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Differences in the chemical composition of dissolved organic matter from waste material of different sources

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Abstract The chemical composition of waste-material-derived dissolved organic matter (DOM) was characterized by chemolytic analyses and ^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectroscopy. Dissolved organic matter was extracted by water from an aerobic fermented urban waste compost, a sewage sludge and a pig slurry and then fractionated using the XAD-8 method. The amount of water-extractable dissolved organic carbon (DOC) ranged from 3% in the sewage sludge to 22% in the pig slurry. Dissolved organic matter isolated from pig slurry was equally distributed between hydrophilic and hydrophobic DOC, whereas in the sewage-sludge-derived material the hydrophobic fraction was predominant. Dissolved organic C from the urban waste compost was mainly within the hydrophilic fraction. Wet-chemical analysis and ^{1}H- and ^{13}C-NMR spectra showed that both DOM fractions from the urban waste compost were low in neutral, acidic and amino sugars as well as in lignin-derived compounds. In turn, the materials were rich in low-molecular-weight aliphatic compounds. The chemical structure of both fractions is probably the result of the intensive transformation of urban waste compost during its fermentation. The hydrophilic fractions of DOM from sewage sludge and pig slurry contained considerable amounts of carbohydrates but were also rich in low-molecular-weight aliphatics. The respective hydrophobic fractions had the largest contents of CuO-extractable phenols which may in part derive from sources other than lignin. By contrast with the other materials, the hydrophobic fraction from the pig slurry seemed to contain polymeric rather than low-molecular-weight material. The ^{31}P-NMR spectrum of the hydrophilic DOM fraction from urban waste compost did not show signals of inorganic or organic P compounds while the spectrum of the hydrophobic fraction revealed traces of monoester P, diester P, and orthophosphate. ^{31}P-NMR spectroscopy suggested that both the hydrophobic and hydrophilic fractions from pig slurry did not contain organic P. The hydrophilic DOM fraction from sewage sludge contained orthophosphate, organic monoester P and a little pyrophosphate. The hydrophobic fraction contained mainly organic diester P and smaller amounts of teichoic acids and organic monoester P. Considering that water-soluble fractions of urban waste compost contained no easily plant-available P and a low content of labile organics, we conclude that this material contains less labile nutrients and is more refractory than the soluble constituents of pig slurry and sewage sludge.

Keywords Waste materials · Dissolved organic matter · Chemical composition · Carbon · Phosphorus

Introduction

Application of organic residues and wastes derived from a wide variety of human activities to arable soils has received worldwide attention because of a potential improvement in soil fertility and increase in the organic matter content. Organic waste materials are rarely applied to the soil in a fresh or raw state. Generally, they are processed to obtain a mature, stabilized organic matter with the production of humic-like materials (Senesi et al. 1996).

In the processed organic materials, a part of the organic substances is water soluble (Gigliotti et al. 1997). For this reason, one immediate impact of the application of organic materials to agricultural land is the release of organic matter into soil solution (Riffaldi et al. 1998; Han and Thompson 1999). Even if the amount of dissolved organic matter (DOM) in soil and waste materials is small compared to the bulk organic matter content, it plays a significant role in the transport of nutrients, metals and

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hydrophobic pollutants, and on the microbial activity in soil (Berggren et al. 1990; Liu and Amy 1990; Qualls and Haines 1991; Zsolnay 1996).

Up to now, little is known about the chemical composition of DOM from composts and waste materials. Chefetz et al. (1998) and Wershaw et al. (1996a, b) found that DOM fractions from leaf litter, municipal solid waste compost and soil water had similar features. Nevertheless, these studies also show that the composition of DOM from different types of composts is different, and prolonged composting changes the composition of DOM significantly. In contrast to DOM from composts, DOM from other waste materials such as sewage sludge and pig slurry is far less well characterized. The decomposition of DOM from sewage sludge and pig manure is different from that of DOM from green manure (Zhou and Wong 2000), and this could be due to differences in the chemical composition (Jandl and Sollins 1997; Namour and Müller 1998).

Leenheer (1981) developed a simple fractionation method that uses XAD-8 resin chromatography to separate DOM into operationally defined hydrophilic and hydrophobic fractions. In soil DOM, the hydrophilic fractions include simple organic acids, polyhydroxy phenols, carbohydrates, amino acids and amino sugars while hydrophobic fractions comprise phenols, hydrocarbons, fatty acids, nucleic acids, and quinones (Qualls and Haines 1991; Guggenberger et al. 1994a). All these compounds are typical products of the decomposition of natural organic matter. In waste material, anthropogenic compounds such as residues of surfactants and plasticizers may also contribute to DOM (Ahel et al. 1996; Fujita et al. 1996; Bauer et al. 1998).

