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DYNAMICS OF ORGANIC C MINERALIZATION AND THE MOBILE FRACTION OF HEAVY METALS IN A CALCAREOUS SOIL INCUBATED WITH ORGANIC WASTES

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Abstract. Organic wastes such as sewage sludge and compost increase the input of carbon and nutrients to the soil. However, sewage sludge-applied heavy metals, and organic pollutants adversely affect soil biochemical properties. Therefore, an incubation experiment lasting 90 days was carried out to evaluate the effect of the addition of two sources of organic C: sewage sludge or composted turf and plant residues to a calcareous soil at three rates (15, 45, and 90 t of dry matter ha^{-1}) on pH, EC, dissolved organic C, humic substances C, organic matter mineralization, microbial biomass C, and metabolic quotient. The mobile fraction of heavy metals (Zn, Cd, Cu, Ni, and Pb) extracted by NH_4NO_3 was also investigated.

The addition of sewage sludge decreased soil pH and increased soil salinity to a greater extent than the addition of compost. Both sewage sludge and compost increased significantly the values of the cumulative C mineralized, dissolved organic C, humic and fulvic acid C, microbial biomass C, and metabolic quotient ($q CO_2$), especially with increasing application rate. Compared to compost, the addition of sewage sludge caused higher increases in the values of these parameters. The values of dissolved organic C, fulvic acid C, microbial biomass C, metabolic quotient, and C/N ratio tended to decrease with time. The soil treated with sewage sludge showed a significant increase in the mobile fractions of Zn, Cd, Cu, and Ni and a significant decrease in the mobile fraction of Pb compared to control. The high application rate of compost resulted in the lowest mobility of Cu, Ni, and Pb. The results suggest that biochemical properties of calcareous soil can be enhanced by both organic wastes. But, the high salinity and extractability of heavy metals, due to the addition of sewage sludge, may limit the application of sewage sludge.

Keywords: biochemical properties, calcareous soil, compost, heavy metals, humic substances C, sewage sludge

1. Introduction

The soils of arid and semiarid regions low in organic C content need organic amendments to improve their physicochemical and biological properties and thus their productivity and natural fertility (Pascual *et al.*, 1997). The most widely used organic amendments are sewage sludge and compost, which have high organic matter, N and P contents, making them suitable for agricultural purposes. However, the use of sewage sludge as agricultural fertilizer has raised numerous environmental and health issues because of the significant concentrations of toxic metals, organic compounds, and pathogens commonly found in these waste materials (McBride *et al*., 1997; Moreno *et al*., 1999; Berrow and Webber, 1972). Soil quality is a complex characteristic, and is determined by the physical, chemical, and biological components of the soil (Johansson *et al*., 1999). Changes in soil biochemical characteristics may be good indicators of soil quality, since they are more dynamic and often more sensitive than physical or chemical soil properties (Friedel *et al*., 2000). Such information is required to detect any possible toxicities resulting from the use of sewage sludge and as an indicator of soil rehabilitation. Pascual *et al*. (1997) demonstrated that the addition of urban organic wastes (municipal solid wastes, sewage sludge and compost) to the soil increases the values of biomass carbon, basal respiration, biomass C/total organic C ratio, and metabolic quotient (qCO_2), indicating the activation of soil microorganisms. It is evident, that heavy metals introduced with sewage sludge or compost cause accumulation of organic matter and decrease the turnover rate of organic matter, presumably because of inhibitory effects on the microbial biomass (Leita *et al*., 1995, 1999; Chander *et al*., 1995; Chander and Brookes, 1991). Moreno *et al*. (1999) found that the addition of cadmium-contaminated sewage sludge compost to the soil decreased microbial biomass C and stimulated the metabolic activity of the microbial biomass. The addition of sewage sludge to soils could affect the potential availability of heavy metals (Wang *et al*., 1997). Mineralization of sludge organic matter may release heavy metals into more soluble forms that may harm sensitive crops and microbes (McBride, 1995). The availability of heavy metals in the sewage sludge and soils treated with sewage sludge depends on many factors such as the properties and amount of heavy metal, the partitioning of heavy metals between solution and solid phase, and soil characteristics (Jin *et al*., 1996). It is widely known that the bioavailability of heavy metals in soil is strongly influenced by the amount and the quality of organic matter that can react with the heavy metals, forming complexes and chelates of varying stability (Leita *et al*., 1999). Soil organic matter is quite effective in retaining heavy metals. Heavy metal-organic associations can occur both in soil solution and at the solid surfaces of either native soil constituents or any added material (e.g., biosolids) (Silveira *et al*., 2003). In a heavy metal-polluted soil, Kiikilä *et al*. (2002) studied the effect of biosolids as organic immoblizing agents and observed that the exchangeable Cu concentration decreased. On the other hand, the heavy metal could be complexed by dissolved organic matter (DOC), which enhances leaching in the field (Moolenaar and Beltrami, 1998).

The aim of this work was to study the effects of increasing rates of two sources of organic matter: sewage sludge and compost applied to an Egyptian calcareous soil on pH, EC, water-dissolved organic C, humic substances C, microbial biomass C, metabolic quotient, organic matter mineralization, and C/N ratio. Additionally, the extractability of mobile heavy metals (Zn, Cd, Cu, Ni, and Pb) was investigated.

