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Carbon Mineralization Potential of Soils Amended with Sludge from Olive Processing

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The treatment and disposal of wastewater coming from the industrial process of extraction of olive-oil, i.e. olive-oil wastewaters, is one of the main problems faced by agriculture in the Mediterranean area, where olive cultivation is widespread and the volume of effluent produced is great. Recycling the olive-oil wastewaters on agricultural land could solve the problem of waste disposal and also conserve natural resources. Since the load of the olive-oil wastewaters is mainly organic, information about the rate of organic carbon (C) mineralization is necessary to predict the fate of this waste in soil and ensure a useful program of waste recycling. Limited information is available on the influence of soil properties on the mineralization process of organic amendments: for example, in incubation experiments the rate of the break down of organic materials was found to be influenced by soil texture (Hébert et al. 1991) and microbial activity (Hattori 1988). Some investigators have found that the proportion of added organic carbon that is mineralized decreases with increased addition rates (Boyle and Paul 1989). However, others have observed no such effects (Levi-Minzi et al. 1990). Although C mineralization of olive-oil wastewaters in soil has been studied (Saviozzi et al. 1990), few data exist on the decomposition processes in soil amended with sludges, which are obtained via natural evaporation of olive-oil wastewaters in lagoons or through physical treatment processes.

The objective of this study was to determine the influence of soil type and application rate on the extent of C mineralization of sludge coming from olive-oil wastewaters.

MATERIALS AND METHODS.

Fourteen agricultural soils from various areas of Tuscany (Italy) were examined. The soil samples, consisting of 20 random sub-samples for each of the 14 soils, were air-dried and passed through a 2 - mm sieve to remove large root fragments. Olive-oil wastewaters were collected from an olive-oil production plant near Pisa, were lyophilized and extensively ground to pass a 1 - mm sieve. Total C (54.7%),

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Table 1. Characteristics of the soils and amount of CO_2-C mineralized (Cm) from the sludge incubated in the soils at a 1.5% loading rate.

Soil	pH	Sand	Silt	Clay	CaCO3	Free Fe	Organic C	Total N	C/N	CEC[1]	AEC[2]	FDA[3]	Cm[4]	Soil Classification
		(%)						(‰)		(meq 100g^{-1})		Abs(nm)	(mg)	
1	5.4	59.5	28.8	11.7	-	0.64	10.61	7.67	13.8	38.1	23.6	0.236	184.9	Fluvaquent
2	8.7	86.3	7.8	5.9	17.3	0.36	0.15	0.25	6.0	11.2	0.5	0.015	70.5	Xeropsamment
3	7.6	61.8	21.5	16.7	0.3	0.48	1.03	1.04	9.9	14.7	3.0	0.091	89.9	Xerorthent
4	5.0	25.5	46.5	28.0	-	0.93	3.08	3.19	9.6	34.8	16.8	0.165	186.1	Chromoxerert
5	5.2	43.8	40.2	16.0	-	0.88	5.58	4.90	11.4	33.3	19.6	0.119	165.4	Fluvaquent
6	6.9	63.2	28.3	8.5	-	0.59	1.63	1.99	8.2	20.8	4.5	0.120	128.5	Xerochrept
7	6.0	25.3	61.9	12.8	-	0.98	1.36	1.74	7.8	20.0	8.6	0.079	129.7	Xerofluvent
8	4.8	87.6	8.5	3.9	-	0.68	24.64	16.00	15.4	33.7	29.0	0.465	153.4	Saprist
9	5.4	80.7	12.9	6.4	-	0.42	2.76	0.90	30.7	11.2	4.7	0.131	85.3	Xerochrept
10	8.1	23.7	51.8	24.5	10.6	0.62	1.11	1.65	6.7	18.0	3.2	0.086	83.5	Xerorthent
11	8.2	19.4	56.6	24.0	12.3	0.67	0.79	1.20	6.6	16.7	4.1	0.031	79.0	Xerorthent
12	5.8	77.9	15.8	6.3	-	0.53	2.08	0.87	23.9	13.7	6.7	0.090	104.6	Xerochrept
13	5.1	97.9	0.2	1.9	-	0.15	0.52	0.42	12.4	2.8	1.4	0.039	54.5	Xeropsamment
14	7.4	47.5	27.5	25.0	4.7	0.54	2.41	2.41	10.0	18.6	5.8	0.086	123.4	Psammaquent