The composition of organic-residue-derived DOM may affect the bioavailability of the substrate as well as the transport of metals and colloids when the residue is applied to soil (Han and Thompson 1999; Zhou et al. 2000). Metal transport relates more to the hydrophilic DOM fraction (Berggren et al. 1990; Guggenberger et al. 1994b) whereas hydrophobic micropollutants preferentially interact with the hydrophobic DOM fraction (Kukkonen et al. 1990; Raber and Kögel-Knabner 1997). Bioavailability of the hydrophilic DOM fraction is higher than that of the hydrophobic fraction (Jandl and Sollins 1997; Namour and Müller 1998). However, knowledge of the nature, composition, and reactivity of DOM from different organic waste materials is incomplete and therefore understanding of the impact of DOM in agricultural soils is limited.

In the present work we studied the chemical composition of fractions of different waste-derived DOM, i.e. urban waste compost, sewage sludge and pig slurry. The DOM samples were characterized by wet-chemical methods and ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. The proportions of hydrophilic organic matter in conjunction with the contents of easily degradable compounds such as low-molecular-weight aliphatic acids and carbohydrates were used to estimate the effects on microbial activity when the materials were applied to agricultural land. The possible effects on plant growth were estimated from the content of P and its chemical binding forms.

Materials and methods

Waste materials

Urban waste compost was collected at the municipal waste treatment plant at Perugia (Italy). It was produced mechanically under aerobic conditions by fast fermentation (25 days) from 70% pre-separated refuse material and 30% sewage sludge. The compost had a total moisture content of 29.5% and a pH of 7.6. On a dry-weight basis, it contained 44.2% ash, 26.2% total organic C, 1.9% total N and 0.9% total P.

Anaerobically-digested sewage sludge was obtained from the municipal waste water treatment plant at Perugia (Italy). It had a total moisture content of 89.5% and a pH of 6.9; the sludge contained 36.4% ash, 26.6% total organic C, 5.7% total N and 1.3% total P on a dry-weight basis. During the wastewater treatment, $AlCl_3$ and lime were added to precipitate all soluble C and P.

Pig slurry was collected on a farm in the south of the Po Valley (Italy) after over 6 months of storage in a lagoon. It had a pH of 8.4 and a moisture content of 99.2%. On a dry-weight basis, it contained 0.48% ash, 22.1% total organic C, 18.2% total N, and 1.9% total P.

Dissolved organic matter extraction

Dissolved organic matter was extracted from urban waste compost and municipal sewage sludge by shaking 0.4 kg urban waste compost and 0.8 kg municipal sewage sludge with 4 l deionized and degassed water overnight at room temperature. After centrifugation (2,000 *g*) the supernatants were separated. Pig slurry DOM was obtained by centrifugation of 20 l at 4,000 *g* for 20 min and collection of supernatant.

The solutions from urban waste compost, sewage sludge and pig slurry were filtered through a 0.7-μm GF/F glass microfiber filter (Whatman, Springfield Mill, United Kingdom) and 0.45-μm Supor-450 polysulfone membranes (Pall Gelman Sciences, Ann Arbor, Mich.), then stored at 2°C for a maximum of 2 weeks.

Dissolved organic matter fractionation

Aliquots of 0.6, 3 and 6 l of extracts of urban waste compost, sewage sludge, and pig slurry, respectively, were used for fractionation of DOM. Each solution was diluted to a volume of 6 l, acidified with 6 M HCl to pH 2, and pumped with a peristaltic pump through a 150-ml glass column filled with Amberlite XAD-8 resin (Rohm and Haas, Philadelphia, Pa.) at a flow rate of 6 ml min^{-1}. The hydrophobic fraction of each sample was adsorbed to the resin, whereas the hydrophilic fraction passed through the column. The hydrophobic fraction was eluted from the resin using 2 bed volumes of 0.1 M NaOH. The hydrophobic and hydrophilic fractions were passed through a strongly acidic cation exchange resin (AG-MP 50, BioRad, Richmond, Va.) in order to protonate the organic substances and to remove all cations other than H^{+}. The samples were then freeze-dried.

Elemental analyses

Dissolved organic C concentrations were measured in the bulk solutions and in the column effluents (hydrophilic fractions) using a TOC-5050 analyzer (Shimadzu, Tokyo, Japan). The distribution of DOC among the hydrophilic and hydrophobic fractions was calculated by difference.

Total C of the freeze-dried DOM fractions was analyzed with an elemental CNHS-analyzer (Vario EL; Elementar, Hanau, Germany). The content of total P was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES, Integra XMP; GBC Scientific Equipment Pty, Dandenong, Victoria, Australia) after heating subsamples at 650°C for 5 h and dissolving the residues in 0.5 M H_2SO_4. All analyses were done in duplicate.

Dissolved organic matter fraction characterization

Xylose, arabinose, ribose, rhamnose, fucose, fructose, mannose, galactose, glucose, glucoronic acid and galacturonic acid were analyzed by capillary gas chromatography according to Amelung et al. (1996). From 10 to 50 mg freeze-dried DOM was hydrolyzed with 4 M trifluoroacetic acid at 100°C for 4 h. The monosaccharides released were separated from the humic residue using an Amberlite XAD-7 resin (Rohm and Haas, Philadelphia, Pa.) and from the cations by the use of a Dowex 50 W X 8 cation exchange resin (Dow ChemicalCo., Midland, Mich.). The carbohydrates were transformed into O-methyloxime trimethylsilyl derivatives and analyzed using a capillary gas chromatograph (HP 6890; Agilent Technologies, Palo Alto, Calif.) equipped with an HP-5 fused silica column (25 m length, 0.25 mm internal diameter and 0.33-µm film; Agilent Technologies, Palo Alto, Calif.), flame ionization detector and split-spitless injector. Myo-inositol was added as internal standard before hydrolyses and methyl-glucose as recovery standard before derivatization.

