## RECYCLING AND UTILIZATION OF ORGANIC MUNICIPAL REFUSE IN BIOCONTROLLED CROP PRODUCTION

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**RESEARCH IN ISRAEL** 

### **RESEARCH IN POLAND**

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### **Executive summary**

#### Introduction

Both quality and quantity of organic matter (OM) in soils affect plant growth and health. Crop residues and root exudates affect the activity of beneficial microorganisms, as well as pathogens. The effects of OM decomposition level in the soil on interactions of beneficial microorganisms and pathogens, and on plant growth have been largely overlooked. Both the mineral fraction and the yearly introduced organic residues, as well as their resulting transformations in soils, play a role in this complex. In addition, humic substances (HS), the most stable organic components in soil, may have both direct and indirect effects on plant growth.

The composting of organic wastes has been defined as a controlled microbial aerobic decomposition process. Recently composting has gained interest in western countries as a result of the accumulation of large amounts of agricultural, industrial and municipal wastes. These wastes create a severe disposal problem involving a number of environmental aspects related to air, soil, ground water and surface water pollution. During the course of the composting process, transformations of various OM fractions can be followed separately without analytical interference from OM already present in the soil. The composting process therefore provides a unique opportunity to evaluate effects of specific OM transformations on plant growth and health and may serve as a model for field soil systems. The main products of aerobic composting are CO<sub>2</sub>, water, minerals and stabilized OM often called humus. Well-composted OM is traditionally used as a source of nutritional elements and/or soil conditioner directly in the field. In the last decade, the demand for peat as a potting medium in horticulture has increased while its availability has decreased. A number of organic wastes such as bark, leaf mold, municipal solid waste (MSW), sewage sludge, sawdust, and treated animal excreta have been introduced as peat substitutes in growth media after proper composting. Some of the well-matured composts have been found to be suppressive of soilborne plant pathogens when utilized as container media.

Composting is a form of waste stabilization that requires special conditions, particularly of moisture and aeration, to yield temperatures conducive to thermophilic microorganisms. It is a controlled biooxidative process that: (*i*) involves a heterogeneous organic substrate in its solid state; (*ii*) evolves by passing through a thermophilic phase and a temporary release of phytotoxins; and (*iii*) leads to production of  $CO_2$ , water, minerals and stabilized OM

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(compost). Compost is the stabilized and sanitized product of composting which is beneficial to plant growth. The OM has undergone an initial, rapid stage of decomposition and is in the process of humification.

Controlled environmental conditions distinguish composting from natural rotting or putrefaction, which often occurs in open dumps, manure heaps, or field soil. The organic wastes, comprised of several components, normally have an indigenous population of microorganisms derived from the atmosphere, water or soil. Once the moisture content of the waste is brought to an appropriate level and the mass is aerated, microbial metabolism speeds up. Energy is obtained by biological oxidation of part of the carbon; some of this energy is used in metabolism, the rest is given off as heat. The end product (compost) is made up of the more resistant residues of the OM, breakdown products, dead and living microorganisms, together with products from further chemical reactions between these materials.

Basically, the process can be divided into four stages: (i) mesophilic stage - an initial phase of 1-2 days, during which the mesophilic strains of microorganisms start to decompose the readily degradable compounds, heat is given off and the temperature rises. The pH falls slightly as organic acids are produced; (ii) thermophilic stage - the second stage, lasting 2-4 weeks, when above 40°C the thermophilic strains take over. If the temperature rises above 60°C, the fungi become deactivated, and the reaction is continued by thermophilic bacteria. In this phase the more readily degradable substances such as sugars, fats, starch and proteins are rapidly consumed and most of the human and plant pathogens are destroyed; the pH becomes alkaline as ammonia is liberated from the proteins. The reaction rate decreases as the more resistant materials are attacked; the compost enters (iii) the cooling-down stage - as the temperature falls, the thermophilic fungi reinvade the composted material from the cooler extremities and start to attack the cellulose, hemicellulose and other polymers. These first three stages of composting last from a few weeks to 2 months, depending on the composted material; the last stage (iv) stability and maturity - requires several months, where little heat is generated and the final pH is normally slightly alkaline. During this phase, mesophilic microorganisms as well as macrofauna colonize the compost, Intense competition for food take place between the microorganisms involving: antagonism and the formation of antibiotics. Humification occurs in the residual OM to produce the stable composted product.

The composting of organic wastes is a dynamic and extremely complicated ecological process in which temperature, pH and nutrient availability are constantly changing. As a consequence, the numbers and species of organisms responsible also change markedly.

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Thermophilic bacteria, particularly *Bacillus* spp. and *B. cereus*, appear to dominate the early phase of high activity, but thermophilic actinomycetes predominate thereafter. The rate of decomposition depends on the rates of microbial activity, the latter being greater when composts are maintained at low (38-55°C) rather than high temperatures (60-70°C). In addition to temperature, optimum starting material values for composting are: C/N ratio 30-35; C/P ratio 75-150; moisture content 50-60%; particle size 15-35 mm; pile size 1.5 m high and 2.5 m wide

Compost maturity is defined as the degree of OM decomposition during composting. Any definition of maturity must be based on the potential use of the compost. For example, compost used in potting mixes (container media) must be mature enough so that no plant growth inhibition occurs within days after formulating of the mix. On the other hand, composts utilized in field agriculture may be applied weeks or months before planting, giving them time to "stabilize" in the soil. Thus, the following definitions are proposed for mature composts: (i) Greenhouse utilization: OM composted to the degree of decomposition which has no adverse effects on container grown plants. (ii) Field application: OM composted to the degree of decomposition that has no adverse effects on the growth of various crops when applied at annual rates of up to 50 tons/ha, at least 6 weeks before sowing or planting (during the warm season, in which decomposition can take place).

#### The following objectives were studied:

1. Chemical and biological characterization of municipal solid waste composting.

Composting of municipal solid waste (MSW) was studied in an attempt to better understand the composting process and define parameters of maturity. Composting was performed in 1-m<sup>3</sup> plastic boxes and the following parameters were measured: temperature, C/N ratio in solid and liquid phase (C/N<sub>(s)</sub> and C/N<sub>(w)</sub> respectively), humic substance fractions and contents, dissolved organic carbon (DOC). Spectroscopic method (DRIFT) was used to study the chemical composition of the bulk organic matter (OM). A bioassay based on cucumber plants growth was correlated to other parameters. C/N<sub>(w)</sub>, C/N<sub>(s)</sub> and DOC showed high rates of change during the first 60 days, then stabilized. Humic acid (HA) content increased to a maximum at 110 days, corresponding to the highest plant dry weight and the highest 1650/1560 (cm<sup>-1</sup>/ cm<sup>-1</sup>) peak ratios from DRIFT spectra. DRIFT spectra showed that the OM transformed to a more aromatic structure. 2. Formation and properties of humic substances originating from composted municipal solid wast.

Composting enables a detailed evaluation of the humification process of various organic wastes within a short period of time (3 to 6 months). Humic substances (HS) constitute a large fraction of the organic matter (OM) in compost, and they are its most active fraction due to their effects on soil ecology, structure, fertility and metal complexes, and plant growth. The formation and properties of HS extracted from composted municipal solid waste were studied. Degradative and non-degradative techniques (FTIR, DRIFT, <sup>13</sup>C-NMR) were used to study the transformation of HS during composting. Time-course studies of composting some of these wastes showed an increase in the relative amount of humic acid (HA) (from 5% to 20% in MSW compost), whereas the formation rate of fulvic acid (FA) was inconsistent. A humification ratio (HR - the ratio of HA/FA) was used to evaluate compost maturity. Values of 0.9 to 3.4 and 3.0 to 9.2 were typical for immature and mature composts, respectively. Another humification index (HI) used to define compost maturity was calculated as the ratio between the non-humified fraction (NHF) and the humified fraction (HA+FA). A HI decrease during composting represents the formation of HS. Elemental- and functional-group analyses indicated only minor differences between HA extracted from composts at various stages. Moreover, these values fell into a wide range, similar to that of soil HA. The <sup>13</sup>C-NMR spectra of the HA exhibited strong bands representing aliphatic structures in various composts (30% in MSW) and a lower level of aromatic components (22% in MSW). The FTIR spectra showed similar trends of strong aliphatic and carbohydrate components. Both techniques provided more qualitative information indicating that HA extracted from mature compost exhibits more aromatic structures and carboxyl groups and less carbohydrate components than that from immature compost.

#### **Results and Conclusions**

#### Experiments in Israel

The level of HS formation reached a maximum within 90 to 120 days of composting without forced aeration. The HS level remained steady in MSW compost, and the HA level increased during composting of MSW, while the NHF level decreased with composting time. Values of C, H and S in HA derived from compost were similar to those found in soils. However, the N levels were higher in compost-derived HA and the C/N ratio was therefore

lower. Total acidity, -COOH and phenolic OH levels were lower in HA derived from composts than the average values-found in soil HA. FTIR and NMR spectra of compost-derived HA were similar, regardless of composting time and exhibited high levels of polysaccharides and aliphatic structures.

Due to the complexity of the materials and processes involved the determination of compost maturity is very difficult. Therefore, several parameters need to be crossbred. This research proves that DRIFT spectroscopy, together with data on HS provide useful information about the OM transformations occurring during the composting process of MSW. Plant bioassay, level of HA and the 1650/1560 DRIFT peak ratio showed the same trend during composting and can therefore be used as maturity indexes. All these parameters exhibited three distinct phases: (*i*) rapid decomposition during the first 30 d; (*ii*) stabilization till day 90; (*iii*) maturation from day 90 onwards. The MSW compost, in our experimental system, was mature and ready to be used as an agricultural substrate after about 110 days of composting. Parameters for compost maturity were developed to the degree that values can be normalized based on criteria, and therefore various production systems can be tested accordingly, thus eliminating the need to calibrate each system separately.

#### Experiments in Poland

MSW compost at different stages of the composting process was used a source of organic matter for plants cultivated in container media. The major experimental plant was crisp lettuce Crispino cv. MSW compost was taken from composting piles at various sampling times during composting and mixed with a loamy sand in doses of 100 t and 400 t/ha. As the control treatments peat substrate and pure loamy soil were recognized. All media were fertilized with macro and microelements. The sphagnum peat was adjusted to pH 6.0 with chalk (12 kg/m<sup>3</sup>) and used as a control. Seeds of lettuce were sown into 5 cm in diameter plastic rings filled with tested media. Two or three seeds were placed per pot, and after emergence the seedlings were thinned to one per pot, and then after ten days transplanted into plastic boxes filled with 10 l of the same media. Four seedlings were grown in each box placed in the hot bed. During cultivation the lettuce was watered three to four times per week.

The experiment was arranged in a randomized complete block design with 4 replicates. Each plot consisted of two boxes and 8 plants. For each cultivation cycle, harvesting was carried out one month from planting date, when the plants started to form heads. Fresh weight of one plant and total yield of lettuce were estimated.

The high ratio of MSW compost in growing media (400 t/ha) had adverse effects on plant growth and health. Independent of the maturity stage of compost, treatment supplied with 400 t/ha of MSW resulted in a reduction of plant population on the plots. Yellowing and tipburn of leaves appeared only in this treatment.

Fresh MSW compost negatively affected plant growth and greatly reduced the weight of the lettuce head as well as the final yield. The composting process improved the quality of the organic matter and decreased its adverse effect on plant growth. In treatments with low application rates of three-month old MSW compost and in the control (pure loamy soil), lettuce produced almost equal yields. A higher dosage of MSW compost (400 t/ha) at the same stage of maturity slightly decreased the yield, but this effect was also not significant. After 9 months of composting the MSW compost had no negative effect on growth of crisp lettuce at all levels used in the experiment. Fresh or partly matured (1 or 3-month old) MSW compost delayed the time of seedlings emergence, but did not influence the final stand of lettuce plants estimated 21 days from date of sowing. The application of this material to the growing medium comprising loamy soil adversely affected the growth rate of plants. Along with the increasing degree of maturation this negative effect became less pronounced, especially if smaller amounts of MSW compost were applied. Nine-month old MSW compost did not adversely affect growth of lettuce plants and in practice may be used as a component of container media for plant cultivation even at high ratios amounting to 400 t/ha. The procedure proposed provides an attractive method for the recycling of MSW.

#### Scientific Impact of Collaboration

This project has significantly enhanced the capacity for research on composting organic matter transformations, and heavy metals binding and uptake in MSW amended soils in Poland as well as in Israel. Techniques for elemental analyses of composts for their organic components as well as electron spin resonance (ESR) and ICP-AES technologies are now being employed in Poland and in Israel after the formulation and approach was transferred to the researchers in Poland.

Prof. Drozd from Poland and Prof. Chen from Israel met during a conference on composting held in Bologna, Italy (June, 1995) and discussed plans and problems related to the Project. During August 1995, Prof. Chen visited Prof. Drozd and his group at the Agricultural University of Wroclaw. The various experiments performed to that date were discussed and summarized. Future experiments were planned. Prof. Chen visited laboratories and discussed

the project with researchers and students from the Polish group. An additional visit took place in July 1996. Prof. Drozd visited Israel in 1993 for a conference on environmental quality and he presented some of the early results of the project. He returned to Israel in 1997 to work jointly on the final report. The collaboration between the groups was very good and this was beneficial to the researchers in both countries.

#### LIST OF PUBLICATIONS RESULTING FROM THIS PROJECT

- 1. Chefetz, B., P.G. Hatcher, Y. Hadar, and Y. Chen. 1996. Chemical and biological characterization of organic matter during composting of municipal solid waste. J. of Environ. Quality 25 (4): 776-785.
- Chen, Y., B. Chefetz, and Y. Hadar. 1996. Formation and properties of humic substance originating from composts. pp. 382-393. <u>In</u>: M. de Bertoldi, P. Sequi, B. Lemmes and T. Papi (eds.) The Science of Composting. Blackie Academic & Professional, Glasgow.
- Chefetz, B., U. Yermiyaho, Y. Hadar and Y. Chen. 1997. Recycling of municipal solid waste (MSW): the composting process and compost utilization in greenhouse agriculture. Dahlia Greidinger Int. Symposium: fertilization and the Environment. Technion, Haifa March 24-27, 1997 (Abstract).
- Chen, Y., Y. Inbar, B. Chefetz and Y. Hadar. 1997. Composting and recycling of organic waste. pp. 341-362. In: D. Rosen, E. Tel-Or, Y. Hadar and Y. Chen (eds.) Modern Agriculture and the Environment. Kluwer Academic Publishers, London, U.K.
- Drozd, J., A. Jezierski and Y. Chen. 1997. Chemical and electron spin resonance properties of municipal solid waste composts. pp. 395-400. <u>In</u>: D. Rosen, E. Tel-Or, Y. Hadar and Y. Chen (eds.) Modern Agriculture and the Environment. Kluwer Academic Publishers, London, U.K.
- 6. Chefetz, B, Y. Hadar and Y. Chen. 1998. Water extractable compounds released during composting of municipal solid waste. Acta Horticulturae (in press)
- Chen, Y., B. Chefetz, F. Adani, P. Genevini and Y. Hadar. 1998. Organic matter transformation during composting of municipal solid waste. pp. 000 In: Proc. 8<sup>th</sup> International Humic Substances Society Conference, Wroclaw, Poland.

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# RESEARCH IN ISRAEL

# Composting and Recycling of Organic Wastes

#### **Introduction**

Both quality and quantity of organic matter (OM) in soils affect plant growth and health. Crop residues and root exudates affect the activity of beneficial microorganisms, as well as pathogens (Chang et al., 1986). The effects of OM decomposition level in the soil on interactions of beneficial microorganisms and pathogens, and on plant growth have been largely overlooked (Hoitink and Fahy, 1986; Chen et al., 1988; Grebus et al., 1994). Both the mineral fraction and the yearly introduced organic residues, as well as their resulting transformations in soils, play a role in this complex. In addition, humic substances (HS), the most stable organic components in soil, may have both direct and indirect effects on plant growth (Stevenson, 1985; Chen and Aviad, 1989; Chen et al., 1994).

The composting of organic wastes has been defined as a controlled microbial aerobic decomposition process. Recently composting has gained interest in western countries as a result of the accumulation of large amounts of agricultural, industrial and municipal wastes (de Bertoldi et al., 1987; de Bertoldi, 1993; Steuteville, 1994a,b; Golsdtein and Steuteville, 1995). These wastes create a severe disposal problem involving a number of environmental aspects related to air, soil, ground water and surface water pollution. During the course of the composting process, transformations of various OM fractions can be followed separately without analytical interference from OM already present in the soil. The composting process therefore provides a unique opportunity to evaluate effects of specific OM transformations on plant growth and health and may serve as a model for field soil systems. The main products of aerobic composting are CO<sub>2</sub>, water, minerals and stabilized OM often called humus. Well-composted OM is traditionally used as a source of nutritional elements and/or soil conditioner directly in the field. In the last decade, the demand for peat as a potting medium in horticulture has increased while its availability has decreased (Chen et al., 1992). A number of organic wastes such as bark, leaf mold, municipal solid waste (MSW), sewage sludge, sawdust, and treated animal excreta have been introduced as peat substitutes in growth media after proper composting (Cull, 1981; Bik, 1983; Lohr et al., 1984; Verdonck, 1984; Inbar et al., 1985; Raviv et al., 1986, Chen et al., 1988; Chen et al., 1992). Some of the well-matured composts have been found to be suppressive of soilborne plant pathogens when utilized as container media (Hoitink and

Fahy, 1986; Hoitink and Kuter, 1986; Chen et al., 1988; Mandelbaum et al., 1988; Hoitink et al., 1993).

#### **Principles of composting**

Composting is a form of waste stabilization that requires special conditions, particularly of moisture and aeration, to yield temperatures conducive to thermophilic microorganisms (Hoitink and Fahy, 1986). Zucconi and de Bertoldi (1987) proposed the following definitions: Composting is a controlled biooxidative process that: (*i*) involves a heterogeneous organic substrate in its solid state; (*ii*) evolves by passing through a thermophilic phase and a temporary release of phytotoxins; and (*iii*) leads to production of  $CO_2$ , water, minerals and stabilized OM (compost). Compost is the stabilized and sanitized product of composting which is beneficial to plant growth. The OM has undergone an initial, rapid stage of decomposition and is in the process of humification.

Controlled environmental conditions distinguish composting from natural rotting or putrefaction, which often occurs in open dumps, manure heaps, or field soil. A simplified flowchart of the overall composting process is shown in Fig. 1. This flowchart illustrates the interactions between the organic waste, microorganisms, moisture and oxygen. The organic wastes, comprised of several components, normally have an indigenous population of microorganisms derived from the atmosphere, water or soil. Once the moisture content of the waste is brought to an appropriate level and the mass is aerated, microbial metabolism speeds up. Energy is obtained by biological oxidation of part of the carbon; some of this energy is used in metabolism, the rest is given off as heat. The end product (compost) is made up of the more resistant residues of the OM, breakdown products, dead and living microorganisms, together with products from further chemical reactions between these materials (Gray and Biddlestone, 1981).

The temperature trend in most composting processes is presented in Fig. 2. Basically, the process can be divided into four stages: (i) <u>mesophilic stage</u> - an initial phase of 1-2 days, during which the mesophilic strains of microorganisms start to decompose the readily degradable compounds, heat is given off and the temperature rises. The pH falls slightly as organic acids are produced; (ii) <u>thermophilic stage</u> - the

second stage, lasting 2-4 weeks, when above 40°C the thermophilic strains take over. If the temperature rises above 60°C, the fungi become deactivated, and the reaction is continued by thermophilic bacteria. In this phase the more readily degradable substances such as sugars, fats, starch and proteins are rapidly consumed and most of the human and plant pathogens are destroyed; the pH becomes alkaline as ammonia is liberated from the proteins. The reaction rate decreases as the more resistant materials are attacked; the compost enters (*iii*) the <u>cooling-down stage</u> - as the temperature falls, the thermophilic fungi reinvade the composted material from the cooler extremities and start to attack the cellulose, hemicellulose and other polymers. These first three stages of composting last from a few weeks to 2 months, depending on the composted material; the last stage (iv) stability and maturity - requires several months, where little heat is generated and the final pH is normally slightly alkaline. During this phase, mesophilic microorganisms as well as macrofauna colonize the compost, Intense competition for food take place between the microorganisms involving: antagonism and the formation of antibiotics. Humification occurs in the residual OM to produce the stable composted product (Gray and Biddlestone, 1981; Diaz et al., 1982; Hoitink and Fahy, 1986; Zucconi and de Bertoldi, 1987; He et al., 1992; Jimenez and Garcia, 1992; Chen and Inbar, 1993; Ciavatta et al., 1993; Inbar et al., 1993; Adani et al., 1995).

The composting of organic wastes is a dynamic and extremely complicated ecological process in which temperature, pH and nutrient availability are constantly changing. As a consequence, the numbers and species of organisms responsible also change markedly. Thermophilic bacteria, particularly *Bacillus* spp. and *B. cereus* (Finstein and Morris, 1975; Kwok et al., 1987), appear to dominate the early phase of high activity, but thermophilic actinomycetes predominate thereafter (Nakasaki et al., 1985). The rate of decomposition depends on the rates of microbial activity, the latter being greater when composts are maintained at low (38-55°C) rather than high temperatures (60-70°C) (Kuter et al., 1985). In addition to temperature, optimum starting material values for composting are: C/N ratio 30-35; C/P ratio 75-150; moisture content 50-60%; particle size 15-35 mm; pile size 1.5 m high and 2.5 m wide

#### <u>Compost maturity</u>

Compost maturity is defined as the degree of OM decomposition during composting. Any definition of maturity must be based on the potential use of the compost. For example, compost used in potting mixes (container media) must be mature enough so that no plant growth inhibition occurs within days after formulating of the mix. On the other hand, composts utilized in field agriculture may be applied weeks or months before planting, giving them time to "stabilize" in the soil. Thus, the following definitions are proposed for mature composts: (i) Greenhouse utilization: OM composted to the degree of decomposition which has no adverse effects on container grown plants. (ii) Field application: OM composted to the degree of decomposition that has no adverse effects on the growth of various crops when applied at annual rates of up to 50 tons/ha, at least 6 weeks before sowing or planting (during the warm season, in which decomposition can take place).

#### Chemical parameters for compost maturity

The chemical nature of the decomposition process and the evaluation of compost maturity are a difficult problem, since several parameters are required to provide a definite evaluation for the readiness of the material for use in horticulture (Morel et al., 1985; Zucconi and de Bertoldi, 1987). Some of the main changes taking place in the solid phase of the OM during decomposition in soils and/or in partially controlled environments such as a compost pile are: an increase in ash content, a decrease in cellulose and hemicellulose, and generally, as a result of concentration, a relative increase in lignin (Harada and Inoko, 1980b; Inoko, 1982).

Several procedures for testing stability or maturity of composts have been proposed. Some examples are: starch content, cellulose content, C/N ratio, C/N ratio in water extracts of composts, concentration of HS, presence of indicator microorganisms, respiration rate, and others (Harada and Inoko, 1980a,b; Chanyasak and Kubota, 1981; Harada et al., 1981; Chanyasak et al., 1982; Lax et al., 1987; Inbar et al., 1989; Inbar et al., 1990b; Inbar and Chen, 1993).

The C/N ratio represents one of the major guidelines for the composting process. However often the C/N ratio of bulk composts does not provide useful information; in wood wastes for example, much of the carbon is not readily biodegradable. For such wastes, availability must be considered. High "available" C/N ratios of immature or

inadequately composted materials cause immobilization of nitrogen and nitrogen deficiency in plants. High microbial activity existing in immature compost requires O<sub>2</sub> and consequently may cause oxygen deficiency to roots. During the decomposition of fresh or partially decomposed OM, adverse effects on plant growth result from toxic fermentation byproducts produced in the early stages of composting. This phenomenon is well-known in relation to the incorporation of crop residues into soils. Lynch et al. (1980) observed a reduction in root growth of young barely plants cultured in different soils amended with straw. They attributed the reduction to an accumulation of acetic acid produced by decomposition of the straw. Toussan et al. (1968) identified benzoic acid and phenylacetic acid as phytotoxins present in the decomposition products of barley sampled in the field. Acetic acid has also been identified as a phytotoxin in immature composts by De Vleeschaawer et al. (1981). Anid (1986) identified high levels of acetic, propionic and butyric acids in immature compost, whereas those volatile acids disappeared when stabilization was achieved. Wong and Chu (1985) noted severe suppression of germination when seeds of Brassica chinesis were treated with extracts of fresh refuse compost. Less adverse effects were found with 6 week-old compost. Differences from the control were not found with the 12 month-old compost. These investigators speculated that many factors could be influencing germination and root elongation including pH, salt and ammonia contents, ethylene oxide concentration, and heavy metals. Zucconi et al. (1981a,b) tested the response of a wide range of plant species in various bioassays to fresh, immature and mature composts. In general, all plants were inhibited by immature compost. Growth usually improved upon contact with mature compost. These authors concluded that phytotoxicity during composting appears to be strictly associated with the initial stage of decomposition and that it is a transient condition, possibly connected to the presence of readily metabolizable material. Low molecular weight organic acids (acetic, propionic, and butyric) were the most toxic compounds found in the early stages of the composting process (De Vleeschauwer et al., 1981; Zucconi et al., 1981a,b; Chanyasak et al., 1983; Hirai et al., 1986). Finally, allelopathic toxins in wastes can cause problems, but they are generally destroyed within a few weeks of composting. Hoitink and Kuter (1986) concluded that the negative responses of plants grown in bark composts were due to high cellulose

content resulting in nitrogen immobilization, allelopathic chemicals, toxic levels of metabolites of anaerobic metabolism, high salt content and, possibly, other factors. They concluded that appropriate curing is essential to stabilize compost and eliminate or reduce negative plant responses (Hoitink and Fahy, 1986). Inbar et al. (1988) measured  $O_2$  consumption by fresh and composted separated manure (CSM) and grape marc (CGM) at various moisture levels, with and without the addition of nitrogen, as a function of composting time in a simulation system. For both materials, cumulative O<sub>2</sub> consumption increased rapidly at first, then leveled off. Maximum O<sub>2</sub> uptake was obtained at moisture levels of 60 to 70% (on a net weight basis). The addition of nitrogen increased the  $O_2$  uptake rate in some instances, more markedly in the CGM which is low in nitrogen content. The O2 uptake rate vs. time approached leveling off after a few days of composting in the pilot-scale system, exhibiting a slow approach to a steady state in microbial activity. As opposed to the fresh OM for both materials, the composted products had low O<sub>2</sub> uptake rates, indicating that O<sub>2</sub> consumption provides a good measure of the rate of decomposition and the degree of stability. A similar relationship between O2 uptake and MSW composting age was observed by Iannotti et al. (1994). This measure, as well as CO2 release, has been used by microbiologists for many years for this purpose. However, leveling off or a lower rate of  $O_2$  uptake is often achieved before compost can be considered mature for greenhouse utilization (Inbar et al., 1988). This may not necessarily be the case for compost applied to soil well ahead of planting, where only some stability is required.

To avoid problems caused by carbon availability, the ratio of water-extractable organic C/organic N was proposed as an indicator of compost maturity by researchers in Japan (Chanyasak and Kobuta, 1981; Chanyasak et al., 1982, 1983). These researchers found values of 5 to 6 for the soluble organic C/organic N ratio of mature compost of MSW. A highly significant negative correlation was established between the cation exchange capacity (CEC) and the soluble C/N ratio. However, this was not confirmed for CSM by Inbar et al. (1989), nor for CGM by Inbar et al. (1990a). It also seems, as proposed by Hoitink and Kuter (1986), that this procedure is not effective for low C/N ratio wastes such as sewage sludge which, after the mixing of raw sludge and bulking agents, already has low ratios in the extract.

#### **Biological parameters of compost maturity**

The ultimate, and probably most attractive evaluation of compost maturity is based on bioassays. Most are based on plant growth over a few days or weeks, and this limits their usefulness. Data given in Table 1 (Hadar et al., 1985) show that extended composting was needed to obtain maximum growth of plants in separated manure. Growth of unfertilized plants was retarded but fertilization alone could not sufficiently enhance growth unless the compost was mature. This suggests that nitrogen deficiency was not the only growth-limiting factor in this immature compost. An experiment conducted using water extracts of CSM (Inbar et al., 1989) showed that tomato seedlings were inhibited in water extracts obtained from composts less than 40 days old. An increase in inhibition resulting from phytotoxic substances was observed in compost extracts prepared during the thermophilic stages of composting (20-40 d). From day 40 onward, growth in compost extract was significantly better than that in a standard nutrient solution. It was concluded that phytotoxic compounds and competition for  $O_2$  in the immature compost were responsible for the inhibition in plant growth. Grebus et al. (1994) reported that 60-70 days of composting were required to destroy the inhibitory growth effect of a yard-trimmings mixture on radish. Plant growth bioassays revealed that ryegrass, cucumber and radish differ in their responses to MSW compost age (Iannotti et al., 1994). These bioassay revealed that ryegrass and radish treated with slow-release fertilizer are sensitive to compost maturity, but cucumber is not. Different results were observed by Chefetz et al. (1995) who reported that a bioassay based on cucumber growth is a sensitive tool for determining MSW compost maturity.

#### Humic substances in composts

HS have attracted the interest of soil scientists due to their importance to soil ecology, fertility and structure and their effects on plant growth (Vaughan and Malcolm, 1985; Chen and Aviad, 1989; Chen et al., 1994). As more agricultural lands throughout the world are treated with composted organic materials such as composts from sewage sludge, municipal refuse, crop residues, and animal excreta, elaboration of the nature of the organic components (especially the HS) present in such composts, as well as of their formation during the composting process, has become essential. HS

are known to be involved in a number of interrelated, chemical processes in soil and to influence plant growth directly as well as, indirectly. Indirectly, humic acid (HA) may improve soil fertility by increasing the availability of plant nutrients or by sequestering heavy metals such as iron, zinc, and manganese in the soil environment, thereby solubilizing these elements for the benefit of plants (Chen and Aviad, 1989). Some reports also suggest that plant roots can take up HS, thereby allowing them to have direct affect on plant growth and metabolism (Vaughan and Malcolm, 1985).

A variety of techniques have been employed to extract HS from soils. The methods vary among researchers, depending upon the nature of the material to be examined, the discipline of the investigators and other arbitrary factors. The common extraction procedures have been reviewed by Hayes et al. (1975), Hayes (1985), Stevenson (1982), Watanabe et al. (1994) and Adani et al. (1995). They stated that aqueous solutions of NaOH are capable of extracting appreciable fractions of OM, including the more complex, high-molecular-weight and less soluble components of humus. Aqueous solutions of NaOH are known to induce slight oxidation of the extracted OM. The alkali solution also dissolves protoplasmic and structural components from fresh organic tissues and these become mixed with the humified OM (Stevenson, 1982). When fresh plant residues and young peat material were extracted with alkali, substances such as hemicelluloses, proteins, alkali-soluble lignin, and tannins entered into the humic fraction. However, as the decomposition proceeded, the fraction of these substances decreased while that of the HS increased (Inbar et al., 1993; Adani et al., 1995). In the case of strongly humified materials, the danger of extracting the admixtures with the HA is practically negligible. To minimize the chemical changes caused by autooxidation during the alkali extraction, all steps should be conducted in the presence of an inert gas (e.g.  $N_2$ ) (Stevenson, 1982).