2. Material and Methods

For the incubation experiment an Egyptian calcareous soil low in organic C (0.31%) and high in $CaCO_3$ content (15.9%) was used. The particle size distribution was 86.8% sand, 3.5% clay, and 9.7% silt. The pH of the soil was 8.16 and electrical conductivity was 2.90 dS m^{-1}. Two sources of organic matter (sewage sludge and compost) were added to this soil, the main characteristics of which are described in Table I. The sewage sludge was collected from the Plieningen sewage treatment plant, Germany. The compost used was prepared by 3-year free air composting of turf and plant residues, which were collected from field and greenhouse. Both sewage sludge and compost were added to the soil at rates of 15, 45, and 90 tonnes of dry matter per hectare. The soil-sludge or compost mixtures (50 g) were put in glass vessels (250 mL), the experiment being carried out in triplicate. Distilled water was added to each soil mixture to bring it to 70% of its water-holding capacity. An unamended soil was used as the control. Small vials with 5 mL of 1 M NaOH solution were placed in the vessels for trapping CO_2. After the addition of NaOH, the vessels were closed air tight and incubated at 35 °C. This temperature was chosen, because it is the average temperature in the South of Egypt in summer time. The NaOH solution in the vials was changed after 0, 6, 15, 27, 43, 60, 76, and 90 days. For day 0, the NaOH solution in the vials was changed after 1 h.

Soil pH and electrical conductivity (EC) were measured with a glass electrode using a soil-to-water ratio of 1:1. The pH and electrical conductivity of sewage sludge and compost were measured using a ratio of 1:10. The soil texture was determined by means of the pipette method (Schlichting *et al.*, 1995).

After 0, 27, 60, and 90 days of incubation, the soil was destructively sampled, and the mobile fraction of Zn, Cd, Cu, Ni, and Pb was measured after extraction of

TABLE I

Characteristics of soil and organic wastes

Characteristics	Soil	Sewage sludge	Compost
pH (H_2O)	8.16	5.9	7.8
Ec (dS m^{-1})	2.9	1.9	0.4
Total organic C (%)	0.31	22.7	9.8
Total N (%)	0.021	3.5	0.6
C/N	14.8	6.5	16.3
Zn (mg kg^{-1})	22.1	1014	126
Cd (mg kg^{-1})	0.38	4.5	0.7
Cu (mg kg^{-1})	17.5	402	38
Ni (mg kg^{-1})	7.7	104	19
Pb (mg kg^{-1})	6.5	230	23

2-g air-dry soil with 50 mL of NH_4NO_3 for 2 h (Schlichting *et al*., 1995). The total content of Zn, Cd, Cu and Ni was determined by an aqua regia microwave digestion method. Heavy metal concentrations were determined by atomic-absorption spectrometry (AAS Perkin Elmer 3100).

All forms of extracted C were measured after 0, 27, 60, and 90 days of incubation. Dissolved organic C (DOC) was measured in an aqueous extract (1:10). The humic substances C were extracted by 0.1 M $Na_4P_2O_7$ at a solid/liquid ratio of 1:10. The fulvic acid C was measured after the precipitation of the humic acid C at pH 2.0 from the Na pyrophosphate extract. The humic acid C was calculated by subtracting the fulvic acid C from C extracted by 0.1 M Na pyrophosphate. Soil microbial biomass C was measured by the fumigation-extraction method (Vance *et al*., 1987). In this technique, three replicates of each treatment were fumigated with ethanol-free chloroform for 24 h at 25 °C. Then the soil samples were extracted with 0.5 M K_2SO_4 for 30 min. Three replicates of non-fumigated soil samples were extracted similarly. All extracted forms of C were determined by an automated procedure, using a DIMA-TOC 100 carbon analyzer. Microbial biomass C was calculated as Ec/kEC, where Ec is organic C extracted from fumigated soils minus organic C extracted from non-fumigated soils and the kEC = 0.45 (Jörgensen, 1996; Wu *et al*., 1990).

CO_2 evolved during the incubation was trapped in 1 M NaOH and the excess of NaOH was titrated with 0.1 M HCl after addition of $BaCl_2$ (Black, 1965). Mineralized C was calculated as cumulative CO_2-evolution (g kg^{-1} soil) (Leifeld *et al*., 2002). The specific respiration activity (qCO_2) was expressed as the production of CO_2-C per unit microbial biomass C and time (Anderson and Domsch, 1978).

For control soil and soil treated with organic amendments, total soil C and N were measured by LECO 2000 CN analyser after 0, 27, 60, and 90 days of incubation. The soil inorganic carbon was determined with a Scheibler apparatus (carbonates were dissolved with 10% HCl and the volume of released CO_2 was measured). After that, the carbonate concentrations were calculated using the universal Gas Law (Schlichting *et al*., 1995). In the soil samples, total organic carbon (TOC) was calculated as differences between total carbon and inorganic carbon.

Differences of means between treatments were tested by separate two-way ANOVAs and subsequent *post-hoc* comparisons of means (LSD test, at $P = 0.05$).