The amino sugars glucosamine, galactosamine, mannosamine, and muramic acid were determined by analyzing 20–100 mg freeze-dried DOM with the method of Zhang and Amelung (1996). After hydrolysis with 6 M HCl for 8 h, the solution was filtered, the pH was adjusted to 6.6–6.8 with 0.4 M KOH, centrifuged at 1,500 *g* for 10 min and the supernatant evaporated to dryness under vacuum at 40°C and then re-dissolved in methanol. Amino sugars were transformed into aldononitrile acetate derivatives and excess acetic anhydride was destroyed with water and 1 M HCl before the amino sugar derivatives were extracted from the aqueous solution with dichloromethane. Amino sugar derivatives were analyzed by capillary gas chromatography using an HP-5 fused silica column of 25 m length and flame ionization detection. Myo-inositol was added as internal standard before hydrolyses and methyl-glucamine as recovery standard before derivatization.

Alkaline CuO oxidation was carried out according to Hedges and Ertel (1982). The method involves oxidation of 10–50 mg freeze-dried sample with CuO and 2 M NaOH at 170°C under pressure for 2 h. After precipitation of humic acids by acidification with 6 M HCl and centrifugation at 2,000 *g*, the generated lignin-derived phenols were purified using an octadecyl (C_{18}) column (500 mg resin) and analyzed as trimethylsilyl derivatives by capillary gas chromatography using an HP-5 fused silica column of 25 m length, flame ionization detector and split-spitless injector. To increase the recoveries, 50 mg glucose was added prior to the CuO oxidation (Amelung et al. 1999). Ethylvanillin was added as internal standard before hydrolysis and phenylacetic acid as recovery standard before derivatization.

Quantification of chromatograms was done by electronic peak area integration. For selected samples, the peak assignment of all used wet-chemical methods was verified using capillary gas chromatography with mass-selective detection.

Liquid-state ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded on an Avance DRX 500 spectrometer (11.7 T; Bruker, Karlsruhe, Germany) at a temperature of 290 K. For measurement, 150 mg each freeze-dried sample were dissolved in 3 ml 0.5 M NaOD/D_2O.

The ^{1}H-NMR spectra were performed using 5-mm sample tubes under the following conditions: spectrometer frequency 500 MHz, homonuclear presaturation for solvent suppression, 1.16 s acquisition time, 1 s delay time, 2 Hz line-broadening factor. Chemical shifts were given relative to the resonance of tetramethylsilane.

The ^{13}C-NMR spectra were recorded using 10-mm sample tubes under the following conditions: spectrometer frequency 125 MHz, inverse-gated decoupling, pulse angle 45°, 0.16 s acquisition time, 1.84 s delay time, 100 Hz line-broadening factor. The measurement conditions were chosen according to recommendations in the literature (Preston 1996). Chemical shifts were given relative to the resonance of tetramethylsilane. Identification of sharp lines resulting from well-defined substances was done at a line-broadening of 10 Hz. The presence of acetic acid was tested by adding a standard solution. Due to the low content of C in the freeze-dried samples of sewage sludge and pig slurry, it was not possible to record reasonable ^{13}C spectra of these materials.

^{31}P-NMR spectra were recorded using 10-mm sample tubes under the following conditions: spectrometer frequency 202 MHz, no proton decoupling, 0.1 s acquisition time, 0.2 s relaxation delay, 20 Hz line-broadening factor. All chemical shifts were measured on the basis of the 85% H_3PO_4 external standard in a 5-mm tube inserted into the 10-mm sample tube before the measurement of each sample.

Signal assignments were made according to literature data (Newman and Tate 1980; Orem and Hatcher 1987; Condron et al. 1990; Kögel-Knabner 1997). The signal areas were calculated by electronic integration.

Results and discussion

In the three waste materials, a considerable amount of the total organic C was found to be water soluble (Table 1). The proportion of extractable C ranged from 3% of the total organic C in the sewage sludge to 22% in the stabilized pig slurry. The low solubility of organic C in the sewage sludge might be due to the addition of Al and lime during the wastewater treatment process. This results in the precipitation of $Al(OH)_3$ and subsequent sorption of DOM (Mazet et al. 1990; Wershaw et al. 1996a). Sorption of organic matter to $Al(OH)_3$ is not easily reversible except under drastic pH conditions (Kaiser and Zech 1999).

