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Effects of medium-term amendment with sewage sludge on soil organic fertility and on heavy metal bioavailability

Gabriella Rossi* and Claudio Beni

Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria – Centro di ricerca Agricoltura e Ambiente (CREA-AA), via della Navicella 4 - 00184 Roma (Italy)

* Correspondence: gabriella.rossi@crea.gov.it; +39-06-7005413

Abstract: The biomass fraction of processed municipal and industrial wastes added to soil can maintain, and in some case improve, the soil's organic fertility. One of the main constraints in the agricultural use of the sewage sludge is its content of heavy metals. In the long term, soil administration of sewage sludge in agriculture could result in a risk of environmental impact. The aim of this research was to evaluate the effects of medium-term fertilization with sewage sludge diversely processed on the soil's organic carbon content and humification – mineralization soil's processes and on the physical and mechanical properties of soil. Furthermore, the heavy metals accumulation in soil, in their total and available form, has been investigated.

After eight years of administration to soil, the use of sewage sludge as an agricultural soil amendment has contributed to maintaining the soil's organic fertility. An increase in concentrations of total Ni and Zn was detected in soil. For bioavailable form (DTPA-extractable) this trend was evidenced for all heavy metals analysed. However, the concentrations of total and available heavy metals in the soil did not exceed the legal threshold established by Italian law for unpolluted soils.

Keywords: sewage sludge recycling; soil organic fertility; heavy metals bioavailability

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1. Introduction

The soil organic matter influences and regulates the cycle of the nutrients in the soil–plant systems, contributing significantly to the maintenance of global soil fertility (chemical, physical and biological). It is involved in fact, both in plant and micro-organism growth and, as a substrate for the mineralization processes, in the promotion of the soil's nutrient availability. Therefore, the quantity, quality and turnover of the organic matter are correlated to the potential fertility, in natural and agricultural soils.

Mediterranean agricultural areas are characterised by low soil organic C (SOC) contents and are often prone to soil degradation and SOC depletion due to change in extensive land use during the last decades and they are highly vulnerable to environmental changes [1,2,3]. Continuously high temperatures during the summer in the Mediterranean lead to a rapid decline in the organic matter content in cultivated soil . The loss of the soil organic matter from the agricultural soil is increasing very rapidly because of the climatic characteristics and the intensive land use which affect processes the processes of humification-mineralization of native soil organic matter.

A greater effort has to be addressed to conservation and enrichment of the organic matter in arable lands. Nowadays, growing concern focuses on the suitability of bio-wastes such as sewage sludge, MSW and animal slurries to be used in agriculture. The promotion of waste recycling and recovery techniques is an urgent necessity. The necessity of linking agricultural practices to sustainable environment management leads to the identification of farm procedures with beneficial effects on the ecosystem. Fertilization practices with organic waste could have a positive influence

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on the soil's organic fertility and the soil's nutrient supply [4,5]. Residual biomasses, such as sewage sludge, slurries and food industry residue can enrich soil with macronutrients such as nitrogen, phosphorus, potassium, sulphur, calcium, magnesium and micronutrients [6,7] which meet the requirements of cultivated crops and enhance the restoration of soil fertility.

Sewage sludge is a potential source of nutrients for the crops but its heavy metal content is one of the hazards to the environment. Nowadays, the environmental directives in many countries regulate the use of sewage sludge in agriculture by limiting the total heavy metal concentration in sludge and soil; in Italy, the use of sludge in agriculture is regulated by Decree-law 99/92 [8] in implementing Directive 86/278/EC. In order to assess the potential for re-use of sewage sludge in agriculture, its contribution to soil organic fertility should be verified [9,10]. In addition, the effects on physical and mechanical characteristics of the soil [11,12,13,14], on the behaviour of heavy metals in soil and in soil-plant system and the hazard of environmental impact [15,16,17,18] should be evaluated.

The aim of this research was to evaluated the effects of medium term fertilization with sewage sludge diversely processed on the soil's organic carbon content and humification – mineralization processes and on the physical and mechanical properties of soil. Furthermore, the heavy metals accumulation in soil, in their total and available form, has been investigated.

2. Results

2.1 Soil caracterization.

The soil was characterised by a middle cation exchange capacity, subalcaline pH, middle nitrogen content, low content of total organic carbon and a low value of the C/N ratio (Table 1).

The total concentrations of copper, lead, zinc and nickel in the soil were below the limits set by Italian law.

