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Soil organic matter composition and pesticide bonding in sandy soils in relation to groundwater protection in the Northwest German Lower Plain

Abstract In sandy gleyic soils with a low groundwater table under arboriculture in Northwest Germany, a wide variation of groundwater pollution by pesticides has been observed. We therefore examined data on microbial activity and soil organic matter composition by wet chemistry, cross-polarization magic-angle spinning and ^{13}C nuclear magnetic resonance, and pyrolysis–field ionization mass spectromy. However, neither microbial activity nor the soil organic matter composition of cultivated topsoils explained the differences in xenobiotic leaching into the groundwater. Data from Anthrosols suggested that these soils have a higher capacity for pesticide bonding because of high amounts of aromatic and carboxylic C moieties in the soil organic matter. However, despite the same pesticide inputs and time of application, the leached output from these soils was higher than that from the Podzols. Initial data from subsoil investigations suggest that the presence of a spodic horizon most likely reduces groundwater pollution by pesticides. Studies to assess fixation capacity and desorption kinetics in Bh horison seem warranted.

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Introduction

Applications of herbicides are used to control weeds in cultivated soils (Cheng 1990; Blume and Ahlsdorf 1993). In Germany maize production and arboriculture require well contrived and intensive herbicide management in order to restrain weeds due to the reduced soil tillage (Heitefuss 1987; Domsch 1992). Apart from weed control, insecticides and nematicides are used to control parasite activity. These practices have induced an accumulation of pesticide residues and/or metabolites in soil or have polluted groundwater and drinking water (Blume and Ahlsdorf 1993). Especially in sandy soils, anthropogenic chemicals are translocated in complex with dissolved compounds in the leaching water (Domsch 1992; Linn et al. 1993). In the Northwest German Holsteinische Geest, a landscape from Pleistocene sands, the soils are used for fodder maize production or for arboriculture (Blume 1986). Because of intensive cultivation the native Podzols are often modified in the topsoil and sometimes in the deeper horizons, and recently were classified as Aric or Cumulic Anthrosols (FAO 1989). In the Holsteinische Geest, Ahlsdorf (1991) discovered a wide range of concentrations of chlortoluron-polluted groundwater under different soil types (Fig. 1). Surprisingly, with similar water regimens and soil properties and despite the highest soil organic matter content (Ahlsdorf 1991) the chlortoluron transfer into the groundwater was considerable higher below the Gleyi-cumulic Anthrosol in comparison to all the other soils (Fig. 1). The behaviour of simazin and aldicarb showed a similar pattern (Ahlsdorf 1991).

Soil organic matter and microbial activity are the most important soil parameters that influence the fixation and/or degradation of organic chemicals, provided the soils are similar in texture and pH (Katan and Aharonson 1989; Senesi and Chen 1989; Cheng 1990; Howard et al. 1991; Blume et al. 1992; Domsch 1992; Linn et al. 1993). Therefore, we examined data on microbial activity as revealed by microbial biomass and enzyme activities, and soil organic matter composition as revealed by wet chemistry, cross-polarization magic-angle spinning ^{13}C nuclear
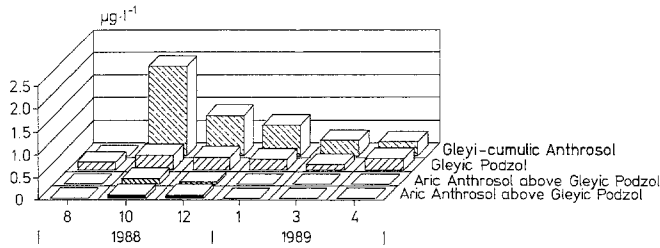
Fig. 1 Concentration of chlortoluron in the groundwater below different soils in the Northwest German Holsteinische Geest from Pleistocene sands (adapted from Ahlsdorf 1991)

magnetic resonance (NMR) spectroscopy, and pyrolysis–field ionization mass spectrometry, in an attempt to understand the findings of Ahlsdorf (1991). Provisional recommendations for landscape planning and possible land use guidelines were deduced from this study.