The distribution of DOC between hydrophilic and hydrophobic DOM fractions in the three materials varied greatly. The distribution was balanced between the two fractions in the pig slurry DOM whereas in the sewage-sludge-derived material the hydrophobic fraction was predominant. The dissolved organic C of urban waste compost was mainly within the hydrophilic fraction. The

Table 1 Dissolved organic carbon (*DOC*) and dissolved P (*DP*) from different waste materials: urban waste compost (*UWC*), sewage sludge (*SS*), and pig slurry (*PSL*). DOC and DP are given as the proportion of total organic C (*TOC*) and total P (*TP*) present in the parent material

Material	DOC % of TOC	Hydrophilic fraction % of DOC	Hydrophobic fraction % of DOC	DP % of TP
UWC	9.9	61	39	5.0
SS	2.8	8	92	6.4
PSL	22.4	53	47	12.6

Table 2 Chemical characteristics of CuO-extractable phenols in the hydrophilic and hydrophobic fractions of dissolved organic matter extracted from urban waste compost (*UWC*), sewage sludge (*SS*), and pig slurry (*PSL*)

Sample	Σ VSC[a] mg g^{-1} C	S/V[b]	(ac/al)$_V$[c]	(ac/al)$_S$[d]
UWC hydrophilic fraction	0.7	0.9	0.4	0.4
UWC hydrophobic fraction	5.8	1.1	0.4	0.4
SS hydrophilic fraction	0.5	0.7	0.1	0.1
SS hydrophobic fraction	5.2	1.2	0.1	0.1
PSL hydrophilic fraction	5.6	0.6	0.1	0.2
PSL hydrophobic fraction	15.1	1.4	0.2	0.2

[a] Sum of vanillyl, syringyl, and cinnamyl CuO oxidation products
[b] Ratio of syringyl to vanillyl units in CuO oxidation products
[c] Acid-to-aldehyde ratios of the vanillyl units in CuO oxidation products
[d] Acid-to-aldehyde ratios of the syringyl units in CuO oxidation products

Table 3 Hydrolyzable neutral and acidic sugars in the hydrophilic and hydrophobic fractions of dissolved organic matter extracted from urban waste compost (*UWC*), sewage sludge (*SS*), and pig slurry (*PSL*)

Sample	Σ neutral sugars[a] mg g^{-1} C	Σ acidic sugars[b] mg g^{-1} C	(Man+Gal)/(Xyl+Ara)[c] mg g^{-1} C
UWC hydrophilic fraction	21.1	2.9	0.8
UWC hydrophobic fraction	16.7	5.7	1.3
SS hydrophilic fraction	174.6	31.9	1.7
SS hydrophobic fraction	38.3	20.0	2.5
PSL hydrophilic fraction	83.1	32.6	1.0
PSL hydrophobic fraction	12.6	3.1	2.0

[a] Sum of neutral carbohydrates
[b] Sum of acidic carbohydrates
[c] Ratio of mannose plus galactose to xylose plus arabinose

latter concurs with the results of Chefetz et al. (1998) who found between 30% and 40% of DOC extracted from composted municipal solid waste in the hydrophobic DOM fractions. We assume that the large proportion of hydrophilic DOM was due to the composting-fermentation processes. In contrast, Zhou et al. (2000) found that the hydrophobic fraction of DOM of sewage sludge was smaller than that of DOM from composted sewage sludge. Of all materials used in our study, the sewage sludge showed the smallest proportions of DOC in the hydrophilic fraction. This supports the finding that in groundwater recharged by reclaimed waste waters only 16% of the DOC was in the hydrophilic fraction (Fujita et al. 1996).

Compared to litter-derived DOM from forests (Guggenberger and Zech 1994; Guggenberger et al. 1998; Kaiser et al. 2001), the DOM fractions from the urban waste compost had small concentrations of lignin-derived CuO-degradation products (Table 2). The values agree with the small proportions of hydrophobic DOC. The lignin-derived phenols released by CuO from the DOM fractions of sewage sludge and pig slurry indicate incomplete degradation of the lignin polymer during digestion of vegetables in the mammal gut.

Further evidence of the incomplete degradation of lignin is given by the acid-to-aldehyde ratios of the vanillyl and syringyl units which ranged from 0.1 to 0.2 in the DOM fractions from sewage sludge and pig slurry (Table 2). Such low values indicate initial oxidative degradation of lignin side chains (Hedges et al. 1985). This contrasts with the higher acid-to-aldehyde ratios of the vanillyl and syringyl units of soluble lignin degradation products in forest floor leachates (Guggenberger and Zech 1994; Guggenberger et al. 1994a; Kaiser et al. 2001). The relatively weak oxidation of the lignin side chains compares well with the results on lignin transformation during aerobic composting of municipal waste (Pichler and Kögel-Knabner 2000).

The ratio of syringyl to vanillyl phenols in all materials was 0.6–1.4 (Table 2) which suggests a predominant contribution of angiosperm-derived lignin to the water-soluble organic matter of all three waste materials (Kögel 1986).