Among the chemical criteria required for the characterization of an stabilized organic waste product (e.g. compost), humus content and quality are highly ranked (Sugahara and Inoko, 1981; Roletto et al; 1982; Roletto and Ottino, 1984; Roletto et al., 1985; Sequi et al., 1986; Saviozzi et al., 1988; Jimenez and Garcia, 1992; Chen and Inbar, 1993). The main trends of several humification parameters (expressed as percentage of variation) over a period of 140 days during the stabilization of wastewater sludge and straw mixtures are shown in Fig. 3 (Saviozzi et al., 1988). The

following humification indexes were suggested: (i) C/N ratio, (ii) CHA - humic acid carbon (percentage of organic C), (iii) CFA - fulvic acid carbon (percentage of organic C), (iv) CHA/CFA ratio, (v) CHA+CFA (percentage of organic C), (vi) HI (index of humification) - the ratio between the organic C of the non-humified fraction (NHF) and that of the HA + FA fraction (after Sequi et al., 1986), (vii) organic C (% DM), (viii) stability index (SI) - the ratio between HA after apolar, polar and acid hydrolysis treatments and NaOH-Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> HA extraction (after Adani et al., 1995). During the first 30 to 60 days changes in HI occurred rapidly; thereafter, the rate of change became progressively slower. All the parameters were reported to be linearly and significantly correlated to the C/N ratio. In their work, Saviozzi et al. (1988) suggested minimum values for some humification parameters indicating maturity of farmyard manure (FYM). FYM containing less than 37.1% organic C, and exhibiting an HI value lower than 0.4, a CHA + CFA higher than 16, and a CHA higher than 9.7, could be considered mature. Time-course studies of the composting of various wastes showed an increase in the relative amount of HA (from 18% to 45% of OM in CSM compost and from 5% to 20% in MSW compost), whereas the formation rate of fulvic acid (FA) was inconsistent. Humification ratio (HR=HA/FA) values of 0.9 to 3.4 and 3.0 to 9.2 were typical for immature and mature composts, respectively. Although the values of the HR for various composts differ, they generally increase by more than 80% during composting, indicating a high degree of OM polymerization, since more polymerized components are found in mature compost. HI decrease during composting represents the formation of HS. Elemental and functional-group analysis of the HA originating from various composts indicated only minor differences between composting stages. Moreover, these values fell into a wide range, similar to that of soil HA. In general, even though HA amounts increased during composting, the elemental and functional groups were similar to "young forms" of HA reported in the literature. The  $E_4/E_6$  ratio was higher in compost HA, indicating a lower molecular weight than that of "model" HA (Chen et al., 1977). Elemental and functional-group analysis of compost FA have been reported in only a few works (Roletto and Luda, 1987; Pandeya, 1992). The compost FA had lower carbon and nitrogen contents but higher amounts of oxygen and carboxyl groups than HA, and the overall elemental and

functional groups extracted from compost were similar to "model" FA (Schnitzer, 1978; Roletto and Luda, 1987; Pandeya, 1992).

## CPMAS <sup>13</sup>C-NMR, FTIR and DRIFT spectroscopies

During the process of compost production, organic materials that are chemically complex and difficult to fractionate are formed. Extraction procedures that are commonly applied to soils and composts remove only a fractions of the C in the system. To profile the organic material of composts during the course of their formation, a method that can be applied to the intact sample is preferable. The only physical method holding some promise for the reliable characterization of such organic materials appears to be nuclear magnetic resonance (NMR) (Wershaw, 1985; Wilson, 1987). Recently, the application of NMR spectroscopy in studies on HA has gained considerable attention. Both <sup>1</sup>H- and <sup>13</sup>C-NMR, in the solid and liquid state, have been used. Wershaw (1985) indicated, that although NMR analysis has been applied for a much shorter period of time than most other techniques, it has provided more definitive structural information than other methods. Recent studies have shown that the technique of solid-state CPMAS (cross polarization magic-angle spinning) <sup>13</sup>C-NMR can provide carbon "fingerprints" of diverse solid samples such as peats (Wilson et al., 1983; Preston et al., 1987), whole soils (Preston and Ripmeester, 1983; Wilson et al., 1983; Preston et al., 1994), composts (Piotrowski et al., 1984; Gerasimowicz and Byler, 1985; Preston et al., 1986; Inbar et al., 1990a, Chefetz et al., 1995), forages (Eflosen et al., 1984), wood (Kolodzieski et al., 1982; Haw et al., 1984), and fossil fuels (Packer et al., 1983), HS isolated from soils, peat, river water, river sediments, lake water, marine waters, and marine sediments as reviewed by Malcolm (1989). An in-depth review of the state of the art of NMR spectroscopy theory, techniques, and applications to a wide range of organic and inorganic geochemistry and soil chemistry studies are discussed by Wilson (1987). Plant and microbial remains are the substrate for OM transformations in the geosphere. The myriad of chemicals which compose plants and microbes can be grouped into six major types: lignins, polysaccharides, proteins, lipids, resins and pigments (Wilson, 1987). The contribution of CPMAS <sup>13</sup>C-NMR assigned chemical shifts for each of these groups is described by Wilson (1987). Wershaw et al. (1986, 1988) compared spectra of HA fractions from several different

environments with published spectra of plant components; they showed that these components, when incorporated into HA retain many of the chemical structural features of the original plant material. They attributed some of the observed bands to lignin-like or melanin-like structures. Sharp and well-defined carbohydrate bands were observed in the spectra of some of the fractions. Lignins are composed of three basic building blocks, namely syringyl, guaiacyl, and p-hydroxyphenolic units. Resonances from these structures can be observed in all lignins. Typical <sup>13</sup>C-NMR assignments to these structures are presented in Fig. 4. A number of structural differences between lignins from various sources have been reported, but in general, many investigators agree that the basic units are those shown in Fig. 4. The intensity in the <sup>13</sup>C-NMR spectral region from 160 ppm to 110 ppm is due to the aromatic ring carbons of lignin. In addition, the signal around 56 ppm is usually attributed to methoxy carbons, principally of lignin origin (Himmelsbach and Barton, 1980; Haw et al., 1984; Wilson, 1987).

The second most important organic precursors to HS are polysaccharides, of which cellulose is the most important. Cellulose consists of long chains of glucose units, each of which is combined by a  $\beta$ -glucoside link to the C4 hydroxyl or another glucose unit (Fig. 5). Enzymatic hydrolysis of cellulose can vary in nature, as can the number of glucose units that are present. It is not uncommon to find 2-4000 glucose units joined together (Wilson, 1987). In the solid state, cellulose exists in at least four forms- the most common of which are cellulose I and II that may have slightly different chemical shifts. Moreover, these cellulose units may exist in various degrees of crystallinity (Haw et al., 1984; Wilson, 1987). The features of cellulose I (the native or natural form of cellulose) are: a peak at 105 ppm attributed to the C<sub>1</sub> carbon of the anhydroglucose repeating unit (Fig. 5); signals at 89 and 84 ppm, resulting from the C<sub>4</sub> carbon of cellulose; the highest absorption intensities for C<sub>2</sub>, C<sub>3</sub> and C<sub>5</sub> carbons in the 70 to 80 ppm region; peaks at 63 to 66 ppm are assigned to the C<sub>6</sub> carbon of cellulose (Haw et al., 1984; Wilson, 1987). Hemicellulose exhibits spectral features which are similar to cellulose. In addition, it exhibits peak at around 103 ppm due to carbons that are structurally analogous to the C1 carbon of cellulose, and signals at 22 and 174 ppm which result from acetate groups present in hemicellulose. Some of the absorption

intensity of the 174 ppm peak could be due to other carbonyl species present in hemicellulose (e.g. CO<sub>2</sub>H groups of uronic acid) (Kolodziejski et al., 1982).

The <sup>13</sup>C-NMR spectra can be divided into five regions (Hatcher et al., 1983). Region I (0-50 ppm) is assigned to paraffinic carbon or carbons that are bonded only to other carbons. Region II (50-112 ppm) is assigned to C-O, C-N bonds as in carbohydrates, alcohols, esters and amines. Region III (112-163 ppm) is assigned to aromatic and phenolic carbons. Region IV (163-190 ppm) represents carboxyl, ester and amide carbons groups. Region V (190-215 ppm) represent the carbonyl carbons. The 0 to 112 ppm region was calculated as aliphatic carbon, the 60 to 112 ppm region as polysaccharide carbon and the 112 to 163 ppm region as aromatic carbon. Total aromaticity was calculated by expressing aromatic C (112-163 ppm) as percentage of aliphatic C (0-112 ppm) plus aromatic C (Hatcher et al., 1981; Kögel-Knabner et al., 1991).

To date, many studies have been conducted on HA compost using CPMAS <sup>13</sup>C-NMR spectroscopy, but only a few used this method to study bulk compost (Inbar et al., 1989; Chefetz et al., 1995). Inbar et al., (1989) reported only minor differences between the spectra of HA from fresh and composted manure (12% increase in carboxyl content; 8% increase in aromatic carbon and 8% decrease in alkyl carbon). During composting of MSW, HA aromatic carbon increased by 39% while the aliphatic carbon content decreased by 19% (Garcia et al., 1992). During composting of MSW, the following distinct changes in the CPMAS <sup>13</sup>C-NMR spectra of the bulk compost resulting from the composting process were noted: (i) Total aliphatic carbon decreased by 14.4% from 74.8% in the raw material to 64.0% in the mature compost; the polysaccharides decreased by 17.0%, from 42.3% to 35.1% in the mature compost; and the alkyl groups (0-60 ppm) decreased by 11.0% during the composting process; (ii) the aromatic components, including aromatic and phenolic carbons, increased by 54%, from 15.9% in the raw material up to 24.5% of the total carbon in the mature compost. Total aromaticity increased by 58.2%, from 17.5% in the raw material to 27.7% in the mature compost; (iii) carboxyl carbon increased by only 9.5%; (iv) the C=O carbonyl carbon increased by 73.7%, from 1.9% in the raw material to 3.3% in the mature compost (Chefetz et al., 1995).

Infrared (IR) spectroscopy and a wide variety of chemical methods are being used to characterize HS. Fourier transform infrared (FTIR) spectroscopy serves as a qualitative tool to nondestructively characterize the principal classes of chemical groups that compose the HA. Negative feedback as to the usefulness of IR spectral analysis is probably due, in part, to the complexity of the IR spectra. However, IR analysis has contributed substantially to the knowledge of HA chemistry (Schnitzer, 1978; Stevenson, 1982; MacCarthy and Rice, 1985), and complements the information obtained from solid-state CPMAS <sup>13</sup>C-NMR spectroscopy (Gerasimowicz and Byler, 1985; Lobartini and Tan, 1988). The structural complexity of humic materials and the abundance of strongly hydrogen-bonded groups have, until recently, severely limited the usefulness of infrared spectroscopy for structural and compositional studies. With dispersive instruments only broad, ill-defined bands have been observed (Gerasimowicz et al., 1986). FTIR spectroscopy, which provides a much higher signal-to-noise ratio and improved accuracy in the frequency of the instrument, increased the information attainable from the spectra (Griffiths, 1983). Gerasimowicz and Byler (1985) and Gerasimowicz et al. (1986) obtained FTIR spectra on solid HA extracted from materials sampled at four selected stages of a municipal wastewater treatment process. From the FTIR spectra, several important differences between the decomposition stages were observed and discussed. Sugahara and Inoko (1981) investigated HA extracted from city refuse at different stages of decomposition by IR spectroscopy. They observed decreases in aliphatic C-H stretching, increases in COO- and decreases in C-O stretching as composting proceeded. On the whole, the shape of the IR spectra of city refuse HA became featureless during composting. Similar changes were observed by Zech et al. (1987) for IR spectra of fresh and decomposed spruce and pine litter. In many instances, CPMAS <sup>13</sup>C-NMR spectroscopy data lend themselves somewhat better to quantitative analysis than do the FTIR results. In particular, the relative aromatic nature of the HA was more evident from the NMR spectra and could not be seen as readily from FTIR data (Gerasimowicz and Byler, 1985). The development of an attachment mounted onto FTIR spectrophotometers has allowed the determination of diffuse reflectance infrared Fourier transform (DRIFT) spectra. Sample preparation for DRIFT spectroscopy is much simpler than for FTIR spectroscopy, interferences due to water adsorption are reduced, and resolution is

improved. The spectra obtained using DRIFT spectroscopy had a higher degree of resolution as compared with FTIR spectroscopy. Moreover, the bands indicative of aliphatic C-H, carboxyl and carboxylate functional groups, aromatic C=C, and the C-O stretch of polysaccharides were prominent and very well resolved. The DRIFT spectra obtained can also be used to fingerprint OM acquired from various sources. Relative concentrations of functional groups were found to be fairly constant regardless of sample concentration. The DRIFT spectra peak intensity ratio can be used to determine the humification process. The application of DRIFT spectroscopy to OM research will prove especially useful for characterizing heterogeneous bulk samples such as peat and composts. A combination of quantitative elemental analysis supplemented by modern, nondestructive NMR, FTIR and DRIFT characterizations could have significant biochemical implications in the study of the nature and properties of HS and other complex heterogeneous matrices (Niemeyer et al., 1992).

#### Raw material used for composting

#### Municipal solid waste:

Problems caused by MSW in modern society have become more severe over the last decade due to increasing amounts of waste and decreasing availability of landfill space (Alter, 1991; Finstein, 1992). The amount of MSW generated in the US rose to 323 million tons in 1994, an increase of 5%, whereas during the period between 1988 and 1994 the number of landfills decreased by more than half (from 8000 to 3558 in 1994). The remaining capacity of the landfills has also decreased and in some states such as Ohio, Missouri, and Vermont the landfills can last another 10 years or less. Together with the decreasing landfill capacity, the tipping fee has increased and can reach up to 75\$ per ton (Steuteville, 1994a,b, 1995). The European community produces more than 2500 tons of garbage a year of which the MSW fraction can reach up to 10%. Thus recycling has become an attractive solution for MSW treatment. The organic fraction in the MSW varies between 30 and 50%. Thus recycling this fraction can reduce the cost of transportation by 50%. For the organic fraction, composting seems to be a desirable option, having the capacity of reducing the volume and weight by approximately 50% and resulting a product which can be useful for agriculture (He et al., 1992). An alternative solution for organic waste management is the waste to

energy program, but its high tipping fee and its minor daily capacity make composting the ideal solution for the organic fraction. The main problems facing MSW compost production and utilization stem from the heterogeneous nature of the raw material. Its composition can change with climate, standard of living, type of garbage collection system and season.

#### Yard waste:

Yard waste can be defined as the amount of leaf fall, grass clippings and wood waste diverted from the MSW stream. In 1988, the EPA estimated that 18% of MSW is yard waste. Yard waste is not homogenized waste and its characteristics vary with weather, area and collection policy. The characteristics of the material affect the collection treatment, the processing equipment and the properties of the end product. Yard waste humidity varies from 30 to 75%, with that of leaves varying between 19 and 28%, of grass from 54 to 64% and of the wood fraction from 17 to 18%. The C/N ratio of yard waste is usually high (90-125) due to the large levels of lignin in woody waste. To reduce the initial C/N ratio to a level suitable for composting (30-35), yard waste is usually mixed with animal manure, sewage sludge, poultry manure or any other waste that can provide additional nitrogen. Recovery of yard waste by composting is an increasingly popular method of recycling solid organic waste (Steuteville, 1995). The common systems used for composting yard waste are static piles and turned windrows. Yard waste compost is useful as a substrate in container media and unlike composts produced from other wastes (MSW and sewage sludge) this compost seems to be "cleaner".

#### Sewage sludge:

The level of sewage sludge, the by product of normal wastewater treatment operations, increasing worldwide. Utilization of sewage sludge in agriculture as an organic fertilizer is regarded as a beneficial and economic process. Chemical properties of sewage sludge indicate high rates of nitrogen and phosphorus. Sewage sludge can be applied to soil as a liquid or solid amendment. An increasing concern over human pathogens in the sludge has enhanced the interest in using composting as a process that can destroy plant and human pathogens and produce useful agricultural products. The main problem facing composting of sewage sludge is its moisture content. Thus before composting, sewage sludge humidity must be brought to less than 60% by drying or by

adding a dewatering agent (lime). Usually sewage sludge cannot be used as only raw material for composting, so yard waste or straw litter are used as bulking agents.

#### Separated cattle manure:

The total amount of organic waste products in the US from livestock and poultry production has been estimated at over 1.5 billion tons per annum (on a dry matter basis). Of this amount, about 1 billion tons is cattle manure (Stevenson, 1985). Because of technological and economic considerations, the monetary value of manures and other wastes has significantly decreased in recent years, with the result that these materials are now regarded as a liability rather than an asset to the total farm operation. Farming has become highly specialized and livestock and poultry production is being concentrated in to large-scale confinement-type enterprises. These changes imply that large volumes of wastes have to be disposed of in a relatively small area (Stevenson, 1985). Stevenson (1985) summarized the limitations regarding the use of farmland for the disposal of animal manure as follows: (i) animal manure as a source of plant nutrients is a bulky, low-grade fertilizer of variable composition; (ii) concentration of nutrients, soluble salts, trace elements, and water vary tremendously and are seldom known. Optimum rates of application are thus difficult to predict; (iii) in many soils, the leaching of nutrients present in high concentrations in manures (especially NO3-) in to the ground water may limit application rates; (iv) on-farm management problems are created by the physical properties of manure. Application techniques are inefficient and time consuming; (v) production of animal manures is continuous, while the need for fertilizers is seasonal; (vi) odor and associated nuisances; and (vii) the presence of some human and plant pathogens and weeds restrict the use of manures by farmers. Development of new management systems which will increase the quality of the products, decrease salt concentration, and improve the physical structure and ease of handling are needed. One of the proposed systems now used on farms is based on separating of the manure into solids and liquid (Huijsmans and Lindley, 1984; Bohnhoff and Converse, 1987). This material can be successfully used, after proper composting, as a peat substitute or complementary product for peat mixtures in container media, while the effluent is used as organic liquid fertilizer (Chen et al., 1984a,b; Levanon et al., 1984; Raviv et al., 1984; Hadar et al., 1985; Chen and Hadar, 1987).

#### Grape marc:

The primary by-product of grape juice processing and wine production is grape marc (GM; pomace). It consists primarily of processed skins, seeds and stems. GM represents as much as 20% of the wet weight of the original fruit and its moisture content is about 65% (Hang, 1988). Annual world production of dried GM is estimated at 7,500,000 metric tons (Aguilera, 1987). Direct incorporation of GM, without any pretreatment, into vineyard soils is a universal practice. However, this method has become a serious problems since degradation materials that are highly incompatible with plant roots are released. Composting GM has the potential to solve the environmental problems related to this byproduct and to create a useful product for greenhouse agriculture.

#### **Conclusions**

Composting seems to be a desirable solution for organic waste management. Readily available wastes such as cattle manure, MSW, sewage sludge, winery waste and yard waste have been found to be suitable materials for composting. The composting process has the capacity to reduce the volume and weight of these wastes by approximately 50% and to produce a product which can be useful in agriculture. Composts produced from various wastes have been found to be suitable materials for container media having the ability to reduce peat and pesticide use thereby solving environmental problems. The positive effects of the composts on plant growth can be explained by their physical, chemical and biological properties. Their physical properties fit well with optimal requirements. In greenhouse setups, where fertigation is continuously applied, the nutrient content is not as important. However, the slow release of nutrients between irrigations, the high contents of HS and the bioactivity of the medium improves plant growth. Mature composts have also been found to be suppressive to several soilborne plant pathogens such as P. aphanidermatum, R. solani and S. rolfsi. As a result, application rates of hazardous pesticides can be reduced or eliminated. Amendment of composts to soils has been shown an increase crop yield, while amendment of compost with mineral fertilizer increases crop yield as compared to the amendment of either compost or mineral fertilizer alone. The positive effects of mature compost on plant growth are connected to its high HS content. The HS formed

during composting seem to have the same characteristics as HS that are formed in soils over long periods. Spectroscopic methods (CPMAS <sup>13</sup>C-NMR, DRIFT and FTIR) are useful tools to determine the transformations of the organic fraction during composting, and can help to define compost maturity. During composting, many parameters must be monitored (temperature, humidity, pH, C/N ratio, aeration), although a number of the parameters stabilize at the maturation stage providing no tools for the actual maturity stage. Only a few parameters can be used to define compost maturity. Many authors have reported that HI, C/N ratio, respiration and microbial activity can be used as maturity indexes. We hypothesize that plant growth may serve as an integrative signal for compost maturity.

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#### **Figures legends**

Fig. 1.

Simplified flowchart of the composting process (after Gray and Biddlestone, 1981).

Fig. 2.

A schematic temperature and processes vs. time of composting.

Fig. 3.

Changes and trends in the humification parameters (expressed as percentage of variation) during the composting of wastewater sludge and straw mixtures (after Saviozzi et al., 1988)

Fig 4.

Structural components of lignin (the numbers indicates typical <sup>13</sup>C-NMR assignments).

Fig. 5.

Structures of anhydroglucose repeating unit and cellobiose (4-O- $(\beta$ -D-glucosepyranosyl)  $\beta$ -D-glucopyranose).

Table 1.

Effects of composting of the solid fraction of a slurry produced from methanogenic fermentation of cattle manure on tomato seedling response (following Hadar et al., 1985).

Table 1. Effects of composting of the solid fraction of a slurry produced from methanogenic fermentation of cattle manure on tomato seedling response (following Hadar et al., 1985).

Treatment	Unfertilized	Fertilized	
	Dry weight (mg/plant)		
Raw material	166b	30c	
Immature compost	319a	486b	
Mature compost	355a	612a	





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fig. 2

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fig 4

SYRINGYL G

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Fig. 5





30e

# FORMATION AND PROPERTIES OF HUMIC SUBSTANCE ORIGINATING FROM COMPOSTS

#### ABSTRACT

Composting enables a detailed evaluation of the humification process of various organic wastes within a short period of time (3 to 6 months). Humic substances (HS) constitute a large fraction of the organic matter (OM) in compost, and they are its most active fraction due to their effects on soil ecology, structure, fertility and metal complexes, and plant growth. The formation and properties of HS extracted from various composts such as municipal solid waste (MSW), grape marc (GM), composted separated cattle manure (CSM), sewage sludge (SS), wood compost (WC) and other organic wastes were studied. Degradative and non-degradative techniques (FTIR, DRIFT, <sup>13</sup>C-NMR) were used to study the transformation of HS during composting of the various organic wastes. Time-course studies of composting some of these wastes showed an increase in the relative amount of humic acid (HA) (from 18% to 45% of OM in CSM compost and from 5% to 20% in MSW compost), whereas the formation rate of fulvic acid (FA) was inconsistent. A humification ratio (HR - the ratio of HA/FA) was used to evaluate compost maturity. Values of 0.9 to 3.4 and 3.0 to 9.2 were typical for immature and mature composts, respectively. Another humification index (HI) used to define compost maturity was calculated as the ratio between non-humified fraction (NHF) and the humified fraction (HA+FA). A HI decrease during composting represents the formation of HS. Elemental- and functional-group analyses indicated only minor differences between HA extracted from composts at various stages. Moreover, these values fell into a wide range, similar to that of soil HA. The <sup>13</sup>C-NMR spectra of the HA exhibited strong bands representing aliphatic structures in various composts (50% of total C in CSM, 30% in MSW and 61% in GM) and a lower level of aromatic components (37% in CSM, 22% in MSW and 22% in GM). The FTIR spectra showed similar trends of strong aliphatic and carbohydrate components. Both techniques provided more qualitative information indicating that HA extracted from mature compost exhibits more aromatic structures

and carboxyl groups and less carbohydrate components than that from immature compost.

Studies on the effects of HS on plant growth showed stimulative effects. Typical response curves indicated enhanced growth with increasing HS concentration in solution, followed by decreases in growth at higher concentrations. In soils, the addition of composts was found to stimulate growth beyond that provided by mineral nutrients, presumably because of the effects of HS.

#### Introduction

Composting can play useful role in global waste management due to the increasing amount of decomposed organic materials such as animal excreta, municipal solid waste (MSW) and sewage sludge (SS) in modern society. Composting has been defined as a controlled microbial aerobic decomposition of heterogeneous raw waste passing through a thermophilic phase with a temporary release of phytotoxins, followed by the production of  $CO_2$ ,  $H_2O$ , minerals and stabilized organic matter (OM) containing a high amount of humic substances (HS). The importance of HS to soil ecology, fertility and structure and their beneficial effects on plant growth (Chen and Aviad, 1990) have caused an increase in the use of compost as an amendment to soils or as a substitute substrate for peat in container media (Avnimelech et al., 1993; Chen et al., 1992; Hoitink, et al., 1993). HS originating from compost form within a shorter period of time than soil HS, therefor better understanding of the chemical and physical characterization and transformation of the compost HS is necessary to study the differences in the formation period. Moreover due to the increase interest in compost as substitute to peat in container media it is essential to study the interactions of HS in the compost-plant system.

The objectives of this article were (1) to compare the rate of decomposition of OM in various composts; (2) to study the rates of formation and decomposition of HS-

humic acid (HA), fulvic acid (FA) and the non-humic fraction (NHF), in various composts; (3) to use humification parameters as maturity indexes; (4) to characterize compost-derived HA using elemental- and functional-group analyses and spectroscopic measurements; (5) to study the effects of compost-derived HS on nutrient solubility and plant growth.

#### **Humic Substance Content**

Among the chemical criteria used to characterize compost maturity, HS content is one of the most common. The amounts of HS fractions in various composts at various stages of composting are reviewed here. The main trends of several humification parameters over a period of 140 days of composting of wastewater sludge and straw mixtures are shown in Fig. 1 (Saviozzi et al., 1988). The following humification indexes (HI) were used to defined compost maturity: (1) HS- amount of total humic substances (HA, FA and NHF) as percent of OM; (2) HA- amount of humic acid as percent of OM; (3) FA- fulvic acid as percent of OM; (4) HR- the HA/FA ratio; (5) amount of the humic materials (HA+FA); (6) HI- the ratio between the NHF and the HA+FA fractions (Sequi et al., 1986); (7) HAp- humic acid percent of HS.

Total HS content follows different trends during the composting of different composts. HS content does not vary during composting of MSW (Sugahara and Inoko, 1981; Das, 1988; Jimenez and Garcia, 1992) These authors found that alkaline extraction of MSW compost at various stages of composting gives a steady value in the range of 19 to 22% of OM. A possible explanation for the presence of HS in the early stages of composting and for the stability of the HS content in MSW compost could be the relatively high content of NHF. Therefore HS in MSW compost cannot be used as an indicator of maturity. In contrast, during the composting of CSM, HS content doubled (from 377 to 710 g/kg OM). The different trends between the composts can be explained by the relatively high amount of HA in CSM (46% of OM),

whereas both HA and FA fractions in MSW compost amount to less than half of the total OM. The trend in HA levels during composting is similar in all composts, its content increasing during composting and reaching up to 46% and 48% of OM in CSM and poplar bark compost, respectively (Roletto et al., 1985; Inbar et al., 1990). In MSW compost, HA increased from 7% - 8% in the raw material to 12% - 14% in mature compost (Jimenez and Garcia, 1992). While the levels of HA increases the amount of FA usually decreases and the HA/FA ratio is therefore often used as an indicator of maturity. This trend of an increasing HA/FA ratio from fresh to composted OM has been reported for poplar bark (Roletto et al., 1985), farmyard manure (FYM), urban refuse (Saviozzi et al., 1988), CSM (Inbar et al., 1990) and MSW (Sugahara and Inoko, 1981; Das, 1988; Jimenez and Garcia, 1992; Gonzales et al., 1993). The value of the HR differs for various wastes but it generally increases by more than 80% during composting, indicating a high degree of OM polymerization, since more polymerized components are found in the mature compost.

Another parameter indicating the role of HS is the HI (NHF/HA+FA) which decreases during composting due to humification of OM (Saviozzi et al., 1988; Inbar et al., 1990). The trend of decreasing HI from fresh to composted materials is similar in all wastes, but the rate of decrease changes according to the amount of NHF in the waste. The HI of grape marc (GM), containing a high level of sugars, drops sharply during composting, in contrast to the HI in CSM (Inbar, 1989). To summarize a large amount of HA forms while FA level usually decreases. The HI and the HR can only be used as maturity parameters when NHF is separated from the fulvic fraction, otherwise these parameters have no meaning.

#### **Elemental- and Functional-Group Analyses:**

The elemental composition, atomic ratios and functional groups of HA extracted from various composts as compared to "model" HA (Schnitzer, 1978) and Leonardite HA are presented in Table 1. The average compositional range of HA

extracted from various composts was similar to those of "model" and Leonardite HA. The C content of HA isolated from compost was lower than that of "model" HA, except in the cases of CSM and GM. This parameter does not change during composting (Roletto and Luda, 1987; Inbar, 1989; Garcia et al., 1992). H content was higher in compost HA than in Leonardite or "model" HA, although it was slightly reduced during composting of CSM and GM. N content was also higher in compost HA. The high N and H contents in the composts may be due to the presence of side chains containing those components. The highest contents of N and H were found in MSW compost (Garcia et al., 1989; Deiana et al., 1990; Garcia et al., 1992), which yielded a relatively low C/N ratio as compared to HA formed in soil or during composting of other stabilized wastes. The H/C ratio represents HA aromaticity (a low ratio indicates an aromatic structure). All compost HA had higher H/C ratios than the "model" or Leonardite HA, indicating that aromatic structures in compost HA are less pronounced and therefore compost HA has identified as "young" HA.

The major differences between "model" or Leonardite HA and compost HA were found in the functional-group analysis. Compared to soil and sediment HA, compost HA contained less fractional oxygen groups (carboxyl, carbonyl and phenolic carbon), due to the relatively short formation time during composting as compared to that required for soil OM transformation. During composting, the carboxyl group content increased (192 to 221 meq/100g in CSM, 176 to 224 meq/100g in MSW, 184 to 264 meq/100g in SS). The carbonyl group content showed the same trend, whereas that of the phenolic group decreased during composting. The total acidity (calculated as phenolic plus carboxyl groups) behaved differently in the various composts: it increased in composts in which the raw material had a stable structure (wood and cattle manure) but decreased in composts in which the raw material had a stable structure (mode and Luda, 1987; Garcia et al., 1992; Kakezaw, 1992). There were no major differences between the elemental composition of HA from the various composts at various stages

of composting and that of "model" HA (Table 1). In general, the elemental and functional groups were similar to "young forms" of HA reported in the literature, even though HA amounts increased during composting.

The  $E_4/E_6$  ratio was higher in compost HA, indicating a lower molecular weight than that of "model" HA (Chen et al., 1977). Elemental and functional group analyses of FA have been reported in only a few works (Roletto and Luda, 1987; Pandey, 1992). The compost FA had lower C and N contents but higher amounts of O and carboxyl groups than HA, and the overall elemental and functional groups extracted from compost were similar to "model" FA (Schnitzer, 1978; Roletto and Luda, 1987; Pandey, 1992).

#### Infrared Spectroscopy (FTIR, DRIFT):

Infrared spectroscopy was used to characterize the HS. FTIR and DRIFT spectroscopy served as qualitative tools to characterize the chemical groups and bands of the HA complex structures. Sugahara and Inoko (1981) investigated HA extracted from city refuse at various stages of composting by IR spectroscopy and found that the aliphatic C-H and C-O stretching decreased while the carboxyl COO- increased during composting. The main absorbance bands were: a broad band at 3400-3300 cm<sup>-1</sup> (H-bonded OH groups); a slight shoulder at 3085-3075 cm<sup>-1</sup> (aromatic C-H stretching); two peaks at 2930 and 2850 cm<sup>-1</sup> (aliphatic C-H stretching); a slight shoulder at 1730-1715 cm<sup>-1</sup> (C=O of carboxyl, C=O of ketonic carbonyl); a well-pronounced peak at 1610-1655 cm<sup>-1</sup> (aromatic C=C stretching); a sharp peak at 1540-1560 (amide II); a peak at 1460-1450 cm<sup>-1</sup> (-CH deformation of -CH<sub>3</sub> and -CH bending of CH<sub>2</sub>); a peak at 1420 cm<sup>-1</sup> (aromatic ring stretch); a peak at 1400-1350 cm<sup>-1</sup> (aliphatic C-H bending); a peak at 1270-1220 cm<sup>-1</sup> (aromatic C-OH and -C-OH stretch and OH deformation of -COOH); a peak around 1100-1020 cm<sup>-1</sup> (C-O stretch of polysaccharides). The interpretations of the IR spectra are based on Inbar et al. (1990), Niemeyer et al.