1 Cation exchange capacity. 2 Anion exchange capacity. 3 Fluorescein diacetate. 4 Cumulative amounts of sludge C mineralized in soil.

total N (2.2%), and pH (5.0) of the resulting sludge, and the main soil characteristics were determined by standard methods and expressed on a dry basis. The anion exchange capacity (AEC) was measured according to the method of Mehlich (1948); fluorescein diacetate (FDA) hydrolytic activity was determined by the Schnurer and Rosswall method (1982) as absorbance at 490 nm on a filtrate from a soil suspension incubated at 24°C with fluorescein diacetate.

A short-term aerobic incubation procedure was used to determine the potential of the soils to mineralize organic C in the sludge; 100 g of soil alone or mixed with 1.5 g of sludge on a dry-weight basis was moistened to 60% of the maximum water holding capacity and incubated at 22°C in 300-ml glass containers closed with rubber stoppers. The 1.5% application rate represents the maximum loading applicable to the soil as established by current Italian legislation (law no. 99 dated 27 January 1992) adopted to conform to European Economic Community directives concerning sludge application to agricultural land. In order to evaluate the effect of application loadings on the mineralization rate of sludge organic C, soil no. 7, chosen for its intermediate characteristics, was incubated during 81 days with doses of sludge varying from 0.37% to 6%. Glass vials containing 20 ml of 0.5N NaOH were placed in the above 300-ml containers to trap evolved CO_2 to measure sludge decomposition daily. Excess alkali was back-titrated with standard 0. 5N HCl after precipitating carbonate with 1.5M $BaCl_2$ solution. Daily opening of the bottles to replenish the NaOH for CO_2 absorption prevented any inhibition of decomposition owing to lack of oxygen. Values of CO_2 from the sludge treated soils were corrected for CO_2 evolved from the native C of soils.

A non-linear least-square regression analysis was used to calculate parameters from cumulative CO_2-C evolution values from the sludge C mineralization. The coefficient of determination (R^2) was used for comparison of model fits. All the results reported are the means of determinations made on three replicates; the mean coefficient of variation was always lower than 5%.

RESULTS AND DISCUSSION

Cumulative amounts of sludge C (C_m) that was mineralized in soil during the 21-day incubation period was determined (Table 1). Values varied considerably among the soil types, ranging from 54.5 mg of sludge C in soil no. 13 to 186.1 mg in soil no. 4, suggesting a strong influence by the soil type on the extent of mineralization. During the incubation period, an amount of carbon ranging from 6.6 to 22.7% of added sludge carbon had been mineralized. Hébert et al. (1991) reported that amount of C mineralized varied among soil-compost mixtures after 28 days of incubation. However, since the conditions of the incubation were more favorable than those usually existing in the field, their values may have overestimated true losses of sludge organic C. Many attempts have been made to describe the dynamics of C mineralization by means of mathematical equations, which we used to describe the mineralization processes in our 14 soils (Table 2).

Table 2. Kinetic models used to describe C mineralization of sludge in soil.

Model	Equation	Reference
First-order	$C_t=C_o(1-e^{-kt})$	Murwira et al.(1990)
First-order E	$C_t=C_o(1-e^{-kt})+C_1$	Jones (1984)
Zero-order	$C_t=kt+intercept$	Seyfried and Rao (1988)
Two simultaneous reactions	$C_t=C_1(1-e^{-kt})+C_2(1-e^{-ht})$	Delphin (1988)

C_t=cumulative amount (mg) of carbon mineralized from sludge after time t (dependent variable); t=time (days) from start of incubation when t=0 (independent variable); C_0, C_1, and C_2=potentially, easily, and slowly mineralizable sludge carbon (mg), respectively; k and h=rate constants (day^{-1}).