The hydrophilic fraction of DOM from forest soils is rich in carbohydrates with polymeric sugars and uronic acids being the major constituents (Guggenberger et al. 1998; Kaiser et al. 2001). Carbohydrates are also abundant in the hydrophobic fraction of DOM from forest soils and they are probably connected to lignin moieties and result from the degradation of lignocellulose (Guggenberger and Zech 1994; Guggenberger et al. 1994a). Compared to DOM from forest soils, the concentrations of neutral and acidic sugars in the hydrophilic and hydrophobic DOM of urban waste compost were low (Table 3) which confirms earlier results (Gigliotti et al. 1997, 1999). A possible explanation is a preferential degradation of carbohydrates during the maturation-fermentation of composts (Chefetz et al. 1998; Pichler and Kögel-Knabner 2000). Also, the total sugar content of the hydrophilic fraction was similar to that of the hydrophobic fraction which contrasts with the results reported on DOM from forests. The concentrations of sugars in the hydrophilic DOM fractions from sewage sludge and pig slurry and that in the hydrophobic fraction of sewage sludge were higher than the concentrations in DOM from urban waste compost and within the range of values reported for DOM from forest soils. An interesting feature of these three fractions was the high concentration of uronic acids which accounted for one third of the total sugars of the hydrophobic fraction of DOM from sewage sludge, possibly because of the strong degradation of carbohydrates. The hydrophobic fraction of DOM from pig slurry had the lowest concentration of sugars of all materials in our study.

The ratios of mannose plus galactose to xylose plus arabinose [(Man+Gal)/(Xyl+Ara)] in the DOM fractions from the waste materials were between 0.7 and 2.5 (Table 3). According to Oades (1984), [(Man+Gal)/(Xyl+Ara)] ratios >2.0 indicate a predominance of carbohydrates from microbial biomass and other sources different from plant tissue. All the hydrophilic fractions and the hydrophobic fraction from urban waste compost had [(Man+Gal)/(Xyl+Ara)] ratios ≤1.7 and thus seemed to contain mainly plant-derived carbohydrates. The hydrophobic fractions from the sewage sludge and the pig slurry had values ≥2.0 which means that there was a stronger contribution of sugars from microbial and other sources. The fractions of DOM in forest floor leachates show a contrasting distribution of hexoses and pentoses with [(Man+Gal)/(Xyl+Ara)] ratios being higher in the hydrophilic than in the hydrophobic fraction (Guggenberger et al. 1998; Kaiser et al. 2001).

Except for the hydrophobic DOM fraction from sewage sludge, all other materials had low concentrations of amino sugars (Table 4) compared to the amino sugar concentrations of DOM from forest soils (Michalzik and Matzner 1999; Kaiser et al. 2001). The amino sugar concentrations in the hydrophobic DOM fractions from the three waste materials were similar to or even greater than those in the hydrophilic fractions, probably as a result of the contribution of weakly degraded microbial cell wall material. Indeed, intact cell wall materials are hydrophobic (Schlegel 1995) whereas amino sugar monomers released during cell wall degradation are hydrophilic. In contrast, amino sugars in DOM from forest soils are mainly in the hydrophilic fraction. This suggests again that a part of the DOM from waste materials represents weakly transformed organic compounds. The content of amino sugars in the hydrophobic DOM fraction from sewage sludge was high and similar to concentrations in the hydrophilic fraction of DOM in forest soils (Kaiser et al. 2001).

Table 4 Hydrolyzable amino sugars in the hydrophilic and hydrophobic fractions of dissolved organic matter extracted from urban waste compost (*UWC*), sewage sludge (*SS*), and pig slurry (*PSL*)

Sample	Σ amino sugars[a] mg g^{-1} C	GluN/GalN[b]
UWC hydrophilic fraction	8.3	1.9
UWC hydrophobic fraction	8.1	1.7
SS hydrophilic fraction	8.8	1.8
SS hydrophobic fraction	37.2	1.8
PSL hydrophilic fraction	3.4	1.7
PSL hydrophobic fraction	7.3	1.4

[a] Sum of amino sugars
[b] Ratio of glucosamine to galactosamine

The ratios of glucosamine to galactosamine of all DOM fractions from the waste materials ranged between 1.4 and 1.9 (Table 4). These low values indicate that microbial amino sugars dominate over fungal amino sugars (Benzing-Purdie 1984; Kögel and Bochter 1985).

The ^{1}H-NMR spectra of the DOM fractions from urban waste compost and sewage sludge (Fig. 1) were dominated by sharp signals due to low-molecular-weight substances (Wilson et al. 1988). Defined compounds detected comprise acetate (1.93 ppm), methanol (3.36 ppm), propionate (1.23, 2.38 ppm), and succinate (2.43 ppm). The sharp signals in the aromatic region of the hydrophobic fraction of DOM from sewage sludge may result from phenols not deriving from biological sources since the concentrations of lignin-derived phenols were low. Phthalic acid esters and alkylphenol polyethoxylate surfactants are common non-biological sources for water-soluble aromatic compounds in waste-materials such as sewage sludge and urban waste composts (Fujita et al. 1996; Bauer et al. 1998). Broad signals denoting the presence of polymeric material only dominated the spectrum of the hydrophobic fraction of DOM from pig slurry, which corresponds to the relatively large concentration of CuO oxidation products in this sample, possibly due to undigested plant-derived material.