3. Results and Discussion

3.1. Effect of Organic Wastes and Incubation Time on Dynamics of pH and EC

For all treatments, soil pH was alkaline (7.5–8.2) during the incubation (Table II). The highest application rate of sewage sludge and compost (90 t ha^{-1}) led to a

TABLE II

Effect of organic wastes on dynamics of soil pH during the incubation experiment

Application rate (t ha^{-1})	Incubation time (days)				
	0	27	60	90	LSD
Compost treatments					
15	8.14	8.17	8.18	8.19	0.05
45	8.06	8.09	8.14	8.16	0.06
90	7.96	7.95	8.02	8.02	0.08
Sewage sludge treatments					
15	8.05	7.95	7.94	7.95	0.09
45	7.83	7.80	7.76	7.76	0.13
90	7.59	7.63	7.60	7.54	0.09
Control treatments					
–	8.16	8.19	8.20	8.20	0.05
LSD treatments					
	0.10	0.08	0.05	0.07	

significant decrease in pH of approximately (0.55–0.66), and (0.18–0.24) units, respectively. The lowest pH values were found for soil treated with sewage sludge at the application rate of 90 t ha^{-1}. This decrease of soil pH is due to the acid effect of decomposable products of organic wastes, especially for sewage sludge. Speir *et al*. (2003) found that high application rates of sewage sludge to a light-textured sandy soil resulted in marked acidification in the zone of sludge incorporation (0–20 cm). Our results showed that pH varied little throughout the incubation period.

The addition of sewage sludge raised the soil salinity level more than the addition of compost (Table III). The soil salinity increased with increasing application rate of organic wastes. The highest increase in soil salinity level was found for soil treated with sewage sludge at the application rate of 90 t ha^{-1}. At the beginning of the experiment (day 0), only the addition of sewage sludge at application rates of 45 and 90 t ha^{-1} raised the soil salinity level significantly, as compared to the control soil. But, with increasing incubation time, the addition of sewage sludge at all rates and compost at 90 t ha^{-1} raised the soil salinity level significantly, mainly as a result of the ions released during the organic matter mineralization process. Wong *et al*. (2001) found that the EC of soil increased significantly due to the addition of sewage sludge. Moreno *et al*. (1999) observed that the addition of sewage sludge compost to an arid soil increased the electrical conductivity of the soil. In fact, high salinity is one of the factors limiting plant growth in soil (Richards, 1960).

TABLE III

Effect of organic wastes on dynamics of electrical conductivity during the incubation experiment

Application rate (t ha^{-1})	Incubation time (days) 0	27	60	90	LSD
Compost treatment					
15	2.93	2.97	2.98	2.96	0.15
45	2.96	2.98	2.98	2.98	0.16
90	2.98	3.14	3.12	3.24	0.08
Sewage sludge treatment					
15	2.95	3.38	3.61	3.70	0.16
45	3.20	3.67	4.10	5.00	0.07
90	3.66	4.77	5.78	5.85	0.10
Control treatment					
–	2.94	2.96	2.97	2.97	0.17
LSD treatment					
	0.15	0.12	0.10	0.12	

3.2. Effect of Organic Wastes and Incubation Time on Dynamics of DOC and Humic Substances C

Higher concentrations of dissolved organic C (DOC) were found in the soil treated with sewage sludge at all application rates (Figure 1). Land application of sewage sludge at agronomic rates increases dissolved organic carbon concentrations in soils (Sloan and Basta, 1995). The results showed that DOC decreased with increasing incubation time, mainly attributed to dissolved organic C being mineralized by microorganisms (Moreno *et al.*, 1999).

The addition of sewage sludge and compost increased significantly humic substances C (humic and fulvic acid C) compared to the control (Figure 1). The fulvic and humic acid C increased significantly with increasing application rate of sewage sludge and compost. During the incubation experiment, the highest increases of fulvic and humic acid C were found for soil treated with sewage sludge at 90 t ha^{-1}. In soil treated with sewage sludge, the fulvic acid C decreased as incubation time increased. This result is explained by a high proportion of easily biodegradable organic compounds in this fraction. In contrast, the humic acid C increased significantly with time, demonstrating the humification and polymerization of sludge organic matter. However, in soil treated with compost, the fulvic and humic acid C did not change significantly with time. This result indicates that the fulvic and humic acid C of compost are more stable as a result of long-time of composting process (3 years).