The coefficient of determination (R^2) was >0.85 (data not shown), for all the equations tested. The first-order E model was the best fit-model (R^2>0.97 for all soils). This model, first proposed by Jones (1984) for N mineralization, if applied to C mineralization, can define a pool of potentially (C_0) and readily decomposable matter (C_1), the latter producing a flush of mineralization during the early stage of incubation. Saviozzi et al. (1993) have already reported better fits to the data of C mineralization of many types of organic materials for the first-order E model compared with other kinetic equations. Parameter estimates according to the first-order E model were calculated (Table 3). As can be seen, the size of the mineralization flush (C_1) depended on the type of soil used, ranging between -19.6 for soil no.4 and 9.6 for soil no. 14. The negative C_1 values could be due to an accommodation by the model of the lag in C mineralization during the initial period of incubation (Ellert and Bettany 1988). The lag-phases, calculated by the equation:

$$\text{lag-phase} = [\ln (C_o / C_o + C_1)] / k \qquad (1)$$

show values ranging between 6.2 hours for soil no.2 to 39.4 hours for soil no. 13 (Table 3). The presence of a lag-phase may be explained in terms of a difficult adaptation of the microbial community in the soil to the acidic sludge, as suggested also by the inverse relation with the rate constant (k). Indeed, the lag in C mineralization of this substrate was generally observed in soils with pH < 6.9 (Table l), with the only exception being soil no. 2. However, measurements of enzyme activities and microbial growth may be required to determine more explicitly the cause of the lag. The potentially mineralizable C (C_o) and the rate constant (k) relative to the decomposition of the organic C of the sludge also displayed variation among 14 soils (Table 3). As can be seen, C_o values varied considerably among soils, ranging from a minimum of 72.7 mg of sludge for soil no. 2 to a maximum of 342.2 mg for soil no. 14.

Table 3. Parameter estimates according to the “First-order E" model for the C-mineralization of sludge in 14 soils.

Soil	C_1 (mg)	C_o (mg)	C_o %added C	k (day^{-1})	Lag-phase (hours)
1	-13.8	267.1	32.6	0.063	20.2
2	-2.5	72.7	8.9	0.136	6.2
3	5.0	93.2	11.4	0.103	-
4	-19.6	228.2	27.8	0.098	22.0
5	-12.1	277.3	33.8	0.047	22.9
6	-8.0	146.8	17.9	0.111	12.1
7	-11.7	236.3	28.8	0.043	28.3
8	-13.7	208.3	25.4	0.072	22.6
9	-6.7	109.4	13.3	0.081	18.6
10	9.4	89.4	10.9	0.078	-
11	8.3	98.5	12.0	0.056	-
12	8.5	142.4	17.4	0.071	-
13	-7.6	90.8	11.1	0.053	39.4
14	9.6	342.2	41.7	0.019	-

For symbol definitions, see Table 2.

When expressed as percentage of added sludge C (Table 3), C_0 ranged from the 8.9% for soil no.2 to 41.7% for soil no. 14. The sludge incubated in soil no. 14 showed, despite its high C_0 value, the lowest rate of decomposition (k = 0.019), with a turnover time (l/k) of 52.6 days. On the contrary, sludge organic C was decomposed at the highest rate (k = 0.136) with a turnover time of one week in soil no. 2, even though C_0 was low. However, no significant correlation was found between k and C_0 values, indicating that the differences in the rates of sludge decomposition in the soils cannot be directly attributed to the differences in the size of the mineralizable C pool.

In Table 4 are reported the significant linear correlations between the C mineralization parameters and the soil characteristics. There is ample evidence (Jenkinson 1977) that organic materials decompose more slowly in strongly acidic soils than in neutral soils; this fact is usually attributed to a shift towards a smaller number of microbial species (DeLaune et al. 1981). Accordingly, in the present study, the high flush of C mineralization was observed in neutral or sub-alkaline soils, as confirmed by the positive correlation coefficient between C_1 and soil pH (Table 4), although the lowest rate was in soil no. 14 which had a pH of 7.4. Although previous studies have reported a more rapid C mineralization in coarsetextured soils (Hébert et al. 1991), our results indicate no relationships between sludge mineralization rate and soil texture.