(1992), Deiana et al. (1990), Sugahara and Inoko (1981), Garcia et al. (1992), Roletto and Luda (1987) and Stevenson (1982).

HA spectra from the various mature composts studied here exhibited similar features: all showed a strong aliphatic nature with aromatic structure and peptide bonds, along with relatively low carboxyl content, similar to young type III HA extracted from fresh soil OM (Stevenson and Goh, 1971). HA extracted at several stages during the composting of various wastes exhibited only minor changes. The main ones consisted of slight reductions of the aliphatic and polysaccharide bands during composting of SS and MSW (Sugahara and Inoko, 1981; Garcia et al., 1989, 1992), whereas during composting of CSM, no changes were observed; during the composting of GM there was a relative increase in aliphatic carbon and a decrease in polysaccharides. The minor changes in HA extracted from CSM during composting are presented in Fig. 2.

#### CPMAS <sup>13</sup>C-NMR Spectroscopy

The use of NMR spectroscopy to study HA has gained prominence over the last few years. Wershaw (1985) showed that although NMR analysis is only applied for a short time, it can provide more definitive structural information than other methods. The <sup>13</sup>C-NMR spectra were divided into the following regions (Hatcher et al., 1983; Malcolm, 1989): 0-50 ppm (alkyl C-methyl, methylene and methine groups), 50-60 ppm (methoxyl C), 60-70 ppm (alcohol), 70-98 ppm (C-O, C-N), 98-112 ppm (anomeric C), 112-145 ppm (aromatic C), 145-163 ppm (phenolic C), 163-190 ppm (carboxyl groups), 190-215 ppm (carbonyl C). The 0-112 ppm region was calculated as aliphatic C, 60-112 ppm as polysaccharide C, 112-163 ppm as aromatic C. Total aromaticity was calculated by expressing aromatic C (112-165 ppm) as percentage of aliphatic C (0-112 ppm) plus aromatic C. CPMAS <sup>13</sup>C-NMR spectra of HA extracted from CSM is presented in Fig. 3. There were only minor differences between the spectra of HA from the fresh and composted manure (12% increase in carboxyl

content; 8% increase in aromatic carbon and 8% decrease in alkyl carbon), similar to the FTIR spectra (Inbar, 1989). During the composting of MSW, changes in HA structure were observed: the HA aromatic carbon increased by 39% while the aliphatic carbon content decreased by 19% (Garcia et al., 1992). Opposite changes occurred in GM HA: while the alkyl region increased, the aromatic carbons decreased, indicating highly oxidizing conditions (Inbar, 1989). The main differences between HA extracted from various composts are present in Table 2. CSM HA seemed to be more aromatic and less aliphatic than MSW and GM HA. The higher aromaticity of the CSM HA can be explained by the high lignin content in this compost (61.5% of dry weight), whereas GM and MSW contain more easily biodegradable OM. These differences in HA structure lead to the conclusion that the raw materials components influence not only the time of composting but also the formation of HS.

#### Humic Substance Effects on Plant Growth

Applying OM as a fertilizer increased plant yield to a higher level than that resulting from the application of the same level of inorganic fertilizer, presumably because of the effects of the HS. In soils, the addition of compost can stimulate growth beyond that provided by mineral nutrient supplements alone (Senesi, 1989; Chen et al., 1994). This improvement can be explained by direct short-term fertilizer effects and some indirect effects. Table 3 presents the typical effects of HA stimulation on wheat growth when given in water or nutrient solution. Addition of FA to the nutrient solution yielded an atypical response curve whereby cucumber root and shoot weights increased with increasing FA concentration up to a FA concentration where shoot and root weights decrease. Chen et al. (1994) found the same trend in melon shoots and roots with increasing concentrations of HS originating from a water extract of CSM. Both experiments showed that higher OM levels result in decreased growth, possibly resulting from a suboptimal concentration of free micronutrients in solution due to an excessive amount of chelators (HS). Complexation of transition metals, such as Cu, Zn, Fe and Mn by HS has been the focus of numerous publications. The solubility of most of the micronutrients in their inorganic forms is limited in soil or nutrient solution. The presence of HS may contribute to improved availability of these elements (Chen and Aviad, 1990). HS not only increased the solubility of Fe in solution but they also affected Fe transport from roots to shoots. Chen et al's (1994) work on HS extracted from CSM indicates that residual concentrations of Fe, Mn and Cu in nutrient solutions that were equilibrated at pH 6.5 and 7.0 increased with increasing concentrations of added OM. With regard to plant nutrition, this data suggests that at low pH, HS may not exhibit beneficial effects, but at pH 7.5 or higher, a high concentration of HS is required to maintain micronutrient availability. The stimulation of ion uptake by the addition of HS led to the proposal that these materials affect membrane permeability related to surface activity of the HS. Another phenomenon related to CSM and GM HS is hormone-like activity (Chen et al., 1994). When mungbean cuttings were placed in nutrient solutions containing OM extracted from CSM, GM and Leonardite, root weight and number were significantly higher as compared to the control. This result supports those of other plant growth assays, in which HS added to a nutrient solution enhanced root formation activity, which could be considered an auxin-like activity. To summarize, the effects of HS on plant growth can be divided into direct and indirect, as follows (Chen and Aviad, 1990):

#### Direct effects:

- 1. Effects on membranes resulting in improved transport of nutritional elements
- 2. Enhanced protein synthesis
- 3. Hormone-like activity
- 4. Enhanced photosynthesis
- 5. Effects on enzyme activity

#### Indirect effects:

 Solubilization of microelements (Fe, Zn, Cu and Mn) and some macroelements (K, Ca, P)

40

- 2. Reduction of active levels of toxic elements
- 3. Enhancement of microbial populations

#### Conclusions

- 1. The level of HS formation reached a maximum within 90 to 120 days of composting without forced aeration.
- 2. HS level increased with composting time in CSM and wood compost (WC), but remained steady in MSW compost.
- 3. HA level increased in CSM, WC, MSW and SS composts.
- 4. FA level remained steady in CSM and decreased in MSW composts.
- 5. NHF level decreased with composting time.
- Elemental- and functional-group analyses indicated only minor differences between HA extracted from composts at various stages of composting.
- Values of C, H and S in HA derived from various composts were similar to those found in soils. However, the N levels were higher in compost-derived HA and the C/N ratio was therefore lower.
- 8. Total acidity, -COOH and phenolic OH levels were lower in HA derived from composts than the average numbers from soil HA.
- FTIR and NMR spectra of compost-derived HA were similar, regardless of composting time.
- 10. FTIR and NMR spectra of compost-derived HA exhibited high levels of polysaccharides and aliphatic structures.
- 11. Biological activity of compost-derived HS resembled that of soil-derived HS.
- 12. Plant-hormone-like activity attributed to HS does not involve auxins, cytokinins or abscisic acid.
- 13. Growth enhancement of plants in nutrient solution and soils by HS may be attributed to the maintenance of Fe, Mn, Cu and Zn in solution at sufficient levels. This effect is pH-dependent, its effectiveness decreasing with increasing pH.

14. The commonly cited conclusion (including 1992 publications) stating that:"Stimulatory effects in nutrient solution of HS can't be ascribed to a supply of elements" may be incorrect.

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- Fig 1: The major relative trends of several humification parameters (expressed as percentage of variation) during 140 days of sludge-straw composting (after Saviozzi et al., 1988).
- Fig 2: FT-IR spectra of HA extracted from separated cattle manure at three stages during composting (after Inbar, 1989).
- Fig 3: CPMAS <sup>13</sup>C-NMR spectra of HA extracted from separated cattle manure at the beginning and after 147 days of composting (after Inbar, 1989).

	CSM <sup>1</sup>	MSW <sup>2</sup>	SS <sup>3</sup>	wc <sup>4</sup>	GM <sup>1</sup>	"model"	Leonardite <sup>2</sup>
						HA <sup>5</sup>	
с	57.8	52	53	50.58	58.2	56.2	61-55.1
Н	5.3	6	5	5.66	5.9	4.7	3.34-3.86
N	3.8	6.3	4.12	3.53	5.8	3.2	1.56-2.43
s	1.1	0	nd	nd	0.66	0.8	0
H/C	1.11	1.4	1.17	1.34	1.21	1	0.66-0.88
C/N	16.6	11.7	13	16.9	14.2	20	52
Total acidity (meg/100 g)	346	498	626	439	413	670	653
COOH (meg/100 g)	221	225	264	247	271	360	279
Phenol OH (meg/100 g)	126	273	362	192	142	390	374
C=O (meq/100 g)	NA	252	288	276	nd	nd	510
E4/E6	7.8	7.1			9.4	4.8	

Table 1. Elemental analysis, H/C and C/N ratios, functional groups and E4/E6 analysis of compost-derived humic acid (HA).

<sup>1</sup> Inbar, 1989

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<sup>2</sup> Garcia et al., 1992

<sup>3</sup> Garcia et al., 1989

<sup>4</sup> Kakezawa et al., 1992

<sup>5</sup> Schnitzer, 1978

Table 2. Carbon distribution in humic acids (HA) extracted from CSM, GM and MSW (as determined by <sup>13</sup>C-NMR).

		_		
		CSM <sup>1</sup>	GM <sup>1</sup>	MSW <sup>2</sup>
Aliphatic C	% of total C	50.4	61	67.3
Aromatic C	% of total C	37.1	22	18.8
Carboxylic C	% of total C	10.6	15	10.2
Aromaticity	% of total C	42.4	27	21.8

<sup>1</sup> Inbar, 1989

<sup>2</sup> Garcia et al., 1992

Culture medium	Plant organ	Fresh weight, mg/plant	Stimulation, %
Water	Root	93	0
	Shoot	185	0
Water + HA	Root	146	57.5
	Shoot	252	36.2
Hoagland's	Root	182	96.3
	Shoot	342	84.9
Hoagland's + HA	Root	203	119.0
	Shoot	390	110.8

Table 3: The effects of 50 mg  $L^{-1}$  humic acid (HA) in water or Hoagland's nutrient solution on wheat growth (after Vaughan and Malcom, 1985).

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## MUNICIPAL SOLID WASTE COMPOSTING: CHEMICAL AND BIOLOGICAL ANALYSIS OF THE PROCESS

#### ABSTRACT

Composting of municipal solid waste (MSW) was studied in an attempt to better understand the composting process and define parameters of maturity. Composting was performed in 1-m<sup>3</sup> plastic boxes and the following parameters were measured: temperature, C/N ratio in solid and liquid phase (C/N<sub>(s)</sub> and C/N<sub>(w)</sub> respectively), humic substance fractions and contents, dissolved organic carbon (DOC). Spectroscopic method (DRIFT) was used to study the chemical composition of the bulk organic matter (OM). A bioassay based on cucumber plants growth was correlated to other parameters. C/N<sub>(w)</sub>, C/N<sub>(s)</sub> and DOC showed high rates of change during the first 60 days, then stabilized. Humic acid (HA) content increased to a maximum at 110 days, corresponding to the highest plant dry weight and the highest 1650/1560 (cm<sup>-1</sup>/ cm<sup>-1</sup>) peak ratios from DRIFT spectra. DRIFT spectra showed that the OM transformed to a more aromatic structure.

#### **INTRODUCTION:**

Problems caused by municipal solid waste (MSW) in modern society have become more severe over the last decade due to increasing amounts of waste and decreasing availability of landfill space (Alter, 1991; Finstein, 1992). Recycling has become an attractive solution for the waste management. For the organic fraction composting seems to be a desirable option having the capacity of reducing the volume and weight by approximately 50% and resulting a product which can be useful for agriculture (He, 1992). One of the main obstacle to successful utilization of MSW compost in agriculture is the lack of reliable quality criteria and understanding the OM transformations throughout the process. Proper evaluation of compost maturity is essential for the establishment of such criteria. Therefore, the objective of this paper is to correlate chemical analyses and DRIFT spectra, with plant performance bioassay.

#### **RESULTS AND DISCUSSION**

Various parameters were followed during composting of MSW. The  $C/N_{(s)}$  ratio decreased rapidly from an initial value of 28 in the raw material to 18 after only 20 days. The ratio continued to decrease, albeit less sharply, to 12.2 after 60 days. From this point on the C/N ratio stabilized at a value of about 12 (11.8-12.8) for the

remainder of process. The C/N<sub>(w)</sub> ratio followed a similar trend, exhibiting three phases: (*i*) rapid decrease from 35 to 8 during the first 20 d; (*ii*) slower decrease to a value of 6, lasting till 70 d; (*iii*) days 70 to the end of the experiment, when it stabilizes at value between 5 to 6. The C/N ratio (C/N<sub>(w)</sub> and C/N<sub>(s)</sub> as well) in itself appeared to be a non reliable indicator of compost maturity. Although it changed dramatically during the second phase of composting, it did not change significantly during the curing phase.

The compost bacterial population is active only in the liquid phase, thus the DOC concentration during composting can indicate the biodegradability of the OM. The changes in DOC concentration followed a trend similar to that of the C/N ratio, exhibiting same three phases: (*i*) rapidly decrease from initial concentration of 28.30 g/Kg to 7.40 g/Kg over the first 20; (*ii*) days 20-60, when the DOC continued to decrease, less sharply, to 2.25 g/Kg; (*iii*) days 60 to the end of the experiment, when the DOC decrease moderately to 1.00 g/Kg.

HA content increased during composting, reaching a stable value after 110 days at 13.5% of the OM while the fulvic fraction (FF) content, including the fulvic acid and the non humic fraction (FA and NHF respectively), decreased. The increasing level of HA may indicate the degree of humification and the maturity of the compost. The humification index (HI=HA/FA) increased to a ratio of 3, and the humification ratio (HR=HA/FF) increased to 1.35. These values differ in other, but in general fresh compost contains low levels of HA and higher levels of FA (Saviozzi et al., 1988; Gonzalez, 1993; Ciavatta et al., 1993). During the composting process the FF decomposed whereas the HA level remained stable.

The distinct differences in the bulk DRIFT spectra resulting from composting, was a reduction of the 1560 cm<sup>-1</sup> peak (amide II) with time probably due to the relatively rapid biodegradabtion of the amino chain. The aromatic region (1650 cm<sup>-1</sup>) became sharper during composting. Peaks in the aliphatic region at 2930 and 2850 cm<sup>-1</sup> decreased, while the 1450 cm<sup>-1</sup> peak, which represents C-H deformation, increased. Another method of monitoring changes during the composting process is the measurement of the intensity of major peaks and the ratios between them (Inbar et al., 1989). The peaks at 2930 cm<sup>-1</sup>, 2850 cm<sup>-1</sup>, 1650 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> were chosen for these calculations. The ratio 1650/2930 (aromatic C / aliphatic C)
increased from 0.88 to 1.10, the ratio 1650/2850 (aromatic C / aliphatic C) increased from 0.79 to 1.54, the 1650/1050 ratio (aromatic C / polysaccharide) increased from 2.39 to 2.80, and the 1650/1560 ratio (aromatic C / amide II bond) increased from 0.94 to 1.52. These increases represent a decrease in polysaccharides, aliphatic and amide components, and an increase in the aromatic structure in the mature compost. The linear correlation between the aromatic to aliphatic peak ratio (1650/2930 cm<sup>-1</sup>/ cm<sup>-1</sup>) and the C/N ratio had a R<sup>2</sup>=0.936 calculated for the equation Y = 1.263 - 0.014X. This correlation indicate that the DRIFT spectra is a useful and reliable tool in the analysis the composting process.

It was hypothesized that plant growth may serve as an integrative single test for compost maturity (Chen and Inbar, 1993, Inbar et al., 1993). Cucumber plants grown in media containing fresh (14 d) compost (50% v/v) exhibited inhibited growth as compared to plants grown on older compost. The dry weight of plants grown in 110 and 132 d old composts were significantly higher than all the others. These results show that as OM decomposed the compost became a better substrate for plant growth. Only highly mature compost supported better plant growth. A correlation's between plants dry weight and other chemical analysis were correlated. A linear correlation between the 1650/1560 (cm<sup>-1</sup>/cm<sup>-1</sup>) DRIFT peak ratio and plant dry weight had  $R^2$ =0.81 calculated for the equation Y = 0.81+0.54X. The linear correlation between HA content in OM and plant dry weight had  $R^2$ =0.70 calculated for the equation Y = 3.59 + 7.78X.

## CONCLUSIONS

Due to materials and processes complexity the determination of compost maturity is very difficult. Therefore, several parameters are needed to be crossbred. This article proves that DRIFT spectroscopy, together with data on HS provide useful information about the OM transformations occurring during the composting process of MSW. Plant bioassay, level of HA and the 1650/1560 DRIFT peak ratio showed the same trend during composting and can therefor be used as maturity indexes. All those parameters exhibited three distinct phases: (*i*) rapid decomposition during the first 30 d; (*ii*) stabilization till day 90; (*iii*) maturation from day 90 and on. The MSW

compost, in our experimental system, was mature and ready to be used as an agricultural substrate after about 110 days of composting.

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# WATER-EXTRACTABLE COMPONENTS RELEASED DURING COMPOSTING OF MUNICIPAL SOLID WASTE

# ABSTRACT

Composting of municipal solid waste (MSW) was studied in an attempt to better understand the composting process and concomitant changes occurring in the watersoluble fraction. Composting was performed in 1-m<sup>3</sup> plastic boxes and the following parameters were measured in the compost liquid phase: C/N ratio, electrical conductivity (EC), pH, dissolved organic carbon (DOC), optical density and soluble nitrogen forms. The C/N ratio and DOC levels exhibited high rates of change during the first 60-70 days, then stabilized. The pH of the compost followed a typical trend during composting, reaching neutrality at the end of the process. The ammonium level peaked during the thermophilic stage, whereas during maturation the ratio between N-NO<sub>3</sub><sup>-</sup>/N-NH<sub>4</sub><sup>+</sup> increased to 4. The increasing level of NO<sub>3</sub><sup>-</sup> during the last stage of composting can be used as an indicator of compost maturity, whereas the C/N ratio can serve only as an indicator of compost stability.

# **INTRODUCTION:**

Problems caused by municipal solid waste (MSW) in modern society have become more severe over the last decade due to increasing amounts of waste and decreasing availability of landfill space (Alter, 1991; Finstein, 1992; Steuteville, 1995). Recycling has become an attractive solution for waste management. For the organic fraction, composting seems to be a desirable option having the capacity to reduce the volume and weight by approximately 50% and to yield a product which could be useful for agriculture (He et al., 1992).

Composting of agricultural and MSW is defined as a biological treatment in which aerobic microorganisms utilize organic matter (OM) as a substrate (Zucconi and de

Bertoldi, 1987). Since microorganisms are only active at the solid-liquid interphase of the compost, a study of this interphase is essential for a better understanding of C and N cycles during composting (Lynch, 1993).

One of the main obstacles to successful utilization of MSW compost in agriculture is the lack of reliable maturity criteria. A proper evaluation of compost maturity is essential for the establishment of such criteria (Chen and Inbar, 1993; Saviozzi et al., 1988). Therefore, the objective of this study was to analyze the chemical properties of the water-soluble fraction of MSW during composting.

# MATERIALS AND METHODS

# **Composting of MSW**

MSW was collected over a 24-h period from the town of Afula in Israel, and mechanically mixed in a MSW classifying facility. After sieving and eliminating the >5-cm fraction, the raw material was divided into three perforated plastic boxes (about  $1-m^3$  each) and composted for 132 days. The compost was turned, mixed, and sampled after manual removal of glass, plastics and metals at 0, 6, 13, 19, 27, 34, 41, 48, 62, 76, 90, 112 and 132 days. Samples (10 L each) were stored at 4°C. Smaller subsamples were dried at 65°C, then ground and sieved.

## Chemical analyses

Aqueous compost extracts were prepared by placing 20 g of compost (dry weight) in 200 mL of distilled water, and shaking (125 rpm) for 2 h at room temperature. The suspension was then centrifuged (10000 g for 30 min) and the supernatant filtered through a 0.45-µm membrane filter (Supor-450, Gelman Sciences). The concentration of dissolved

organic carbon (DOC) was measured immediately after extraction or fractionation using a total carbon monitor (TCM 480, Carlo Erba Instruments, Milan, Italy).

Total N, organic N and  $NH_4^+$  were measured using an automatic Kjeldahl system (Kjeldahl System 1030, Tecator, Hsiganas, Sweden).  $NO_3^-$  levels were measured using specific electrodes. Optical density at 465 nm was measured with a Philips Pye Unicam PU 860 UV/VIS spectrophotometer (Pye Unicam Ltd., Cambridge).

## **RESULTS AND DISCUSSION**

The pH during MSW composting (Fig. 1) exhibited a typical pattern for composting processes (Diaz et al., 1982): it dropped slightly at the beginning of the composting process (thermophilic stage) due to the accumulation of organic acids (e.g., low-molecular-weight fatty acids). The accumulation of organic acids reflects the high rate of OM degradation, and these acids are used later on as substrates by other microorganisms (Inbar et al., 1993). During the cooling down and maturation stages (day 50 and on) the pH dropped to a neutral value.

The EC levels dropped from a value of 5.4 to 2.9 after 20 days of composting (Fig. 1). The EC trend during MSW composting was opposite to that found in separated cattle manure composting (Inbar et al., 1993). The reduction of the sum of ions as reflected by the EC measurements was due to the leaching of concentrated ion liquids from the compost boxes during the first stage of composting.

The C/N ratio exhibited three phases during composting: (*i*) a rapid decrease from 35 to 8 during the first 20 days; (*ii*) a slower decrease to a value of 6, lasting till day 70; (*iii*) stabilization at a value between 5 and 6 from day 70 to the end of the experiment. The C/N ratio measured in the liquid phase has been used as an indicator of compost

maturity (Chanyasak et al., 1982; Jimenez and Garcia, 1992). In this study the C/N ratio changed dramatically during the second phase of composting, but did not change significantly during the curing phase. Moreover, the C/N ratio measured in the compost solid phase followed a similar trend, and neither ratio showed a correlation with a plant-growth bioassay (Chefetz et al., 1996).

The total amount of soluble N decreased during composting (Fig. 2). Decreased levels of organic N represent mineralization. During the thermophilic stage, the ammonium-N levels were high, indicating a high rate of degradation of organic-N compounds by microorganisms. The high ammonium levels during rapid thermophilic decomposition can produce an odor problem. During maturation, the ammonium-N levels continue to decrease while the nitrate-N levels increase. The ratio of N-NO<sub>3</sub><sup>-</sup>/N-NH<sub>4</sub><sup>+</sup> increased to 4 at this stage.

Because the compost's bacterial population is active only in the liquid phase, the DOC concentration during composting can serve as an indication of OM biodegradability. The changes in DOC concentration (Fig. 3) followed a trend similar to that of the C/N ratio, exhibiting the same three phases: (*i*) a rapid decrease from an initial concentration of 28.3 g/kg to 7.4 g/kg over the first 20 days; (*ii*) a continuing, but more gradual decrease from days 20-60, to 2.2 g/kg; (*iii*) a moderate decrease from day 60 to the end of the experiment, to 1.0 g/kg. The DOC pattern indicates a high rate of bioavailable OM which is utilized during the thermophilic stage. The readily available, water-soluble OM is transformed to  $CO_2$  whereas the stable OM remains in the solution. The water extract from MSW compost samples was brown and color changes were monitored at an absorbance of 465 nm (Inbar et al., 1993). The A<sub>465</sub> highly correlated to DOC in the range of 100 to 1000 mg/l (Fig. 3, insert). However, higher DOC concentrations exhibited

during the first 20 days of composting deviated from the correlation curve. High concentration of soluble sugars, peptides and amino acids, which have low  $A_{465}$  values, exist in the water-soluble fraction during this time.

## CONCLUSIONS

The composting process is defined as a biological treatment in which aerobic microorganisms utilize OM. Since microorganisms are only active at the solid-liquid interphase of the compost, this study was performed to better understand this interphase's composition. The C/N ratio and the DOC concentration exhibited three distinct phases: (*i*) rapid decomposition during the first 20 days; (*ii*) a more gradual change till day 60-70; (*iii*) stabilization from day 60-70 on. These parameters appear to be reliable indicators of compost stability. Although they changed dramatically during the active phase of composting, they did not change during the curing phase. They can therefore not be used as indicators of maturity. The only parameter exhibiting a change during the curing phase was the nitrate level which increased from day 80 on. The physico-chemical conditions during the curing stage appear to be suitable for the activity of nitrifying bacteria. Nitrate levels can therefore be used as indicator of compost maturity.

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# **FIGURES LEGENDS**

- Fig. 1. Electrical conductivity (EC), NO<sub>3</sub><sup>-</sup> concentration and pH during the composting of municipal solid waste (measured in a 1:10 solid:water extract).
- Fig. 2. Water-soluble nitrogen forms (total, organic, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) during the composting of municipal solid waste (measured in a 1:10 solid:water extract).
- Fig. 3. Dissolved organic carbon (DOC) concentration during the composting of municipal solid waste (measured in a 1:10 solid:water extract), and the linear correlation between the absorbance at 465 nm and the DOC at various stages of composting (insert).

Fig. 1

₹' -



Composting time (days)

62a



Composting time (days)

4/4

Fig. 3



Composting time (day)

# CHEMICAL AND BIOLOGICAL CHARACTERIZATION OF ORGANIC MATTER DURING COMPOSTING OF MUNICIPAL SOLID WASTE

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## ABSTRACT

Composting of municipal solid waste (MSW) was studied in an attempt to elaborate transformations of organic matter (OM) during the process and define parameters for the degree of maturity of the product. Composting was performed in 1-m<sup>3</sup> plastic boxes and the following parameters were measured in 13 samples during 132 days of composting: temperature, C/N ratio, ash content, humic substance contents and fractions (humic acid, fulvic acid and non humic fraction - HA, FA and NHF respectively). Spectroscopic methods ( CPMAS <sup>13</sup>C-NMR, DRIFT) were used to study the chemical composition of the OM. A bioassay based on growth of cucumber plants was correlated to other parameters. The C/N ratio and ash content showed a typical high rate of change during the first 60 days and reached a plateau thereafter. The HA content increased to a maximum at 112 days, corresponding to the highest plant dry weight and the highest 1650/1560 (cm<sup>-1</sup>/cm<sup>-1</sup>) peak ratios calculated from DRIFT spectra. <sup>13</sup>C-NMR and DRIFT spectra of samples taken from the composting MSW during the process showed that the residual OM contained an increasing levels of aromatic structures. Plant-growth bioassay, HA content and the DRIFT spectra indicated that MSW compost described in this study, stabilized and achieved maturity after about 110 days.

Problems caused to modern society by municipal solid waste (MSW) have become more severe over the last decade due to increasing amounts of waste and decreasing availability of landfill space (Alter, 1991; Finstein, 1992). Recycling has become an attractive option for MSW management. For the organic fraction composting seems to be a desirable treatment having the capacity of reducing the volume and weight by approximately 50% and resulting a stable product which can be beneficial to agriculture (He et al., 1992). The main obstacles facing the production of MSW compost and its utilization stem from the heterogeneous nature of the raw material. The composition of MSW can vary with climate, standard of living, type of garbage collection systems and season.

The composting process consists of a biological treatment in which aerobic thermophilic microorganisms utilize organic matter (OM) as a substrate. The main products of the composting process are fully mineralized materials such as  $CO_2$ ,  $H_2O$ ,  $NH_4^+$  stabilized OM (mostly humic substances) heavily populated with competitive microbial biomass and ash. Compost has the potential of improving soil structure, increasing cation exchange capacity, suppressing soil borne plant pathogens and enhancing plant growth (Saviozzi et al., 1988; Chen et al., 1989; Hoitink et al., 1993). The chemical and microbiological properties of MSW compost have been widely studied and the following parameters have been proposed as maturity and stability indexes: C/N in solid and in water phase (Chanyasak et al., 1982; Jimenez and Garcia, 1992), cation exchange capacity (Harada et al., 1981), humification indexes (Jimenez and Garcia, 1992) and oxygen and  $CO_2$  respirometry (Iannotti et al., 1994). Chemical and spectroscopic analyses of OM transformations during composting in relation to compost maturity of various raw materials have been recently reviewed (Chen and Inbar, 1993).

One of the main obstacles to successful utilization of MSW compost in agriculture is the lack of reliable quality criteria and understanding the OM transformations throughout the process. Proper evaluation of compost maturity is essential for the establishment of such criteria. Therefore, the objective of this research was to study the transformation of OM during composting of MSW and to correlate chemical analyses and <sup>13</sup>C-NMR and DRIFT spectra, with plant performance bioassays.

## **MATERIALS AND METHODS**

# Composting of MSW

MSW was collected over a 24 h period from the town of Afula in Israel, and mechanically mixed in a MSW classifying facility. After sieving and eliminating the >5-cm fraction, the raw material was divided into three perforated plastic boxes (about  $1-m^3$ each) and composted for 132 days. The compost was turned, mixed, and sampled after removal of glass, plastics and metals by hand-picking at 0, 6, 13, 19, 27, 34, 41, 48, 62, 76, 90, 112 and 132 days. Samples (10 L each) were stored at 4°C. Smaller subsamples were dried at 65°C, then ground and sieved. Particles smaller than 1-mm in diameter were used for analyses. Temperature was measured at 4 h intervals by thermocouples connected to a data logger until reaching ambient temperature (~ 15 to 20°C), then, larger intervals (4 d) were applied between temperature readings.

## Chemical analyses

Total organic carbon was measured by loss of weight on ignition at 550°C for 8 h (C organic calculated as 58% of the OM). Organic nitrogen was measured by a Tecator Automatic Kjeldahl System (Kjeldahl System 1030, Tecator, Hsiganas, Sweden).

For studies on humic substances (HS) 20 g of compost were extracted with 200 ml 0.1 N NaOH under N<sub>2</sub>. The supernatant solution containing the soluble HS was separated by centrifugation at 15,000×g and the residue was resuspended in 0.1 N NaOH. This procedure was repeated eight times. The combined solutions were acidified with 6 M HCl to pH~1 and allowed to stand at room temperature for 24 h. The supernatant solution

containing the extracted fulvic fraction (FF) was separated from the humic acid (HA) by centrifugation (2,500×g for 30 min.). The fulvic fraction was separated into fulvic acid (FA) and non-humic fraction (NHF) by adsorption of the FA onto Amberlite XAD-8 resin (mesh size 20-60, Sigma, St. Louis, USA). The Amberlite XAD-8 resin was cleaned before use according to the method described by Thurman and Malcolm (1981). The FA was passed through the column at a flow rate of about 15 pore volumes per hour. The column was then washed by 0.65 pore volumes of distilled water. At this stage the FA adsorbed to the resin while the NHF was eluted. Carbon concentrations of the FF and NHF were determinated by a total carbon monitor (TCM 480, Carlo Erba Instruments, Millano, Italy). FA content was calculated as the FF minus NHF. The following humification parameters were calculated: (i) humification ratio (HR)=HA/FF; (ii) humification index (HI)=HA/FA; (iii) HA percentage (HP)=100×HA/HS.