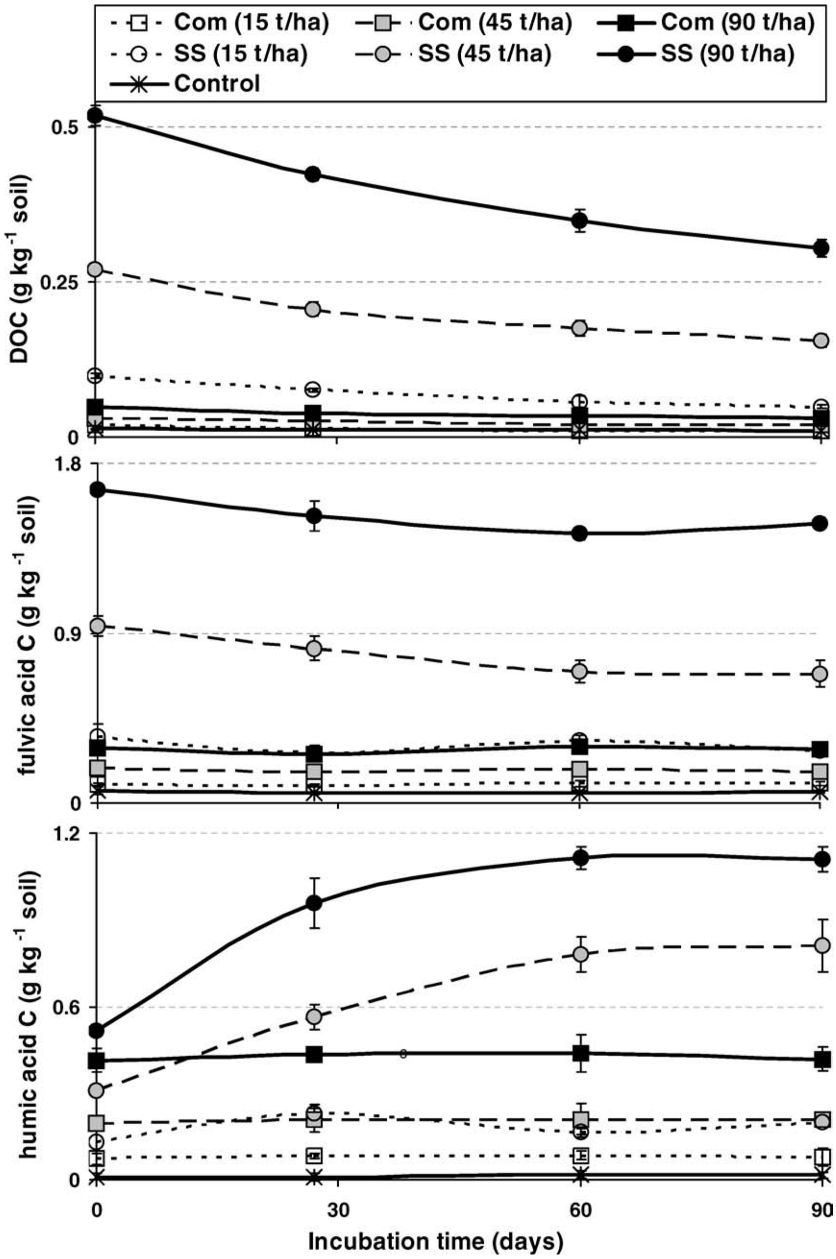

Figure 1. Effect of organic wastes on dynamics of dissolved organic carbon (DOC) and humic substances C during the incubation experiment. Control soil; (com) soil treated with compost at application rates of 15, 45, and 90 t ha^{-1}; (SS) soil treated with sewage sludge at application rates of 15, 45, and 90 t ha^{-1}. Average ± S.D.; where absent, bars fall within symbols.

3.3. EFFECT OF ORGANIC WASTES AND INCUBATION TIME ON DYNAMICS OF C_{org} MINERALIZATION, MICROBIAL BIOMASS C, METABOLIC QUOTIENT, AND C/N RATIO

The C_{org} mineralization during the experiment was recorded as cumulative CO_2-evolution (g kg^{-1} soil). The addition of sewage sludge and compost led to a significant increase in C_{org} mineralization compared to unamended soil (Figure 2). The cumulative amount of C mineralized increased with increasing application rate of sewage sludge and compost. The highest C_{org} mineralization was found for sewage sludge. During the three months of incubation, the cumulative C mineralized amounted to 0.23, 1.28, and 2.93 g kg^{-1} soil for control soil, compost (90 t ha^{-1}), and sewage sludge (90 t ha^{-1}), respectively. The high loss of organic C by mineralization in sewage sludge amended soil could have been due to the high microbial activity as a consequence of the high concentration of dissolved organic C introduced with sewage sludge. The dissolved organic C is the most important source of energy for microorganisms. Pascual *et al.* (1999) attributed the high microbial activity in municipal waste-amended soil to the high level of water-soluble C of amended soil.

Before incubation, the C/N ratios of sewage sludge and compost were 6.5 and 16.3, respectively (Table I). These values are below 20, which is commonly accepted as a threshold for net N mineralization from organic residues. Among two organic wastes, sewage sludge application significantly decreased the initial C/N ratio of the soil compared to the control (Table IV), mainly due to much lower C/N ratio of sewage sludge than that of the compost. As incubation time progressed, the C/N ratio of the soil significantly decreased also in compost treatments compared to the control. For the soil treated with organic wastes, the C/N ratios tended to decrease significantly with time. This result attributed to soil organic matter mineralization and decrease of total organic C with time.

The soil microbial biomass C was used as a sensitive indicator of changing soil conditions (Leita *et al.*, 1999). The addition of both organic wastes (sewage sludge and compost) caused a significant increase in microbial biomass C (Figure 3). This result is explained by the increased number of microorganisms after addition of organic wastes (Goyal *et al.*, 1993; Pascual *et al.*, 1997). The soil microbial biomass C declined during the three months of incubation. This result suggested that the easily biodegradable pool of organic C was gradually exhausted. Chander *et al.* (1995) found that the soil microbial biomass C increased after sewage sludge addition and this initial increase of biomass C declined with prolonged incubation.