The distribution of the signal intensities (Table 5) was largely similar to those of DOM from soil, surface and groundwaters (Leenheer 1994; Ma et al. 2001). Aromatic structures were low in all hydrophilic fractions whereas signals due to aromatic H were more abundant in the spectra of the hydrophobic DOM fractions. Signals due to carbohydrate structures comprised 19–38% of the H moieties in the spectra of hydrophilic DOM and 12–21% of the H moieties in the spectra of hydrophobic DOM.

Table 5 Distribution of hydrogen moieties in hydrophilic and hydrophobic fractions of dissolved organic matter extracted from urban waste compost (*UWC*), sewage sludge (*SS*), and pig slurry (*PSL*) according to liquid-state ^{1}H-NMR spectroscopy

Sample	H moieties (%)		
	Olefinic/aromatic H 10.0–5.5 ppm	Carbohydrate H 5.5–3.0 ppm	Aliphatic H 3.0–0.0 ppm
UWC hydrophilic fraction	1	19	80
UWC hydrophobic fraction	13	12	75
SS hydrophilic fraction	5	36	59
SS hydrophobic fraction	8	20	72
PSL hydrophilic fraction	6	38	56
PSL hydrophobic fraction	12	21	67

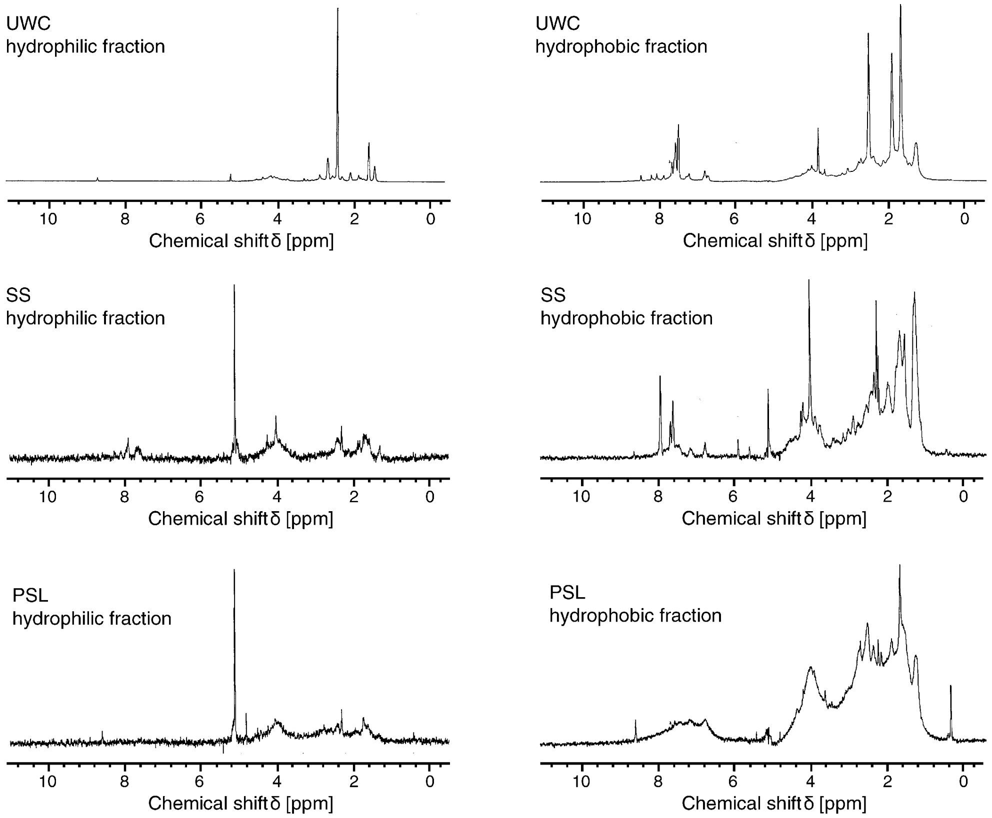

Fig. 1 Liquid-state ^{1}H-NMR spectra of hydrophilic and hydrophobic fractions of dissolved organic matter extracted from urban waste compost (*UWC*), sewage sludge (*SS*), and pig slurry (*PSL*)

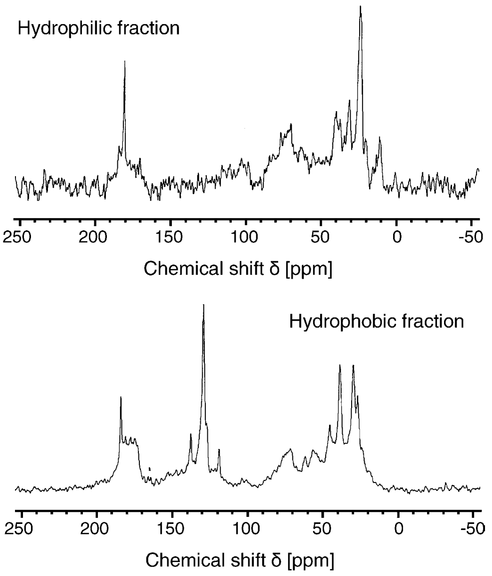

Fig. 2 Liquid-state ^{13}C-NMR spectra of hydrophilic and hydrophobic fractions of dissolved organic matter extracted from urban waste compost

The ranges corresponded well to the wet-chemical characterization of these materials. The DOM fractions from the urban waste compost were rich in aliphatic structures contrarily to DOM from soils, ground and surface waters. Resonances of aliphatic H moieties comprised 75% of the spectrum of the hydrophilic fraction and 80% of the spectrum of the hydrophobic fraction. The low concentration of carbohydrates and the large abundance of low-molecular-weight aliphatic compounds characterized DOM from the urban waste compost as a typical end product of anaerobic fermentation (Schlegel 1995).