# 13C Nuclear Magnetic Resonance Spectroscopy

Solid state C-13 NMR spectra with CPMAS (Cross Polarization Magic Angle Spinning) were obtained using a Chemagnetics M-100 NMR-spectrometer, located at Pennsylvania State University. The spectrometer operates at a <sup>1</sup>H frequency of 100 MHz and a <sup>13</sup>C frequency of 25.2 MHz. Pertinent experimental parameters were the following: contact time of 1 ms; recycle delay time of 1 s; sweep width of 14 kHz (562.5 ppm) and line broadening of 30 Hz. Dried sieved compost samples were placed into a rotor and spun at a frequency of 3.5 kHz at the magic angle (54.7° to the magnetic field).

The <sup>13</sup>C-NMR spectra were divided into five regions (Hatcher et al., 1983). Region I (0-50 ppm) is assigned to paraffinic carbon or carbons that are bonded only to other carbons. Region II (50-112 ppm) is assigned to C-O, C-N bonds as in carbohydrates, alcohols, esters and amines. Region III (112-163 ppm) is assigned to aromatic and phenolic carbons. Region IV (163-190 ppm) represents carboxyl, ester and amide carbons groups. Region V (190-215 ppm) represents the carbonyl carbons. The region 0-112 ppm was calculated as aliphatic carbon, 60-112 ppm as polysaccharide carbon and 112-163 ppm as aromatic carbon. Total aromaticity was calculated by expressing aromatic C (112-163 ppm) as percentage of the aliphatic C (0-112 ppm) plus aromatic C (Hatcher et al., 1981).

# Diffuse Reflectance Infrared Fourier-Transform (DRIFT) Spectroscopy

The DRIFT spectra of MSW compost at twelve stages of the process were obtained for a wavenumber range of 4000 to 400 cm<sup>-1</sup> in a Nicolet 550 Magna-IR<sup>TM</sup> spectrometer (Nicolet Instruments Corporation, Madison, WI, USA). Bulk samples were prepared for analysis according to the methods of Niemeyer et al. (1992), using 15 mg of dried bulk compost mixed with KBr for a total sample weight of 310 mg. The samples were transferred to a macro-sample holder and smoothed with a glass slide. To obtain DRIFT spectra, 400 scans were collected. Spectra of the residual ash obtained after ignition at 550°C for 8 h and loss of the OM were recorded using the same methodology. To compare one spectrum to another a linear baseline correction was applied using 4000 cm<sup>-1</sup>, 2000 cm<sup>-1</sup> and 860 cm<sup>-1</sup> as zero absorbance points. The major peaks data (intensity and wavenumber) were found by using the OMNIC software (Nicolet Instruments Corporation). The spectra of the ash free OM was calculated by subtracting the spectrum of the ash from that of the bulk materials, using the OMNIC software.

# Plant-growth bioassay

Ten cucumber seeds (*Cucumis Sativus* L., cv. dlila, Zeraim-Gedera, Israel) were placed in 0.5-L pot containing 50% MSW compost (various stages of composting) and 50% of perlite (Habonim, Israel, no. 4). Each treatment consisted of five replicates. The plants were irrigated every two days with equal amounts of tap water without fertilizer. After one week the seedlings were thinned, leaving the best three plants per pot. These plants were grown for one month. Wet and dry weights of the plants in each pot were determined.

#### Statistical analysis

Ash content, C/N ratio and temperature results are presented as the average value of three replicates of the three composting boxes, while the data for each box is the average of three replicates with standard errors. HA, FA and NHF content and spectroscopic analyses were determined on a mixed sample from the three composting boxes. The plant bioassay statistical analysis was performed using the Duncan test at p = 0.05.

#### RESULTS

## Composting of MSW

As reported earlier (Harada et al., 1981; Jimenez and Garcia, 1992; Inbar et al., 1993) three typical phases of composting were observed by temperature measurements during the process (Fig. 1): (*i*) a mesophilic phase, during the first 2 d in which temperature rose to  $45^{\circ}$ C; (*ii*) a thermophilic phase lasting 4 weeks in which the temperature increased to a maximum of 72°C; further temperature increases were avoided by turning and mixing the compost once a week; (*iii*) after 60 d of composting the compost temperature equaled that of the ambient. It is interesting to note that the highest temperature during thermophilic phase was over 70°C while the mean and minimum ambient temperatures were only 10-15°C and 0°C respectively.

The change in the C/N ratio and ash content reflects OM decomposition and stabilization during composting (Fig. 2). The C/N ratio decreased rapidly from an initial value of 28 in the raw material to 18 after only 20 days. The ratio continued to decrease, albeit less sharply, to 12.2 after 60 days. From this point on the C/N ratio stabilized at a

value of about 12 (11.8-12.8) for the remainder of process. The initial ash content of the compost was relatively high (~45%) since the raw matter had been collected from a residential area without on-site separation. The change in ash content followed a trend similar to that of the C/N ratio, exhibiting three phases: (*i*) lasting over the first 20 d, when most of the OM decomposed; (*ii*) days 20-80; (*iii*) days 80 to the end of the experiment, the period at which the curing stage began and the rate of decomposition of OM was extremely low.

## Humic Substance Content

Humic substances (HS) comprise the most important fraction of OM due to their effects on soil ecology, structure, fertility and plant growth. NaOH extracted HS from composts can be separated into humic acid (HA), fulvic acid (FA) and a non-humic fraction (NHF) (Chen and Inbar, 1993). The levels of HA, FA and NHF in MSW compost at various stages of the process represent the humification process (Fig. 3). Total levels of HS did not change during the composting process, maintaining values of 14.2% to 18% of the OM. The FA level remained steady at 7.5% of OM for the first 20 days, then decreased to 4.5% in the mature compost. The HA level increased during the composting process, reaching 14% of the OM after 112 days maintaining this value till the end of the process. The NHF decreased rapidly from 8.7% to 4.4% at 60 days of composting probably since it consisted of polysaccharides and fats which are readily decomposed. All three humification parameters (HR, HI and HP) increased during the composting as follows (Table 1): (i) HR increased from 0.42 in the raw MSW to 1 after 30 days, stabilized at 1-1.18 until day 90, then sharply increased to 1.35 in the mature compost; (ii) HI increased rapidly from 0.91 in the raw material to 2 within 30 days, then gradually increased to a final value of 3 at the end of the process; (iii) HP values exhibited a similar trend. The increasing trend of these parameters indicated that during composting HA became the main fraction of HS.

### Spectroscopic Methods

## **DRIFT Spectra**

The use of DRIFT spectra represents a new approach in studies of the structure of heterogeneous materials such as plant tissue and bulk compost samples. The development of an attachment mounted onto FTIR spectrophotometers has allowed the determination of DRIFT spectra. Sample preparation for DRIFT spectroscopy is much simpler than for FTIR spectroscopy, interferences due to water adsorption are reduced, and resolution is improved. The spectra obtained using DRIFT had a higher degree of resolution as compared with FTIR. Moreover, the bands indicative of aliphatic C-H, carboxyl and carboxylate functional groups, aromatic C=C, and the C-O stretch of polysaccharides were prominent and very well resolved. The DRIFT spectra can also be used to fingerprint OM acquired from various sources. Relative concentrations of functional groups were found to be fairly constant regardless of sample concentration. The DRIFT spectra peak intensity ratio can be used to determine the humification process (Niemeyer et al., 1992).

All five bulk MSW compost spectra samples from different stages (raw, 34, 76, 90 and 132d) of composting exhibited similar peaks (Fig. 4). The main absorbance bands were: a broad band at 3300-3400 cm<sup>-1</sup> (H-bonds, OH groups), two distinct peaks at 2930 and 2850 cm<sup>-1</sup> (C-H asymmetric, C-H stretch of -CH), a peak at 2520 cm<sup>-1</sup>, a sharp peak at 1800 cm<sup>-1</sup>, a slight shoulder around 1740 cm<sup>-1</sup>, a wide peak at 1650 cm<sup>-1</sup> (C=C in aromatic structure), a shoulder at 1560 cm<sup>-1</sup> (amide II bonds), a strong peak at 1450 cm<sup>-1</sup> (C-H deformation of CH<sub>2</sub> or CH<sub>3</sub> groups), a peak in the 1100-1000 cm<sup>-1</sup> range (C-O stretch of polysaccharide, Si-O stretch) and a sharp peak at 870 cm<sup>-1</sup> (aromatic CH out of plane bending) (Baes and Bloom, 1989; Inbar et al., 1989).

The distinct change in the spectra resulting from the composting process was a reduction of the 1560  $cm^{-1}$  peak with time probably due to the relatively rapid

biodegradation of the amino chain. The aromatic region and the 1800 cm<sup>-1</sup> peak became sharper during composting. Peaks in the aliphatic region at 2930 and 2850 cm<sup>-1</sup> decreased, while the 1450 cm<sup>-1</sup> peak increased. The spectra of MSW compost (wavenumbers 4000-400 cm<sup>-1</sup>) were different from spectra of composts from other sources that were reported earlier (Niemeyer et al., 1992; Inbar et al., 1989). The main differences between the spectra of MSW compost and the other composts were in the following regions: (i) a sharp peak and a shoulder at 2520  $\text{cm}^{-1}$  and 2580  $\text{cm}^{-1}$ respectively which does not appear in spectra reported for other composts; (ii) a narrow sharp peak at 1800 cm<sup>-1</sup> that appears as a small shoulder at 1710 to 1720 cm<sup>-1</sup> in spectra of other composts; (iii) the peak at 1450 cm<sup>-1</sup> had become the main peak in the spectra of MSW compost instead of the aromatic or the polysaccharide peaks in other composts; (iv) an intense and sharp peak at 870  $\text{cm}^{-1}$  that does not appear in spectra of other compost. According to Pouchert (1981) the peak at 2520 cm<sup>-1</sup> can be attributed to S-H stretch of aromatic or nonaromatic mercaptans and sulfides, the absorbance at 1800 cm<sup>-1</sup> can be attributed to the C=O stretch of the conjugated carbonyl group of aromatic esters and lactones. Both these organic compounds should not appear in composts for the following reasons: (i) S-H bonds can be related to proteins which are rapidly biodegraded; (ii) sulfides form only under anaerobic conditions; (iii) esters and lactones are biodegraded relatively rapidly by many microorganisms.

Spectra of residual ash samples were recorded in order to verify whether these peaks are related to OM or to minerals forms in the compost. The spectra of the residual ash were in similar to the spectrum of calcite (CaCO<sub>3</sub>) exhibiting major absorption bands at 2983 cm<sup>-1</sup>, 2874 cm<sup>-1</sup>, 2580 cm<sup>-1</sup>, 2512 cm<sup>-1</sup>, 1800 cm<sup>-1</sup>, 1420 cm<sup>-1</sup> and 874 cm<sup>-1</sup>. The ash also exhibited peaks in the 1100-950 cm<sup>-1</sup> region and sharp peaks at 680 cm<sup>-1</sup> and 620 cm<sup>-1</sup> which can be attributed to phosphate minerals or to Si-O components (Kodama, 1985). Thus, it is concluded that the mineral matter is responsible for the unusual peaks observed in the spectra of the MSW compost. To correct and reduce the

contribution of the mineral component, subtraction of the residual ash spectrum from the bulk spectrum was performed. The spectra of the ash free MSW compost at two stages of composting are presented in Fig. 5. The spectrum of the mature compost is generally similar to spectra of other composts (Niemeyer et al., 1992) with specific differences at: (*i*) the polysaccharide region peak (1000-1100 cm<sup>-1</sup>) which was smaller in MSW than in other composts; and (*ii*) the OM in MSW compost was more aliphatic (and less aromatic) than pine bark compost, hardwood bark compost and compost from separated cattle manure (CSM) reported by Niemeyer et al. (1992). Various differences between the raw materials and mature compost as revealed by comparing the subtracted spectra can be pointed out: (*i*) reduction of the 1560 cm<sup>-1</sup> peak; (*ii*) reduction and transition to a small shoulder of the 1738 cm<sup>-1</sup> peak (CO<sub>2</sub>H groups) in the mature compost; (*iii*) a sharp decrease in the aliphatic region (2930 cm<sup>-1</sup> and 2850 cm<sup>-1</sup>); and (*iv*) an increase in the aromatic region (1650 cm<sup>-1</sup>).

Following Inbar et al. (1989) we monitored the changes in the IR spectra by calculation of the ratio between the intensity of major peaks. The peaks at 2930 cm<sup>-1</sup>, 2850 cm<sup>-1</sup>, 1650 cm<sup>-1</sup>, 1560 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> were chosen for these calculations. The ratio 1650/2930 (aromatic C / aliphatic C) increased from 0.88 to 1.10, the ratio 1650/2850 (aromatic C / aliphatic C) increased from 0.79 to 1.54, the 1650/1050 ratio (aromatic C / polysaccharide) increased from 2.39 to 2.80, and the 1650/1560 ratio (aromatic C / amide II bond) increased from 0.94 to 1.52. These ratios were calculated for spectra of ash free OM. The changes reflect a decrease in levels of polysaccharides, aliphatic and amide components, and an increase in levels of aromatic structures in mature compost. We believe that the increase in aromatic structures is relative and it resulted from decomposition of aliphatic moieties. The linear correlation between the aromatic to aliphatic peak ratio (1650/2930) and the C/N ratio (Fig. 6) exhibited R<sup>2</sup>=0.936 calculated for the equation Y = 1.263-0.014X. This correlation indicates that DRIFT is a useful and reliable tool in the analysis of OM decomposition during composting.

# CPMAS <sup>13</sup>C-NMR

During the process of compost production, organic materials that are chemically complex and difficult to fractionate are formed. Extraction procedures that are commonly applied to soils and composts remove only a part of the C in the system. To profile the organic components of composts during the course of their formation, a method that can be applied to the intact sample is preferable. The only physical method holding some promise for the reliable characterization of such organic materials appears to be nuclear magnetic resonance (NMR) (Wershaw, 1985). The CPMAS <sup>13</sup>C-NMR technique has been reported to provide useful information on transformation of OM during composting (Chen and Inbar, 1993). The major peaks exhibited in the CPMAS <sup>13</sup>C-NMR spectra of samples representing five stages in the composting process (0, 34,76, 90 and 132 d) (Fig. 7) are at: 30 ppm (methylene C), 55 ppm (methoxyl C), 72 ppm (carbohydrate or aliphatic alcohols), 105 ppm (anomeric carbons of polysaccharides), 130 ppm (C-substituted aromatic C), 150 ppm (O- substituted aromatic C) and at 175 ppm (carboxyl carbon) (K3gel-Knabner et al., 1991).

The distinct changes in the spectra resulting from decomposition of OM were: reduction of the 30 ppm peak; appearance of the 55 ppm peak as a shoulder in the mature compost and an increase of the aromatic region peak (130 and 150 ppm peaks). The relative changes in the level of carbon containing groups are presented in Table 2. The following changes should be noted: (*i*) total aliphatic carbon (0-112 ppm) decreased by 14.4% from 74.8% in the raw material to 64.0% in the mature compost; polysaccharides (60-112 ppm) decreased by 17.0% from 42.3% to 35.1% in the mature compost; and alkyl groups (0-50 ppm) decreased by 11.0% during the composting process; (*ii*) aromatic components, including aromatic and phenolic carbons, increased by 54%, from 15.9% in the raw material to 27.7% in the mature compost; (*iii*) carboxyl carbon increased by only 9.5%; (*iv*) the C=O carbonyl carbon increased by

73.7%, from 1.9% in the raw material to 3.3 % in the mature compost. It should be noted however, that this carbonyl C represents a small fraction of total C and the peaks were poorly resolved.

# Plant-growth bioassay

To establish that a compost is mature, devoid of phytotoxic compounds and ready for use for plant production, several chemical parameters have been suggested as maturity indices. However, so far only a plant bioassay can provide reliable results (Hoitink and Kuter, 1986; Inbar et al., 1993). The dry weight of cucumber plants grown in composts of various ages are presented in Fig. 8. Plants grown in media containing fresh (14 d) compost exhibited inhibited growth compared to plants grown on older compost. The dry weight of plants grown on samples taken after 28 to 84 d of composting were statistically similar. However, the dry weight of plants grown in 112 and 132 d old composts were significantly higher than all the others. These results show that as OM decomposed the compost became a better substrate for plant growth. Only mature compost supported better plant growth.

The highest plant dry weight was achieved after 112 days of composting. This corresponds to the sample in which maximum amount of HA were present, and to the time at which the 1650/1560 DRIFT peak ratio has stabilized at a maximum height. The linear correlation between the 1650/1560 ratio and plant dry weight exhibited a  $R^2=0.81$  calculated for the equation Y = 0.81 + 0.54 X. The linear correlation between HA content in OM and plant dry weight exhibited a  $R^2=0.70$  calculated for the equation Y = 3.59 + 7.78 X.

## DISCUSSION

In this article we studied transformations of OM during composting of MSW, aiming to define compost maturity and to correlate the chemical and spectroscopic analyses to plant growth. Although the C/N ratio is the most common parameter used to define decomposition levels of OM it appears to be a non reliable indicator of compost maturity (Harada et al., 1981). This ratio changed dramatically during the second phase of composting performed in our study (from 28 to 12 within 60 d), it did not change significantly during the curing phase. Only minor changes in the C/N ratio occurred during the curing stage whereas instability of the OM was observed in spectra obtained by DRIFT and NMR. A C/N ratio of 10-12 is usually considered to be an indicator of stable and decomposed OM (Jimenez and Garcia, 1992). The fact that no changes took place during the curing phase challenges the use this ratio as a ultimate parameter. The level of HS in the compost did not change during composting of MSW. This observation agrees with that of Sugahara and Inoko (1981), Das (1988), and Jimenez and Garcia (1992), but contradicts the report of Inbar et al. (1989) who showed that HS levels increased significantly with time of composting in CSM. This suggests that the type of raw material is of major importance to the humification process during composting. In this study the HA content increased during composting, reaching a stable value of 13.5% of the OM after 112 days, whereas the FF level decreased. The increasing level of HA represents the degree of humification and maturity of the compost. HI and HR are commonly used to analyze the humic fraction (Jimenez and Garcia, 1992; Inbar et al., 1989). We found that the HI increased to a ratio of 3, and the HR increased to 1.35. The trend of change of these values is similar in various wastes although specific values differ in other wastes. In general as well as in our present study, fresh composts contain low levels of HA and higher levels of FA (Harada et al., 1981; Saviozzi et al., 1988; Inbar et al., 1989; Gonzalez et al., 1993; Ciavatta et al., 1993a; Ciavatta et al., 1993b). The HP increased to a level higher than 73% in the mature compost indicating that the fraction defined as FA, extracted from heterogeneous materials such as MSW, contains relatively high levels of biodegradable OM that was decomposed mainly during days 20 to 40 (Fig. 3).

DRIFT spectra provide useful information about the transformation of OM. The main absorbance bands indicate changes in OM structure are at 2930 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> (aliphatic groups), 1650 cm<sup>-1</sup> (aromatic structure), and 1100-1000 cm<sup>-1</sup> (polysaccharide). The relative height of the aromatic peak at 1650 cm<sup>-1</sup> increased with composting time and stabilized at a later stage of the process similar to the level of HA. The increase in the 1650/2930, 1650/2850 and 1650/1560 ratios also indicates that the easily degradable OM constituents such as aliphatic chains, polysaccharides and alcohols are chemically or biologically oxidized, and therefore the mature compost contained more aromatic structures of higher stability. The DRIFT spectra of the bulk MSW compost provide information not only on the OM bonds but also on the minerals in the raw material. The relative level of these materials increased (1800 cm<sup>-1</sup> and 1450 cm<sup>-1</sup>) during composting in parallel to the increase in ash. Based on our measurements with MSW compost one should bear in mind that when analyzing high ash containing wastes, spectra of the ash should be subtracted from those of the bulk material.

CPMAS <sup>13</sup>C-NMR spectroscopy is a powerful technique for the analysis of chemical transformations of the OM during composting. <sup>13</sup>C-NMR spectra determined in this research also indicate that the OM structure become more aromatic while carbohydrates, polysaccharides, alcohols, lipids and protein decomposed, along with the relative increase of all other components (HA). These findings are in general agreement with the data obtained from the DRIFT spectra except for the carbonyl and carboxyl regions that, according to the NMR data, increased during composting by 73.0% and 9.5%, respectively. In the DRIFT spectra the carbonyl and carboxyl carbon (1740-1720 cm<sup>-1</sup>) peak intensities were smaller or subjected to a shift. A comparison between <sup>13</sup>C NMR spectra of CSM (Inbar et al., 1989; Inbar et al., 1991) and those of the MSW

compost reveals consistent trends observed in the various carbon-containing functional groups. The only exception was the carboxyl region that increased by 90% during composting of CSM whereas in MSW compost, the carboxyl region increased by 9.5% only. The general similarity in the transformation of OM during composting of these two different raw materials as analyzed by DRIFT and NMR suggest that the composting process transforms heterogeneous raw OM to a compositionally uniform product at the end of the process.

The aim of the plant-growth bioassay (Fig. 8) was to obtain biological criteria for compost maturity. We hypothesized that plant growth may serve as an integrative single parameter for compost maturity. The results of the plant-growth bioassay were similar to those of Zucconi et al. (1981), Chanyasak et al. (1983), and Inbar et al. (1993). In all of these studies plant growth in immature compost was inhibited and it generally improved in the mature compost. These authors suggested that in immature composts low molecular weight organic acids induce phytotoxicity in addition to competition for oxygen and nutrients, due to high rates of OM decomposition. The correlation between the HA level, the 1650/1560 DRIFT peak ratio and plant biomass suggested that these parameters could indicate compost maturity.

## CONCLUSIONS

Compost maturity is very difficult to define by only one parameter usually several parameters are needed to be crossbred. This article demonstrates that <sup>13</sup>C-NMR and DRIFT spectroscopy, together with data on HS provide useful information on the OM transformations occurring during the composting process. Plant-growth bioassay, level of HA and the 1650/1560 DRIFT peak ratio exhibited the same trend during composting and can therefore be used as maturity indices. All these parameters exhibited three phases: (*i*) rapid decomposition during the first 30 d; (*ii*) the stabilization stage till day 90; and (*iii*)

the maturation phase from day 100 on. The MSW compost, described in this study, was mature and ready for use as an agricultural substrate after about 110 days of composting. The understanding of compost maturity has to be improved by investigations of additional parameters for maturity such as the biochemistry of humic components and reactions of the OM occurring in the interface between solid and aqueous phases (Chanyasak et al., 1983; Chen and Inbar, 1993).

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Composting Time	HI	HR	НР
(uays)			
0	0.91	0.42	47.57
13	1.25	0.67	55.51
19	1.36	0.76	57.66
27	2.01	1.02	66.80
34	2.07	1.01	67.47
41	2.14	1.13	68.14
48	2.18	1.17	68.54
62	1.95	1.08	66.07
76	2.59	1.18	72.12
90	2.77	1.12	73.50
112	2.82	1.35	73.84
132	2.99	1.32	74.96

Table 1. Humification index (HI=HA/FA), humification ratio (HR=HA/FF) and percentage of humic acid (HP= $100 \times$ HA/HS) during composting of MSW.
Table 2. Distribution of carbon containing groups during composting of MSW as determined by CPMAS <sup>13</sup>C-NMR (percent of total carbon).

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Composting Time (days)		0	13	34	76	132	
Chemical shift	Carbon containing		Percent	Change from raw			
(ppm)	group				1		material
0-50	Alkyl	26.9	25.5	24.7	23.6	23.6	-12.3%
50-112	O-alkyl	47.9	52.1	46.5	42.4	40.4	-16.0%
112-145	Aromatic	11.6	10.5	13.6	19.0	16.9	+45.6
145-163	Phenolic	4.3	3.6	4.9	6.6	7.6	+76.7
163-190	Carboxyl	7.4	6.6	8.2	8.0	8.1	+9.5%
190-215	Carbonyl	1.9	1.6	2.1	3.4	3.3	+73.0%

### **Figures legends**

- Fig. 1. Ambient and compost temperature vs. composting time of MSW.
- Fig 2. C/N ratio and ash content during composting of MSW.
- Fig. 3. Relative content of the humic acid (HA), fulvic acid (FA) and non humic fraction (NHF) as percent of organic matter vs. composting time of MSW.
- Fig. 4. DRIFT spectra of bulk MSW compost at five stages of composting (raw, 34, 76, 90, 132 d).
- Fig. 5. DRIFT spectra of the ash free OM in MSW compost at two stages of composting (raw and 132 d). Ash spectra were subtracted from those of the bulk materials.
- Fig. 6. DRIFT peak intensity ratio (1650/2930 cm<sup>-1</sup>/cm<sup>-1</sup>) vs. C/N during composting of MSW. Peak ratio was calculated from twelve subtracted spectra at various stages of composting, using the same method as in Fig. 5 (dotted lines represent the 95 confidence interval).
- Fig. 7. CPMAS <sup>13</sup>C-NMR spectra of MSW compost samples at five stages during composting of MSW (raw, 13, 34, 76, 132 d).
- Fig. 8. Dry weight of cucumber plants grown in MSW compost samples at eight stages during composting time. Data followed by the same letter are not significantly different (p = 0.05).

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Fig. 2



Fig. 3

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Fig. 8



Composting Time (days)

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## CHARACTERIZATION OF DISSOLVED ORGANIC MATTER EXTRACTED FROM COMPOSTED MUNICIPAL SOLID WASTE

## ABSTRACT

The properties and transformation of dissolved organic matter (DOM) extracted from municipal-solid-waste (MSW) compost at five stages (days 47, 77, 105, 126 and 187) of composting were studied using a chemical-fractionation scheme. We fractionated the DOM into hydrophobic or hydrophilic neutrals, acids and bases, and obtained solid-state cross polarization magic angle spinning (CPMAS) <sup>13</sup>C-NMR spectra of the unfractionated DOM and of the different fractions. The hydrophobic acid (HoA) fraction was the dominant hydrophobic fraction, exhibiting a moderate increase during composting. The hydrophobic neutral (HoN) fraction increased sharply from less than 1% to 18% of the total DOM at 187 days of composting. The opposite trend was exhibited by the hydrophobic bases (HoB). The hydrophilic neutrals (HiN) represented the major fraction of the hydrophiles till 120 days of composting, decreasing thereafter by 38%. The hydrophilic acids and bases (HiA and HiB, respectively) exhibited no consistent trend during composting. <sup>13</sup>C-NMR spectra of the unfractionated DOM taken from the composting MSW revealed an increasing level of aromatic structures in the residual DOM with time. The <sup>13</sup>C-NMR spectra of the HoA fraction suggested a polyphenol-humic structure, whereas the HoN spectra exhibited strong aliphatic features. The spectra of the HiN fraction confirmed its polysaccharide nature and the HiB contained mainly proteins and carbohydrate-amino complexes. A comparison between the <sup>13</sup>C-NMR spectra of HoA and fulvic acid (FA) indicated the former to be the most soluble FA fraction. The steady DOM concentration and the relative decrease of HiN as the HoA and HoN fractions increased indicates that DOM at the final stage of composting contained less available OM and more macromolecules related to humic substances. The constant level of DOM observed during the curing and maturation stages represents a steady-state situation during which the chemical composition is continually changing.

## **INTRODUCTION**

The amount and the properties of organic matter (OM) change dramatically during composting. Approximately 50% of the OM becomes fully mineralized, mostly due to the degradation of easily degradable compounds such as protein, cellulose and hemicellulose, which are utilized by microorganisms as C and N sources. The residual OM contains newly formed macromolecules along with non-degradable OM, jointly forming the humic substance (HS)- the main stable fraction of mature compost. Although the transformation of OM during composting has been widely studied (Aoyama, 1991; Chefetz et al., 1996; Chen and Inbar, 1993; Chen et al., 1989; Ciavatta et al., 1993; Frimmel et al., 1994; Jimenez and Garcia, 1992), most of the reports have focused on NaOH-extracted HS.

Composting of agricultural and municipal solid wastes (MSW) is defined as a biological treatment in which aerobic microorganisms utilize OM as a substrate (Zucconi and de Bertoldi, 1987). Since microorganisms are only active at the solid-liquid interphase of the compost, a study of this interphase is essential for a better understanding of C and N cycles during composting (Lynch, 1993). Moreover, characterization of the composition of the dissolved organic matter (DOM), the active OM fraction, may be a better indicator of the overall transformation of the OM. In addition, DOM in compost is well known to enhance plant growth due to its maintenance of Fe, Mn, Cu and Zn in solution at sufficient levels (Chen et al., 1994). In soils, DOM is related to C and N availability (Gressel et al., 1995; Stevenson, 1994; Zech et al., 1994), metal complexation and enhanced plant growth (Chen and Aviad, 1990).

A determination of DOM composition is difficult because it contains a mixture of lowmolecular-weight compounds (free amino acids and sugars) and chemically heterogeneous macromolecules (enzymes, amino-sugar complexes, polyphenols and HS). Thus, preliminary fractionation is essential to better understanding the variety of different physicochemical and biological compounds (Leenheer, 1981). The objectives of this study were to investigate the transformation of DOM fractions during MSW composting, using solid-state <sup>13</sup>C-NMR with the intention of determining whether the plateau concentration level of DOM recorded during compost maturation results from its steady composition.

## MATERIAL AND METHODS

#### **DOM** extraction

Aqueous compost extracts were prepared by placing 1 kg compost (wet weight) in 10 L of distilled water, and shaking (125 rpm) for 2 h at room temperature. The suspension was then centrifuged (10000 g for 30 min) and the supernatant filtered through a 0.45-µm membrane filter (Supor-450, Gelman Sciences). The concentration of dissolved organic carbon (DOC) was measured immediately after extraction or fractionation using a total carbon monitor (TCM 480, Carlo Erba Instruments, Milan, Italy).

### Preparative fractionation

Preparative DOM fractionation was performed according to Leenheer (1981) with some modifications. Step 1: 10 L of the compost-water extract were pumped with a peristaltic pump at a flow rate of 10 to 15 pore volumes per hour through a glass column containing 300 mL of Amberlite XAD-8 resin (Sigma). Following the sample, 500 mL of distilled water were passed through the resin. To obtain the organic fraction that had adsorbed onto the resin (hydrophobic base; HoB), it was flushed with a 0.25 pore volume of 0.1 N HCl, followed by 1.5 pore volumes of 0.01 N HCl. Step 2: The sample effluent was combined with the distilled water effluent. This solution was acidified to pH 2.0 with 6 N HCl then cycled over three connected columns containing: Amberlite XAD-8 resin, cation exchanger Amberlyst 15

(Merck) and anion exchanger Amberlyst A-21 (Merck), respectively. The flow rate was 10 pore volumes per hour, the hydrophobic/hydrophilic break (k'0.5r) of the XAD-8 resin was 20-25, the amount of ion exchangers was calculated as 150% of the ion concentration estimated by electrical conductivity. Following the sample, 1500 mL of distilled water were passed through the combined columns. The effluent contained the hydrophilic neutral (HiN) fraction. Step 3: The hydrophobic acid (HoA) fraction was displaced from the XAD-8 resin with a 0.25 pore volume of 0.1 N NaOH, followed by 1.5 pore volumes of distilled water. The HoA was desalted by loading onto a protonated cation exchanger Amberlyst 15 glass column. Step 4: The hydrophobic neutral (HoN) fraction was desorbed from the XAD-8 resin by Soxhlet extraction with 5 pore volumes of methanol. The excess methanol was removed by vacuumrotary evaporation at 40°C. Step 5: The hydrophilic acid (HiA) fraction, which had adsorbed onto the anion exchanger Amberlyst A-21, was released by washing the column with 2 pore volumes of 1 N NaOH. Protonation of this fraction was performed by the same method used for the HoA. Step 6: The hydrophilic base (HiB) fraction was desorbed from the cation exchanger Amberlyst 15 column by elution with 1 pore volume of 0.1 N NH4OH. Excess NH4<sup>+</sup> was removed by vacuum-rotary evaporation at 40°C. All of the fractions were freeze-dried for further analysis.