Microbial biomass C as a percentage of total organic C has been proposed as a sensitive indicator of changes in organic matter and it has also been used effectively to follow the state of a soil's organic matter content after the addition of organic materials (Pascual *et al.*, 1997). Generally, the application of organic matter to the soil causes an increase in the ratio of microbial biomass/TOC (Powlson *et al.*, 1987). In the control soil, the ratio of microbial biomass C/TOC ranged between

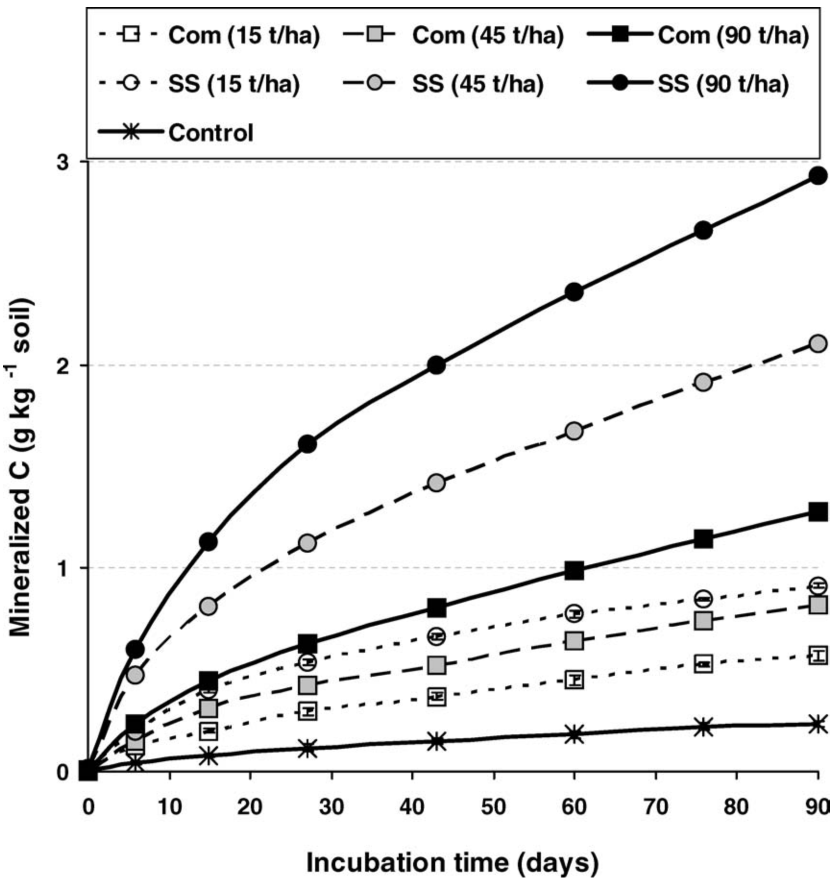

Figure 2. Effect of organic wastes on the cumulative amount of C mineralized during the incubation experiment. Control soil; (com) soil treated with compost at application rates of 15, 45, and 90 t ha^{-1}; (SS) soil treated with sewage sludge at application rates of 15, 45, and 90 t ha^{-1}. Average ± S.D.; where absent, bars fall within symbols.

0.93 and 1.57 during the incubation time (Figure 3). The addition of both organic wastes caused a significant increase in this ratio, indicating a high availability of organic matter to soil microorganisms (Chander *et al*., 2001). This ratio decreased significantly as incubation time increased. This result concurs with that of Pascual *et al*. (1997) who found that the values of microbial biomass C/TOC in the soil amended with various urban wastes decreased with incubation time. The soil treated with sewage sludge showed a high decrease in microbial biomass C and biomass C/TOC during the incubation experiment. This result indicates greater availability of the mineralizable material at the beginning and stabilization of sludge organic matter with increase of incubation time. Of the two organic wastes, the addition of sewage sludge at any application rate caused the higher initial values of biomass C and biomass C/TOC. However, as incubation time increased, these values of biomass C

TABLE IV

Effect of organic wastes on dynamics of C/N ratios during the incubation experiment

Application rate ($t\ ha^{-1}$)	Incubation time (days) 0	27	60	90	LSD
Compost treatment					
15	14.1	13.2	12.4	12.0	0.9
45	13.1	12.0	11.0	10.8	1.5
90	13.7	12.4	11.5	10.8	0.9
Sewage sludge treatment					
15	9.0	8.0	7.6	7.3	0.8
45	8.0	6.6	5.9	5.5	0.5
90	7.5	6.2	5.6	5.3	0.6
Control treatment					
–	14.4	13.8	13.8	13.7	1.1
LSD treatment					
	1.1	0.8	1.0	0.6	

and biomass C/TOC in sewage sludge amended soil decreased and reached values within the range of those in compost amended soil. For both organic wastes, the values of microbial biomass C and biomass C/TOC were still significantly higher than those of the control soil at the end of the incubation.

