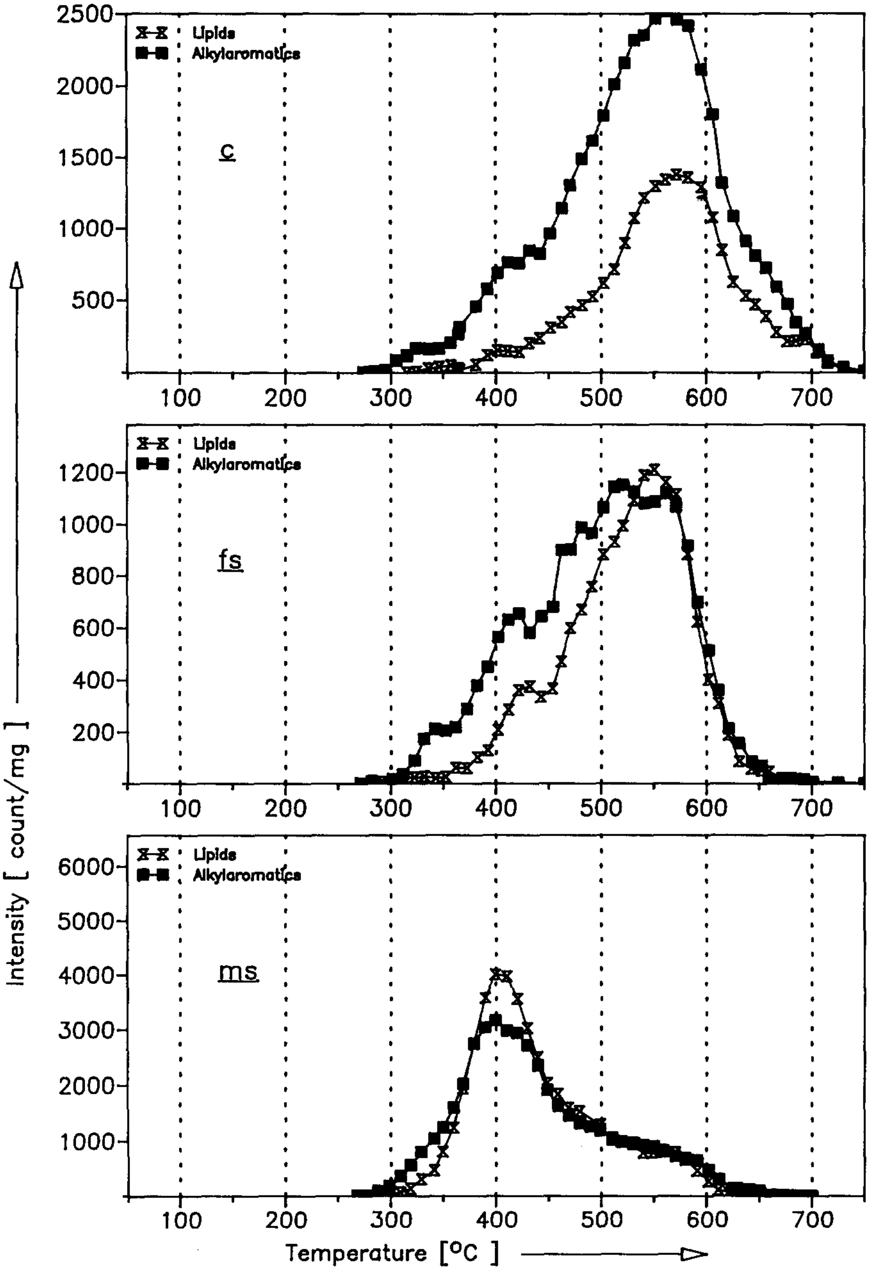

Fig. 5a. Temperature profiles for lipids and alkylaromatics of SOM in different particle-size fractions *c*, *fs* and *ms* from the 13th experimental year (see Fig. 3a).