The following is a simplified scheme of the fractionation procedure:

Hydrophobic fraction - sorbed to XAD-8 (Ho):

• Ho Base (HoB) - desorbed with 0.1 N HCl

• Ho Acid (HoA) - desorbed with 0.1 N NaOH

• Ho Neutrals (HoN) - desorbed with MeOH

Hydrophilic fraction - not sorbed to XAD-8 (Hi) (obtained after sample elution through XAD-8 column):

- Hi Base (HiB) sorbed to  $H^+$  cation exchange resin, desorbed with 0.1 N NH<sub>4</sub>OH
- Hi Acid (HiA) sorbed to anion exchange resin, desorbed with 1.0 N NaOH
- Hi Neutrals (HiN) remaining in deionized-water solution after all column separation.

#### Analytical fractionation

Analytical fractionation (1 L of water extract from each compost sample in two replicates) was performed by the same method used for the preparative fractionation. The DOC concentration of each fraction was calculated as the DOC content of the influent minus that of the effluent.

#### Fulvic acid (FA) extraction

For FA studies, 20 g of compost were extracted with 200 mL 0.1 N NaOH under N<sub>2</sub>. The supernatant was collected following centrifugation at 15000 g for 30 min and the residue was resuspended in 0.1 N NaOH. This procedure was repeated eight times. The combined supernatants were acidified with 6 M HCl to pH~1 and left at room temperature for 24 h. The supernatant containing the extracted fulvic fraction was separated from the humic acid (HA) by centrifugation (2500 g for 30 min). The FA was further purified by adsorption to Amberlite XAD-8 resin following the same method used to purify the HoA fraction.

## <sup>13</sup>C-Nuclear magnetic resonance (NMR) spectroscopy

Solid-state <sup>13</sup>C NMR spectra with CPMAS (cross polarization magic angle spinning) were obtained using a Chemagnetics M-100 NMR spectrometer, located at Pennsylvania State University. The spectrometer was operated at a <sup>1</sup>H frequency of 100 MHz and a <sup>13</sup>C frequency of 25 MHz. Pertinent experimental parameters were the following: a contact time of 1 ms; a recycle delay time of 0.8 s; a sweep width of 14 kHz (562.5 ppm) and a line broadening of 30 Hz. Dried samples (48 h at 65°C) were placed into a rotor and spun at a frequency of 3.5 kHz at the magic angle (54.7° to the magnetic field).

#### RESULTS

#### DOM concentration and fractionation

Changes in DOC concentration during composting occurred in three phases: (*i*) a rapid decrease from the initial concentration of 47.27 g×kg<sup>-1</sup> (dry weight) to 7.37 g×kg<sup>-1</sup> (dry weight) over the first 33 days; (*ii*) days 33-105, when the DOC continued to decrease moderately to  $3.75 \text{ g×kg}^{-1}$  (dry weight); (*iii*) days 105 to the end of the experiment, during which the DOC concentration reached a plateau ( $3.75-3.67 \text{ g×kg}^{-1}$  dry weight). The question arising from this data is whether the DOC concentration plateau recorded during maturation actually reflects a steady DOM composition or a steady-state situation. A spectroscopic study, starting with quantitative fractionation into well-defined groups, was suggested as a logical approach to answering this question.

The hydrophobic fractions increased from 30% of the total DOM at 47 days of composting to 40% at 161 days of composting (Fig. 1). The HoB fraction decreased sharply from 13.9% to less than 1% of the total DOM after 105 days of composting, whereas the opposite trend was exhibited by the HoN fraction, which increased to 18% on day 161 of composting. The HoA fraction remained the dominant hydrophobic fraction throughout the process. The HiN fraction was the major fraction of the total DOM till 126 days of composting; thereafter it decreased by 38% (from 34.3% to 21.2% of total DOM), while HiA became the dominant hydrophilic fraction. The HiA and HiB fractions showed no consistent trends during composting.

#### Solid-state NMR

In all experiments, the <sup>13</sup>C-NMR spectra were divided into five regions (Hatcher et al., 1983). Region I (0-50 ppm) was assigned to paraffinic carbon or carbons that are bound only

to other carbons; region II (50-112 ppm) was assigned to C-O and C-N bonds, as in carbohydrates, alcohols, esters and amines; region III (112-163 ppm) was assigned to aromatic and phenolic carbons; region IV (163-190 ppm) to carboxyl, ester and amide carbon groups; region V (190-215 ppm) to the carbonyl carbons. The 0-112 ppm region was calculated as aliphatic carbon, 60-112 ppm as polysaccharide carbon, and 112-163 ppm as aromatic carbon. Total aromaticity was calculated by expressing aromatic C (112-163 ppm) as percentage of the aliphatic C (0-112 ppm) plus aromatic C (Hatcher et al., 1981).

CPMAS <sup>13</sup>C-NMR spectra of the unfractionated DOM are shown in Fig. 2. The major peaks were at: 25 ppm (microbial deoxy sugars or methyl C), 30 ppm (methylene C, protein), 40 ppm (methyl C), 56 ppm (methoxyl C), 75 ppm (carbohydrates or aliphatic alcohols), 105 ppm (anomeric C of polysaccharides), 115 ppm (protonated aromatic C), 130 ppm (Csubstituted aromatic C), 145 ppm (C3 and C5 in etherified phenolic syringyl units), 145-150 ppm (O-substituted aromatic C), and 175 ppm (carboxyl C) (Gutierrez et al., 1996; Kögel-Knabner et al., 1991; Wilson, 1981).

Distinct changes in the unfractionated DOM spectra during composting were: a decrease of the 75-ppm and 105-ppm peaks; an increase in the aromatic C peak (130 ppm); and the development of the 145- and 115-ppm peaks. The relative changes in the levels of C-containing groups are presented in Table 1. The following changes should be noted: (*i*) polysaccharides (60-112 ppm) decreased by 16.2%, from 33.5% to 28.1% in 187-day compost, the C-O and C-N group area (70-98 ppm) decreased by 19.5%; and alkyl-group compounds (0-50 ppm) stayed at a relatively constant level (31.2-33.1% of total C) during composting; (*ii*) aromatic components, including aromatic and phenolic carbons (112-163 ppm) increased by 51%, from 10.8% in the 47-day DOM to 16.5% of the total C in the mature compost; total aromaticity increased by 48.2%, from 12.9% to 19.2% in the mature compost.

Due to the empirical nature of the fractionation procedure used, the fractions showed different structural features as detected by the solid-state <sup>13</sup>C-NMR (Fig. 3). The HoN fraction exhibited four well-resolved peaks at 25-30 ppm, 75 ppm, 130 ppm and 178 ppm, and a shoulder at 145 ppm. The alkyl C-containing group is the dominant structure in the spectra (48.6-44.3%). The main changes in the HoN spectra during composting were: the appearance of the 75-ppm and 145-ppm peaks, a 33% increase of the 60-98 ppm region (alcohols and aliphatic alcohols), and a 12.4% increase of the aromaticity of the C-containing groups in the 187-day spectrum. Due to the relatively small amount of HoB fraction purified from compost from 80 days on, NMR spectra could only be detected with the 47-day sample. The HoB spectrum exhibited four well-resolved peaks at 30 ppm, 56 ppm, 75 ppm and 175 ppm. The HoB fraction proved to have high aromatic structures making up 25% of the C-containing groups. In addition, this fraction contained 30% paraffinic C and 29% carbohydrates and amines. The spectra of the HoA fractions (47 and 187 days) exhibited less aliphatic structures than the HoN fraction and revealed the following changes during composting: a decrease in the 25- and 56-ppm peaks and a relative increase in the aromatic C-containing group region (10.4%) in the 187-day spectrum.

The spectra of the HiN fractions exhibited four well-resolved peaks at 25, 75, 112 and 178 ppm. The configuration of the spectra indicated that this fraction contains mainly polysaccharides. The only difference between the 47- and 187-day spectra was a 23% decrease of the 60-112 ppm region (from 55.6% to 42.8%). The presence of a carbonyl peak (175 ppm) indicates that the polysaccharides are probably polyuronides.

The HiB spectra exhibited three dominant peaks at 25, 65 and 175 ppm and one poorly resolved peak at 130 ppm. The solid-state NMR spectra of the HiB fraction indicated strong C-O and C-N C-containing groups and a strong carboxyl C. Moreover, the chemical property

of this fraction as obtained in the fractionation procedure indicated that it contains mainly proteins or amino-sugar biopolymers. The main changes in the HiB spectra during composting were: the appearance of peaks in the alkyl region (30 and 40 ppm) in the 187-day spectrum and a small increase in the aromatic region from 13.2 to 15.9%.

The HoA fraction is usually considered to be identical to the FA fraction (Grossl and Inskeep, 1996; Wershaw et al., 1995) due to the similar extraction methods used for their purification (adsorption onto XAD-8 resin and desorption by alkaline solution). To study the differences between the water-soluble hydrophobic acid fraction (HoA) and the NaOH-soluble hydrophobic acid fraction (FA), their two spectra were compared (Fig. 4). The two fractions showed similar NMR spectra, exhibiting peaks at 175, 130, 75 and 30 ppm. These spectra suggest a mixture of aliphatic and aromatic structures with a high amount of carboxylic C-containing groups. The main differences between them were: the 150, 75 and 56 ppm peaks, which appeared distinctly in the FA spectrum and did not appear in the HoA spectrum. The aromatic C- containing groups represent 25% of the total C in the FA spectrum and only 15% in the HoA spectrum. A similar trend of changes can be observed between the two fractions at the methoxy C- and anomeric C-containing groups.

### DISCUSSION

In this research we followed the properties of DOM during the composting of MSW in an attempt to understand DOM transformations during the curing stage of composting. The properties of the DOC fractions of composted MSW are compared, in this discussion, to DOC fractions of well-humified OM extracted from soils. The DOM fractionation results suggest the

importance of HoA and HoN as the main organic compounds remaining in the liquid phase of the mature compost. The HoA fraction represented 22.4% of the total DOM, whereas in DOM from forest soil this fraction makes up 50-55% (Qualls and Haines, 1991; Zech et al., 1994). McLaughlin et al. (1996) reported dominance of HoA fraction (70-90%) in forest and mineral soil solutions. Similar HoA fraction dominance has been reported in lake DOC (Roila et al., 1994). The chemical nature of the HoA fraction as suggested by Qualls and Haines (1991), consists of tannins, polyphenols, oxidized polyphenols and humic-bound carbohydrates. The suggested polyphenol-humic structure of the HoA fraction explains its higher proportion in soils exhibiting higher humification indexes than those of compost (Chen at al., 1996). Moreover, the HiN fraction from compost represented 21-34% of the total DOM, whereas in the aqueous soil solution this fraction represents only 0-10% (Cook and Allan, 1992; Qualls and Haines, 1991; Zech at al., 1994). These differences can be explained by the structure and formation of this fraction. The HiN fraction is composed mainly of poly- and oligosaccharides resulting from plant-derived and microbial polysaccharides (Guggenberger and Zech, 1994; Leenheer, 1981; Stevenson, 1994; Zech et al., 1994). This suggested structure was validated by the solid-state NMR spectra (Fig. 3). Carbohydrates represent the most easily degradable structure class of DOM (Garcia et al., 1991; Qualls and Haines, 1991). Thus, the HiN fraction is expected to be dominant in biologically decomposed OM, whereas in ecosystems where slow degradation takes place (soils and lakes) HiN is expected to represent a lower proportion of the DOM. The steady concentration of the HiN fraction during 120 days of composting could represent a steady-state condition in which the carbohydrates originate from both degradable OM and microbial biomass. The decrease in the HiN fraction at the last stage of composting (120 days on) represents deficient carbon availability (low levels of polysaccharides).

According to the literature and to our FTIR measurements the HiA fraction consists of organic compounds with a high degree of biological oxidation, or humic-like substances of low molecular weight (David et al., 1989; Qualls and Haines, 1992; Wershaw et al., 1995). The amount of this fraction changes only slightly during the composting process and represents a DOM percentage similar to that reported for soil DOM (Zech at al., 1994). At the last stage of composting, the HiA fraction became the dominant hydrophilic fraction, suggesting relatively low bioavailability to microorganisms active in compost degradation. The HiB fraction contains mainly proteins, peptides and amino-sugar polymers carrying a positive charge at pH 2. The strong protein feature of this fraction is seen in the NMR spectra as high carboxylic and C-N peaks. No significant differences in HiB fraction content were observed during composting. We assume that during the rapid decomposition process (till day 80) (Chefetz et al., 1996), the HiB fraction contains mainly active enzymes and proteins, while activity at later stages of the process have been reduced.

In general, DOM concentration declines during composting (Inbar et al., 1993). Two important fractions also declined in their relative concentrations (HoB and HiN). However, the relative amount of HoN increased from the very beginning of composting. In fact it almost doubled in concentration from days 105 to 187. Based on the fractionation procedure and NMR data, we conclude that the HoN fraction consists of highly apolar compounds with 48-44% aliphatic structures. It contains the least-soluble organic molecules from the DOM and may be closely related to the HA fraction, which is not soluble in water. According to Cook and Allan (1992) and Zech et al. (1994), in soils the HoN fraction represents 5 to 10% of the total DOM in soils. The contribution this fraction makes to the mature compost is much higher (16-18%) than in soils. This may be due mainly to the fact that this fraction represents an intermediate stage in the humification process and thus, these apolar compounds are more likely to be included.

Based on the studies of Guggenberger and Zech (1994), the HoA fraction exhibits a polymeric structure with covalently linked carbohydrates. Similar features were observed in the compost HoA fraction, but contrary to Wershaw et al.'s (1995) suggestion, this fraction was not identical to the compost or soil FA. The relative proportion of the HoA-fraction increase during composting indicated stability toward microbial degradation. The presence of the methoxy C peak in the 47-day HoA suggests that this fraction was originally the soluble fraction of lignocellulose-degradation products. Similar conclusions were reached by Grossl and Inskeep (1996), who characterized the HoA fraction isolated from wheat straw. A comparison of the HoA fractions isolated from soil, wheat straw and compost indicated that the compost HoA fraction is at an intermediate stage between raw OM (lignocellulose complex) and that which has been degraded and gone through humification processes (soil FA). Moreover, the differences between the HoA and FA fractions revealed HoA to be the most soluble fraction of the compost FA.

DOM in compost at various stages of decomposition contains heterogeneous organic compounds. Being the phase most readily accessible to microorganisms, DOM is the organic fraction containing the organic materials used as an energy source, bio-originating macromolecules (enzymes, polysaccharides and proteins), breakdown products, and the repolymerized compounds eventually contributing to HS formations. The proposed structure and formation of the DOM fractions enable a better understanding of the differences between the <sup>13</sup>C-NMR spectra of unfractionated DOM at different stages of composting. The decrease in carbohydrate C-containing groups seen in the 187-day NMR spectrum of the unfractionated DOM parallels the trend followed by the percentage of the HiN fraction. During composting,

the easily degradable organic-compound decreased while the relative proportion of the resistant fraction increased. Thus, the aromatic C-containing groups (aromatic C, protonated aromatic C and etherified phenolic syringyl units - 130 ppm, 115 ppm and 145 ppm, respectively) increased during composting by more than 50%. Similar reduce of carbohydrate C exhibited in composted and stockpiled manure extracts (Liang et al., 1996).

Monitoring the relative concentrations of the various DOM fractions, and studying the chemical structure of these fractions, revealed that the plateau concentration level of the DOM (days 105-187) does not reflect a steady composition. The relative concentrations of the HoN, HoB and HiN fractions change significantly during the curing stage of MSW composting.

## CONCLUSIONS

DOM represents the most active fraction of compost, both biologically and chemically. It is therefore the organic fraction most subject to change, and as such directly reflects the OM transformation process. In this study we used chemical fractionation and solid-state NMR methods to follow OM transformation during the cooling-down and curing phases of MSW composting. Chemical fractionation and the NMR spectra of the unfractionated DOM indicated degradation of the HiN fraction, resulting in relatively high levels of aromatic and aliphatic structures in the residual DOM. The increasing levels of the HoN and HoA fractions at the last stage of composting may represent the humification process of the compost. The differences between the FA and HoA fractions indicated that HoA is the most mobile and therefore the most active part of the FA fraction. The decrease in HiN from day 120 and the increase in HoN from roughly the same period, may be of relevance to plant-growth enhancement. Improved uptake of elements (increased HoN concentration) or the removal of compounds toxic to plants (reduced HiN concentration) could be the mechanisms involved. Monitoring the chemical and biological changes in DOM during the composting process, in particular during the maturation stage, can improve our knowledge of the transformation of OM during the process of rapid humification.

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Table 1. Distribution of DOM carbon-containing groups during composting of MSW as determined by CPMAS <sup>13</sup>C-NMR (percent of total carbon).

Jacob Contraction

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Composting time (days)		47	77	105	126	187	
Chemical shift	Carbon-containing		Percen	Change with			
(ppm)	group						time (%)
0-50	Alkyl	31.2	28.5	29.5	30.4	33.1	+6.0
50-112	O-Alkyl	42.0	44.7	41.5	38.1	36.3	-13.6
112-145	Aromatic	7.3	6.8	9.8	9.7	11.0	+50.2
145-163	Phenolic	3.5	2.9	4.2	4.6	5.5	+54.1
163-190	Carboxyl	16.4	17.6	14.7	15.3	13.8	-15.4

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## **FIGURES LEGENDS**

- Fig. 1. Fractionation of DOM extracted from MSW compost at six stages of composting (47, 77, 105, 126, 161 and 187 days). Bars represent the standard deviation of three replicates.
- Fig. 2. CPMAS <sup>13</sup>C-NMR spectra of unfractionated DOM extracted from MSW compost samples at five stages of composting (47, 77, 105, 126 and 187 days).
- Fig. 3. CPMAS <sup>13</sup>C-NMR spectra of DOM fractions (HoN, HoA, HoB, HiN and HiB) extracted from MSW compost samples at two stages of composting (47 and 187 days). The HoB fraction approached zero concentration from day 77 on, and the 187-day spectrum is therefore not shown. Spectra of the HiA fraction were poorly resolved due to high salt concentrations and are therefore not shown.
- Fig. 4. CPMAS <sup>13</sup>C-NMR spectra of the fulvic acid (FA) and hydrophobic acid (HoA) fractions purified from 187-day MSW compost.



Fig. 2







and the second second



fig. 4



# RECYCLING OF MUNICIPAL SOLID WASTE (MSW): THE COMPOSTING PROCESS AND COMPOST UTILIZATION IN GREENHOUSE AGRICULTURE
#### ABSTRACT

Composting of municipal solid waste (MSW) was studied in an attempt to better understand the composting process, define parameters of maturity and to determine the potential use of the compost in container media. Composting was performed in 1-m<sup>3</sup> plastic boxes and the following parameters were measured: temperature, C/N ratio in solid and liquid phase (C/N<sub>(9)</sub> and C/N<sub>(w)</sub> respectively), humic substance fractions and contents, and dissolved organic carbon (DOC). Spectroscopic method (DRIFT) was used to study the chemical composition of the bulk organic matter (OM). A bioassay based on the growth of cucumber plants was correlated to other parameters. C/N<sub>(w)</sub>, C/N<sub>(s)</sub> and DOC showed high rates of change during the first 60 days, then stabilized. Humic acid (HA) content increased to a maximum at 110 days, corresponding to the highest plant dry weight and the highest 1650/1560 (cm<sup>-1</sup>/ cm<sup>-1</sup>) peak ratios from DRIFT spectra. DRIFT spectra showed that the OM transformed to a more aromatic structure.

Two greenhouse experiments were performed using cucumber (dlila) and spurge (enjelica) plants aiming to determine the potential use of the MSW compost in container media. Dry weight of cucumber plants grown on MSW compost mixed with coal ash or tuff (60% coal ash or tuff and 40% compost) resembled that of plants grown on substrate containing composted cattle manure (CSM) as the organic fraction. The heavy metals concentration in the cucumber leaves was below toxicity of the plants and the food chain. The number of spurge cuttings showed no significant difference between MSW compost and CSM as organic fractions of a substrate.

Substrate	dry weight (g)	number of fruits
CMSW + Coal Ash	8.2 ± 1.7 A	28.4 ± 1.3
CMSW + Tuff	$6.0 \pm 2.8 \text{ A}$	24.0 ± 3.4
CSM + Tuff	5.6 ± 3.1 A	$21.6 \pm 1.5$

## Effects of substrate composition on cucumber plants growing.

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Substrate	Pb	Cr	Cd	Fe	Мо	Mn	Zn	Cu
CMSW + Coal Ash	0.97 A	0.40 A	0.48 A	60.7 A	10.6 B	26.2 B	67.0 A	11.3 A
CMSW + Tuff	0.87 A	0.34 AB	0.44 A	54.8 A	11.3 B	22.3 B	71.4 A	11.8 A
CSM + Tuff	0.54 C	0.31 B	0.41 A	49.1 A	4.4 A	35.5 A	48.7 B	10.7 A

Heavy metals concentration levels in leaves of cucumber plants grown on various substrate (mg/kg dry matter).

# RESEARCH IN POLAND

#### 1. Introduction and aim of the work

Municipal solid wastes are the onerous ballast which negative influences on the human environment. Because of increasing the quantity and variety of the wastes' content, making them productive properly becomes very serious problem. On the base of present results of the researches, municipal wastes may be used in different way, depending on their kind and noxiousness. Because storing wastes is a very serious emergency for the surrounding environment, so they have been looking for solutions which can stop this danger. Present solutions of this problem are various (burning, gas production, composting) and do not answer which of them is the best and the most reasonable.

Among many different ways of the municipal wastes utilization more and more popular becoming making them productive by composting process. Composting connected with using received product is very important part of the environment protection because it is contributing to:

- decreasing weight and capacity of the wastes,

- limiting the area of wastes dump,

- eliminating sanitary emergency connected with wastes removing,

- including municipal wastes to the organic manure balance.

During the composting process, a very intense transformations of the organic matter are occurring as a result of the integrated microbiological activity. Its include mineralisation of the organic wastes till the final product representing various forms of macro and microelements, as well as humification processes of which effect are forming humus compounds. They can characterise different participation of particularly humus connections, various physico-chemical properties pointing on differentiation of their structure, and their biological activity. Conditions and term of the composting are the main factors which decide about character of these products.

According many nowadays investigations these products can regressive or stimulative influence on growth and development of plants. Because of that, cognition of composts chemical composition and properties of humus substances can be the base of proper estimation of the composting products quality.

The aim of the investigations was to determine maturity indexes of the compost received form municipal solid wastes on the base of some parameters characterizing directions of the organic matter transformation.

#### 2. Material and methods

Researches included municipal solid wastes (MSW) from the big urban agglomeration in Upper Silesia. To the particular experimental analysis was used raw material leaving Dano technological line. Material taken in December 1994 was composted in plastic containers during 90 days, with a moisture about 50% w.w. and temperature of the environment 12-15  $^{\circ}$  C. During continuing the experiment each day was measured the temperature of the compost in the centre of the container (Fig. 30). In the composted material was determined moisture and content of the water was completed till the established level. In every 10-14 days composting material was aerated by turnover and the samples were taken to analyse. Together were taken 8 samples: raw material, and after 14, 28, 38, 52, 62, 76 and 90 days of the experiment (tab.1).

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#### Table 1

Characteristic of the compost samples (MSW) in different stages of maturity

No of sample	Stages of compost maturity
K0	Initial material (raw material) after leaving technological line
K1	Material after 14 days of composting process
K2	Material after 28 days of composting process
К3	Material after 38 days of composting process
K4	Material after 52 days of composting process
K5	Material after 62 days of composting process
K6	Material after 76 days of composting process
K7	Material after 90 days of composting process

In the compost samples taken in different stages of maturity were made the following determinations: moisture, dry matter, ash content.

In the water extract prepared in 1:10 (compost:water) were determined:

-dissoluble forms: C<sub>w</sub>, N<sub>w</sub>, N-NH<sub>4</sub>, N-NO<sub>3</sub>, Cl, PO<sub>4</sub>, K, Ca, Mg, Na, SO<sub>4</sub>, Cu, Zn, Mn, Fe, Pb, Cd, Cr and Ni,

-EC (mS/cm)

- pH

 $-C_w/N_w$  ratio

In the compost samples dried on the air were determined:

- Ct (total carbon),

- C<sub>ox</sub> (oxidizable carbon),

- C<sub>ac</sub> dissoluble in 0,1 N HCl (FF fraction),

- C<sub>NHF</sub> non humic fraction,

- Calk dissoluble in 0,1 N NaOH (alkaline-extractable carbon in 0,1 N NaOH),

- C<sub>HA</sub> humid acid-like carbon,

- C<sub>FA</sub> fulvic acid-like carbon,
- HR1 humification ratio 1 ( $C_{HA}/C_{FA}$ ),
- HR2 degree of humification ( $C_{ac}$ +  $C_{alk}/C_{ox} \times 100$  in ash free),
- HI index of humification  $(C_{ac}/C_{alk})$ ,
- $P_{HA}$  percentage portion of HA ( $C_{HA}/C_{alk}x$  100),
- $P_{FA}$  percent of FA ( $C_{FA}/C_{alk} \times 100$ ),
- Ct/Nt ratio in solid phase of compost,
- CEC (dmol /kg in ash free),
- ESR spectra and determination of free radicals.

Some chemical and physico-chemical properties of humus fractions extracted using procedure recommended by the IHSS, among others:

- separating of FF fraction to C-NHF and C-FA using XAD-8. FA fraction separated by 0,1 M HCl was joining with FA fraction isolated by 0,1 M NaOH and after separating on the cation exchanger they were lyophilizated. Humic acids ( $C_{HA}$ ) defecated by treated them many times with HCl+HF mixture according method recommended by Schnitzer, were dialysed and freeze-dried. In such way received preparations FA and HA were determined elementary composition (C,H,N) and IR spectra in the range of the waves number 625-4000 cm<sup>-1</sup>.

#### 3. Results of investigations

3.1. Total forms of macro and microelements in the composts (MSW) in different stages of maturity (Tab.2 and Fig. 1-6)

During composting process it has been found increase of percentage portion of macroelements Nt, P, K, Mg and Ca in comparison with their content in the initial material (Tab. 2). Only content of Na was on the similar level during whole researching period.

Analogously microelements (Cu, Zn, Mn, Fe, Pb, Cd, Cr), their content was significantly increasing in the following stages of composting in comparison to the raw material (Tab. 2).

3.2. Dissoluble forms of macro and microelements, reaction and salinity of water extracts (1:10) in different matured composts (Tab. 3 and Fig. 7-18)

During the composting process significantly decreased content of dissoluble carbon (Cw) in the water extract from 1434 mg Cw in the initial material till 132 mg Cw after 90 days of composting (Tab. 3). We can also observe changes in quantity of dissoluble Nw. Nw is the highest in the initial material and after 14 days of composting, and next significantly reduces with two minimum after 28 and 76 days of transformation process. With advance of the composting process content of mineral nitrogen enlarged from 19% in the initial material till 60% after 90 days of composting. These changes were accompanied by increase of N-NO<sub>3</sub> as well as decrease quantity of forms N-NH<sub>4</sub>. The last component characterize two obvious maximum: from the very beginning (till 14 days) and during the period of 38 till 62 days of transformation. Content of Na and S dissoluble in water, enlarged. Among determined dissoluble in water forms of microelements Cu, Cd and Cr increased insignificantly during composting, but contents of Zn, Fe, Mn, Pb and Ni were expressively decreasing in this period (Tab. 3).

Salinity of composts generally decreased in the last part of composting process in comparison to the initial material.

3.3. Characteristic of organic matter and humus compounds in different matured composts (Tab. 5 and Fig. 19-20).

During composting MSW deep transformations of organic matter were observed (Tab. 4). Expression of these changes is decrease of  $C_{ox}$  (oxidizable) from 22.11% in the raw material till 15.9% after 90 days of maturing. Decrease of the organic carbon was connected with its mineralization. It was confirmed by increase of ash in more matured composts from 54% in the initial material till about 68% after 90 days of composting process. In the opposite to the carbon is total nitrogen. Changes of  $C_{ox}$  and Nt decided of decrease of C/N ratio in longer maturing composts. During the composting time, decrease of low molecular organic bound ( $C_{ac}$ ) in more matured composts was also observed. This group of compounds is called fulvic fraction (FF) and consist of non humic fraction (NHF) and fulvic acids (FA). FF was divided by XAD-8 resin for NHF and FA. The quantity of NHF decreased in the composting time (Fig. 21).

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Content of humic substances extracted by 0.1 NaOH ( $C_{alk}$ ) increased with degree of compost maturity. This group consist of humic (HA) and fulvic acids (FA). Humic acids increased during composting time, but the most amounts of fulvic acids were observed between 38 and 76 days of composting process. Ratio  $C_{HA}/C_{FA}$  was significantly increasing with the compost maturity. CEC was also significantly increasing time.

## 3.3.1. Determination of semiquinone free radicals in different matured composts by electron spin resonance (EPR)

EPR spectra were obtained with either an SE Radiopan or an ESP 300E Bruker Spectrometer operating at x-band (ca. 9.2 GHz) frequencies (Fig. 22). Measurements were performed on solid air-dried samples of composts at different maturities at ambient temperature. TEMPO and DPPH free radicals were used as standards for guantitative measurements of semiquinone free radicals (SFRs) concentration.

The initial, rapid stage of composting was accompanied by a decrease in SFRs concentration (Fig. 23). Temperature stabilisation (30-50 days) was connected to additional production of SFRs and an increase in intensity of the ESR radical signal. The next local temperature maximum (at about 65 days) was also accompanied by a decrease in SFRs concentration. Temperature stabilisation in more matured compost (70-90 days) paralleled stabilisation of the ESRs concentration at a higher level. The ESR was significantly correlated ( $r = 0.73^*$ ) only with CEC (Fig. 24).

3.3.2. IR spectra of fulvic acids (FA) and humic acids (HA)

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FA were isolated from composts acc. IHSS method and they were separated by XAD-8 resin after lyofilization at a temperature  $-20^{\circ}$  C and pressure  $10^{-4}$  mm Hg, FA were mixed with KBr and the tablets were prepared. IR spectra of FA (obtained at a wave number 4000 to 400 cm<sup>-1</sup>) are presented on Fig. 25. HA were isolated from composts by 0.1 M NaOH, after previously extraction of FF acc. IHSS method. The solution was separated by centrifugation, next was filtrated to remove solids, acidified with 6.0 M HCl to pH 1 and the supernatant containing the extracted FA was separated from precipitated HA by centrifugation. The HA were purified by HCl-HF method five times. After that the HA were dialysed against distilled water until the dialysate was free of Cl. In this point the HA were freeze-dried and the tablets mixed with KBr were prepared. IR spectra of HA at wave number 4000 to 400 cm<sup>-1</sup> are presented on Fig. 26.