The ^{13}C-NMR spectra of the DOM fractions of urban waste compost (Fig. 2) confirm the results of both the ^{1}H-NMR and wet-chemical analyses. The hydrophilic DOM showed almost no signals due to aromatics and phenols. The highest signal intensities occurred in the alkyl region indicating that about half of the C was in aliphatic compounds (Table 6). As the addition of a standard proved (spectrum not shown), the sharp signal in the carbonyl region at 181 ppm and the corresponding sharp signal in the alkyl region at 23 ppm results from a single

Table 6 Distribution of carbon moieties in hydrophilic and hydrophobic fractions of dissolved organic matter extracted from urban waste compost (*UWC*) according to liquid-state ^{13}C-NMR spectroscopy

Sample	C moieties (%)			
	Carbonyl C 200–160 ppm	Aromatic C 160–110 ppm	O-alkyl C 110–60 ppm	Alkyl C 50–0 ppm
UWC hydrophilic fraction	13	8	33	46
UWC hydrophobic fraction	18	26	19	36

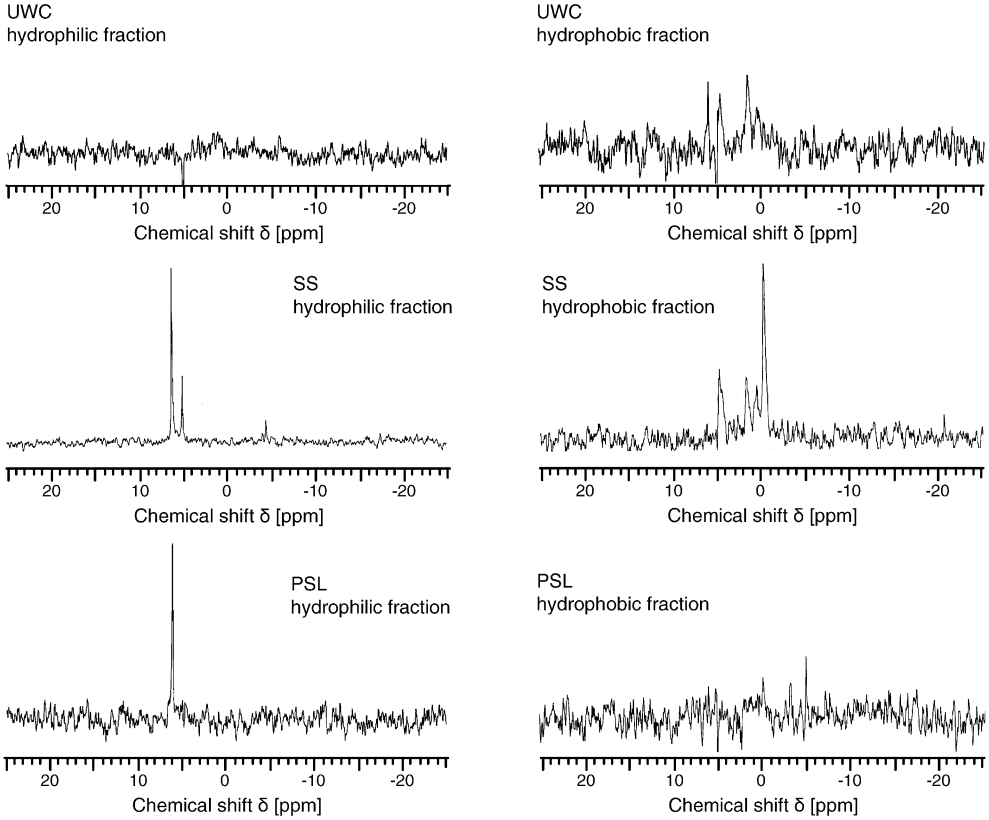

Fig. 3 Liquid-state ^{31}P-NMR spectra of hydrophilic and hydrophobic fractions of dissolved organic matter extracted from urban waste compost (*UWC*), sewage sludge (*SS*), and pig slurry (*PSL*)

substance, acetic acid produced by the oxidative fermentation (Schlegel 1995). The strong signals at 25 ppm with the relatively low signal intensities in the O-alkyl C region suggest the presence of methyl C other than in deoxy sugars. The signal at 40 ppm indicates methyl C and amino acids, while the strong signal at 30 ppm indicates methylene C and proteins.