Table 1. Physical and chemical characteristics of control soil and limits established by the Italian Law for the use of sewage sludge on an agricultural soil (D.L. 27/01/1992 n.99). Concentrations are referred to dry weight.

Parameter	Value	Limits	Parameter (mg kg^{-1})	Value	Limits
Sand %	23		Available P	16	
Silt %	55		Total Cu	68.2	≤ 100
Clay %	22		Total Ni	43.8	≤ 75
Texture (USDA)	Silt loam		Total Pb	14.9	≤ 100
pH	7.8	7.5>pH>6	Total Zn	78.5	≤ 300
SOC (g kg^{-1})	9.0				
Total N (mg kg^{-1})	1,180				
C/N	7.6				
C.E.C. (cmol kg^{-1})	13.8	> 15			

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2.2. Soil organic carbon behaviour in amended plots.

Table 2. Concentration of SOC, TEC and C-(HA+FA) in soil (g kg^{-1} d.w.).

Treatment	SOC	TEC	C-(HA+FA)
T	8.6 a	5.1 a	3.3 a
L	10.8 b	6.0 ab	4.1 b
D	11.0 b	7.1 b	4.2 b
C	10.8 b	8.0 bc	5.1 c

Within each column, different letters indicate significant differences at p≤0.05 (LSD test), n=12

The sludge processing seemed to influence organic carbon pools and humification processes, as shown in table 2 and figure 1. The soil organic carbon (SOC), total extractable carbon (TEC) and humified carbon contents [C-(HA+FA)] were higher in amended plots than in control (Table 2). The most likely explanation is the yearly addition to soil of organic carbon in the form of organic fraction of sewage sludge. No significant differences in SOC and TEC were found in amended plots. In plots treated with compost sludge, the concentrations of TEC and humic and fulvic acids carbon C- (HA + FA) were higher in comparison with other treatments.

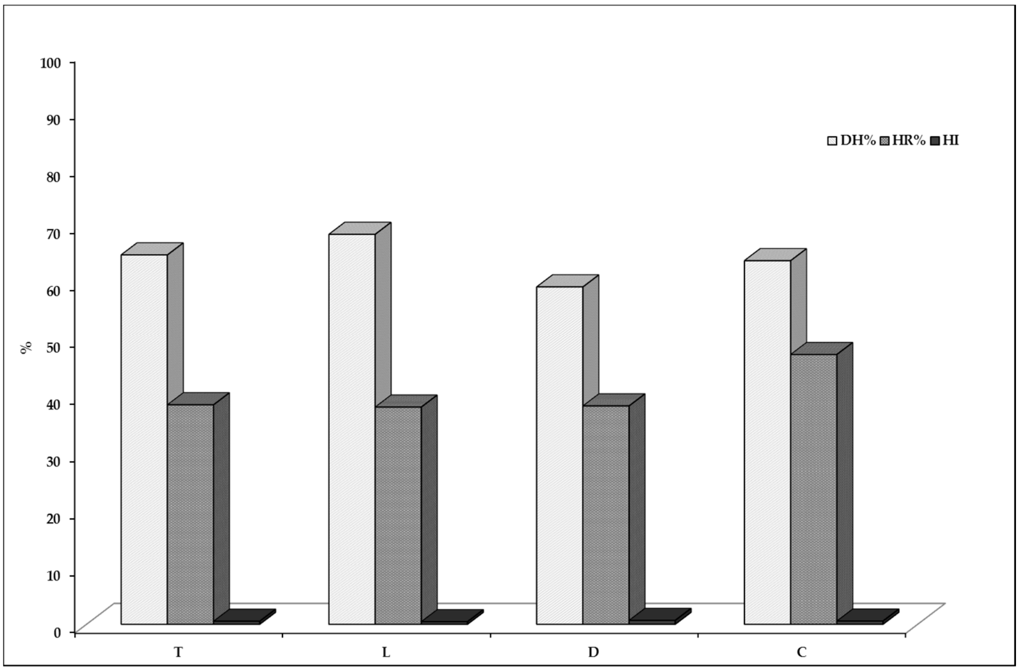

Figure 1. **DH %**, humification degree; **HR %**, humification rate; **HI**, humification index.