The metabolic quotient (qCO_2) is a relationship between soil respiration and microbial biomass and is expressed as mg CO_2-C $h^{-1}g^{-1}$ microbial biomass C (Anderson and Domsch, 1978). The metabolic quotient is related to the hypothesis of energy optimization and it can be used as an indicator of environmental stress since it is calculated from parameters which are very sensitive to environmental changes (Anderson and Domsch, 1993). At the beginning of the experiment (day 0), the control soil had an initial metabolic quotient value of 7.8 mg CO_2-C h^{-1} g^{-1} biomass C (Table V). This value increased significantly due to the addition of sewage sludge at all application rates and compost at the high application rate. The highest increase of the metabolic quotient was found in sewage sludge-amended soil, mainly due to the high proportion of easily biodegradable compounds in sewage sludge. In all treatments, the values of the metabolic quotient decreased with incubation time, indicated by the lower CO_2 evolution per biomass unit. During the three months of incubation, in the soil amended with sewage sludge at 45 and 90 t ha^{-1}, the values of the metabolic quotient always remained significantly higher than those of the control and soil amended with compost. Leita *et al.* (1999) reported that the increase of metabolic activity occurred by the addition of municipal refuse compost may have been due to stress induced by heavy metals, even if these were below toxic levels. Although the initial value of metabolic activity increased significantly

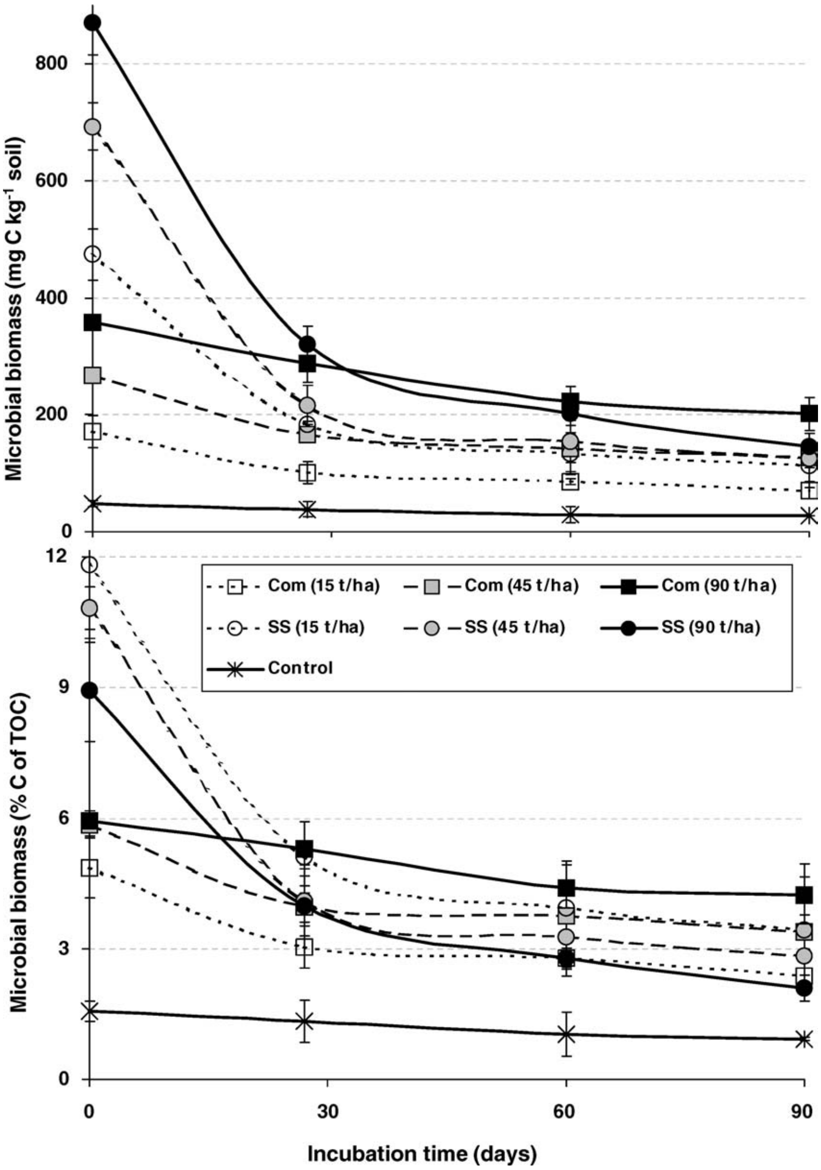

Figure 3. Effect of organic wastes on dynamics of microbial biomass C and microbial biomass C/TOC during the incubation experiment. Control soil; (com) soil treated with compost at application rates of 15, 45, and 90 t ha^{-1}; (SS) soil treated with sewage sludge at application rates of 15, 45, and 90 t ha^{-1}. Average $\pm$ S.D.; where absent, bars fall within symbols.

due to the addition of compost at high application rate of 90 t ha^{-1}, this increase of metabolic activity was not found as incubation time increased; mainly due to the added material's stability with composting. This fact suggested that not only the amount of TOC added to the soil, but also the quality of the organic matter affected

TABLE V

Effect of organic wastes on dynamics of qCO_2 (mg CO_2-C h^{-1} g biomass C) during the incubation experiment

Application rate (t ha^{-1})	Incubation time (days) 0	27	60	90	LSD
Compost treatment					
15	7.5	3.2	2.2	1.8	0.9
45	9.0	2.4	2.0	1.9	0.7
90	10.2	2.2	2.0	2.0	1.6
Sewage sludge treatment					
15	12.1	2.5	2.0	1.8	0.8
45	13.8	4.9	4.1	4.4	0.9
90	15.1	5.2	4.4	5.4	0.5
Control treatment					
–	7.8	3.7	2.8	1.4	2.5
LSD treatment					
	2.2	0.4	0.3	0.7	

the metabolic quotient (Leita *et al.*, 1999). Pascual *et al.* (1997) found that the metabolic quotient was higher after the addition of sewage sludge and municipal solid waste than after compost addition.

