J Therm Anal Calorim (2010) 99:981–986
DOI 10.1007/s10973-010-0692-1

Agricultural valorisation of de-inking paper sludge as organic amendment in different soils

Thermal study

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MEDICTA2009 Special Issue

Abstract The objective of this study is to study the influence of de-inking paper sludge (DPS) and sewage sludge (SL) mixtures addition at different rates (2, 4 and 8%) in two soils. Incubation experiments were performed during 60 days and the influence of treatments in physical soil properties was determined by soil porosity and stability of aggregates. Differential thermal analysis (DTA) of amended soils after incubation was performed. Experimental results show that amendment increased biological soil activity, soil porosity and stability of aggregates. DTA analysis shows that the first exothermic peak generally increases with the dosage of DPS:SL due to the addition of immature organic matter. Moreover, the second peak enlarges probably due to the humification process during incubation.

Keywords De-inking paper sludge · Agricultural valorisation · Thermal analysis

Introduction

Climate and inadequate land management in Mediterranean area had led to a reduction in the organic soils content [1]. This fact can cause a negative effect on the chemical, biological and physical properties of the soils. Indeed, the application of organic residues to agricultural soils is a widespread practice in Mediterranean areas [2].

On the other hand, paper pulp manufacturing generates important amount of waste materials. In recent years, an increasing proportion of recycled fibres are used in paper industries due to their important environmental and economical benefits. A ton of pulp produced from recycled paper requires 60% less energy to manufacture than a ton of bleached virgin kraft pulp [3]. However, paper recycling leads to large amounts of de-inking paper sludge (DPS) composed by cellulose fibres, removed inks, clay fillers and other chemical additives. The production of this type of waste material is very important around the world [4, 5]. For example, Spanish paper industry generated more than 200.000t of DPS in 2006.

Due to their high organic matter content, DPS could be used as amendment to improve soil fertility and biological functioning [6]. The application of DPS can markedly improve physical properties as macroaggregate stability [7] or water holding capacity [8] reducing the risk of soil erosion. Also, DPS can increase cation exchange capacity [9], decrease soil acidification and soil metal pollution [10] and improve biological activity [8]. Moreover, DPS can be use in the reintroduction of woody species as alder or aspen in the restoration and revegetation of degraded sites [11]. However, C/N ratio of DPS can be quite high (100–300) and their soil application could originate a temporary immobilization of soil nitrogen [12]. Indeed, co-composting of DPS with poultry manure and chicken broiler litter [13] or wastewater sludge [14] has shown a complete stabilization of the material. Other source of nitrogen can be sewage sludges (SL) which have been used in agricultural soils as an alternative to traditional mineral fertilisers due to their

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high contents in organic matter and essential nutrients such as nitrogen and phosphorous [2].

The objective of this study is to study the influence of DPS and SL mixtures addition at different rates (2, 4 and 8%) in two soils with different pH, texture and organic matter content. An incubation experiment was performed during 60 days and final samples were analysed by differential thermal analysis (DTA).

Experimental

Soil characterization

The two selected soils named SA and SN were sampled in Madrid Region (Spain). Soil SA is located in Valdeolmos city and SN in San Sebastián de los Reyes city. Soil SA is classified as Typic Palexeralf by USDA-SSS Soil Taxonomy and as Luvisol by FAO, while Soil SN is classified as Typic Haploxeralf by USDA-SSS Soil Taxonomy and as Luvisol by FAO.

Both samples were air-dried, crushed and sieved through a 2 mm mesh. Soil metal content was determined using a Perkin Elmer 2280 atomic absorption spectrophotometer after sample extraction by digestion with 3:1 (v/v) concentrated HCl/HNO_3 following 3051a method [15]. Initial pH and electrical conductivity (EC) were determined in a ratio soil:water of 1:2.5 (g mL^{-1}). pH was measured using a Crison micro-pH 2000 [16] and EC with a Crison 222 conductivimeter following Rhoades' method [17]. Soil total organic carbon (TOC) was determined by ashing samples at 540 °C [18]. Nitrogen content was determined by the Kjeldahl method [19] with a Büchi 435 digestor. Soil cation exchange capacity (CEC) was determined with $NH_4OAc/HOAc$ at pH 7.0 [20]. Soil cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) moved with $NH_4OAc/HOAc$ at pH 7.0 were measured using a Perkin Elmer 2280 atomic absorption spectrophotometer. $CaCO_3$ content was measured by treating samples with HCl and measuring the evolved CO_2 manometrically. Soil texture was determined following Bouyoucos methodology [21] and soil moisture characteristics according to Richards [22].