The IR spectra of FA representing different stages of compost maturity from MSW exhibited similar features regardless of the composting time (Fig. 25). The main absorbency bands were: a broad zone at  $3400 - 3300 \text{ cm}^{-1}$  (H-bonded OH groups); a slight shoulder at 3085 cm<sup>-1</sup> (aromatic C-H stretch); a sharp peak at 2934 cm<sup>-1</sup> and a

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slight shoulder at 2850 cm<sup>-1</sup> (aliphatic C-H stretch); a slight shoulder at 1710-1720 cm<sup>-1</sup> (C=O of COOH, C=O of ketonic carbonyl groups); a pronounced peak at 1650 cm<sup>-1</sup> (C=C aromatic, COO<sup>-</sup>, C=O hydrogen-bounded and N-H groups, a slight shoulder at 1540 cm<sup>-1</sup> (N-H bound in amines), sharp peaks at 1510-1520 cm<sup>-1</sup> (C=C of aromatic rings); 1460 cm<sup>-1</sup> (aliphatic C-H and 1420 cm<sup>-1</sup> (aromatic ring stretch and COO-); 1385 cm<sup>-1</sup> (aliphatic C-H bounds in CH<sub>3</sub> groups); a broad peak at 1210 cm<sup>-1</sup> region (-C-O- stretch of OH deformation of COOH groups), a slight shoulder at 1160 cm<sup>-1</sup> (C-O-C stretch of various groups, C-OH bounds of phenols) and a peak around 1100 - 1020 cm<sup>-1</sup> (C-O stretch of polysaccharides). The IR spectra of HA representing several stages during the composting of MSW express similar features regardless the composting time (Fig. 26). The IR spectra of HA are generally similar to IR spectra of FA. Both in case of FA and HA decrease aliphatic C-H stretch (at 2930 and 2850 cm<sup>-1</sup>) during composting time was observed. This changes were stronger in HA in comparison to FA. In last two stages of maturity in HA disappeared clear zone absorbance at 1710-1720 cm<sup>-1</sup>. In more matured composts higher intensity of absorbency in zone at 1650 cm<sup>-1</sup> and 1540 cm<sup>-1</sup> (connected with presence of N-H bounds) were observed.

#### 3.3.3. Elementary analysis of FA and HA

Elementary analysis of FA and HA are presented in Tab. 6 and 7. Decrease of C and H content in composition of FA and HA during composting time were observed. The content of N enlarges in molecules of FA in composting time. More matured molecules of FA and HA have a high degree of aromaticity what is confirm by less H/C ratio. These results showed interesting changes in molecules of humic substances developed during composting process.

#### 3.4. Statistical interpretation of the chemical changes in compost

Significant correlation coefficients between the analyzed parameters, at a level p<0.05, are presented in table 8. Among many investigated dependencies, the most interesting are these one which indicate important changes of the parameters during composting process. It is especially according  $C_{ox}$  (r = - 0.96), humus compounds (FF) extracted by solution of acid  $C_{ac}$  (r = -0.85), humification index HI (r = -0.82) and  $C_{ox}/N_t$  ratio (r = -0.99). The values are decreasing with composting days. Transformation of MSW during composting process leads to the significant increase of some parameters. This is particularly marked in N (r = 0.91), ash (r = 1.00), phosphorus (r = 0.80), Mg (r = 0.73), Zn (r = 0.85), Mn (r = 0.82) and CEC (r = 0.89). Among humus indices only humic acids are significantly correlated with the period of composting (r = 0.76).

These results indicate that composting process may be a reason of increasing some heavy metals in the last stages of the municipal wastes' transformations.

## 3.5. Suitability of compost from municipal solid wastes (MSW) in different stages of maturity as a container medium for vegetables cultivation

In the end of March 1994 was founded a new experiment concerned the influence of different moisture level (50 and 60 % w.w.) and different N manuring (0,25 and 0,5% of N in form of urea) in the beginning of composting municipal wastes (MSW) process. The experiment was founded in the plastic containers of about 1 m<sup>3</sup> capacity and the composting control was leading at the same time on the pile as it is mostly used.

The experiment involved the following combinations:

0 - composting process in the pile

I - composting process at 50% w.w. of water

II - composting process at 60% w.w. of water

III - composting process at 50% w.w. of water + 0,25% N (in form of urea)

IV - composting process at 50% w.w. of water + 0,5% N (in form of urea)

In the pile and in plastic boxes the temperature was measured daily and every 10-15 days after turnover of the compost were taking mean samples in which were made chemical analysis.

In the compost samples taken in different maturity stage from all combinations were made the following determinations: moisture, dry matter and ash content. In the water extract prepared in relation 1:10 (compost : water) were made analysis:

- dissoluble forms: Cw, Nw, N-NO<sub>3</sub>, N-NH<sub>4</sub>, PO<sub>4</sub>, SO<sub>4</sub>, Cl, K, Ca, Mg, Cu, Zn, Mn, Fe, Pb, Cd, Cr and Ni

 $- EC (mSxcm^{-1})$ 

- pH

 $- C_w/N_w$  ratio

Compost from the pile, in various maturity stages was used in the biological experiments as the component of the container medium for horticultural cultivation.

The experiment was carried out to determine the suitability of media prepared by mixing of loamy soil with municipal solid waste compost at various stages of its maturity as a container medium for vegetables cultivation. The experimental plant was lettuce - species susceptible to deficiencies of organic matter in the soil and with tendency for accumulation heavy metals in the crop.

There was used the compost at following stages of decomposition:

1. fresh compost,

2. compost after 1 month of maturing

3. compost after 3 months of maturing

4. compost after 9 months of maturing (still under investigation).

The compost pile was initiated on 1st April and parts of composting material were taken for the experiment on 5th April, 5th May, 5th June and 5th January.

In the experiment there were estimated the media comprised loamy soil with addition of MSW compost in the amount : 0-100 t/ha and 400 t/ha. As the control there was used sphagnum peat substrate recognised as a superior and very popular medium in Poland for soiless plant production and pure loamy soil taken from the field without any addition of organic matter.

3.5.1 Effect of maturity stage of compost (MSW) on the emergence of lettuce seedlings

Germination and emergence test. Seeds of crisp lettuce Crispino cv. were sown into plastic boxes filled with 10 l of estimated mediums. Before seed sowing all media used in experiment were fertilized with MIS-4 fertilizer mixture, containing NPK and Mg in the amount of 1 kg per 1 m<sup>3</sup> of the medium. The peat substrate was additionally adjusted to pH 6.0 by incorporation 12 kg of ground chalk per 1m<sup>3</sup> of peat. In each box 50 seeds were sown in 3 replications. The seeds were placed on the surface, pressed into the medium and afterwards covered with thin layer of the same medium mixed with sand and put into the greenhouse.

The emergence counts were taken after 7 and 21 days from sowing. There were determined the number of raised seedlings developed leaves, height and fresh weight of plants.

Fresh MSW compost slightly delayed germination and emergence of lettuce (Tab. 9). After seven days from sowing the number of raised seedlings in medium with 100 t and 400 t/ha of such MSW compost was lower than number of plants cultivated in peat or pure loamy soil. One three or nine months old MSW composts used at the rate of 100 t/ha had no the negative effect on seedling emergence. The higher quantity of MSW compost in medium (400 t/ha) caused some prolongation of lettuce raising at early stages of maturity, while usage of fully matured material, after 9 months of composting did not influence on the plant stand in 7th day from sowing date. Estimation of seedlings emergence done three weeks after seed sowing in every cycle of test showed that the number of raised seedlings in four investigated mediums was similar. MSW compost independently from maturity stage and its dose had no disadvantageous effect on the final emergence of lettuce seedlings.

Type of medium significantly affected the growth rate of lettuce seedlings (Tab.10). The highest fresh weight and shoot height of seedlings were obtained in treatment with peat substrate while plants grown in pure loamy soil reached about 80-

60.1% lower fresh weight of 100 seedlings. The addition of fresh MSW compost resulted in serious growth retardation of lettuce plants. The seedlings grown in mediums with added fresh MSW compost in dose 100 t and 400 t/ha were shorter and developed number of leaves. The colour of its leaves was very plain. Increasing stage of maturity of compost improved the quality of seedlings. The difference in total fresh weight of seedlings grown in pure loamy soil and in soil with addition 3 months old MSW compost in the amount 100 t and 400 t/ha was not significant. Similarly, both tested doses of 9 months old MSW compost had no detrimental effect on estimated features of seedlings: their height, number of leaves and fresh weight.

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3.5.2. Influence of maturity stage of compost (MSW) on plant growth and health of lettuce

In the second experiment the MSW compost at different stages of composting process was used as a source of organic matter in medium provided for plant cultivation in containers. The experimental plant was crisp lettuce Crispino cv.

MSW compost was taken from composting pile on 5th April, 5th May, 5th June, 5th January and in doses 100 t and 400 t/ha mixed with loamy soil. As the control treatments peat substrate and pure loamy soil were recognised. All media were fertilized with MIS-4, part A fertilizer  $(1,0 \text{ kg/m}^3)$  containing macroelements.

Microelements were supplied as a part B of the same fertilizer in the amount of  $135 \text{ g/m}^3$  of medium. The sphagnum peat was adjusted to pH 6,0 with chalk (12 kg/m<sup>3</sup>). Seeds of lettuce were sown into 5 cm in diameter plastic rings filled with tested media. Two or three seeds were placed per pot, and after emergence the seedlings were thinned to one per pot. At the moment when three truth leaves were developed transplantations together with plastic rings were put into plastic boxes filled with 10 l of the same media as in the pots. Four seedlings were grown in one box placed in the hot bed. During cultivation lettuce was watered three, to four times per week.

The experiment was arranged in a randomized complete block design with 4 replications. Each plot consisted of two boxes and 8 plants. For each cultivation cycle the harvest was done one month from planting date when the plants started to form the heads (Phot. 1). Fresh weight of one plant and total yield of lettuce were estimated.

High ratio of MSW compost in growing media (400 t/ha) had the derminal effect on plant growth and health. Independently on the maturity stage of compost, in treatment supplied with 400 t/ha of this material there was observed reduction of plant population on the plots. Also yellowing and tipburn of leaves appeared only in this treatment.

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Fresh MSW compost negatively affected plant growth and greatly reduced weight of lettuce head as well as final yield (Tab. 11). In treatment supplied with 400 t/ha of fresh MSW compost growth of lettuce was suppressed by 98.8% in comparison to peat substrate. Composting process improved quality of compost and decreased its adverse effect on growth of plants. In treatment with lower amount of three months old MSW compost and in control with pure loamy soil medium lettuce produced almost equal yields. Higher dosage of Msw compost (400 t/ha) at the same stage of maturity slightly decreased yielding but this effect was also not significant. After 9 months of composting process MSW compost had no negative effect on growth of crisp lettuce at all amount used in the experiment. Fresh or partly matured (1 or 3 months old) MSW compost delayed time of seedlings emergence but did not influence the final stand of lettuce plants estimated 21 days from date of sowing. The application of this material to the growing medium comprising loamy soil adversely affected the growth rate of plants. Along with the increasing degree of maturation this negative effect became less pronounced, especially if smaller amounts of MSW compost was applied. Nine months old MSW compost did not adversely affect growth of lettuce plants and in practice may be used as a component of medium for plant cultivation even in heavy ratios amounted 400 t/ha.

#### 4. Present realisation of the work - field experiment

After had been finishing the second phase of the investigations, 3rd and 4th part of the researches were leading. So in the spring of 1995 was founded the field experiment which aim was to determine influences of different doses of compost from municipal solid wastes on soil properties as well as quantity and quality of the plant harvest cultivated as a main crop - lettuce, and second plant headed cabbage. Analysis of soil samples and plant material will be continued in 1996.

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#### Sector Contents

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Table 2

## Total content of macro and microelements in compost from municipal solid wastes (MSW) in different stages of maturity

Macro and Microelements			Da	ys of comp	osting			
	1	14	28	38	52	62	76	90
Nt (% of dry matter)	0.848	0.864	0.870	0.877	0.935	1.024	1.039	1.229
P % of d.m.	1.227	1.341	1.408	1.534	1.462	1.493	1.407	1.788
K % of d.m.	5.348	5.304	5.302	5.554	5.573	5.001	5.069	6.081
Mg % of d.m.	5.605	6.467	7.342	7.964	7.792	7.834	7.600	7.549
Ca % of d.m.	30.756	32.886	39.418	41.672	41.668	41.876	41.750	41.759
Na % of d.m.	4.519	4.475	4.699	4.950	4.977	4.558	4.500	4.454
Cu mgxkg⁻¹ d.m.	275.0	291.0	285.0	387.0	312.0	315.0	303.0	364.0
Zn mgxkg <sup>-1</sup> d.m.	1753.0	1725.0	1725.0	1975.0	1875.0	1850.0	2150.0	2132.0
Mn mgxkg⁻¹ d.m.	495.0	497.0	515.0	513.0	561.0	715.0	644.0	633.0
Fe mgxkg <sup>-1</sup> d.m.	23733.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	31788.0
Pb mgxkg <sup>-1</sup> d.m.	496.0	644.0	796.0	532.0	568.0	502.0	611.0	828.0
Cd mgxkg <sup>-1</sup> d.m.	6.1	6.4	6.0	7.0	7.8	6.3	7.0	6.4
Cr mgxkg <sup>-1</sup> d.m.	75.0	77.0	87.0	92.0	100.0	76.0	81.0	79.0
Ni mgxkg <sup>-1</sup> d.m.	59.0	56.0	68.0	75.0	63.0	59.0	58.0	66.0

Chemical composition of the water extracts (1:10) from composts of municipal solid wastes (MSW)

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Parameter			Days	of compo	sting			
	1	14	28	38	52	62	76	90
Cw mgx100 <sup>-1</sup> g of d.m.	1434	607	491	222	265	207	140	132
Nw mgx100 <sup>-1</sup> g of d.m.	143.2	118.0	50.8	70.3	78.4	77.6	51.2	64.0
$N-NO_3$ mg×100 <sup>-1</sup> g of d.m.	0.7	1.5	3.1	3.5	2.0	5.2	35.7	35.2
N-NH₄ mgx100 <sup>-1</sup> g of d.m.	26.8	27.1	11.7	20.3	35.8	41.5	5.8	3.4
NO₃/NH₄ ratio x10	0.26	0.55	2.64	1.7	0.55	1.24	61.5	103.3
Nmin %	19.2	24.2	29.1	33.8	48.2	60.1	81.1	60.3
P mgx100 <sup>-1</sup> g of d.m.	8.8	6.4	2.1	2.2	2.1	1.6	1.1	1.4
K mgx100 <sup>-1</sup> g of d.m.	342	368	318	354	374	380	375	415
Ca mg/100 g of d.m.	1123	224	170	148	142	130	145	154
Mg mgx100 <sup>-1</sup> g of d.m.	456	389	308	321	329	312	307	316
Na mgx100 <sup>-1</sup> g of d.m.	83	330	269	290	309	315	320	346
S mgx100 <sup>-1</sup> g of d.m.	425	476	435	476	506	514	470	489
Cw/Nw ratio	9.9	5.14	9.7	3.2	3.4	2.7	2.7	2.1
Cu mgxkg <sup>-1</sup> d.m.	1.4	1.8	2.3	2.3	3.3	3.4	4.5	5.1
Zn mgxkg <sup>-1</sup> d.m.	133.0	28.1	19.8	20.1	28.0	23.3	8.9	9.4
Fe mgxkg <sup>-1</sup> d.m.	280.0	135.2	42.8	43.5	29.7	24.8	18.6	20.9
Mn mgxkg <sup>-1</sup> d.m.	66.2	8.5	4.5	4.6	4.1	3.6	2.8	2.1
Pb mgxkg <sup>-1</sup> d.m.	10.7	5.3	2.9	3.0	3.2	2.3	0.7	1.1
Cd mgxkg <sup>-1</sup> d.m.	0.4	0.4	0.3	0.3	0.4	0.8	0.8	0.8
Cr mgxkg <sup>-1</sup> d.m.	0.9	0.8	0.6	0.7	0.8	1.9	2.0	1.9
Ni mgxkg <sup>-1</sup> d.m.	3.3	1.1	0.9	1.2	1.2	1.9	0.7	0.8
pH in H₂O	7.0	7.0	8.2	8.4	7.9	6.7	6.4	6.4
EC (mSxcm <sup>-1</sup> , 25°C)	4.4	2.7	2.55	2.51	2.20	2.35	2.4	2.4

Component	Days of composting1142838526276906.52.82.61.21.51.20.80.816.913.65.88.08.37.54.95.20.080.170.350.400.210.500.340.283.163.131.342.313.824.050.550.270.70.50.150.140.140.10.080.086.46.96.06.46.77.67.56.83.60.680.430.350.340.310.340.378.36.34.24.04.24.04.04.11.87.35.75.86.26.97.17.8												
-	1	14	28	38	52	62	76	90					
C <sub>w</sub> /C <sub>ox</sub>	6.5	2.8	2.6	1.2	1.5	1.2	0.8	0.8					
N <sub>w</sub> /N <sub>t</sub>	16.9	13.6	5.8	8.0	8.3	7.5	4.9	5.2					
N-NO <sub>3</sub> /N <sub>t</sub>	0.08	0.17	0.35	0.40	0.21	0.50	0.34	0.28					
N-NH₄/Nt	3.16	3.13	1.34	2.31	3.82	4.05	0.55	0.27					
P <sub>w</sub> /P	0.7	0.5	0.15	0.14	0.14	0.1	0.08	0.08					
K"/K	6.4	6.9	6.0	6.4	6.7	7.6	7.5	6.8					
Ca <sub>w</sub> /Ca	3.6	0.68	0.43	0.35	0.34	0.31	0.34	0.37					
Mg <sub>w</sub> /Mg	8.3	6.3	4.2	4.0	4.2	4.0	4.0	4.1					
Na <sub>w</sub> /Na	1.8	7.3	5.7	5.8	6.2	6.9	7.1	7.8					
Cu <sub>w</sub> /Cu	0.5	0.6	0.8	0.6	1.0	1.1	1.5	1.4					
Zn <sub>w</sub> /Zn	7.6	1.6	1.1	1.0	1.5	1.2	0.4	0.4					
Mn <sub>w</sub> /Mn	13.4	1.7	0.9	0.9	0.7	0.5	0.4	0.3					
Fe <sub>w</sub> /Fe	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06					
Pb <sub>w</sub> /Pb	2.1	0.8	0.4	0.6	0.6	0.5	0.1	0.1					
Cd <sub>w</sub> /Cd	6.5	6.2	5.0	4.2	5.1	12.6	11.4	12.5					
Cr <sub>w</sub> /Cr	1.2	1.0	0.7	0.8	0.8	2.5	2.5	2.4					
Ni <sub>w</sub> /Ni	5.6	1.9	1.3	1.6	1.9	3.2	1.2	1.2					

## Percentage portion of dissolved forms in total content of macro and microelements (MSW)

# Fractional composition of humus compounds and some physico-chemical properties of compost from municipal solid wastes (MSW)

Parameter			Days	of compo	osting			
	1	14	28	38	52	62	76	90
C <sub>ox</sub> (oxidizable) % of d.m.	22.11	21.69	18.78	17.97	17.46	16.81	16.34	15.6
C <sub>ac</sub> extracted by 0,1 M HCl								
(% C <sub>ox</sub> )	4.3	4.0	2.4	2.1	2.1	2.0	2.0	1.8
C <sub>alc</sub> extracted by 0,1 M								
NaOH (% С <sub>ох</sub> )	9.2	9.5	12.0	13.1	13.8	12.2	12.5	12.1
C <sub>HA</sub> (% C <sub>ox</sub> )	3.4	3.9	5.5	5.9	5.7	5.5	5.1	6.2
C <sub>FA</sub> (% C <sub>ox</sub> )	5.8	5.6	6.5	7.2	8.1	6.7	7.4	5.9
HR1 (C <sub>HA</sub> /C <sub>FA</sub> )	0.58	0.69	0.84	0.82	0.7	0.82	0.69	1.05
HI (C <sub>ac</sub> /C <sub>alc</sub> )	0.48	0.42	0.2	0.16	0.15	0.16	0.16	0.14
HR2 (C <sub>ac</sub> +C <sub>alc</sub> x100)	27.9	27.3	29.7	32.1	34.4	30.7	30.5	30.2
Р <sub>НА</sub> % (С <sub>НА</sub> /С <sub>аlc</sub> x100)	36.9	41.5	45.5	45.1	41.5	45.1	40.6	47.3
P <sub>FA</sub> % (C <sub>FA</sub> /C <sub>alc</sub> x100)	63.1	58.5	54.5	54.9	58.5	54.9	59.4	52.6
C <sub>ox</sub> /N <sub>t</sub>	26.0	25.1	21.6	20.5	18.6	16.4	15.7	12.7
CEC dmolxkg <sup>-1</sup> of ash free	51.4	52.7	52.2	57.0	58.5	58.8	76.1	82.1
Ash % of d.m.	54.3	56.2	61.4	62.0	62.3	63.6	65.7	68.2
Ignition loss % of d.m.	45.7	43.8	38.6	38.0	37.7	36.4	34.3	31.8

### Table 6

# Elementary composition of fulvic acids from compost (MSW) in different stages of maturity

Parameter			Days	of compo	sting			
	1	14	28	38	52	62	76	90
N % of ash free	2.88	3.63	4.27	3.93	4.38	4.57	3.55	4.36
<u>C %</u>	50.08	45.44	45.0	41.65	43.97	42.43	38.28	42.47
Н%	6.97	6.05	5.75	5.04	6.03	5.13	5.40	5.25
C/N	17.39	12.52	10.54	10.58	10.04	9.27	10.78	9.73
<u>C/H</u>	7.18	7.50	7.82	8.26	7.29	8.26	7.08	8.08
N ( in atomic %)	0.20	0.25	0.30	0.28	0.31	0.32	0.25	0.31
C (in atomic %)	4.17	3.78	3.75	3.47	3.66	3.53	3.19	3.52
H (in atomic %)	6.97	6.05	5.75	5.04	6.03	5.13	5.40	5.25
H/C	1.67	1.60	1.53	1.45	1.64	1.45	1.69	1.49
N/C	0.05	0.06	0.08	0.08	0.08	0.09	0.08	0.09

### Table 7

Elementary composition of humic acids isolated from compost (MSW) in different stages of maturity

.

Parameter			Days	of compo	osting						
	1	14	28	38	52	62	76	90			
N % of ash free	4.51	4.66	7.40	7.07	6.76	6.65	6.36	6.00			
C %	55.71	51.46	50.25	50.08	49.05	49.32	48.93	48.33			
<u> </u>	8.26	7.32	6.50	6.43	6.70	6.69	6.44	5.93			
C/N	12.35	11.04	6.79	7.08	7.25	7.41	7.69	8.05			
C/H	6.7	7.0	7.7	7.7	7.3	7.3	7.5	8.1			
N (in atomic %)	0.32	0.33	0.52	0.50	0.48	0.47	0.45	0.43			
C (in atomic %)	4.64	4.23	4.19	4.17	4.09	4.11	4.08	4.03			
H (in atomic %)	8.26	7.32	6.50	6.43	6.70	6.69	6.44	5.93			
H/C	1.78	1.72	1.55	1.54	1.63	1.62	1.58	1.47			
N/C	0.07	0.08	0.12	0.12	0.12	0.11	0.11	0.11			

Variable	N total	Р	Mg	Cu	Zn	Mn	Cr	Ni	Cox	Cac	Caik	C <sub>HA</sub>	CFA	HR1	н	HR2	Рна	P <sub>FA</sub>	C <sub>ox</sub> /Nt	CEC	Ash	Ignition Loss
Days	0.91*	0.80*	0.73*		0.85*	0.82*			- 0.96*	-0.85*		0.76*			-0.82*				-0.99*	0.89*	1.00*	-1.00*
N total		0.81*			0.77*	0.76*			-0.78*					0.71*					-0.91*	0.92*	0.80*	-0.80*
Р				0.79*					-0.79 *	-0.75 *		0.84*		0.93*	-0.72 *		0.80*	-0.80 *	-0.82 *	0.71*	0.80*	-0.80 *
ĸ													_									
Mg									-0.87*	-0.95*	0.93*	0.92*			-0.97*	0.78*	0.70*		-0.75*		0.80*	-0.80*
Cu								0.71*				0.71*										
Zn	_	_							-0.79*										-0.82*	0.93*	0.80*	-0.80*
РЬ																						
Cd							0.77*						0.84*			0.82*						
Cr											0.75*		0.79*			0.84*						
Ni																						
C <sub>ox</sub>										0.97*	-0.82*	-0.88*			0.95*				0.97*	-0.76*	-1.0*	1.0*
C <sub>ac</sub>										_	-0.92*	-0.95*			1.0*	-0.74*	-0.7*	0.7*	0.88*		-0.9*	0.9*
L C <sub>alk</sub>												0.89*	0.85*		-0.94*	0.93*					0.70*	-0.70*
CHA														0.78*	-0.96*	0.73*	0.80*	-0.80*	-0.79*		0.90*	-0.90*
CFA																0.90*						
HR1	ļ																0.90*	-0.90*			0.70*	-0.70*
<u> </u>																-0.77*			0.85*		-0.90*	0.90*
HR2	<u> </u>																					
PHA																		-1.0*				
PFA														-								
· C <sub>ox</sub> /Nt																				-0.86*	-1.0*	1.0*
CEC																					0.80*	-0.80*
Ash																						-1.0*

Correlations coefficients between some determined features\*

\* - Marked correlations are significant at p < 0.05

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Table 8

Correlations	coefficients	between	some	determined	features	(continuation)
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		1				Timeu	Tealure		illinuali	<u>un)</u>	
Variable	C <sub>w</sub>	N <sub>w</sub>	N-NO	3 N-NH₄	N-NO <sub>3</sub> /N-NH <sub>4</sub>	Nmir	Pw	K,,	Ca <sub>w</sub>	Mg,	, Na <sub>w</sub>
Days	-0.82*	-0.72*	0.80*		0.77*	0.91	-0.83	0.76		-0.76	*
N total			0.84*		0.89*	0.76*	,	0.85	,		
Р	-0.73*										
ĸ										+	
Mg	-0.94*	-0.86*					-0.95*		-0.87	-0.94	* 0.75*
Cu											
Zn			0.89*		0.83*	0.81*					
Pb				-0.72*							
Cd										+	
Cr							1			†	
Ni										+	
Cox	0.87*	0.84*				-0.86*	0.94*	0.87*	<u> </u>	+	
Cac	0.89*	0.91*			_	-0.73*	0.98*		0.76*	0.94*	,
C <sub>alk</sub>	-0.80*	-0.81*					-0.88*			-0.84	
СНА	-0.85*	-0.85*					-0.92*		-0.76*	-0.89	,
CFA											
HR1										†	
HI	0.90*	0.91*					0.98*		0.79*	0.95*	·
HR2										0.00	
PHA	-0.72*		_				-0.72*		-0.73*	-0.76*	
PFA	0.72*						0.72*		0.73*	0.76*	
Cox/Nt	0.81*	0.74*	-0.76*		-0.74*	-0.89*	0.85*	-0 73*	0.70	0.70	
CEC			0.97*		0.96*	0.82*	0.00	0.77*		0.77	
Ash	-0.86*	-0.85*	0.75*		0.73*	0.84*	-0.92*	0.77		-0.86*	
Ignition loss	0.86*	0.85*	-0.75*		-0.73*	-0.84*	0.92*			0.86*	——
C,		0.84*				-0.72*	0.93*		0.95*	0.93*	-0.92*
N <sub>w</sub>							0.95*		0.80*	0.96*	
N-NO <sub>3</sub>				-0.74*	0.95*	0.79*					
N-NH₄					-0.75*						
Nmin							-0.74*				
Pw									0.85*	0.99*	-0.75*
Ca <sub>w</sub>										0.90*	-0.95*
Mg <sub>w</sub>											-0.78*

Correlation coefficients between some determined features (cont	ntinuation)
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	TCIALIO		001100	500000								
Variable	Sw	C <mark>"∕N</mark> "	Cu <sub>w</sub>	Znw	Mnw	Few	Pbw	Cd <sub>w</sub>	Cr₩	Niw	рН <sub>w</sub>	EC
Days		-0.79*	0.98*			-0.79*	-0.85*	0.80*	0.80*			
N total			0.93*					0.85*	0.84*			
P			0.75*									
ĸ												
Mg		-0.71*		-0.84*	-0.86*	-0.96*	-0.89*					-0.89*
Cu												
Zn		-0.73*	0.86*									
Pb												
Cd												
Cr											0.75*	
Ni												
C		0.73*	-0.90*	0.72*		0.88*	0.89*					0.74*
C <sub>ac</sub>			-0.77*	0.76*	0.76*	0.93*	0.90*					0.80*
Calk						-0.85*	-0.76*					-0.76*
				-0.76*	-0.76*	-0.89*	-0.84*					-0.79*
CEA												
			-0 73*	0.78*	0.79*	0 94*						0.83*
			-0.75	0.70	0.73	0.34	0.30					0.00
				0.74*	0.74*	0.75*	0.72*					
				-0.74	-0.74	-0.75	-0.72					
				0.74*	0.74*	0.74*	0.72*	0 70+	0 701			
C <sub>ox</sub> /N <sub>t</sub>		0.75*	-0.97*			0.79*	0.84*	-0.78*	-0.78*			
CEC			0.94*					0.79*	0.80*			
Ash		-0.71*	0.93*	-0.75*	-0.71*	-0.87*	-0.91*					-0.74*
	0 72*	0.71*	-0.93*	0.75*	0.71	0.07	0.91	-		0 92*		0.74
	-0.73	0.01	-0.73	0.95	0.95	0.90	0.97			0.03		0.90
			0.87*	0.05	0.00	0.52	0.92	0 77*	0.79*	0.75		0.00
N-NO <sub>2</sub> /N-NH			0.85*					0	0.71*			
Nmin		-0.73*	0.91*				-0.76*	0.85*	0.86*			
Pw			-0.75*	0.86*	0.85*	0.98*	0.96*			0.74*		0.87*
Kw.	0.73*	-0.83*	0.77*					0.75*	0.72*			
Ca <sub>w</sub>				0.99*	1.00*	0.94*	0.92*			0.89*		0.99*
Mgw				0.90*	0.90*	0.98*	0.96*			0.79*		0.91*
Naw	0.73*	-0.77*		-0.96*	-0.96*	-0.86*	-0.88*			-0.88*		-0.95*
Sw		-0.87*										-0.72*
C <sub>w</sub> /N <sub>w</sub>			-0.72*				0.71*					
Cuw							-0.78*	0.82*	0.81*			
Zn <sub>w</sub>					0.99*	0.94*	0.95*			0.93*		0.97*
Mn <sub>w</sub>						0.94*	0.93*			0.90*		0.99*
Fe <sub>w</sub>							0.98*			0.82*		0.96*
Pbw										0.86*		0.93*
Cd <sub>w</sub>									0.99*		-0.85*	
Crw											-0.84*	
Niw												0.86*

#### Table 9

### The effect of maturity stage and rate of MSW compost on the energence of lettuce seedlings after seven and twenty one days from sowing (%)

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	Fresh	MSWC	1month	old MSWC	3 month	old MSWC	9 month	old MSWC	
Treatments	Estimation of seed emergence after								
	7 d <b>ays</b>	21 days	7 days	21 days	7 days	21 days	7 days	21 days	
Sphagnum peat substrate	93.2	100.0	94.6	100.0	97.2	98.0	92.0	96.7	
Loamy soil	90.06	98.0	92.6	100.0	97.2	96.0	94.0	96.5	
Loamy soil + MSWC 100 t/ha	80.0	96.0	95.2	100.0	86.0	95.2	86.6	92.0	
Loamy soil + MSWC 400 t/ha	80.0	98.0	81.2	100.0	77.2	93.4	95.2	97.5	

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### Quality of lettuce seedlings as affected by the type of media