Materials and methods

Soils and site

Selected soil properties are summarized in Table 1. The general determinations were carried out according to Schlichting et al. (1995). Soil texture was analyzed by a combination of sieving and elutriation, pH was measured in 0.01 M CaCl$_2$, total organic C after dry combustion (see Wet chemistry), and total N by Kjeldahl digestion and determined as NO$_3^-$ in a flow-injection analyzer (Jones 1991). Detailed data on the spodic horizons are given in Beyer (1996).

Microbiology

Microbial biomass was determined according to the substrate-induced respiration method suggested by Anderson and Domsch (1978). After conditioning at 22 °C for 1 week (storage at 4 °C), a moist soil sample equivalent to 50 g oven-dry soil was amended with a powder mixture containing 150 mg glucose and 500 mg talcum. The CO$_2$ evolution rate was measured hourly, using the method described by Heinemeyer et al. (1989), where each sample was continuously purged with air (250 ml min^{-1}). The CO$_2$ evolved was measured using an infrared detector. Soil microbial biomass C was calculated from the maximum initial respiratory response in terms of mg C g^{-1} soil as 40.04 mg CO$_2$ g^{-1} +3.75 (Anderson and Domsch 1978). Dehydrogenase activity was determined according to the classical 2,3,5-Triphenyltetrazolium chloride (TTC) method from Casida et al. (1964) with modifications from Thalmann (1968). Moist soil (5 g) was weighed into a glass tube and treated with TTC. The tubes were purged with N$_2$ and sealed with a rubber plug. The content of each tube was mixed and incubated for 24 h at 30 °C in the dark. After incubation the red triphenylformazan (formed by the reduction of TTC was extracted and determined at 485 nm in a photometer. Alkaline phosphatase activity was determined according

to Hoffmann (1966). About 10 g moist soil was placed in a 100-ml Erlenmeyer flask and treated with toluol and bisodiumphenylphosphate in a buffer solution. The content was mixed, and the flasks were sealed with rubber plugs and incubated for 5 h at 37 °C in the dark. After incubation the cleaved phenol was coloured by adding 2,6-dibromoquinone imide chloride and determined at 578 nm in a photometer.

Wet chemistry

Air-dried, ground (<2 µm) soil samples were treated according to Beyer et al. (1993a). Organic C in the solid and liquid state was measured by dry combustion in a Coulomat 702 (Ströhlein Instruments, Kaarst, Germany). Dry soil samples or freeze-dried extracts were heated (600 °C) in an induction furnace under O$_2$; CO$_2$ was trapped in Ba(OH)$_2$. The determination of methoxyl groups in order to quantify lignin was carried out by the Zeisl–Pregl procedure (Hauptmann 1992). The OCH$_3$-C in soils was demethylized into methyl iodide by boiling each sample with hydroiodic acid. Methyl iodide was hydrolysed into methanol and silver iodide, which was determined gravimetrically. Lignin was estimated as seven times the OCH$_3$ content. Proteins were estimated by multiplying α-NH$_2$-N by 6.25. The α-NH$_2$-N was determined after extraction with 10 M HCl and 1 M formic acid (10:1) according to Stevenson and Cheng (1970) by using the ninhydrin reaction (triketo-hydrindine hydrate). Lipids, resins, and waxes were extracted with ethanol/benzene. Polysaccharides were extracted successively in inorganic acids. The humic fractions were extracted by the classical NaOH procedure (Schlichting et al. 1995). Further details of the extraction have been presented by Beyer (1995).

Solid-state cross-polarization magic-angle spinning ^{13}C NMR spectroscopy

These ^{13}C-NMR spectra were taken at 2.3 Tesla (25.2) MHz in a Bruker MSL 100 equipped with a commercial 7-mm cross-polarization magic-angle spinning probe at a rotation frequency of 4 kHz. A contact time of 1 ms was used. Due to short T$_{1H}$ (relaxation time) in soil organic matter a recycle delay of 0.3 s was chosen. The chemical shift is given in TMS (tetramethylsilane) (0 ppm) scale. Quantitative data were obtained with the integration routine of the spectrometer. The subdivision of the spectra follows the internationally used scheme (Wilson 1987): alkylic units (0–46 ppm), O-alkylic units (46–110 ppm), aromatic units (110–160 ppm), and carboxylic units (160–210 ppm). Further details are given by Fründ and Lüdemann (1989). Distribution of the extracted litter compounds among the various NMR subunits was carried out according to Beyer (1995) as follows: alkyl region: 100% of lipid C, 41% of protein C; O-alkyl region: 100% of polysaccharide C, 24% of protein C, 44% of lignin C; aromatic region: 5% of protein C, 56% of lignin C; and carboxyl region: 30% of protein C.