Organic waste materials characterization

De-inking paper sludge and SL wastes were air-dried, crushed and sieved through a 2 mm mesh. Total organic carbon (TOC) of wastes was determined by ashing samples at 540 °C [18]. Nitrogen content was determined by the Kjeldahl method [19]. $CaCO_3$ content was measured by treating samples with HCl and measuring the evolved CO_2 manometrically. Total content of Cr, Ni, Cu, Zn, Cd, Pb and Ca, Mg, Na and K was determined following 3051a method [15] using a Perkin Elmer 2280 atomic absorption spectrophotometer.

Treatments

Soils were amended with mixtures of DPS and SL (1:1 mass) at three different rates (2, 4 and 8%) leading to SA20, SA40 and SA80 treatments for SA soil and SN20, SN40 and SN80 treatments for SN soil.

Treatment evaluation

The biological activity of different treatments was evaluated by C mineralization in soil (cumulative CO_2 evolution), total mineralization coefficient (TMC) and humification index (HI_{60}).

The CO_2 evolved was evaluated during 60 days at a temperature of 28 ± 2 °C as follows: the decomposition rate was determined by passing CO_2 and NH_3 free air through the respiration vessels, trapping the evolving CO_2 in 50 mL of 1 M NaOH and periodic titration of the CO_2 trapped with 1 M HCl after $BaCl_2$ precipitation of carbonates. Triplicate CO_2 measurements were taken periodically. Another three vessels without soils were used as blanks for each measure of evolving CO_2 [23].

Total humic substances after incubation were extracted with a mixture of 1 M $Na_4P_2O_7$ and 0.1 M NaOH, centrifuged at 3,000 rpm and filtered. An aliquot of this extract was acidified with concentrated H_2SO_4 to pH = 1, centrifuged to separate coagulated humic acids (HA) and then, the HA were re-dissolved with 0.1 M NaOH [23]. The non-coagulated fraction with H_2SO_4 is referred to as fulvic acids ($C_{FA\,60}$). The C contents of the THS ($C_{THS\,60}$) and HA ($C_{HA\,60}$) were determined by the Walkley–Black method [24].

Total mineralization coefficient (TMC) was calculated according to [25] as follows:

$$\mathrm{TMC} = 100 * \sum \mathrm{mg\ C{-}CO_2\ Evolved/Initial\ TOC}$$

Humification index (HI) was calculated as follows:

$$\mathrm{HI} = C_{\mathrm{THS}}/\mathrm{TOC}$$

The influence of treatments in physical soil properties was determined by soil porosity, stability and size distribution of aggregates. Soil aggregate stability was determined by water stability of aggregates between 1 and 2 mm using a wet sieving method according to [26]. Also, the size distribution of aggregates was studied by sieving using a Microcomputer Screener FT-97. Soil porosity was measured by mercury intrusion porosimetry.

Finally, DTA of samples after incubation during 60 days was carried out in a thermobalance Labsys Setaram. About 80 mg of samples were heated at 15 °C min^{-1} until 850 °C in air atmosphere using a flow rate of 40 mL min^{-1}.

Table 1 Soil Properties

	SA	SN
pH	5.89	7.41
EC (1:2.5)/µS cm^{-1}, 25 °C	207	387
TOC/%	2.61	1.88
$N_{Kjeldahl}$/%	0.12	0.08
Ratio C/N	21.8	23.5
CEC/cmol$_{(+)}$ kg^{-1}	20.47	15.80
CaCO$_3$/%	–	0.31
Soil moisture at 33 kPa/%	21.9	15.9
Soil moisture at 1,500 kPa/%	8.4	6.9
Cu/mg kg^{-1}	9	9.14
Ni/mg kg^{-1}	18.6	9.48
Cd/mg kg^{-1}	0.38	0.20
Zn/mg kg^{-1}	17	36.55
Pb/mg kg^{-1}	24.8	6.26
Clay (<0.002 mm)/%	20	12
Silt (0.002–0.05 mm)/%	34	20
Sand (0.05–2 mm)/%	46	68
Texture	Loam	Sandy-loam

Table 2 De-inking paper sludge (DPS) and sewage sludges (SL) properties

	SL	DPS
pH	6.88	7.93
EC (1:2.5)/µS cm^{-1}, 25 °C	5.810	790
TOC/%	30	27.5
$N_{Kjeldahl}$/%	3.21	0.43
Ratio C/N	10	64
CEC/cmol$_{(c)}$ kg^{-1}	64.90	25.37
CaCO$_3$/%	–	24.4
Cu/mg kg^{-1}	225	367
Ni/mg kg^{-1}	30	170
Cd/mg kg^{-1}	1.6	9.8
Zn/mg kg^{-1}	785	1,918
Pb/mg kg^{-1}	114	57

Results and discussion

Main soil properties are shown in Table 1. Differences between soils are mainly related with pH, TOC and texture which are parameters that can influence in the soil respiration process and consequently, in the soil biological activity. SA was an acid soil whereas SN could be classified as neutral. TOC and N content were higher for SA than SN. The metal content of both soils did not exceed the limit values for soil metal concentration fixed by European [27] and Spanish regulations [28].