Treatments	Number of developed leaves	Height of plant	Total fresh weight of 100 seedlings (g)	Relative weight of seedlings (%)*					
Sphagnum peat substrate	3.0	11.8	60.5	100					
Loamy soil	2.0	5.6	12.8	21.3					
Loamy soil + 100 t/ha MSWC <sub>0</sub>	1.5	3.1	4.4	7.0					
Loamy soil + 400 t/ha MSWC <sub>0</sub>	1.5	2.8	2.6	4.3					
$LSD\alpha = 0.05$	7.43								
MSWC <sub>0</sub> = fresh m	nunicipal								
solid waste cor	mpost								
Sphagnum peat substrate	3.0	13.7	102.0	100.0					
Loamy soil	2.0	6.9	16.8	16.4					
Loamy soil + 100 t/ha MSWC <sub>1</sub>	1.5	3.9	11.2	11.0					
Loamy soil + 400 t/ha MSWC <sub>1</sub>	1.5	4.0	9.0	8.8					
$LSD\alpha = 0.05$ 15.66									
$MSWC_1 = 1$ month old									
MSW comp	MSW compost								
Sphagnum peat substrate	4.0	13.7	102.0	100.0					
Loamy soil	3.0	11.5	40.6	39.8					
Loamy soil + 100 t/ha MSWC <sub>3</sub>	3.0	9.3	31.4	30.7					
Loamy soil + 400 t/ha MSWC <sub>3</sub>	3.0	8.9	27.2	26.6					
$LSD\alpha = 0.05$	LSDa = 0.05 22.9								
MSWC <sub>3</sub> = 3 months old									
MSW compost									
Sphagnum peat substrate	4.0	4.3	44.6	100.0					
Loamy soil	2.0	5.0	7.4	16.6					
Loamy soil + 100 t/ha MSWC <sub>9</sub>	3.0	5.4	8.4	18.8					
Loamy soil + 400 t/ha MSWC₀	3.0	6.6	10.2	22.9					
$LSD\alpha = 0.05$	LSD <sub>α</sub> = 0.05 2.76								
MSWC <sub>9</sub> = 9 months old									
MSW compost									

\*- Relative weight of seedlings was counted in relation to sphagnum peat substrate

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## Effect of maturity stage and rate of MSW compost on yielding of crisp lettuce

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Treatments	Yield kg/m <sup>2</sup>	Weight of plant (g)	Relative yield (%)						
Sphagnum peat substrate	5.82	165.3	100.0						
Loamy soil	2.29	64.9	39.3						
Loamy soil + 100 t/ha MSWC <sub>0</sub>	1.45	41.3	24.9						
Loamy soil + 400 t/ha MSWC <sub>0</sub>	0.07	2.2	1.2						
$LSD\alpha = 0.05$	0.53	15.12							
$MSWC_0 = fresh municipal$									
solid waste cor	npost	_							
Sphagnum peat substrate	8.49	240.8	100.0						
Loamy soil	4.20	119.2	49.5						
Loamy soil + 100 t/ha MSWC <sub>1</sub>	3.36	101.2	39.6						
Loamy soil + 400 t/ha MSWC <sub>1</sub>	2.43	73.0	28.6						
$LSD\alpha = 0.05$	$LSD\alpha = 0.05$ 0.57 16.28								
MSWC <sub>1</sub> = 1 month old MSW compost									
Sphagnum peat substrate	8.06	228.7	100.0						
Loamy soil	4.17	118.5	51.7						
Loamy soil + 100 t/ha MSWC <sub>3</sub>	3.92	113.0	48.6						
Loamy soil + 400 t/ha MSWC <sub>3</sub>	2.82	79.9	35.0						
LSDα = 0.05	1.56	44.57							
MSWC <sub>3</sub> = 3 months old MSW compost									
Sphagnum peat substrate	3.38	96.0	100.0						
Loamy soil	1.67	47.5	49.5						
Loamy soil + 100 t/ha MSWC <sub>9</sub>	1.41	50.2	41.9						
Loamy soil + 400 t/ha MSWC <sub>9</sub>	1.61	45.8	47.7						
$LSD\alpha = 0.05  0.25  7.05$									
MSWC <sub>9</sub> = 9 months old MSW compost									



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Fig. 1 Changes of K and Mg in compost (MSW) of different stages of maturity

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Fig. 2 Changes of N and P in compost from MSW in different stages of maturity

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Fig. 3 Changes of Zn and Mn during composting MSW in different stages of maturity

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Fig. 4 Changes of Cu and Pb during composting MSW in different stages of maturity



Fig.5 Changes of Cr and Ni during composting MSW in different stages of maturity

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Fig.6 Changes of Cd during composting MSW in different stages of maturity



## Fig.7 Changes of Cw and Nw in the water extract (1:10) during composting MSW in different stages of maturity

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# Fig. 11 Changes of P in the water extract (1:10) during composting municipal solid wastes in different stages of maturity

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## Fig. 12 Changes of K, Ca and Mg in the water extract (1:10) during composting MSW in different stages of maturity

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## Fig.14 Changes of Zn and Fe in the water extract (1:10) during composting MSW in different stages of maturity



## Fig. 15 Changes of Cu and Pb in the water extract (1:10) during composting MSW

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Fig.16 Changes of Mn in the water extract (1:10) during composting MSW

# Fig. 17 Changes of Cr and Ni in the water extract from compost (MSW) in different stages of maturity





Fig. 18 Changes of pH (H<sub>2</sub>O) in the water extract (1:10) during composting MSW



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Fig. 21 Changes of NHF and FA in FF fraction during composting time

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Fig. 22 EPR spectra of composts in different stages of maturity





















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Fig. 23 IR spectra of fulvic acids (FA) isolated from different matured composts



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Fig. 24 IR spectra of humic acids (HA) isolated from different matured composts

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Fig. 25 Temperature evolution (dashed line) and ESRI (solid line) during composting municipal wastes



Figure 3. Regression between CEC and ESRI

Fig. 26 Regression between CEC and ESRI





Days of composting

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Days of composting









Days of composting

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# Fig. 31 Correlations between CEC and days during composting MSW CEC = 45.827 + .33846 \* Days Correlation: r = .89464 at p < 0.01



Days of composting



Days of composting



Fig. 33 Correlations between Nmin (water extract) and days during composting MSW Nmin = 15.495 + .64278 \* Days

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Days of composting

\*







Fig. 36 Influence of composts in different stages of maturity on growth of lettuce A- raw compost, B- 1month old compost, C- 3 months old compost MSW 1 - compost dose 100 t/ha MSW 4 - compost dose 400 t/ha

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## Chemical and electron spin resonance properties of municipal solid waste compost

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Keywords: Compost maturity, municipal wastes, electron spin resonance, semiquinone free radicals

#### Abstract

Quantitative electron spin resonance (ESR) measurements were performed on samples of composted municipal refuses various stages of maturity (up to 90 days of composting). Results were compared with selected humification indexes: amount of humic acids (CHA), humification ratio  $HR_1$  (CHA/CFA) and cation exchange capacity (CEC). Among the investigated parameters, the most significant correlation with intensity of the free radical signal (ESRI) was found with CEC.

#### Introduction

The stage of compost maturity is an important criterion for its utilization in agriculture (Inbar et al. 1990, Iglesias Jimenez and Perez Garcia 1992, Sophon 1978). When applied to soils, fresh (immature) compost can raise microbiological activity and introduce phytotoxic compounds (Viel et al. 1987, Wong 1985). During composting the organic matter is decomposed and new products are created. The transition forms of these organic substances have different properties (Inbar et al. 1990, Iglesias Jimenez and Perez Garcia 1992, Sugahara and Inoko 1981). The humic substances formed during composting carry various functional groups, as well as semiquinone free radicals (SFRs) (Almendroz et al. 1987, Senesi 1990). The latter are very sensitive to pH, ionic strength, hydrolysis, redox reactions and interaction with metal ions (Senesi et al. 1986, 1992). These radicals play an important role in the polymerization and depolymerization reactions involved in humification. The signal intensity of electron paramagnetic resonance can change during the transformation of organic material.

The aim of this work was to study relationships between composting time, humification indexes and free radical signals, as a way of determining compost maturity and evaluation it for agricultural use.

#### Materials and methods

Studies were conducted on municipal solid wastes (MSW) from the greater metropolian area in Upper Silesia (Poland). The municipal refuse was initially prepared according to Dano technology. Composting was performed in a closed fermentative chamber, which also served as a grinding machine. The material was ground by crushing and blowing and its temperature was raised to about 45°C. After 24 hours a product having some physical properties resembling compost was obtained.

This fresh material which contained a high level of organic matter, was composted in 100 dm<sup>3</sup> plastic containers. Its temperature was measured daily for 90 days and water was added to a maintain a moisture level of ca. 50% of the compost's weight. Every 10-14 days the compost was turned over and samples were taken. These samples were airdried and the following determinations were made: Ct - total oxidizable carbon, Nt - total nitrogen according to Kjeldahl, cation exchange capacity (CEC) according to Harada and Inoko (1980), humic and fulvic-like carbon (CHA and CFA respectively), humification ratio HR<sub>1</sub> (CHA/CFA) and electron spin resonance (ESR) spectra. The ESR spectra were obtained with either SE Radiopan or an ESP 300E Bruker Spectrometer operating at x-band (ca. 9,2 GHz) frequencies. Measurements were performed on solid air-dried samples of composts in different maturities at ambient temperature. TEMPO and DPPH free radicals were used as standards for quantitative measurements of SFR concentration.

#### **Results and discussion**

During the composting of MSW, marked qualitative and quantitative changes in organic matter were observed (tab. 1).  $C_t$  content decreased and  $N_t$  increased, effecting a reduction in the C/N ratio. Humification increased the amount of CHA with compost maturity. The interdependence between investigated parameters and composting time is presented in a correlation matrix (tab. 2). The most significant correlation coefficients with degree of compost maturity (composting time) were found with  $C_t$ ,  $N_t$ , C/N ratio, CEC and CHA. This observation confirms the suggestion that organic matter transformation is very closely connected with the degree of compost maturity. The most visible changes in these parameters were observed in the first 4 to 6 weeks. After this time, transformation rate was distinctly slower. ESR spectra consisted of a broad-line signal due to the presence of Fe (III) bound to organic and mineral substances, and a narrow-line signal (R) at G = 2.0035, attributed to SFRs (fig. 1).

The above mentioned changes were influenced by microbiological activity and strongly characterized an exothermic process, as evidenced by the pattern of temperature evolution during composting (fig. 2). The temperature of the compost markedly increased during the first 3 weeks of transformation. It decreased gradually till about 6 weeks, after which it was dependent upon ambient conditions.

The initial, rapid stage of composting (lasting about 20 days and during which temperature increased markedly) was accompanied by a decrease SFR concentration (fig. 2). Temperature stabilization (30-50 days) was connected to additional production of SFRs and an increase in ESRI (intensity of the ESR radical signal). The next local temperature maximum (at ~ 65 days) was also accompanied by a decrease in SFR concentration. Temperature stabilization in the mature compost (70-90 days) paralleled stabilization of the SFR concentration at a higher level (fig. 2).

These phenomena contrast those found with isolated humic substances: in the case of isolated fulvic and humic acids, an increase in temperature resulted in an increase in SFR concentration (Senesi, 1992). In our system the production of SFR was connected with the intensity of the composting processes (a humification process).

The ESRI was significantly correlated (r = 0.73) with CEC (fig. 3). This last parameter was correlated with composting time (fig. 4). Free radicals may therefore be an important index in evaluating compost maturity. A final estimation of this parameter requires further investigations, to confirm this suggestion.

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Table 1:	Values of investigated parameters at different stages of maturity of
compost	from municipal wastes.

	Composting time (days)								
Parameters	1	14	28	38	52	64	78	90	
C <sub>t</sub> (% of d.m.)	22.11	21.69	18.78	17.97	17.46	16.81	16.34	15.60	
N <sub>t</sub> (% of d.m.)	0.85	0.86	0.87	0.88	0.93	1.02	1.04	1.23	
C <sub>t</sub> /N <sub>t</sub>	28.6	25.1	21.6	20.5	18.6	16.4	15.7	12.7	
CHA (% of d.m.)	3.4	3.9	5.5	5.9	5.7	5.5	5.1	6.2	
HR1 (CHA/CFA)	0.58	0.69	0.84	0.82	0.70	0.82	0.69	0.89	
CEC (dmol x kg <sup>-1</sup> )	51.4	52.7	52.2	57.0	58.5	58.8	76.1	82.1	
ESRI $(10^{16} \text{ spins x g}^{-1})$	19.2	16.3	14.1	18.4	16.2	13.2	20.2	23.5	

Table 2:Correlation matrix

Parameter	days	Ct	Nt	$C_t/N_t$	CEC	CHA	HR <sub>1</sub>
Ct	-0.9556 <sup>1</sup>	1.0000					
Nt	0.9029 <sup>1</sup>	-0.7822 <sup>1</sup>	1.0000				
C/N <sub>t</sub>	-0.9860 <sup>1</sup>	0.9761 <sup>1</sup>	-0.8647 <sup>1</sup>	1.0000			
CEC	0.8916 <sup>1</sup>	-0.7644 <sup>1</sup>	0.92611	-0.8263 <sup>1</sup>	1.0000		
CHA	0.7473 <sup>1</sup>	-0.8847 <sup>1</sup>	0.5620	-0.83271	0.5036	1.000	
HR <sub>1</sub>	0.5562	-0.6593	0.5196	-0.6674	0.3640	0.8371 <sup>1</sup>	1.0000
ESRI	0.3829	-0.2386	0.5748	-0.2802	0.7295 <sup>1</sup>	0.0836	0.0090

1) Significant correlation coefficient at  $\alpha = 0.05$ ; n = 8.



Figure 1. ESR spectrum of a compost sample after 90 days of maturation. R-semiquinone free radical signal. Based on the R signal intensity, the ESRI parameter was calculated.



Figure 2. Temperature evolution (dashed line) and ESRI (solid line) during composting of the municipal wastes



Figure 3. Regression between CEC and ESRI



Figure 4. Regression between CEC and composting time

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## THE INFLUENCE OF DIFFERENT MATURITY OF COMPOSTS FROM MUNICIPAL AND AGRICULTURAL WASTES UPON THE GERMINATION AND GROWTH OF *LEPIDIUM SATIVUM*

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#### Keywords: biological tests, composts, maturity of composts, utilization of wastes

Abstract: The aim of this work was to determine the influence of water extracts (1:10) of composted municipal wastes (MSW) and of poultry farm wastes (PSM) upon the germination and growth of Lepidium sativum. Extracts from less mature composts inhibited germination of seeds and growth of Lepidium s. Stronger inhibiting influence occurred in the case of PSM extracts, but after diluting them 5x and 10x the adverse effect vanished.

#### Introduction

The maturity of composts is an essential criterion in their agricultural application (Wong 1985, Wong and Chu 1985). It is especially important, when they are applied directly to soil before the cultivation takes place (Kropisz et al. 1978, Nogales et al. 1984), or used as media in pots (Chanyasak et al. 1983a and b).

Immature composts cause higher biological activity in the soil (Mandelbaum et al. 1988), and at the same time they potentially block the available nitrogen (Chanyasak et al. 1983, Inbar et al. 1990). The immature compost introduces phytotoxic elements to soil (Inbar et al. 1990, Purves et al. 1974, Wong 1985, Zucconi et al. 1984), such as low-molecular carboxyl acids, NH<sub>3</sub> etc. It also brings about the decrease of  $O_2$  content in soil, which facilitates reduction processes. Consequently, it may lead to an increase of solubility of e.g. heavy metals, excessive concentration of which inhibits seed germination and plant growth (Giordano et al. 1975, Lutz 1981).

Especially important role is played by compounds soluble in water, which are characterized by the highest biological activity (Chanyasak and Kubota 1981, Hunt et al. 1973, Inbar et al. 1990). Testing their influence upon the initial stages of germination and plant growth may be an introductory evaluation of compost maturity, and determination of their applicability for fertilizer purposes (Hadar et al. 1985).

The aim of the research was to determine the influence of water extracts from composts produced of municipal wastes (MSW) and poultry farm wastes (PSM) at different degree of maturity, upon the germination and growth of *Lepidium s*.

#### Objects and research methods

The samples of municipal wastes composts (MSW) were taken from the fresh material after 24 hours of processing in the biostabilizer chamber according to Dano technology

(dispertion, mixing and the initial thermophilic process) and from composts after 7, 14, 30, 90 and 180 days of composting, being at different degrees of maturity.

The research included also composted wastes from a poultry farm (PSM). The samples were taken from fresh material and composts at different degrees of maturity after 7, 14, 30, 60 and 90 days of the composting process, and from the commercial product. Because of the high moisture content in the poultry farmwastes, straw was added in quantities allowing keeping the moisture content level at approximately 50%. The composting process was carried out according to the Okada technology, in concrete ditches, in which the wastes were mechanically mixed. After 90 days CaCO<sub>3</sub>, brown coal and special sorbents were added, and the commercial product was prepared.

In the samples taken from composts the content basic fertilizer elements was determined (total forms: N, P, K, C and ash) and water extracts were made from them in 1:10 proportion (initial extract). In these extracts the macro- ( $C_w$ ,  $N_w$ , P, K) and microelements ( $C_u$ , Pb, Cr), the soluble forms of N-NH<sub>4</sub> and N-NO<sub>3</sub>, as well as electrical conductivity and pH were determined.

Lepidium s. seeds were used for biological tests, they were placed on Petri dishes with filter tissues, soaked with 7 ml of water extract from composts at different degree of maturity. As a control, some seeds of Lepidium sativum were placed on tissue soaked with sterile distilled water. The growth of plants on the compost extracts was expressed as percentage in comparison to the control.

#### **Research** results

The results show that composts produced from municipal (MSW) and agricultural wastes (PSM) at different degree of maturity have a varying chemical composition (tab.1). Composts of municipal wastes (MSW) are characterized by a lower content of N, P, and K and higher content of ash in comparison with composts produced from agricultural wastes. The more mature composts contain a lower amount of organic matter, and at the same time they contain more nitrogen. Especially worth mentioning is the difference in the number of soluble forms in MSW and PSM. Water extracts from the composted municipal wastes (tab.2) contain much lower amount of N-NO<sub>3</sub> and N-NH<sub>4</sub> and of other macroelements (tab. 2). In the composed agricultural wastes (PSM) occur large amounts of N-NH<sub>4</sub> (tab. 2), many times higher than in MSW composts, which can turn out to be a crucial factor inhibiting the germination of seeds (Inbar et al. 1990). As the composts ripe, the above form of nitrogen slowly vanishes, and at the same time the intensity of nitrification process increases. It led to the increase of the amount of nitrate forms of nitrogen. Occurrence of large amounts of soluble forms of nitrogen, especially of N-NH<sub>4</sub> in the compost produced of agricultural wastes PSM and their higher salt content may be the reasons that inhibit the germination and growth of Lepidium s., particularly in the first stages of its maturity (Inbar et al. 1990).

The different chemical composition of the tested composts and their water extracts was mirrored in the results of the biological tests. The water extracts of the initial extract from the composted municipal wastes (MSW) at different degree of maturity had initially (up to 36 hours) a inhibiting effect upon the germination and growth of *Lepidium s*. (Fig. 1a). In extracts produced of less mature composts (fresh material, after 7 and 14 days of composting), the inhibiting effect lasted for a longer period of time (42-56 hours). The plant growth inhibiting effect was clearly weaker as the composts grew riper. After 62 hours of water extracts from the MSW composts influence stabilized at the level of 110 - 130% in comparison to the control assumed as 100%. The extracts from composts produced of municipal wastes gave the plants the necessary elements, and after a longer period of time, their stimulating effect upon plant growth and development became visible (Fig. 1a).

Water extracts from composted poultry farm wastes (PSM) at different degree of maturity, had definitely more inhibiting influence upon the germination and growth of the test plant (Fig. 1b). Water extract of PSM after one day of composting had the most inhibiting effect on germination and growth. In the presence of that extract even after 80 and 86 days only single seeds germinated, and the plants growing out of them were strongly deformed. As the PSM compost grew riper, the plant growth factor increased. However, after 90 days of maturing, it reached after 80 - 86 hours only 50 - 60% of the control value, a large quantity of plants were deformed and started to wither (Fig. 1b). The reason for that could be the too intense saturation of elements in water extracts from these composts, which inhibited plant growth (Inbar et al. 1990).

Water extracts PSM solved 1:1, especially those from composts after 1, 14 and 30 days of maturing, had also inhibiting effect in the initial period of test plant growth (Fig. 2a). After 62 hours the adverse effect vanished and a stimulating effect was observed upon the test plant growth in comparison to the control. Dilution the initial extract of PSM in proportion 1:5 and 1:10 did not have so adverse effect upon the test plant. It was observed that after 42 hours the solution of 1:5 (Fig. 2b) and after 36 hours the solution of 1:10 (Fig. 2c) had a clearly positive effect upon initial plant growth in comparison with the control assumed at 100. The research carried out shows a great differentiation of the analyzed composts and demonstrates the need of controlling them before application for fertilizer purposes.

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#### Conclusions

On the basis of the research carried out the following conclusions can be drawn:

- 1. Composts produced from municipal wastes (MSW) and agricultural wastes (PSM) had different chemical composition and different influence upon the *Lepidium sativum* germination.
- 2. Water extracts from less mature composts from municipal wastes at the biginning inhibited and then stimulated the *Lepidium sativum* seeds germination.
- 3. Water extracts from composted agricultural wastes (PSM) at all degrees of maturity strongly inhibited the germination of *Lepidium sativum* seeds, and their stimulating effect appeared only after solving the extract in proportion of 1:5 and 1:10.

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The contents of ash and macroelements (in % of dry matter)

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		MSW compost									
Prope	rty	Composting time (days)									
-	1	7	14	30	90	180					
ash	54.3	55.6	56.2	62.6	64.7	71.9					
Ct	24.28	23.51	22.73	20.75	18.10	15.34					
Nt	0.85	0.88	0.90	1.09	1.13	1.30					
Р	0.21	0.20	0.23	0.28	0.23	0.28					
Κ	0.54	0.50	0.50	0.74	0.56	0.69					
C <sub>t</sub> /N <sub>t</sub>	28.6	26.7	25.2	25.2 19.0		11.8					
			PSM con	npost							
Prope	rty	Composting time (days)									
-	1	14 <sup>1)</sup>	30	60	90	CP <sup>2)</sup>					
ash	56.7	47.0	52.2	53.5	56.7	59.7					
Ct	20.06	24.51	22.97	22.75	19.64	23.46					
$N_t$	2.96	1.87	1.84	2.05	2.56	2.08					
Р	4.43	4.61	4.72	4.64	4.83	4.62					
Κ	4.16	3.98	4.11	3.79	4.42	3.97					
$C_t/N_t$	3.8	13.1	12.5	11.1	7.7	13.3					
1)	after addition of s	straw;									
<sup>2</sup> )	commercial prod	uct after add	ition of CaCC	) <sub>3</sub> , sorbents a	nd brown co	al					

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The contents of macro- and microelements dissolved in water extract (1:10)

			r i r			
Property		(	Composting	g time (day	s)	
	1	7	14	30	90	180
$C_{\rm w}$ (mg 100 g <sup>-1</sup> d.m.)	1413	831	. 859	281	248	131
N <sub>w</sub> (mg 100 g <sup>-1</sup> d.m.)	143	123	199	90	80	76
N-NO <sub>3</sub> (mg 100 g <sup>1</sup> d.m.)	8.7	8.5	1.3	7.3	9.3	41.5
N-NH₄ (mg 100 g <sup>-1</sup> d.m.)	26.8	13.2	91.6	36.2	26.7	3.6
P (mg 100 g <sup>-1</sup> d.m.)	8.8	4.7	4.0	2.6	2.4	0.9
K (mg 100 g <sup>-1</sup> d.m.)	342	326	384	509	441	406
C <sub>w</sub> /N <sub>w</sub>	9.9	6.7	4.3	3.1	3.1	1.7
Cu (mg 100 kg <sup>-1</sup> d.m.)	1.4	1.3	1.6	2.8	4.8	1.4
Pb (mg 100 kg <sup>-1</sup> d.m.)	10.7	6.3	9.2	10.0	9.0	4.8
Cr (mg 100 kg <sup>-1</sup> d.m.)	9.0	7.0	3.2	3.3	2.4	2.4
EC (m S.cm <sup>-1</sup> , 25 °C)	4.4	4.3	3.1	2.5	2.5	2.9
pH	7.0	7.1	7.4	7.9	7.8	7.8

MSW compost

## PSM compost

Property		(	Composting	g time (day	s)	
·	1	14 <sup>1)</sup>	30	60	90	CP <sup>2)</sup>
$C_{w}$ (mg 100 g <sup>-1</sup> d.m.)	774	706	874	874	561	108
N <sub>w</sub> (mg 100 g <sup>-1</sup> d.m.)	1531	935	853	803	553	384
N-NO <sub>3</sub> (mg 100 g <sup>-1</sup> d.m.)	5.1	1.6	1.1	1.2	1.2	21.1
N-NH₄ (mg 100 g <sup>-1</sup> d.m.)	850	233	122	127	55	100
P (mg 100 g <sup>-1</sup> d.m.)	157	292	252	224	178	478
K (mg 100 g <sup>-1</sup> d.m.)	2934	2884	3643	3334	3612	3221
C <sub>w</sub> /N <sub>w</sub>	0.5	0.75	1.0	1.0	1.0	0.3
Cu (mg 100 kg <sup>-1</sup> d.m.)	8.5	10.0	18.3	21.9	16.9	10.2
Pb (mg 100 kg <sup>-1</sup> d.m.)	6.9	4.7	3.6	3.2	3.9	2.3
Cr (mg 100 kg <sup>-1</sup> d.m.)	4.8	4.5	4.1	3.5	3.1	2.4
EC (m S.cm <sup>-1</sup> , 25 °C)	5.2	5.1	6.2	6.5	7.0	6.2
pH	8.4	8.5	8.2	8.1	9.0	8.2

<sup>1), 2)</sup> see table 1

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Eafter 36 hours Bafter 42 hours Dafter 56 hours Dafter 62 hours Bafter 80 hours Clafter 86 hours



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## Pot experiment

1. Germination and emergence test

Fresh MSW compost slightly delayed germination and emergence of lettuce (Tab. 1). After seven days from sowing the number of raised seedlings in media with 100 T and 400 T x ha<sup>-1</sup> of MSW compost was lower than number of plants cultivated in peat or pure loamy soil. One, three and nine months old MSW compost used in the rate of 100 T had no negative effect on seedling emergence.

The higher quantity of MSW compost in media (400 T x ha<sup>-1</sup>) caused some prolongation of lettuce raising. Estimation of seedling emergence done 21 days after seed sowing in every cycle of test showed that the number of raised seedlings in four investigated media was similar. MSW compost independently from the maturity stage and its dose had no disadvantageous effect on the final emergence of lettuce seedlings.

Type of the medium significantly affected the growth rate of lettuce seedlings (Tab. 2). The highest fresh weight and shoot height of seedlings were obtained in treatment with peat substrate whilst plants grown in a pure loamy soil reached about 80-60.1% lower fresh weight of 100 seedlings. The addition of fresh MSW compost resulted in a serious growth retardation of lettuce plants. The seedlings grown in media with fresh MSW compost added in dose 100 T and 400 T x ha<sup>-1</sup> were shorter and developed lower number of leaves. The color of their leaves was very plain.

Increasing stage of maturity of compost improved the quality of seedlings The difference in total fresh weight of seedlings grown in pure loamy soil and in soil with addition of the 3-month old MSW compost in the amount of 100 T and 400 T x ha<sup>-1</sup> was not significant.

2. Effect of maturity stage and rate of MSW compost on yielding of crisplettuce

The high ratio of MSW compost in growing media (400 T x ha<sup>-1</sup>) had the determining effect on the plant growth and health. Regardless on the maturity stage of compost, in treatment supplied with 400 T x ha<sup>-1</sup> of this material there was observed a reduction of plant population on plots. Also yellowing and tipburn of leaves appeared only in this treatment.

Fresh MSW compost negatively affected the plant growth and greatly reduced the weight of lettuce head as well as final yield (Tab. 3). In the treatment supplied with 400 T x ha<sup>-1</sup> of fresh MSW material the growth of the lettuce was suppressed by 98.8% in comparison to peat substrate. The composting process improved the quality of compost and decreased its adverse effect on growth of plants. In a treatment with lower amount of three months old MSW compost and in control with pure loarny soil medium, lettuce produced almost equal yields. The higher dosage of the MSW compost (400 T x ha<sup>-1</sup>) at the same stage of maturity slightly decreased the yielding but this effect was also not significant.

3. Effect of maturity stage and rate of MSW compost on the content of macro- and microelements in crisp lettuce

Comparison of chemical composition of lettuce produced on various media (peat, loamy soil, loamy soil  $\div$  100 T MSWc x ha<sup>-1</sup> and loamy soil  $\pm$  400 T MSWc x ha<sup>-1</sup>) shows an important influence of those media on the content of macro- and microcomponents in the test plant (Tab. 4.1-4). The influence of the MSW compost on the macro- and microcomponent contents depends on the stage of its maturity and on its dosage.

- macroelements

A loamy soil medium with an addition of fresh material of 100 T x ha<sup>-1</sup> MSW compost caused a significantly increase of values of K contents in lettuce (Tab. 4.1). Contents of N and Mg in the test plant on the loamy soil + 100 T x ha<sup>-1</sup> of MSW compost was lower in comparison with the pure loamy soil medium (Fig. 1).

Addition to the loamy soil the MSW compost after 1 and 3 months of maturation had an significantly influence on the content of K at the rates of 100 and 400 T x ha<sup>-1</sup> and N at its higher dose (Tab. 4.2- 4.3). Application of the compost after 9 months of maturation in the media did not influenced significantly on the higher contents of N, P, K, and Mg in investigated test plant (Fig. **1**).

#### - microelements

Addition of fresh MSW before composting to the medium (Tab. 4.1) caused a significant increase of Zn content in lettuce at the rate of 100 T x ha<sup>-1</sup> as well as Cd, Ni, Pb, Cr, and Zn at the dose of 400 T x ha<sup>-1</sup> (Fig 1 and 3). When MSW compost after 1 month of maturation was applied in the medium, a significant increase of Zn in lettuce was found at both compost rates as well as Cr at the dose of 400 T x ha<sup>-1</sup> (Tab. 4.2). The MSW compost after 3 months of maturation added to the media caused only an increase of Zn in lettuce at the rate of 400 T x ha<sup>-1</sup>.

The doses of 100 and 400 T x ha<sup>-1</sup> of MSW compost after 9 months of maturation introduced to the media did not affect significantly on the changes of microelements under study in lettuce.

The above results show that application of mature composts in horticultural media does not affect increasingly the microelements gaining, including heavy metals by plants.

Simultaneously, the study shows that the very popular media, commonly used in a horticultural production, e.g. that containing peat, with addition of macro- and microelements in form of mineral fertilizers can arrange conditions that favour uptaking of some heavy metals by plants.

Field experiment

1. Effect of different doses of MSW compost on yielding of plants

#### - Lettuce

The field experiment results showed an effect of the applied doses of MSW compost on a yielding of lettuce (tab. 5). The crops of this plant from plots fertilized with 30, 60, and 120 T x ha<sup>-1</sup> of MSW compost were significantly higher in comparison with control objects. The highest total yield (3.03 kg/m<sup>2</sup>) has been obtained on the object where 30 T x ha<sup>-1</sup> of MSW compost + 70 kg/ha of mineral nitrogen were applied. A comparably high crop (2.96 kg/m<sup>2</sup>) was obtained on an object fertilized only with mineral nitrogen at the rate of 70 kg N/ha.