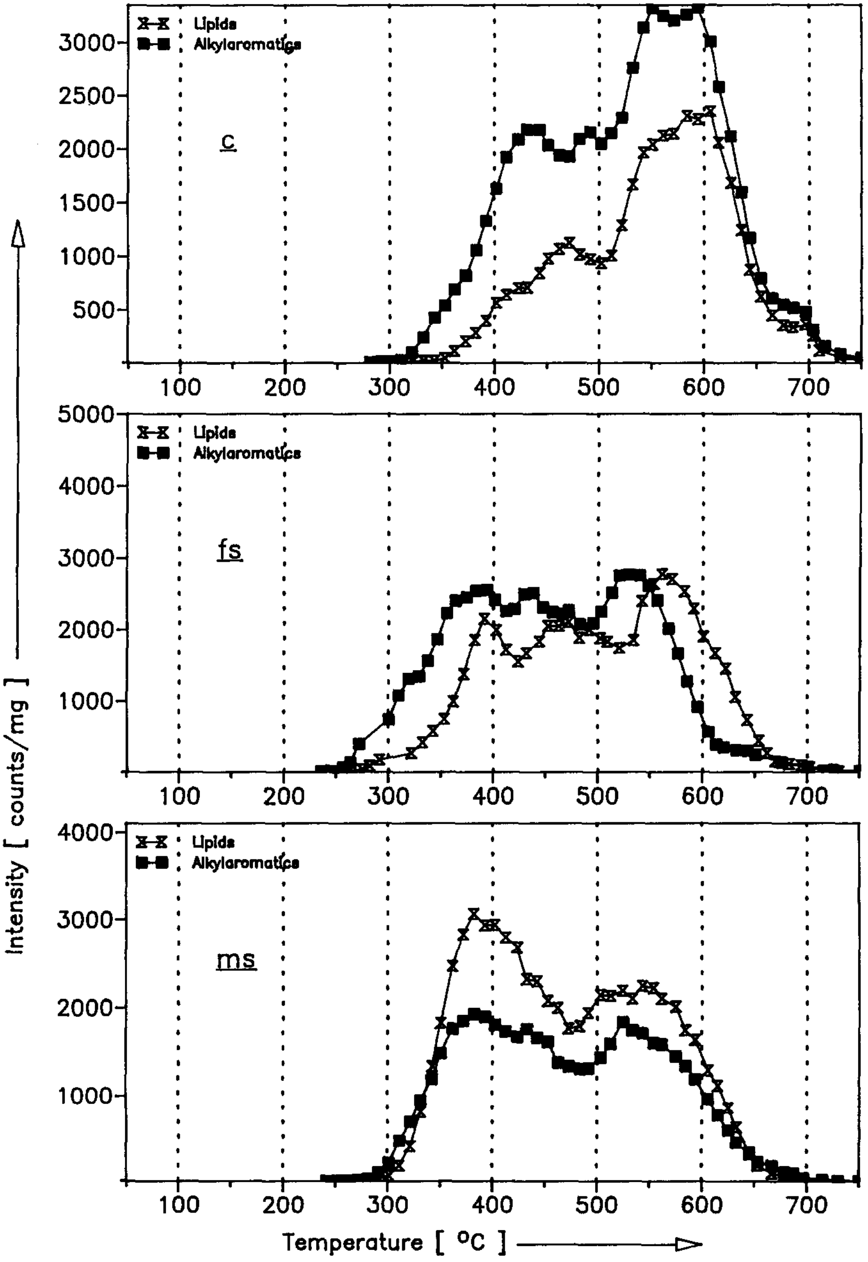

Fig. 5b. Temperature profiles for lipids and alkylaromatics of SOM in different particle-size fractions *c*, *fs* and *ms* from the 34th experimental year (see Fig. 3a).

very similar, showing an approximately Gaussian-distribution of ion intensities in the 13th year. The maxima of thermal release are at 560—580 °C in clay and show a shift toward lower temperatures in fine silt (520—550 °C) and medium silt (400 °C). The samples from the 34th experimental year also show bimodal evolution curves, resulting from low- (380—480 °C) and high-temperature pyrolysis (520—600 °C).

With aging, the development of SOM is indicated by the lower-temperature evolution of phenols, lignin monomers, carbohydrates, N-containing compounds and alkylaromatics in clay and fine silt of the 34th year. On the other hand, the comparison of the corresponding curves from the 13th and 34th year also shows that lignin dimers, alkylaromatics and lipids are registered at increased pyrolysis temperatures in all three fractions in the 34th year. This indication of increased thermal energy for evolution is to a lesser extent also observed for phenols, lignin monomers, and N-containing compounds in clay and fine silt (see Figs. 3, 4 and 5).