Table 2 summarizes main properties of DPS and SL used in this study. TOC was similar for two wastes. Main differences are related to C/N ratio, EC and CaCO$_3$ content. DPS shows elevated C/N ratio due to their lower N content whereas the high EC of SL could produced soil salinization. For this reason, the mixture of both sludges is necessary for their agricultural application (Table 3).

Table 3 summarizes the effect of DPS:SL addition in EC, pH, TOC, $N_{Kjeldahl}$ and C/N of soils. The increase of the dosage logically produced an increment on the TOC and $N_{Kjeldahl}$ of soils. C/N ratio was stabilized between 17 and 20 which are recommendable values to soils. pH evolution is different according to soil initial pH. In the case of SN, pH was buffered according to Rato Nunes et al. [12] that observed this tendency in soils with high initial pH. On the other hand, pH of SA increased 0.7 units for the highest dosage due to the CaCO$_3$ added with the DPS:SL mixture. Therefore, this amendment could be a liming agent for acid soils.

Experimental results obtained during incubation process of amended soils show that all treatments presented the same mineralization pattern which was satisfactorily described (r: 0.965–0,997) by means of a power model CO$_2$–C $= a \cdot t^b$ [23] (Table 4; Fig. 1). The initial mineralization rate ($a \cdot b$; $t = 1$) increased with the treatments for the two soils due to the increment of supplied TOC. The percentage of CO$_2$ evolved for highest dosage was higher

Table 3 Main properties of the different treatments and mixture DPS-SL

	EC (1:2.5)/µS cm^{-1} (25 °C)	pH	TOC/%	$N_{Kjeldahl}$/%	Ratio C/N
DPS-SL (1:1)	2,900	7.5	29.15	1.26	23
SN	387	7.4	1.88	0.08	23
SN20	515	7.4	2.30	0.12	19
SN40	642	7.3	2.75	0.16	17
SN80	1,005	7.3	3.51	0.2	18
SA	207	5.9	2.61	0.12	22
SA20	378	6.3	3.12	0.17	18
SA40	666	6.5	3.66	0.20	18
SA80	956	6.6	4.75	0.24	20

Table 4 Parameter estimates for cumulative CO_2–C evolved (mg C kg^{-1} dry mass) for the different treatments

	$C = a \cdot t^{b}$	r	$a \cdot b$ (t = 1)/mg C kg^{-1} day^{-1}	Mineralization rate
SN	$C = 72.41 \cdot t^{0.181}$	0.997	13.11	$dC/dt = 13.11 \cdot t^{-0.819}$
SN20	$C = 141.82 \cdot t^{0.175}$	0.993	24.82	$dC/dt = 24.82 \cdot t^{-0.825}$
SN40	$C = 170.38 \cdot t^{0.156}$	0.977	26.58	$dC/dt = 26.58 \cdot t^{-0.844}$
SN80	$C = 186.82 \cdot t^{0.276}$	0.980	51.56	$dC/dt = 51.56 \cdot t^{-0.724}$
SA	$C = 12.80 \cdot t^{0.525}$	0.971	6.72	$dC/dt = 6.72 \cdot t^{-0.475}$
SA20	$C = 31.80 \cdot t^{0.470}$	0.965	14.95	$dC/dt = 14.95 \cdot t^{-0.530}$
SA40	$C = 64.19 \cdot t^{0.493}$	0.975	31.65	$dC/dt = 31.65 \cdot t^{-0.507}$
SA80	$C = 184.41 \cdot t^{0.323}$	0.992	59.56	$dC/dt = 59.56 \cdot t^{-0.677}$

for SA than for SN (Fig. 2). This percentage was in the same range that data obtained for other authors in a soil amended by similar rate of manure [29]. This fact is according to increment in the TMC (Table 5). HI_{60} slightly decreased and $C_{FA\ 60}$ increased with the dosage. These results indicate that, although the mineralization increased, the HI_{60} decreased due to the addition of increasing amounts of less evolutionated organic matter from DPS:SL mixtures. Indeed, DPS:SL organic matter humification during incubation tended to promote the formation of FA substances and a weak transformation of more resistant HA and non-extractable substances, principally consisting of lignin from sawdust and other resistant compounds with a high molecular size found in the residues [23].