The most heavy heads of lettuce with weight over 200g were produced on plots fertilized with MSW compost at the rate of 120 T/ha and 30 T/ha in treatment amended with compost at the rate 30 T/ha + 70 kg N/ha and supplementary fertilized with 70 kg N/ha.

#### - Cabbage

Different methods of nutrition had a significant effect on yielding of white head cabbage (Tab. 6). The highest total and marketable yields were found in treatment supplied with 30 T/ha MSW compost and supplemental nitrogen fertilization of the rate of 180 kg N/ha.

The high rate of MSW compost (120 T/ha) was sufficient source of nitrogen for growth and development of white head cabbage and gave the yield as high as in the treatment fertilized with ammonium nitrate at rate of 180 kg N/ha. The yields from plots supplied with compost at the rates 30 and 60 T/ha were similar to those obtained in non-fertilized control while significantly lower when compared to mineral fertilize use only. That means that at such rates it was not the sufficient source of nitrogen for cabbage.

The results of experiments showed that mineral fertilization with ammonium nitrate applied in one preplant dosage of 180 kg N/ha or with MSW compost in the amount of 30 T/ha produced the heads with the highest tendency for cracking. The yields of cracked heads from plots fertilized with MSW compost alone in doses of 30-120 T/ha were considerably lower and amounted within 5.5-6.2% of the total yield.

2. Effect of different doses of MSW compost on content of macroelements and microelements in plants

#### - lettuce

Results of the study show that lettuce cultivated on the plots with various doses of compost contained different contents of some macro- and microelements (Tab. 7). The significant effect of organic fertilization by MSW compost and ammonium nitrate on the content of N, K, Mg, and Zn have been found for lettuce.

The content of nitrogen in lettuce was significantly higher on the plots fertilized with  $NH_4NO_3$ , 30 T x ha<sup>-1</sup> of MSW compost +  $NH_4NO_3$  and 120 T MSW compost in comparison to non-fertilized control. Plants harvested from plots fertilized with 30 T of MSW compost contained significantly lower amount of nitrogen, whilst at 60 T dose of MSW compost they did not differ in nitrogen content with those from the control plots.

Significant increase of potassium content in lettuce was found only on the plots fertilized with 30 T/ha of MSW compost + 70 kg/ha  $NH_4NO_3$ . The magnesium and zinc contents in lettuce on every plot fertilized with MSW compost and mineral nitrogen was significantly higher in comparison with the control object.

#### - cabbage

Fertilization with MSW compost and mineral nitrogen had no significant effect on the content of macro- and microelements in cabbage. In all plots fertilized with MSW compost and  $NH_4NO_3$  the content of components under study, i.e. N, P, K, Mg,

Zn, Mn, Fe, Cu, Cd, Ni, Pb, and Cr did not differ significantly from their amount in cabbage from the control plots (Tab. 8).

#### - root celery

Analysis of celery roots indicates that the applied variants of fertilization had an effect on the content of some determined mineral components (Tab. 9). Celery derived from plots fertilized with various doses of MSW compost did not differ in nitrogen content from control. Significant increase of nitrogen was found only in celery roots derived from plots fertilized with mineral nitrogen in a form of nitrate (200 kg N x ha<sup>-1</sup>) and 30 T/ha of compost with an addition of 200 kg/ha of nitrogen in a form of ammonium nitrate.

No significant effect of MSW compost dosage has been found on the phosphorus and copper content in celery roots, whilst there was a marked influence of mineral fertilization as well as that of 30 T of MSW compost + mineral N fertilization, on the decrease of contents of these components.

In celery roots from objects fertilized with MSW compost a considerable decline of manganese content was found. The contents of remaining components: K, Mg, Zn, Fe, Cd, Ni, and Cr in celery roots did not significantly differ from those in the control.

The study shows that the most pronounced effect of the MSW compost fertilization was observed for the first plant, i.e. lettuce. As a result of the increasing dose of MSW compost the Mg content increase, and among heavy metals, that of Zn. There was no significant increase of heavy metals in plants cultivated after lettuce harvesting on the plots fertilized with various rate of MSW compost (cabbage, celery). The detailed analysis of these results leads to conclusion that for second and third plant cultivated on the plots fertilized with MSW compost there is a considerable decrease of many macrocomponents and heavy metals.

#### 3. Effect of various MSW compost dosage on some properties of soil

## - contents of microelements

In Tables 10, 11, and 12 there are presented contents of total form of microcomponents: Cd, Cu, Cr, Fe, Mn, Ni, Pb, Zn, and  $pH_{KCl}$  in soil layers of 0-20 and 20-40 cm for which the field experiment was carried out. The data shown there allow for conclusion that application of various rates of MSW compost had a significant effect on the content increase of some microcomponents in the soil. After lettuce harvesting in both soil layers: 0-20 and 20-40 cm there was a significant increase of Cu, Fe, Mn, Ni, Pb, and Zn contents. On the all objects fertilized with MSW compost there was an considerable increase of Cu, Fe, Pb, and Zn contents in the 0-20 cm layer, whilst amount of Mn increased significantly only on the object fertilized with a dose of 120 T x ha<sup>-1</sup> of MSW compost. It should be noted that significant increase of Cu, Pb, and Zn in relation to the control was observed also on the objects fertilized only with mineral nitrogen (70 kg N/ha).

In the layer of 20-40 cm a significant increase of Cu was found in the object fertilized with 30, 60, ad 120 T of MSW compost and 70 kg of mineral nitrogen. A significant increase of Fe and Mn in this depth was observed at higher rates of MSW composts: 60 and 120 T, whilst Ni and Pb at the rate of 120 T. There was no considerable increase of zinc in comparison with the control object in the depth of 20-40 cm.

Contents of Cd and Cr were not affected significantly on the objects fertilized with MSW compost, with respect to the control.

After cabbage harvesting in both soil horizons there were also determined signi ficant changes in the contents of some microelements depending on MSW compost fertilization. In the layer of 0-20 cm a significant increase of Cu, Mn, Pb, and Zn was found on the objects fertilized with 30, 60, and 120 T of MSW compost. There was also found a considerable increase of Ni on the objects fertilized with 60 and 120 T of MSW compost as well as Zn, also on the objects fertilized with 180 kg N and 30 T of

MSW compost + 180 kg N/ha. In the layer of 20-40 cm only significant increase of Pb on all objects was found in relation to the control, whilst Zn content increased on the objects with 60 and 120 T doses and Cu and Ni - at the highest rates - 120 T of MSW compost. The Fe and Mn contents on this depth even decreased in comparison to the control objects.

After celery harvesting, the soils fertilized with MSW compost indicated also significant differentiation in contents of some microelements, but only in the 0-20 cm layer. It concerns particularly Pb content for which a significant increase was observed on all objects fertilized with MSW compost and mineral nitrogen. All applied rates of MSW compost had an significant effect on Mn increase, whilst in the object with the highest compost rate only significant increase of Zn was found.

- physical properties of soil

In table 13 and in fig. 4-6 results of bulk density, total porosity, field water capacity at pF 2.54 and water retention in range of pF 1,0 - 2.9 were presented.

Statistical analysis of these results (tab. 13) shows that only at the MSW compost rate of 120 T x ha<sup>-1</sup> there was significant decreasing effect on the bulk density. Lower MSWc rates (30 and 60 T/ha) as well as fertilization with N did not influence on changes of this property.

Applaying of MSW compost in rate 120 T/ha influence on increase of water retentionability in field of pF 1,0 - 2.9 (fig.4-6). This positive effect was the most marked after harvesting of lettuce (fig.4) and weaker after harvesting of cabbage (fig.5) and celery (fig.6).

The remaining physical properties such as total porosity and water retention at pF 2.54 were not significantly changed under influence of the applied doses of MSW compost and mineral N.

Table 1

The effect of maturity stage and rate of MSW compost on the emergence of lettuce seedlings after seven and twenty one days from sowing (%)

	Fresh 1	MSWC	1month c	Id MSWC	3 month o	old MSWC	9 month old MSWC		
Treatments		<b>-</b>		<u>Es</u> t	<u>imation of</u>	seed emerger	ice after		
	7 days	21 days	7 days	21 days	7 days	21 days	7 days	21 days	
Sphagnum peat substrate	93.2	100.0	94.6	100.0	97.2	98.0	92.0	96.7	
Loamy soil	90.06	98.0	92.6	100.0	97.2	96.0	94.0	96.5	
Loamy soil + MSWC 100 t/ha	80.0	96.0	95.2	100.0	86.0	95.2	86.6	92.0	
Loamy soil + MSWC 400 t/ha	80.0	98.0	81.2	100.0	77.2	93.4	95.2	97.5	

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Quality of lettuce seedlings as affected by the type of media

Treatments	Number of developed leaves	Height of plant	Total fresh weight of 100 seedlings (g)	Relative weight of seedlings (%)*
Sphagnum peat substrate	3.0	11.8	60.5	100
Loamy soil	2.0	5.6	12.8	21.3
Loamy soil + 100 t/ha MSWC <sub>n</sub>	1.5	3.1	4.4	7.0
Loamy soil + 400 t/ha MSWC <sub>0</sub>	1.5	2.8	2.6	4.3
LSDa = 0.05			7.43	
MSWC <sub>0</sub> = fresh mur	nicipal solid waste cor	npost		
Sphagnum peat substrate	3.0	13.7	102.0	100.0
Loamy soil	2.0	6.9	16.8	16.4
Loamy soil + 100 t/ha MSWC <sub>1</sub>	1.5	3.9	11.2	11.0
Loamy soil + 400 t/ha MSWC <sub>t</sub>	1.5	4.0	9.0	8.8
LSDa = 0.05			15.66	
$MSWC_1 = 1$ month of	old MSW compost			
Sphagnum peat substrate	4.0	13.7	102.0	100.0
Loamy soil	3.0	11.5	40.6	39.8
Loamy soil + 100 t/ha MSWC3	- 30	9.3	31.4	30.7
Loamy soil + 400 t/ha MSWC3	3.0	8.9	27.2	26.6
LSDa = 0.05			22.9	
$MSWC_3 = 3$ months	old MSW compost			
Sphagnum peat substrate	4.0	4.3	44.6	100.0
Loamy soil	2.0	5.0	7.4	16.6
Loamy soil + 100 t/ha MSWC <sub>2</sub>	3.0	5.4	8.4	18.8
Loamy soil + 400 t/ha MSWC <sub>2</sub>	3 0	6.6	10.2	22.9
LSDa = 0.05			2.76	
$MSWC_9 = 9 months c$	old MSW compost			

\*- Relative weight of seedlings was counted in relation to sphagnum peat substrate

Effect of maturity stage and rate of MSW compost on yielding of crisp lettuce in pot experiment

	Treatments	Yield kg/m²	Weight of plant (g)	Relative yield (%)
	Sphagnum peat substrate	5 82	165.3	100.0
	Loamy soil	2.29	64.9	39.3
I	Loamy soil + 100 t/ha MSWC <sub>0</sub>	1.45	41.3	24.9
I	.oamy soil + 400 t/ha MSWC <sub>0</sub>	0.07	2.2	1.2
	LSDa = 0.05	0.53	15.12	
М	SWC <sub>0</sub> = fresh mur	nicipal solid waste co	mpost	
	Sphagnum peat substrate	8.49	240.8	100.0
	Loamy soil	4.20	119.2	49.5
L	oamy soil + 100 t/ha MSWC <sub>1</sub>	3.36	101.2	39.6
Ĺ	oamy soil + 400 t/ha_MSWC1	2.43	73.0	28.6
	LSDa = 0.05	0.57	16.28	
MS	$SWC_1 = 1 month c$	old MSW compost		
	Sphagnum peat substrate	8.06	228.7	100.0
	Loamy soil	4.17	118.5	51.7
L	oamy soil + 100 t/ha MSWC3	3.92	113.0	48.6
Lo	oamy soil + 400 t/ha MSWC3	2.82	79.9	35.0
	LSDa = 0.05	1.56	44.57	
MS	$SWC_3 = 3$ months	old MSW compost		
S	phagnum peat substrate	3.38	96.0	100.0
	Loamy soil	1.67	47.5	49.5
Lo	oamy soil + 100 t∕ha MSWC₀	1.41	50.2	41.9
Lo	amy soil + 400 t/ha MSWC <sub>2</sub>	1.61	45 8	47.7
	LSDa = 0.05 0	.25	7.05	
MS	$WC_9 = 9 \text{ months c}$	old MSW compost		

## Table 4.1

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Influence of different doses of various maturity composts on contents of macro- and microelements in lettuce Pot experiments - Fresh material

Medium	Macro	pelements	g x kg <sup>-1</sup>			Microelements mg x kg <sup>-1</sup>						
	N	Р	K	Mg	Cu	Zn	Mn	Cd	Ni	Pb	Fe	Cr
Peat	17.9	2.6	19.6	2.9	5.6	61,2	126,0	0.2	0.8	2.3	89.8	0.4
Loamy soil	24.1	1.9	41.6	5.3	5.6	39.9	52.2	0.7	2.0	3.2	200.0	0.6
Loamy soil +	21.9	2.0	51.9	3.6	6.1	73.2	40.0	0.4	1.9	3.3	171.1	0.6
of compost												
Loamy soil +	n.đ	n.d	n.d	n.d	5.3	143.7	32.6	1.1	3.3	7.4	211.1	1.5
400 t x ha <sup>-1</sup>												
of compost												
$I.SD \alpha = 0.05$	8.32	0.78	5.77	0.61		4.72		0.16	1.3	2.61		1.17
T	้ถ	bl	le	- 4	.2							
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Influence of different doses of various maturity composts on contents of macro- and microelements in lettuce Pot experiments - 1 month old compost MSW

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Medium	Macro	oelements	g x kg <sup>-1</sup>				Mic	roelemen	ts mg_x kį	y-1		
	N	Р	K	Mg	Cu	Zn	Mn	Cd	Ni	Pb	Fe	Cr
Peat	14.2	3.0	14.3	2.8	5.0	60.1	155.0	0.3	2.3	2.8	168.0	0.7
Loamy soil	20.9	2.6	29.0	4.7	6.9	45.9	67.5	0.6	5.0	3.9	364.8	0.9
Loamy soil + of compost	19,6	2.1	45.0	3.5	8.8	83.0	65.6	0.5	5.9	4.5	452.4	1.1
Loamy soil + 400 t x ha <sup>-1</sup> of compost	23.7	1.97	52.92	3.53	7.3	135.1	64.1	0.6	5.7	6.1	517.7	1.2
$LSD \alpha = 0.05$	9.7	0.9	14.4	0,44		10.8				4.3	188.4	0.22

#### Table 4.3

Influence of different doses of various maturity composts on contents of macro- and microelements in lettuce Pot experiments - 3 months old compost MSW

Medium	Macro	pelements	g x kg <sup>-1</sup>				Mi	croelemen	ts mg x kį	,-) ,-)		
	N	Р	K	Mg	Cu	Zn	Mn	Cd	Ni	Pb	Fe	Cr
Peat	12.8	3.1	17.4	5.2	9.2	200.9	478.1	1.6	1.5	4.4	159.4	0.7
Loamy soil	20.8	2.4	32:4	4.7	8.9	55.9	63.8	0.6	6.8	<u>3,</u> 3	268.8	1.0
Loamy soil +	20,7	2,3	42.1	4.4	97	93.2	57.5	0.5	6,1	5.2	292.2	1.0
of compost												
Loamy soil +	26,95	2.6	56.14	3.53	4.4	115,3	28.5	0.4	1.2	4.1	118.8	0.7
400 t x ha <sup>-1</sup>										1		
of compost			_									
$LSD \alpha = 0.05$	3.33	1.2	10.1	0.44		55.7		0.19	0.76		35.3	
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Table 4.4

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Influence of different doses of various maturity composts on contents of macro- and microelements in lettuce Pot experiments - 9 months old compost MSW

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Medium	Macro	elements	g x kg <sup>-1</sup>		Microelements mg x kg <sup>-1</sup>								
	N	Р	К	Mg	Ĉu	Zn	Mn	Cd	Ni	Pb	Fe	Cr	
Peat	31.3	2.1	47.5	3.7	17.7	351.0	495.3	0.9	1.7	5.5	135.2	0.7	
Loamy soil	26.0	1.3	43.7	4.1	10.2	248.4	53.8	0.3	4.2	5.2	342.2	0.8	
Loamy soil +	24.2	1.2	41.9	4.4	9.7	176.7	54.7	0.4	2.9	4.6	239.9	0.8	
of compost													
Loamy soil +	25	1.19	47.35	4.16	8.4	265.5	\$6.6	0.4	4.4	5,9	318.8	0.9	
400 t x ha <sup>-1</sup>											•		
of compost													
$I.SD \alpha = 0.05$	5.16	0.78		0.48		<b> </b>	166.6	0.31	0.76		122.35	0.12	

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Effect of different compost (MSW) doses on yield of lettuce

<u>_</u>	Total yield	Yield o	f heads with	n weight	Average weight of
Object	T x ha <sup>-1</sup>	>200 g	100-200 g	< 199 g	lettuce head (g)
Control	1.52	0.32	0.86	0.34	158
Nmin.	2.96	2.25	0.63	0.08	246
$70 \text{ kg x ha}^{-1}$					
MSWC	1.95	0.85	0.85	0.25	162
30 T x ha-1					
MSWC	2.18	1.06	0.90	0.22	181
60 T x ha <sup>-1</sup>					
MSWC	2.65	2.00	0.50	0.15	220
120 T x ha <sup>-1</sup>					
MSWC	3.03	2.30	0.76	n.d.	252
30 T x ha <sup>-1</sup> + N min					
LSD $\alpha = 0.05$	0.10	0.12	· ·		7.5

#### field experiment

Table	6											
Effect	of	diff	eren	t	compost	(MSV	/) doses	on	yield	of	cabbag	e
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	Total yield	Marketable	Small	Cracked	Heads with	% of marketable yield	% of cracked heads
Object	T x ha <sup>-1</sup>	yield	heads	heads	symptoms of	in total yield	in total yield
					diseases		
Control	31.10	30.40	0.00	0.00	0.70	97.7	0
Nmin.	49.79	42.20	0.00	5.34	2.25	84.7	10.7
70 kg x ha <sup>-1</sup>							
MSWC	35.54	32.90	0.43	2.21	0.00	92.6	6.2
<u> </u>							
MSWC	36.51	34.00	0.59	1.92	0.00	93.1	5.3
60 T x ha <sup>-1</sup>							
MSWC	45.24	41.10	0.25	2.50	1.39	90.6	5.5
120 T x ha <sup>-1</sup>							
MSWC	54.63	45.40	0.00	6.36	2.87	83.1	11.6
$30 \text{ T x ha}^{-1} + \text{N min}$							
LSD $\alpha = 0.05$	8.27	7.67			0.34		

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	N	P	K	Mg	Zn	Mn	Fe	Cu	Cd	Ni	Pb	Cr
Object		g_x	kg <sup>-1</sup>					mg x	kg <sup>-1</sup>			
Control	22.1	5.05	55.49	2.15	33.7	36.3	352.3	5.6	0.4	1.1	4	1.5
Nmin.										_		
70 kg x ha <sup>-1</sup>	29.03	5.31	56.55	2.55	40.9	38.7	385.3	5.5	0.47	1.5	4.2	1.7
MSWC												
30 T x ha-1	20.87	4.81	55.06	2.27	41.2	36.8	356	5.4	0.43	1.4	4.3	1.7
MSWC												
60 T x ha <sup>-1</sup>	21.37	4.89	54.32	2.41	43.1	34	308.3	5.5	0.4	1.2	3.9	1.6
MSWC												
120 T x ha <sup>-1</sup>	24.63	4.82	56.56	2.53	54.3	36.7	354	6.4	0.47	1.4	5.7	1.57
MSWC												
$30 \text{ T} \text{ x ha}^{-1} + \text{N} \text{ min}$	29.47	5.15	59.15	2.87	46.2	38.3	400	6.7	0.4	1.37	5.7	1.7
$LSD \alpha = 0.05$	0.87		1.34	0.03	3.58	1				0.19		

 Table 7

 Effect of different compost (MSW) doses upon content of macro- and microelements in lettuce - field experiment

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Table 8	1		
Effect of different compost (MSW) doses upon	n content of macro-	- and microelements in cabba	ge - field experiment

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	N	Р	К	Mg	Zn	Mn	Fe	Cu	Cd	Ni	Pb	Cr
Object		gx	kg <sup>-1</sup>					nıg x	kg <sup>-1</sup>			
Control	22.1	5.05	55.49	2.15	33.7	36.3	352.3	5,6	0.4	1.1	4	1.5
Nmin.												
70 kg x ha <sup>-1</sup>	29.03	5,31	56.55	2.55	40.9	38.7	385.3	5.5	0.47	1.5	4.2	1.7
MSWC												
30 T x ha-1	20.87	4.81	55.06	2.27	41.2	36.8	356	5.4	0.43	1.4	4.3	1.7
MSWC												
$60 \text{ T} \text{ x ha}^{-1}$	21.37	4.89	54.32	2.41	43.1	34	308.3	5.5	0.4	1.2	3.9	1.6
MSWC												
$120 \text{ T x ha}^{-1}$	24.63	4.82	56.56	2.53	54.3	36.7	354	6.4	0.47	1.4	5.7	1.57
MSWC												
$30 \text{ T x ha}^{-1} + \text{N min}$	29.47	5.15	59.15	2.87	46.2	38.3	400	6.7	0.4	1.37	5.7	1.7

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	N	Р	К	Mg	Zn	Mn	Fe	Cu	Cd	Ni	Pb	Čr
Object		g x	kg <sup>-1</sup>					mg x	kg <sup>-1</sup>			
Control	16.00	10.96	50.25	1.84	50.20	22.10	56.80	14.90	0.57	0.75	3.10	0.52
Nmin.												
70 kg x ha <sup>-1</sup>	19.70	9.33	51.13	1.64	52.90	21.50	63.10	12.00	0.62	0.75	3.00	1.85
MSWC												
30 T x ha-1	16.47	11.61	48.08	1.90	53.40	19.50	65.60	14.60	0.62	0.95	3.00	2.10
MSWC												
60 T x ha <sup>-1</sup>	16.50	11.05	47.26	1.77	54.30	20.00	52.80	13.70	0.57	0.72	2.90	0.47
MSWC												
120 T x ha <sup>-1</sup>	16.45	10.37	49.33	1.81	59.70	20.10	55.80	14.30	0.62	0.82	3.60	3.40
MSWC												1
$30 \text{ T x ha}^{-1} + \text{N min}$	20.70	8.46	52.27	1.61	49.30	20.50	58.40	10.30	0.60	0.72	3.20	1.37
LSD $\alpha = 0.05$	2.46	1.52				1.13		1.39	1			

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Effect of different compost (MSW) doses upon content of macro- and microelements in celery - field experiment

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Table 9

Table 10

Effect of different doses of compost MSW upon contents of microelements in soil from field experiment
after applying of composting material in growing of first testing plant - lettuce

	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn	рПксі
Object	mg x kg <sup>-1</sup> d.m.								
	layer 0-20 cm								
Control	0.983	33.125	15,350	12062.5	192,75	20.75	41.50	99.70	6,69
Nmin.									
70 kg x ha <sup>-1</sup>	0.917	36.125	15,983	12425	187.25	20.00	46.57	115.25	6.66
MSWC									
30 T x ha '	1.075	35,500	16,617	12975	187.35	20.87	53,45	118.40	6.74
MSWC									
60 T x ha <sup>-1</sup>	1.083	38.375	15.917	13425	194.12	20.00	57,12	150.40	6,75
MSWC									
120 T x ha <sup>-1</sup>	1.017	41.000	16.117	13825	210.37	20.75	59.66	182.10	6,79
MSWC									
$30 \text{ T x ha}^{-1} + \text{N min}$	0.950	34.665	15,883	12766.5	184,40	20.20'	43,40	118.85	6.7
LSD q= 0.05		2.23		760.8	3.3		3,86	7.22	
			<b></b>	lay	er 20-40 e	cm	L	L	L
Control	0.917	21.90	15.37	13487.5	130.75	18.5	33,15	73.9	<b>_</b> _
Nmin.								]	
70 kg x ha <sup>-1</sup>	0.900	22.90'	16.42	12425	109.65	20.2	33.60	80.9	
MSWC								1	
<u>30 T x ha-1</u>	0.733	24.40	15.77	10987.5	140.9	18.0	30.20	81.7	
MSWC								1	
60 T x ha <sup>-1</sup>	0.833	25.90	15.27	13883.3	154.75	21.2	37.10	88.6	
MSWC							1		
<u>120 T x ha<sup>-1</sup></u>	0.900	27.40	15.42	14581.2	165.5	23.0	51.10	97.9	
MSWC							<u> </u>	1	†
$30 \text{ T x ha}^{-1} + \text{N min}$	0.783	22.25	16.68	12600	136.65	19.0	37.00	67.1	
LSD <sub>14=0.05</sub>		1.39		384.89	17.08	4.5	17.95	24.1	

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والمستقلاف والمانية فالمتهم ومترا والمراجع والمنافع والأفار فالعارين ومعادرت والمتلافعة المارين ودورستم ومردس وسرور السرور والمستعار والم

Effect of different doses of compost MSW upon contents of microelements in soil from field experiment after applying of composting material in growing of second testing plant - cabbage

	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn	рН <sub>ксі</sub>
Object	$mg x kg^{-1} d.m.$								
	layer 0-20 cm								
Control	0.863	28.75	16.038	12379.15	191.2	17.35	39.95	98.1	6.66
Nmin.									
$-70 \text{ kg x ha}^{-1}$	0.950	32.60	16.738	12568.75	187.45	18.75	40.75	102.1	6.68
MSWC									
<u>30 T x ha<sup>-1</sup></u>	1.050	35.35	17.45	12518.75	210.15	19.10	54.05	118.9	6.68
MSWC									
<u>60 T x ha<sup>-1</sup></u>	1.125	35.60	16.638	12543.75	221.65	20.00	50,35	159.5	6.70
MSWC									
<u>120 T x ha<sup>-1</sup></u>	1.138	43.15	17.863	13987.5	221.85	21.10	77,10	216.65	6.70
MSWC									
$30 \text{ T x ha}^{-1} + \text{N min}$	0.933	32.40	17.163	12575	174.25	18.10	43.15	116.9	6.64
$LSD_{n=0.05}$		3.85			3.85	2.29	2.79	3.4	
				lay	er 20-40 c				L
Control	0.888	22.40	17.588	12837.5	190.9	19.40	29.25	75.65	
Nmin,									
70 kg x ha <sup>-1</sup>	0.850	24.85	16.475	12231.2	114.65	19.75	35.05	76.15	
MSWC									
30 T x ha <sup>-1</sup>	0.938	19.90	16.788	12768.7	107.15	20.50	40.35	82.25	
MSWC									
<u>60 T x ha<sup>-1</sup></u>	0.825	21.40	16.088	12018.7	95.15	19.00	41.45	84.65	
MSWC									†
120 T x ha <sup>-1</sup>	0.913	<b>30</b> .00	16.188	12729.1	171.75	20.60	44.95	95.65	
MSWC								1	1
$30 \text{ T x ha}^4 + \text{N min}$	0.825	22.40	17.025	12290	131.65	19.60	36.65	72.65	
LSD a= 0.05		8.5		340.1	19.15	1.1	5.8	6.6	

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Effect of different doses of compost MSW upon contents of microelements in soil from field experiment after applying of composting material in growing of third testing plant - celery

	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn	рН <sub>ксі</sub>
Object	mg x kg <sup>-1</sup>								
	layer 0-20 cm								
Control	0.938	29,45	16.49	15222.5	223.9	21.8	44.4	118.6	6.06
Nmin.									
70 kg x ha <sup>-1</sup>	0.888	27.10	16.15	16568.7	218.0	22.0	47.4	116.8	6.4
MSWC									
30 T x ha <sup>-1</sup>	1.025	31.35	16.36	15425	231.1	21.2	49.2	120.6	6.52
MSWC									
60 T x ha <sup>-1</sup>	1.125	31.35	16.81	15893.7	232.9	23.1	50.6	129.4	6.54
MSWC									
120 T x ha <sup>1</sup>	1.113	32.00	16.39	16581.2	237.1	21.9	59.5	154.5	6.55
MSWC							_		
<u>30 T x ha<sup>-1</sup> + N min</u>	1.013	27.75	15.92	16065	217.5	22.8	51.8	124.1_	6.58
LSD a= 0.05				940.2	3.67		1.22	18.94	
				lay	yer 20-40 a	em			
Control	0.975	20.10	16.54	14881.2	141,60	21.1	30.1	88.7	
Nmin.									
70 kg x ha <sup>-1</sup>	0.925	17.10	16.87	17345	121.20	22.1	46.9	86.6	
MSWC									
30 T x ha <sup>-1</sup>	0.938	19.00	15.92	14295	151.10	21.6	36.6	75.1	
MSWC									
<u>60 T x ha<sup>-1</sup></u>	1.083	19.80	16.96	15630	130.00	21.3	39.1	68.3	
MSWC									
$120 \text{ T x } \text{ha}^{-1}$	0.963	18.50	16.8	17185	123.90	23.0	43.2	72,6	
MSWC									
<u>30 T x ha<sup>-1</sup> + N min</u>	0.925	20.65	16.53	16230	148.20	21.4	37.3	59,7	
$LSD_{w=0.05}$									

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Influence of application of different doses of compost MSW upon some physical properties of soil - layer 0-20 cm

Object	Lettuce	Cabbage	Celery						
	Total porosity (in vol. %)								
Control	42.19	42.88	42.73						
Nmin	42.12	41.17	44.00						
30T MSWC	41.84	43.06	39.61						
60T MSWC	43.45	42.42	42.51						
120T MSWC	46.40	47.56	42.70						
30T MSWC + N	44.17	41.16	45.50						
Bulk density ( T x m <sup>-3</sup> )									
Control	1.55	1.39	1.56						
Nmin	1.535	1.39	1.47						
30 t MSWC	1.54	1.35	1.59						
60 T MSWC	1.47	1.33	1.62						
120 T MSWC	1.38	1.26	1.53						
30T MSWC + N	1.44	1.37	1.53						
$LSD \alpha = 0.05$		0.12							
	Retention at pF 2.54 c	of field water cape	ıcity (in vol. %)						
Control	25.07	23.23	26.39						
Nmin	24.97	22.01	25.98						
30T MSWC	26.15	23.51	26.69						
60T MSWC	26.18	23.5	27.02						
120T MSWC	27.42	25.3	26.46						
30T MSWC+N	26.965	23.82	25.93						





Fig. 1 Relative contents of N, P, K and Mg in lettuce growing on various mediums, expressed as the percentage of the content of the element in the lettuce growing on loamy soil (the content of N, P, K and Mg in test lettuce growing on loamy soil is 100)

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Fig. 2. Relative contents of Cu, Zn, Mn and Cd in lettuce growing on various mediums, expressed as the percentage of the content of 00, Zn, Mn and Cd in lettuce growing on loamy soil is 100)

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Fig. 3 Relative contents of Ni, Pb, Fe and Cr in lettuce growing on various mediums, expressed as the percentage of the content of the element in lettuce growing on loamy soil (the content of Ni, Pb, Fe and Cr in lettuce growing on loamy soil is 100)







# Figure 5 Changes of water retention at pF 1 - 2.9 after harvesting second testing plant- cabbage (field experiment)



# Figure & Changes of water retention at pF 1 - 2.9 after harvesting first testing plant - lettuce (field experiment)

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