3.4. Effect of Organic Wastes and Incubation Time on Dynamics of Mobile Fractions of Heavy Metals

In our soil, the total content of heavy metals (Zn, Cd, Cu, Pb, and Ni) can be considered as normal for a non-contaminated soil (Table I). Scheffer and Schachtschabl (2002) gave the following values of heavy metals in non-contaminated soil: 10–80 ppm for Zn, 0.1–0.5 ppm for Cd, 2–40 ppm for Cu, 5–50 ppm for Ni, and 2–60 ppm for Pb. The heavy metals extracted with NH_4NO_3 give an indication of the heavy metals included in the mobile fraction of the soil (Zeien and Brümmer, 1989). The percentages of NH_4NO_3-extractable Zn, Cd, Cu, Ni, and Pb were calculated with respect to their total content (Figure 4). Soils act as buffer systems, and can immobilize heavy metals. The degree of buffering depends both on the kind of heavy metal and the soil (Welp, 1989, 1999). Our results showed that the initial percentage of heavy metals extracted with NH_4NO_3 lay in the range of 0–29% of the total content. This percentage differs from one heavy metal to another depending on its mobility. The order of mobility of the heavy metals was: Cd > Cu > Ni > Pb > Zn. During the three months of incubation, the mobility of heavy metals showed significant changes for all treatments. Most changes in extractability of mobile heavy metals occurred at

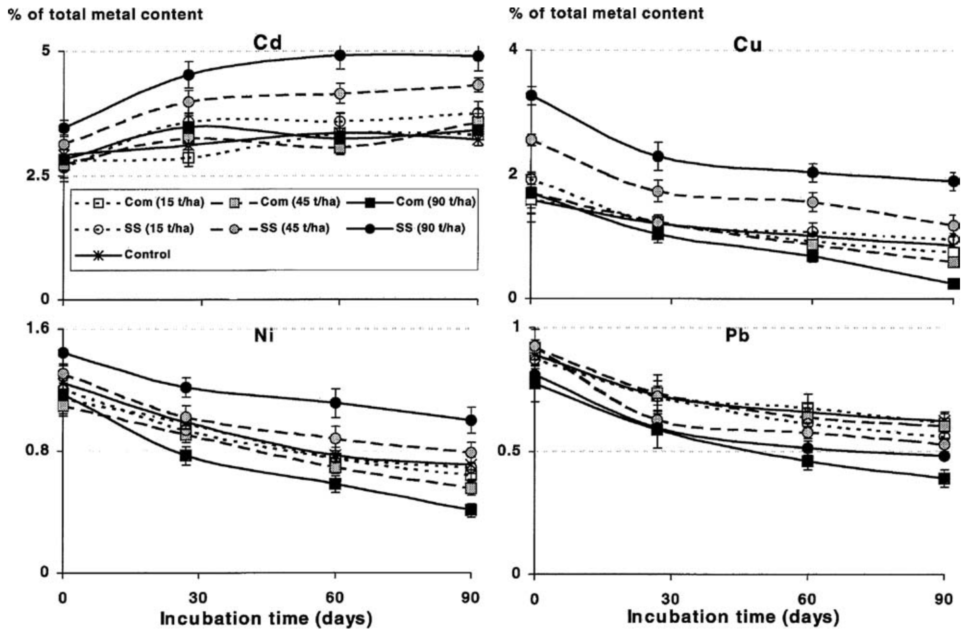

Figure 4. Effect of organic wastes on dynamics of mobile fraction of heavy metals during the incubation experiment. Control soil; (com) soil treated with compost at application rates of 15, 45, 90 t ha^{-1}; (SS) soil treated with sewage sludge at application rates of 15, 45, and 90 t ha^{-1}. Average $\pm$ S.D.; where absent, bars fall within symbols.