The spectrum of the hydrophobic fraction was characterized by low signals of O-alkyl C indicating the scarce presence of carbohydrates in this fraction (Fig. 2, Table 6). The signals due to aliphatic compounds at 25, 30, and 40 ppm were less pronounced than for the hydrophilic fraction whereas signals of aromatic structures were more intense. The aromatic signals were predominantly sharp thus indicating the presence of low-molecular-weight substances rather than the presence of polymeric matter. The signature of the sharp signals at 120, 130, 140 ppm did not resemble those typical for lignin-derived compounds (Wilson 1987). According to the position of the signals, phthalic acid esters are most likely the compounds inducing the large distinct resonances in the aromatic region. Another possibility is alkylphenol polyethoxylate and linear alkylbenzene sulfonate surfactants (Ahel et al. 1996; Brunner et al. 1988). All the substances may contribute to the signals in the aromatic as well in the alkyl region.

The spectra of both DOM fractions differed largely from those obtained in DOM fractions of forest floor leachates. In the latter, the hydrophilic fractions are usually dominated by signals in the O-alkyl C region and show less resonances of alkyl C. The hydrophobic DOM fractions of forest floor leachates also contain more O-alkyl C than the hydrophobic DOM fraction of urban waste compost (Kaiser et al. 1997, 2001). Moreover, both the hydrophilic and the hydrophobic fraction from the urban waste compost were lower in O-alkyl C than DOM fractions extracted from leaf litter composts (Wershaw et al. 1996a, b) and other municipal waste composts (Chefetz et al. 1998; Pichler et al. 2000). The small amount of O-alkyl C and the high content of alkyl C suggested again an advanced decomposition of carbohydrates (Chefetz et al. 1998; Pichler and Kögel-Knabner 2000; Pichler et al. 2000) and simultaneous production of aliphatic acids during the aerobic fermentation of the urban waste compost.

The ^{31}P-NMR spectrum of the hydrophobic DOM fraction from pig slurry showed no signals due to P confirming the results of the elemental analyses, which showed that P was below the detection limit. The only signal in the spectrum of the hydrophilic DOM fraction from pig slurry was due to orthophosphate (Fig. 3, Table 7). The spectrum of the hydrophilic DOM fraction from sewage sludge showed signals due to orthophos-

Table 7 Distribution of detected phosphorus moieties in hydrophilic and hydrophobic fractions of dissolved organic matter extracted from different waste materials (*UWC* urban waste compost, *SS* sewage sludge, *PSL* pig slurry) according to liquid-state ^{31}P-NMR spectroscopy

Sample	P moieties (%)				
	Ortho-phosphate 6.2 ppm	Monoester P 5.6–4.1 ppm	Teichoic acid P 2.0–1.0 ppm	Diester P 0.5 to –1 ppm	Pyro-phosphate –4.8 ppm
UWC hydrophilic fraction	–	–	–	–	–
UWC hydrophobic fraction	–	–	–	–	–
SS hydrophilic fraction	55	33	–	–	12
SS hydrophobic fraction	–	25	37	38	–
PSL hydrophilic fraction	100	–	–	–	–
PSL hydrophobic fraction	–	–	–	–	–

phate, organic monoester P, and a small signal of pyrophosphate. In the spectrum of the hydrophobic DOM fraction from sewage sludge the most abundant signal was that of organic diester P. In addition, there were smaller signals of teichoic acids and organic monoester P, which can derive from plant and microbial sources. The lack of signals of inorganic species in the hydrophobic fraction depends on the fractionation procedure, which concentrates inorganic P in the hydrophilic fraction. The occurrence of P species, especially of orthophosphate, in the DOM fractions of the sewage sludge is surprising because of the addition of Al during wastewater treatment which should result in the formation of insoluble Al phosphates. The ^{31}P-NMR spectrum of the hydrophilic DOM fraction from urban waste compost showed no pronounced inorganic or organic P signals while the spectrum of the hydrophobic fraction revealed traces of monoester P, diester P, and orthophosphate (Fig. 3). This corresponds with the low solubility of P in the urban waste compost (Table 1).

Conclusions

The results showed that the water-soluble fractions of urban waste compost had different properties from the soluble constituents of pig slurry and sewage sludge. They contained neither organic nor inorganic P and were low in carbohydrates and amino sugars. Thus, application of urban waste compost to soil offers no easily plant-available P and no labile organic matter that might serve as an energy source for microbial growth. The water-soluble fractions of sewage sludge contained more P, carbohydrates and amino sugars than urban waste compost. We assume that in terms of immediate effects on plant nutrition and biological activity, the application of sewage sludge is preferable to urban waste compost.

The set of samples studied is limited to a few sources. However, because of similar underlying processes, the treatment of waste materials leads to qualitatively similar products. For instance, its chemical composition characterizes the DOM from the urban waste compost studied as a typical product of aerobic fermentation. Therefore we expect similar results also for waste materials from comparable sources and processing. At least, our results suggest that processing waste materials does not necessarily lead to a product of superior properties (i.e. easily plant-available elements and/or labile organic matter) compared to the source material.

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