In soil treated with composted sludge (C), DH% and HI showed values (DH%= 63.7, HI=0.57) close to the control T (DH%= 64.7, HI=0.54); this trend indicates that the addition of composted sludge has not altered the natural process of soil humification; the latter is favoured by the higher concentration of humified carbon [C-(HA+FA)] (table 2) and is also evidenced by the highest value of humification rate (HR%=47.2). The liquid sludge (L) administration also contributes to keeping the humic fraction stable (HI = 0.46 e DH% = 68.3). By contrast, dehydrated sludge (D) did not contribute to the humification processes. These treatments gave the highest value of humification index (0.69). The result, due to an increase of the not-humic extracted C in comparison with the

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humic C, indicates a drop in the humification level. It is strengthened by the lowest DH% value observed in this treatment (59.1).

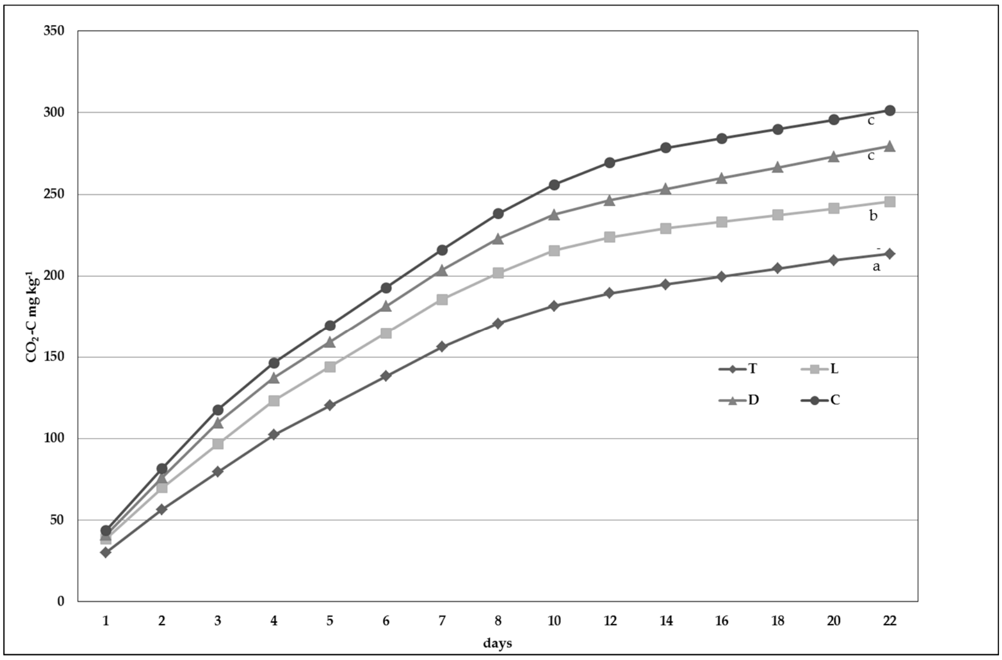

Figure 2. Cumulative CO_2-C evolution from soil (mg kg^{-1})

Different letters indicate significant differences at $p \leq 0.05$ (LSD test), n=12

The cumulative amounts of CO2-C evolved from control (T) from amended plots were determined (Figure 2).

The application of the amendments to soil induced a remarkable effect on the cumulative mineralized C.

In amended plots, the total amount of CO2-C mineralised increased significatively respect to soil not treated (T). The CO2-C curves of differently treated soil indicated that plots amended by composted and dehydrated sludge gave the highest values of mineralized C. Particularly, respiration rates were higher in C and D than in control (T), 41% and 31% respectively.). Levi-Minzi [19] suggested that the amendments which present a complementary mineralization rate of about 5% are good enough to maintain an effective amount of OM in the soil. Samples of soil treated with dehydrated or composted sludge for eight years, presumably, contain different quantities of not humified and more labile C fraction, easily decomposable in respect to T and L.

2.2. Effects of sewadge sludge on on the physical characteristics of the soil

All the physical-mechanical parameters are improved following the use of composted sewage sludge, compared to other treatments. In fact, in C treatment, the deformation was lower at both 10 daN and 200 daN, showing a higher bearing capacity of the soil while shear strength and penetration resistance were lower, demonstrating the greater soil workability and water retention capacity was higher, compared to other plots (Table 3).

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Table 3. Soil physical and mechanical parameters after eight years of sludge administration.

Treatment	Soil deformation at 10 daN (%)	Soil deformation at 200 daN (%)	Shear strength (kPa)	Cone penetration resistance at 100 mm depth (MPa)	Maximum hydraulic capacity (%)
T	24.13 b	38.8 b	19.65 b	2.89 b	28.72 a
L	27.42 b	39.12 b	20.32 b	3.14 b	27.43 a
D	25.18 b	37.11 b	20.14 b	2.77 b	29.15 a
C	18.33 a	27.42 a	15.54 a	1.81 a	34.68 b

Within each column, different letters indicate significant differences at $p \leq 0.05$ (LSD test), n=12.