Table 4. Significant correlation coefficients between the sludge C-mineralization parameters of the first-order E model and soil characteristics.

Parameters	pH	Free Fe	Total N	CEC	AEC	FDA
C_1	0.798**	-	-	-	-0.607*	-
C_0	-	0.576*	-	0.664**	0.620*	-
C_m	-	0.730**	0.603*	0.955**	0.847**	0.604*

, * Significant at P<0.05 and P<0.01, respectively. For symbol definitions, see Tables 1 and 2.

The amount of mineralized C (C_m) was found to be positively related to the total N content of soil, perhaps because when the organic C is added to soil the microorganisms need the nutrients from the soil for their growth and activity. As can be seen in Table 4, C_0 and C_m were found to be strictly correlated to the exchange capacity (CEC and AEC) and to free iron content, Mingelgrin and Prost (1989) observed that surface kinetics favoured transformations involving adsorbate organic materials, suggesting that mineralizable carbon may be the fraction of sludge C that is adsorbed most by sites of exchange on soil colloids. As expected, C_m was found to be positively related with fluorescein diacetate (FDA) hydrolytic activity, representing a measure of the total microbial activity in soil.

The effect of application loadings on the mineralization rate of sludge organic C in soil no. 7 is reported in Fig. 1. Total evolved C increased with incremental sludge addition, but reduced decomposition became apparent at the 6% rate, perhaps because of a nitrogen deficiency in the soil. This explanation is supported by the findings of Saviozzi et al. (1991), who noted an immobilization of N in soil treated with olive-oil wastewaters at 80-320 $m^3 ha^{-1}$. Aspitarte et al. (1973) reported that N supplement to soil treated with sewage sludge increased the CO_2 evolution. When the percentages of the added carbon mineralized were compared (Fig. 1), the data indicated decreasing efficiency as application rates increased. Comparing efficiency between treatment rates revealed a 10-fold decrease between the 0.37 and the 6% rate. Accordingly, in a study on the dynamics of carbon during olive-oil wastewaters decomposition, Saviozzi et al. (1990) observed decreased efficiency in the C mineralization as loading rates increased.
The results of this study demonstrate that the soil characteristics influence the extent of sludge mineralization and that the dynamics of the process is well described by the first-order E kinetic model.

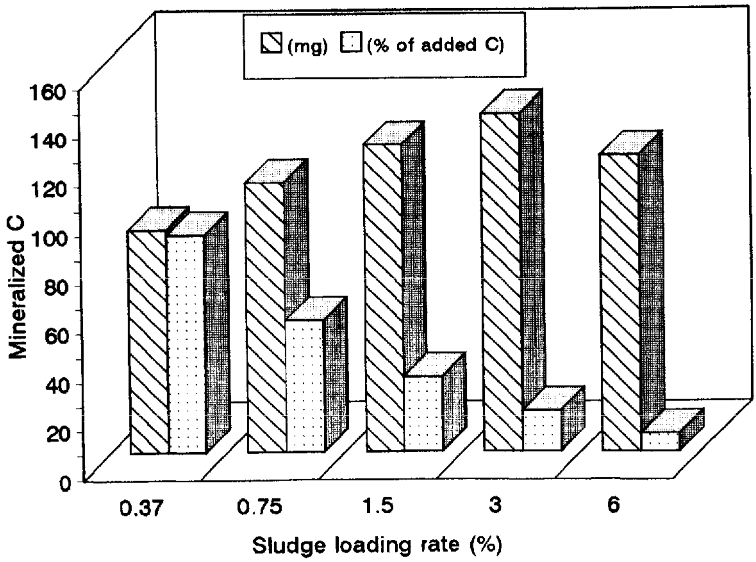

Figure 1. Cumulative amount of C mineralized from sludge in soil no.7 after 81 days of incubation.

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