high application rates of sewage sludge and compost. Among all treatments, the soil treated with sewage sludge showed a significant increase in extractability of mobile Cd, Cu, Zn and Ni as compared to the control, especially with the highest application rate. In contrast, the addition of sewage sludge at 45 and 90 t ha^{-1} caused a significant decrease in mobile Pb compared to the control. Possible explanations for the increase of mobile Zn, Cd, Cu, and Ni in soil amended with sewage sludge are: (i) the high content of heavy metals in sewage sludge; (ii) formation of soluble heavy metals-organic associations (iii) the decrease in soil pH. Sloan *et al.* (1997) found that the application of sewage sludge increased the percentages of Ni, Zn, and Cd in the exchangeable fraction. Chander *et al.* (1995) noted that the amounts of Cd, Zn, Ni and Cu extracted with 0.5 M K_2SO_4 increased with increasing sludge application rate. Our results showed that the addition of sewage sludge led to a reduction in soil pH and an increase in water dissolved organic C and fulvic acid C. This result confirms that the mobility of heavy metals can be increased by the addition of sewage sludge. Several investigations have revealed that soluble organics are able to raise the mobility of heavy metals (Temminghoff *et al.*, 1998; Amrhein *et al.*, 1992; Neal and Sposito, 1986). McBride (1995) reported that heavy metal complexes with fulvic acids are soluble. The soil pH has also been shown to govern the concentrations of soluble and plant available heavy metals (Brallier *et al.*, 1996). Heavy metal solubility increases at lower pH and decreases at higher pH values (Chuan *et al*., 1996). In our investigation, the soil treated with compost at high application rate showed the lowest mobility of Cu, Ni, and Pb during the incubation experiment. This result suggests that the quality of organic matter affects the availability and mobility of heavy metals. It is widely known that the availability of heavy metals in soil is strongly influenced by the amount and the quality of organic matter which can interact with the heavy metals, forming complexes and chelates of varying stability (Leita *et al*., 1999). At the end of the incubation (90 days), mobile Cu, Ni, and Pb decreased significantly from 0.85%, 0.70% and 0.62% of total content for the control to 0.24%, 0.41% and 0.39% of their total content for the soil treated with compost at the highest application rate, respectively. It was observed that the highest decrease was pronounced for Cu. In this connection, organic matter from compost may have a significant impact on reducing Cu availability. Many studies have shown that copper has the ability to form strong complexes with organic matter (Van Dijk, 1971; McBride, 1978; Tyler and McBride, 1982). The importance of soil organic mater in limiting Pb availability has also been demonstrated (Strawn and Sparks, 2000). Brown *et al*. (2003) reported that the application of biosolids composts effectively reduced the Pb availability. For all treatments, the mobility of Cu, Ni, Zn, and Pb decreased as incubation time increased. This is attributed to the tendency of soluble Cu, Ni, Zn, and Pb to be precipitated by $CaCO_3$ in calcareous soil or to bind with the organic matter due to the addition of sewage sludge and compost.

The concentration of the mobile fraction of Zn in this soil was actually below the detection limit (0.01 mg L^{-1}) of the ASS instrument. This result indicates that $CaCO_3$ in soils led to Zn precipitation as $ZnCO_3$. Osman *et al*. (1980) demonstrated that $CaCO_3$ plays an important role in Zn deficiency which is found in Egypt's calcareous soils. Morera *et al*. (2002) found that the availability of Zn was remarkably low in soil with high carbonate content. In this investigation, however, the addition of sewage sludge at 45 and 90 t ha^{-1} raised the initial extractability of mobile Zn by 0.08% and 0.11% of total content, respectively (data not shown). This result concurs with that of Almas *et al*. (2000) who found that addition of organic matter increased the solubility of Zn by formation of organo-metallic complexes. Our result provides good evidence that the mobilization of unavailable zinc in calcareous soil can be increased by the addition of sewage sludge. It was observed that the initial increase of extractable Zn decreased with increasing incubation time. Among heavy metals, the highest mobility was found for Cd with addition of sewage sludge. The initial extractability of mobile Cd increased significantly up to 27 days of incubation in the soil treated with sewage sludge. After that, the extractability of mobile Cd almost remained constant up to the end of the incubation. At the end of incubation (90 days), mobile cadmium increased significantly from 3.2% of total content for control to 3.7%, 4.3% and 4.9% of total content for soil amended with sludge at application rates of 15, 45, and 90 t h^{-1}, respectively. This increase of mobility of Cd can be due to the mineralization of Cd from organic sewage sludge or the formation of soluble organo-metallic complexes. It is possible that high DOC concentrations in soil treated with sewage sludge inhibited precipitation of Cd (Sloan *et al.*, 1997). Holm *et al.* (1996) found that DOC inhibited precipitation of $CdCO_3$ in agriculture soil. Neal and Sposito (1986) reported that the solid soil sorption of Cd was reduced by the formation of soluble-organic associations in the aqueous solution. Our results suggest that sewage sludge-applied Cd is easy to extract from soil and can be available for plants. In contrast, the mobility of Cd was unaffected by the addition of compost as compared to untreated soil.

4. Conclusion

The addition of organic wastes (sewage sludge and compost) to the calcareous soil increased the values of dissolved organic C, humic substances C, C_{org} mineralization, microbial biomass C, and qCO_2. The C_{org} mineralization is related with decrease of C/N ratio during the incubation experiment. The addition of sewage sludge at high application rate caused a high decrease in soil pH of approximately (0.55–0.66). Our result provided good evidence that the mobilization of unavailable Zn in calcareous soil can be increased by the addition of sewage sludge. Both sewage sludge and compost addition enhanced the studied biochemical properties of calcareous soil. However, the addition of sewage sludge at high application rate led to a high increase in soil salinity and extractability of Cd, Ni, and Cu. The high EC and extractability of heavy metals in sludge amended soil at high sludge application rate may pose an inhibitory effect on plant growth in calcareous soil. This reason may limit the use of sewage sludge as amendments for calcareous soil. Therefore, more studies are needed to investigate the effect of sewage sludge on plant growth and uptake of heavy metals under field condition.

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