2.3 Heavy metal bioavailability

Table 4. Total Cu, Pb, Ni and Zi in soil (mg kg $^{-1}$ d.w.).

Treatment	Cu	Pb	Ni	Zn
T	79.0 a	18.50 a	38.42 a	95.25 a
L	89.63 a	18.37 a	42.0 b	98.0 a
D	89.19 a	20.89 a	41.21 b	120.63 b
C	87.13 a	19.84 a	41.28 b	113.0 b

Within each column, different letters indicate significant differences at $p \leq 0.05$ (LSD test), n=12

With regard to total heavy metals (Table 4), Cu and Pb did not differ from control (T) in any treatment. Ni and Zn instead showed a quite different behaviour. The Ni soil concentration increased significantly in L, D and C, compared to control (T). However no differences were observed among composted, liquid and dehydrated treated plots. Zn content was significantly higher in D and C.

Table 5. DTPA- extractable Cu, Pb, Ni and Zi in soil (mg kg $^{-1}$ d.w.).

Treatment	Cu-DTPA	Pb-DTPA	Ni-DTPA	Zn-DTPA
T	14.29 a	2.36 b	0.44 a	2.52 a
L	16.71 ab	1.84 a	0.79 b	5.22 bc
D	18.49 b	2.68 b	1.08 c	6.82 c
C	17.33 b	2.24 b	0.90 b	4.87 b

Within each column, different letters indicate significant differences at $P \leq 0.05$ (LSD test), n=12.

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With regard to DTPA-extractable heavy metals, bioavailable forms (Table 5), Cu content was significantly higher in D and C respect to T and L while Pb concentration was significantly lower in L compared to other treatments. For Ni and Zn there was an overall increase with respect to control (T). The percentages of bioavailability of copper and lead did not show significant variations between the control and the theses treated, reaching around 18 and 20% for copper and 10 and 12% for lead respect to total forms. Zinc and nickel showed different behaviour. For Ni, the percentage of bioavailable form respect to total has varied from 1,15% (T) to 2,62% in D and 2,18% in C; in the case of Zn the percentage of bioavailability was 2.65% in T, 5.33% in L, 5.65% in D and 4.31% in C.

3. Discussion

After eight years of administration to soil, the use of sewage sludge as agricultural soil amendment has contributed to maintaining the soil organic fertility. The analysis of humification parameters and soil respiration activity showed us that different sludge processing techniques are likely to result in different effects on soil carbon pools and the trend of mineralization of the soil's organic carbon.

In amended soil, tillage is a fundamental factor in influencing soil quality, plant behaviour and the sustainability of farming systems [11] because it can alter the soil physical properties and the soil's profile depth. Many authors use the soil penetration resistance measurements as a tool for characterizing soil strength after tillage [12,13]. The deformation response of a soil under different load conditions is used to predict how the soil stability changes after the application of an effective stress [13]. Soil moisture content depends also on the organic matter content, influenced by the amendment. Soil moisture content during tillage affects the distribution of aggregates' size and those aggregates formed at low moisture content have three to four times more resistance to crushing than those formed at greater moisture contents [14]. The results obtained on the sewage sludge administration on the physical and mechanical parameters of soil showed an improvement of the soil tillage indexes in the soil treated with compost sludge in comparison with other treatments.

An increase in concentrations of total nickel and zinc was detected in soil. For bioavailable form (DTPA-extractable) this trend was evidenced in all heavy metals analysed.

These results suggest that long-term soil amendment with sewage sludge might shift the soil heavy metals residual forms to forms that are potentially more mobile, labile and available to soil organisms and plants. In fact, the soil inorganic and organic components may form different kinds of bonds with micronutrients and heavy metals influencing their bioavailability [20,21, 22]. However, after eight years, the concentrations of total and available heavy metals in the soil did not exceed the legal threshold established by Italian law for unpolluted soils.

In conclusion, the prolonged amendment with compost sludge gave better results than the other treatments because the added organic fraction contributed to keeping the organic humification-mineralization process in equilibrium (organic fertility) and to improving the physical and mechanical qualities of the treated soil. Moreover, after eight years, the risk of environmental impact has not been highlighted with regard to the heavy metals considered.