Pyrolysis–field ionization mass spectrometry

The pyrolysis-field ionization mass spectra of the Bh horizons were recorded using a double-focusing Finnigan MAT 731 mass spectrometer, using a heatable/coolable direct-introduction system with electronic temperature-programming (IGT, Much, Germany), adjusted to

Table 1 Selected properties of topsoils under cultivation in the Northwest German Holsteinische Geest

No.	Soil type	Sand (g kg^{-1})	Silt (g kg^{-1})	Clay (g kg^{-1})	pH (CaCl$_2$)	TOC (mg g^{-1})	Total N (mg g^{-1})	C:N
CW5	Gleyic Podzol	710	230	60	5.2	26	1.6	16.3
CW6	Gleyic Podzol	820	140	40	4.7	34	3.2	10.6
CW7	Gleyi-cumulic Anthrosol	770	180	50	4.7	14	1.6	8.8
CW8	Gleyi-cumulic Anthrosol	790	180	50	5.8	15	1.6	9.4

the +8 kV potential of the ion source. The sample weights were increased with decreasing total organic C concentrations to produce strong, approximately equal total ion intensities. The sample weights ranged from 4.9 to 11.7 mg air-dried, ground soil samples. To determine the percentage of volatilized matter, all samples were weighed before and after each analysis (error±0.01 mg). The samples were heated in a high vacuum from 50 °C to 650 °C at a heating rate of approximately 0.5 °C s^{-1}. About 60 magnetic scans were recorded for the mass range 16–1000 daltons during the heating. These single spectra were integrated by the Finnigan MAT SS 200 data system, resulting in a summed spectrum for each measurement. Three replicates were carried out for each sample. The summed spectra were averaged to one survey spectrum.

The assignment of pyrolysis products was based on studies of model compounds (Sorge et al. 1993a), plant materials (Simmleit and Schulten 1989), extracted humic fractions (Schulten and Schnitzer 1992), and soils (Hempfling and Schulten 1990, 1191; Sorge et al. 1993b), using several pyrolysis measurements. On the basis of these studies, signals of soil organic matter biomarkers in pyrolysis–field ionization mass spectra of humic fractions and soils have been proposed (Schnitzer and Schulten 1992). Nominal masses were tentatively assigned to six classes of biomarkers (carbohydrates, phenols and monomeric lignin units, dimeric lignin units, lipids, alkylaromatics, and N-containing pyrolysis products). Detailed descriptions of the procedure for analyses of terrestrial and aquatic humic fractions (Schulten 1987) and whole soil samples (Schulten 1993) have been published.

Results

Table 2 summarizes the microbiological data obtained from Ap horizons. There were no clear differences between soils in the values for microbial parameters in the bulk soil samples (Table 2). However, in the Podzols total organic C was a little higher (Table 1), which obviously affected the microbial biomass level. Thus, the ratio of microbial C to total organic C (Table 2) reflects the higher percentage of microbial C in the Cumulic Anthrosols (Anderson and Domsch 1985, 1989) and suggests a significantly higher microbial C turnover in these soils, as suggested by Wu and Brookes (1988). Pesticide decomposition in the topsoil was not affected by these differences. Surprisingly, the soils with high microbial activity were characterized by a high pesticide output, even though equal pesticide inputs were applied at all four sites and the applications were made at the same time (Ahlsdorf 1991). This observation is in contrast to other results reported recently (Cheng 1990; Linn et al. 1993).

The litter and humic compound distribution reflects a different pattern in the two soil types (Table 3). The high lipid fraction is typical of the native Podzols, but these molecules affect aggregate stability (Hempfling et al. 1990) rather than xenobiotic fixation (Senesi and Chen 1989). However, a high yield of humic acids in the Glcyiv Podzols suggests a high binding capacity, provided these fractions are rich in phenolic units or aromatic carboxyl acids, whereas high polysaccharide and fulvic acid contents in the Anthrosols suggest a higher percentage of carboxyl C (Beyer 1995), which is another chemical structure that can bond with organic pesticides (Senesi and Chen 1989).