Various models have been proposed to explain the stability of organic compounds in the soil environment. Jenkinson (1981) distinguished between resistant plant material, physically protected and chemically stabilized organic matter. In an ecosystem model for grasslands, Parton et al. (1988) subdivided the organic C pool into metabolic and structural C from plant residues, into active soil C, slow soil C and passive soil C. However, a distinct and quantitative separation of these very complex and heterogenous pools from soil and their analysis is difficult (Christensen 1992). The present study shows that physical fractionation according to particle size followed by temperature-resolved Py-FIMS enabled the monitoring of thermal properties of selected important SOM constituents which correspond to changes in the stability of chemical bonds. The maximum thermal evolution of carbohydrates (370—380 °C, fine and medium silt), and of phenols and lignin monomers (360—400 °C) (Figs. 3 and 4) are in line with decomposition studies of various lignocellulosic materials by thermogravimetry (Bilbao et al. 1987, 1989a, b). Accordingly, grass residues from the long-term pot experiment were largely pyrolyzed at 400 °C (Schulten et al. 1992). Moreover, these temperature profiles confirm results of integrated spectra for distinct temperature-ranges, in particular the view that not only aromatics, such as lignin components, but also aliphatics and N-containing compounds can contribute to high-temperature pyrolysis of SOM (Leinweber et al. 1992). The shifts of the evolution maxima toward higher temperatures in passing from medium silt to clay indicate that a larger amount thermal energy is required for the evolution of the observed substances in finer size fractions. It is suggested that these substances are either stabilized by C-C bonds in the humic structures or more strongly bound to the mineral matrix. The latter follows from the shift of evolution maxima toward higher temperature with higher specific surfaces and a larger content of three-layer silicates (Table 1). However, the influence of particle size on mass transfer of the pyrolysis products has to be considered too as recent observations of mixtures of humic substances with basalt, quartz, iron oxide and different clay minerals showed (Schulten & Leinweber 1993). Thus, further experimental evidence of a thermal stabilization of SOM compounds due to organomineral bonding is needed.

Two different trends were observed by DTA, TG (Leinweber & Schulten 1992) and Py-FIMS (Figs. 3—5) for the influence of the duration of SOM development (13th year versus 34th year) on the thermal evolution of SOM associated with size fractions.. These were an enrichment of thermolabile substances with time on the one hand and a shift of SOM decomposition toward higher temperature on the other. The thermolabile and/or loosely bound substances, enriched with clay and fine silt during the last two decades of the experiment, are identified as carbohydrates, N-containing compounds, phenols, lignin monomers and alkylaromatics. This is explained by the input of plant constituents and their microbial turnover products, that enter clay and fine silt during decomposition of roots and stubble, as can also be concluded from the redistribution patterns in Fig. 2. The shift of DTA effects and TII maxima toward higher temperature, observed most clearly in medium silt (Leinweber & Schulten 1992), results largely from lignin dimers, alkylaromatics and lipids. Obviously, these molecular building blocks reach a higher energetic status during 'maturation' of SOM. This can be explained by their three-dimensional crosslinking, whereby arylalkyl combinations seem to be of particular importance. Among the above listed substances, alkylaromatics were recently proposed as major building blocks of humic substances (Schulten et al. 1991; Schulten & Schnitzer 1992, 1993b). The present data indicate that the incorporation of molecular subunits into a stable, three-dimensional network appeas to be a principal biogeochemical process during formation and maturation of humic substances. Surprisingly, in terms of soil formation, this seems to progress rather rapidly. Finally, from the methodological point of view, it is important to mention that we found so far no indication of catalytic effects of the soil clays during SOM pyrolysis.

Concluding remarks

On the basis of the present study, it is only possible to offer some preliminary conclusions about the influence of the mineral matrix on the molecular-chemical composition of SOM and about the types of chemical bonds between soil organic constituents and between SOM and minerals. This is due to our limited knowledge of the influence of mineral matrices (particle size, mineral species) on mass transfer during pyrolysis and on the SOM structure/pyrolysate relationship. However, our initial results indicate a major influence of the mineral matrix on newly formed SOM:

(1) Stronger differences are found between size fractions representing samples with different reactive surface and mineral composition than between whole soil samples from different experimental years;
(2) Relationships exist between the specific surface and the mineral composition of a distinct fraction and the quality of SOM associated with it: clay fractions, richer in three-layer silicates, appear to accumulate N-containing compounds, phenols, lignin monomers and carbohydrates. Medium and fine-silt fractions, containing more quartz and feldspars and less three-layer minerals, yield more intense signals for lignin dimers and lipids;
(3) In addition to (2), strong differences between the size fractions are observed for the thermal energies required for the evolution of the selected SOM constituents from humic- and/or organomineral-bonding sites. High energy is required to release lignin subunits, lipids and alkylaromatics from clay. Less energy is required to evolve the same compounds from medium silt;
(4) Organic substances in different size fracations undergo different transformations over a 20-year-period of SOM development in a steady-state C_{org} level. Especially, SOM constituents characterized by a low level of energy required for thermal evolution, such as phenols, lignin monomers, lignin dimers, lipids, carbohydrates and N-containing compounds from plant residues in medium silt, are partly lost from this fraction and transfered to finer-sized fractions and/or are incorporated into bonds of a higher thermal stability.

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