4. Materials and Methods

Field trials were settled as a long term experiment with the aim of monitoring the benefits and drawbacks of sewage sludge administration to soil.

Municipal and partially industrial sewage sludge was obtained from the waste treatment plant in Italy near Rome. The concentration of heavy metals in the sludge did not exceed the limits imposed by the D.L. 99/92 (Italian law). Anaerobically digested dewatered (D, 24% d.w.), liquid (L, 3% d.w.) and composted (C, 62% d.m. 9:1 w:w sludge to straw "before-composting" ratio) sludges were applied every year at a rate of 0 (control, T) and 15 t ha^{-1} d.w. (L, D, C). The sludge used has been characterized annually and has always been within the limits of the Italian law (D.L. 99/92).

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Sludge was incorporated into the 0 - 30 cm plough layer every autumn. The experiment was carried out following a completely randomised block design. Plots of 7x7 m were laid out in 4 blocks and each treatment had a single replicate per block.

After eight years, three sub-samples (0-30 cm) for each replicate for each treatment were collected. Samples were air-dried at ambient temperature, and the analyses were made on the <2 mm dried soil fraction after sieving.

Soil pH was determined with a glass electrode in a 2.5:1 water to soil ratio (v/w), as to particle size by the sedimentation procedure, cation exchange capacity (CEC) by ammonium acetate procedure, total nitrogen by the Kjeldahl method [23] and available P with a spectrophotometer using the Olsen method [24]. Soil organic carbon (SOC) was determined with the Springer and Klee [25], and total extractable carbon (TEC), and humic and fulvic acid carbon (HA + FA) were determined by the dichromate oxidation method [26]. Not humified and more labile C fraction (NHC) was calculated by the difference [TEC− (HA + FA)], and not extractable organic carbon (NEC), conventionally defined as humin (a pool of organic carbon recalcitrant to microbial degradation), by the difference (SOC−TEC). Humification parameters DH (degree of humification), HR (humification rate), and HI (humification index) were determined according to Sequi et al. [27] and Ciavatta et al. [28]. DH% is given by (HA + FA × 100)/TEC, HR% by (HA + FA × 100)/SOC, and HI (dimensionless) by [TEC – (HA + FA)]/(HA + FA). To measure soil microbial respiration, 25 g of sample were placed in closed glass jars and incubated in the dark at field capacity and 30 °C. The CO2 evolved was trapped by 0.5 N NaOH daily for the first week of incubation and every two days for the next two weeks, and determined by titration of the excess NaOH with 0.5 N HCl [29].

The soil's physical and mechanical parameters were characterized according to the official methods of the Ministry of Agriculture [30]: monoaxial compression test on soil [31] was detected with a oedometer apparatus (Controls, mod. T302) under vertical loads (10 and 200 daN) for evaluating the plastic soil deformation during a 24-h test; soil shear strength was measured by using a vane shear test meter (Controls, torsion wrench 0–32 Nm, diameter 25 mm, vane height 50 mm). For each plot, 20 measures were taken on topsoil (at depths of 0.35–0.70 m); shear resistance (kPa) was calculated with the Terzaghi and Peck [32] relationship to applied torque; soil penetration resistance was measured on each treatment and on the control areas using a hand penetrometer (Controls, Italy) with a 60◦ cone and base area of 100 mm2; maximum hydraulic capacity was measured using the Richards' method [33].

Soil total heavy metal (Cu, Zn, Ni, Pb and Cd) were extracted by wet digestion with a HNO3-HClO4 mixture (2.5:1 ratio) at 140 °C for 40 hours. The DTPA- extractable heavy metals were determined according to the Lindsay and Norvell procedure [34]. This method is utilised to estimate the amount of soil heavy metals available to plant roots in both natural and cropped, neutral or alkaline soils [35]. The soil concentration of bioavailable fraction of the heavy metals was analysed because it is of great interest in studies of soil contamination as it is the most mobile fraction.

Trace elements in the extracts were analysed by Inductively Coupled Plasma Emission Spectroscopy (ICP).

Mean values were compared with the Least Significance Differences Test (LSD) choosing a confidence level of 95% to test significance ($p \leq 0.05$).

Author Contributions:.

The aspects regarding conceiving, designing and performing the experiments, statistical analysis and paper writing were shared between the authors.

Conflicts of Interest:

The authors declare no conflict of interest and there has been no significant financial support for this work that could have influenced its outcome.

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