The NMR spectra of all soil samples look very similar (Fig. 2), whereas the quantitative data (Table 4) confirmed the higher alkyl C content of the Podzols suggested by the wet chemical lipid fractions (Table 3). Parts of these structures may be derived from lipidic moieties in the humic compounds (Wilson 1987; Schulten and Schnitzer 1992). Beyond this, the higher carboxyl content in the Anthrosols suggested by the oxidized (wet chemical) polysaccharide and fulvic acid fractions (Table 3) was also found with NMR spectroscopy. However, the humic substances in the Podzol soil organic matter did not appear to contain the high proportion of aromatic structures suggested by the high humic acid fraction (Table 3). In contrast to the relative soil organic matter composition, discussed so far, Fig. 3 shows the mean absolute amounts of soil organic matter units in the cultivated soil layer from 0 to 30 cm

Table 2 Microbial parameters in topsoils under cultivation in the Northwest German Holsteinische Geest (*TPF* triphenyl formazan, *TOC* total organic C, *PN* phenol)

No	Soil type	Microbial biomass		Dehydrogenase activity		Alkaline phosphatase activity	
		mg kg^{-1} soil	mg C g^{-1} TOC	mg TPF kg^{-1} soil	mg TPF g^{-1} TOC	mg PN kg^{-1} soil	mg PN g^{-1} TOC
CW5	Gleyic Podzol	333	13.1	189	7.4	261	10.2
CW6	Gleyic Podzol	370	11.7	168	5.3	164	5.2
CW7	Gleyi-cumulic Anthrosol	266	18.5	86	6.1	202	14.4
CW8	Gleyi-cumulic Anthrosol	320	21.3	110	7.3	104	6.9

Table 3 Soil organic compounds (mg C g^{-1} total organic C) in topsoils under cultivation in the Northwest German Holsteinische Geest (*CW5 CW6*, Gleyic Podzols; *CW7 CW8*, Gleyi-cumulic Anthrosols)

Soil no.	Lipids	Polysaccharides	Protein	Lignin	Fulvic acids	Humic acids	Humins
CW5	144	79	33	123	42	438	141
CW6	215	62	34	92	37	446	114
CW7	51	128	40	115	66	350	240
CW8	55	145	41	140	54	306	259

Table 4 Cross-polarization magic-angle spinning ^{13}C nuclear magnetic resonance C units, expressed as a percentage of total organic C, in topsoils under cultivation in the Northwest German Holsteinische Geest (*Alkyl* alkylic units, *Aromat* aromatic units, *Carboxyl* carboxylic units)

No.	Soil type	Alkyl-C) (0–46 ppm)	*O*-Alkyl-C (46–110 ppm)	Aromat-C (110-160 ppm)	Carboxyl-C (160–210 ppm)
CW5	Gleyic Podzol	38	45	10	7
CW6	Gleyic Podzol	37	45	11	7
CW7	Gleyi-cumulic Anthrosol	31	46	16	9
CW8	Gleyi-cumulic Anthrosol	28	45	19	10
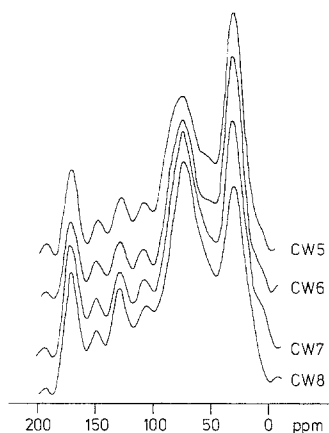
Fig. 2 Cross-polarization magic-angle spinning ^{13}C nuclear magnetic resonance spectra of sandy topsoils under cultivation in the Northwest German Holsteinische Geest (*CW5 CW6*, Gleyic Podzols; *CW7 CW8* Gleyi-cumulic Anthrosols)
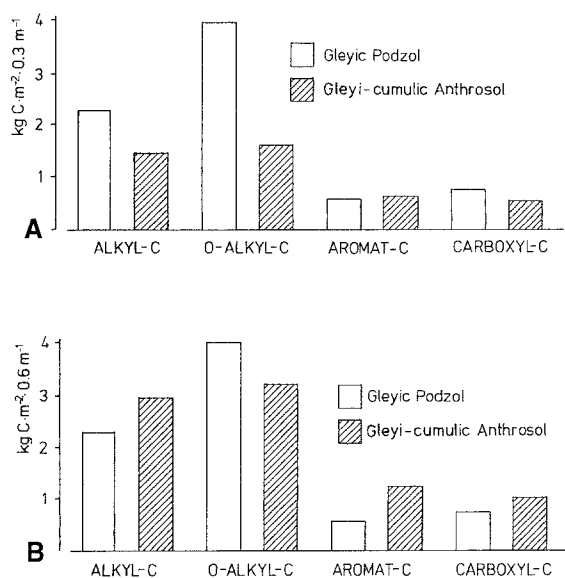
Fig. 3 Mean cross-polarization magic-angle spinning ^{13}C nuclear magnetic resonance (CPMAS ^{13}C-NMR) C units in sandy soils of the Northwest German Holsteinische Geest: **A** cultivated layer (0–30 cm); **B** rooting zone (0–60 cm). *ALKYL* alkylic units, *AROMAT* aromatic units, *CARBOXYL*, carboxylic units

(Fig. 3a) and the rooting zone from 0 to 60 cm (Fig. 3b). Regardless of the higher total organic C contents in the Podzols (Table 1), the relative differences in the aromatic

and carboxylic structures (Table 4) disappeared in the cultivated layer. However, these differences were observed with regard to the total rooting zone in both soil types (Fig. 3b) because the Cumulic Anthrosols contain considerable amounts of soil organic matter in the subsoil (Beyer et al. 1993b). The data from the Anthrosols suggest a higher capacity for pesticide bonding, because of the high amounts of aromatic and carboxylic C moieties (Senesi and Chen 1989).

Discussion

In summary, neither the microbial activity data nor parameters describing the quality of soil organic matter in the Ap horizons sufficiently explained the differences in pesticide leaching presented in Fig. 1. However, only the Gleyi-cumulic Anthrosols had no spodic horizon. In Aric Anthrosols this horizon is preserved despite man-made soil modifications (Ahlsdorf 1991). Therefore we assumed that the presence of a spodic horizon in the subsoil probably causes a higher fixation of anthropogenic organic compounds and reduces their leaching into the groundwater. Figure 4 shows the mean litter and humic compound composition of the cultivated layers (Ap) investigated together with data from typical spodic horizons (Bh) obtained by wet chemistry for comparison. The Bh horizons are characterized by very high amounts of fulvic acids, accumulated by translocation during the podzolization process in former times.

The NMR data for total soil organic matter do not indicate these differences between Ap and Bh horizons clearly (Fig. 5), because the classical humic fractions are rather weakly defined mixtures of several chemical C units (Bey-
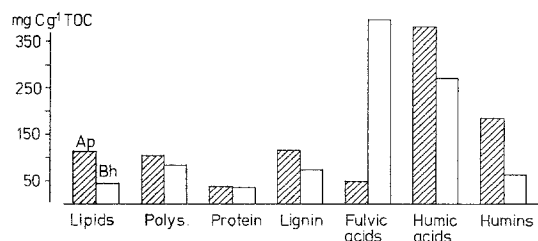
Fig. 4 Mean litter and humic compound composition in sandy topsoils under cultivation (means of Table 3) and spodic horizons (*n* = 18) (data from Beyer 1996). *TOC* total organic C, *Polys.* polysaccharides
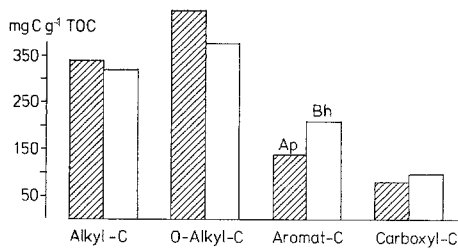
Fig. 5 Mean distribution of CPMAS ^{13}C-NMR C units of total soil organic matter in sandy topsoils under cultivation (means of Table 4) and spodic horizons ($n=10$) (data from Beyer 1996). For further explanations, see Figs. 3, 4
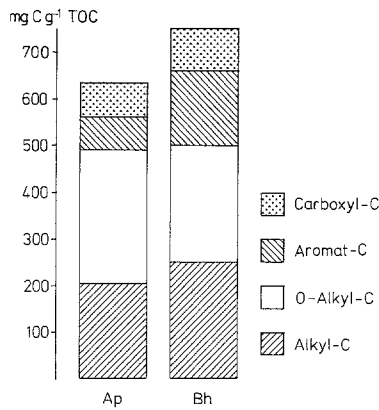

Fig. 6 Mean distribution of CPMAS ^{13}C-NMR C units of the humic matter in sandy topsoils under cultivation and spodic horizons. For further explanations, see Figs. 3, 4

er 1995). However, Fig. 5 suggests a higher aromaticity in the Bh horizons. In Fig. 6 the amounts of C that were not

detected as litter compounds are shown as the remainder after subtraction of the litter substances from the NMR data for total soil organic matter (see Methods). In contrast to the classical humic fractions (Fig. 4), the humified material was chemically characterized and confirmed the considerable importance of non-lignin aromatic structures.

Figure 8 shows averaged pyrolysis–field ionization mass data from Ap horizons of 20 agricultural soils (Sorge et al. 1993b). The volatilized organic matter shows typical signals of carbohydrates, phenols, and lignin monomers, lignin dimers, n-C10 to n-C20 alkyl diesters, n-C16 to Cn-C34 fatty acids, n-C27 to n-C30 alkanes, sterols, and alkylaromatics and N compounds. Additionally, seven Bh horizons from Podzols in Northwest Germany were analyzed by pyrolyis–field ionization mass spectrometry. The two selected spectra of Fig. 7 confirm the suggested soil organic matter composition deduced from wet chemistry and NMR spectroscopy. Beneath the polysaccharide peaks (m/z 82, 96, 110, 132, 144), signals from aromatic units derived from monomeric lignins and phenols (m/z 180, 182, 194), dimeric lignins (m/z 270, 294, 310, 326), and alkylic units derived from lipids (m/z 230, 244, 256), sterols (m/z 396) and alkylaromatics (m/z 206, 218) dominate the spectra. This soil organic matter composition was also determined in recent pyrolysis–field ionization mass spectrometry analyses of spodic horizons (Beyer et al. 1993c; Sorge et al. 1994; Beyer 1996). Mainly alkylic and aromatic components and their combined molecules were detected. Due to the specific soil organic matter composition of the spodic horizons, pesticides are obviously fixed by direct binding as polar species (Senesi and Chen 1989) at the aromatic structure. These moieties are probably responsible for the high binding capacity (Cheng 1990), whereas the alkylic units in the humic matter connect the stiff-ben-

Fig. 7 Thermograms and pyrolysis–mass spectra of spodic horizons (**a** Bsh, **b** Bhs) of a Haplic Podzol in the Northwest German Holsteinische Geest (adapted from Beyer et al. 1993c). *Rel* relative
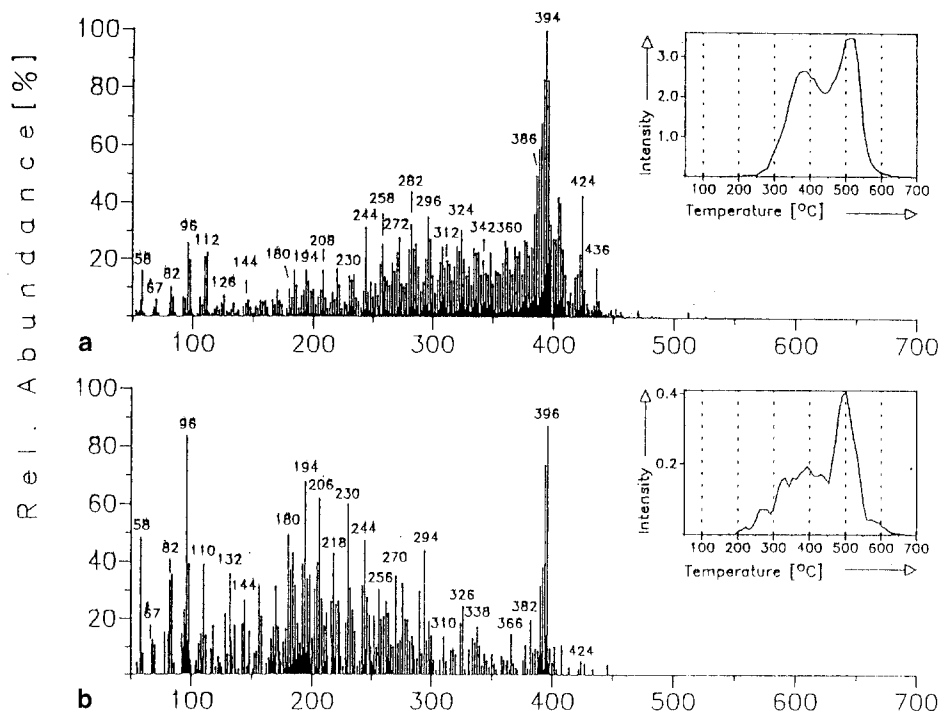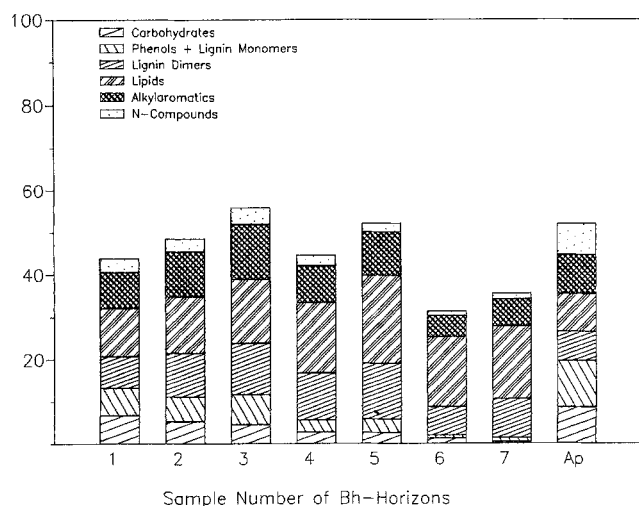
Fig. 8 Relative intensities of selected biomarkers of pyrolysis–field ionization mass spectrometry in sandy spodic horizons in Haplic Podzols (1–7) and the mean of cultivated layers (Ap) in the Northwest German Holsteinische Geest (TII total ion intensity)

zene rings to a flexible, sponge-like molecular system, and organic compounds might be physically trapped in these voids (Schulten 1995). Beyond this, spodic horizons often have high livels of amorphous iron and aluminum hydroxides (Blume 1986) with a variable surface charge that can change greatly with changes in pH, and thus these constituents may serve as a sink for pesticide components under certain circumstances (Beyer 1996).

We conclude that in the sandy gleyic soils of the Northwest German Holsteinische Geest, neither microbial acitivity nor the soil organic matter composition in the cultivated layer were sufficient to explain the different behaviour of herbicides leaching into the groundwater. Nevertheless, in Germany pesticide behaviour in soil has been predicted recently by the humus content in the topsoil layer, provided pH levels and soil textures are similar (Blume et al. 1992). Our preliminary studies, however, suggest that in sandy soils with an intact spodic horizon in the subsoil, the groundwater contamination is much lower. Therefore we assume that the presence of a spodic horizon may prevent, but in any case reduces, groundwater pollution by herbicides in the soils of the Holsteinische Geest with a low groundwater table of 60–100 cm below the soil surface.

Further lysimeter and adsorption/desorption investigations in the laboratory and the field are necessary in order to obtain a better understanding of the processes involved. In Germany, recent soil maps contain adequate information about the presence of spodic horizons (Blume 1992) which could be valuable for landscape planning. If our observations are verified, pesticide applications should be restricted only to soil with an intact spodic horizon, due to the ecotoxicological risk of drinking-water pollution. Moreover, federal land use guidelines should oblige farmers to reduce ploughing depths in order to preserve spodic soil horizons in the unameliorated native Podzols.

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