The addition of the amendments increased the water stability of soil aggregates (Table 6) and the aggregate size (Fig. 2) due to the addition of organic matter according to results obtained by other authors [30]. Soils treated with the high rates of DPS:SL presented the higher occurrence of soil aggregates longer than 8 mm. This increment of stability could be also related with the addition of stable organic compounds as humic-like materials and cellulose and with the higher biological activity [31]. These results indicated that addition of organic materials plays an

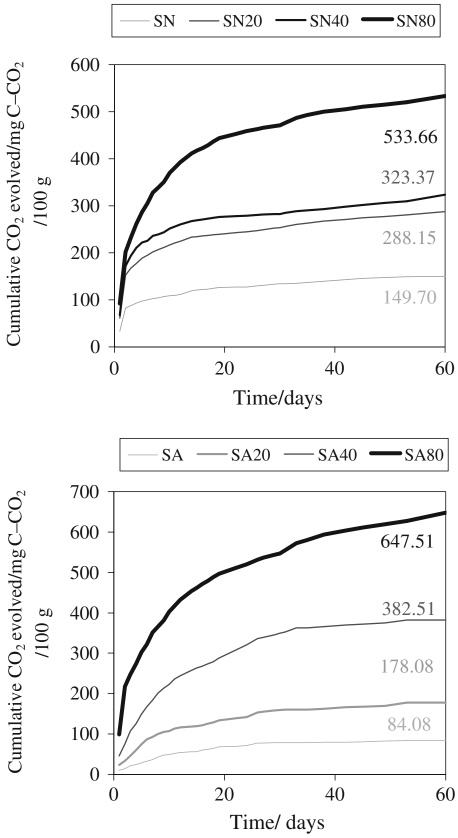

Fig. 1 Cumulative curve of CO_2 evolved during the incubation experiments

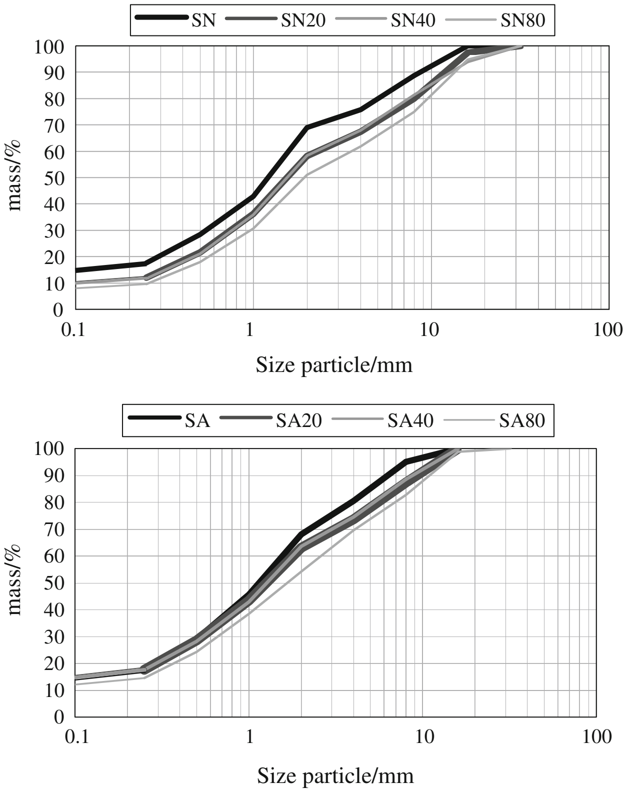

Fig. 2 Size distribution of soil aggregates after incubation experiments

Table 5 Total mineralization coefficient (TMC) and organic matter transformation after incubation after 60 days ($_{60}$)

	TOC$_{60}$/%	TMC/%	C$_{THS\ 60}$/%	C$_{HA\ 60}$/%	C$_{FA\ 60}$/%	HI$_{60}$
SN	1.6	7.9	0.37	0.13	0.24	0.23
SN20	2.0	12.5	0.44	0.15	0.29	0.22
SN40	2.7	11.7	0.50	0.17	0.33	0.19
SN80	3.3	15.2	0.65	0.23	0.42	0.19
SA	2.6	3.1	0.77	0.50	0.27	0.30
SA20	2.8	5.3	0.79	0.55	0.24	0.28
SA40	3.0	9.8	0.82	0.53	0.29	0.27
SA80	4.7	12.5	0.98	0.43	0.55	0.21

Table 6 Water stability of soil aggregates and soil porosity (%)

	Ag$_{estables}$ H_2O/%	Hg total porosity/%
SN	34.04	33.46
SN20	34.99	38.51
SN40	36.65	43.89
SN80	44.89	42.62
SA	37.54	41.62
SA20	36.91	42.75
SA40	42.34	47.51
SA80	69.37	52.44

important role to prevent soil physical degradation by soil crust formation and erosion [30].

Soil porosity increased more than 5% for the highest rates (Table 6). These results were similar to that obtained with compost [31] but better than obtained with olive-mill wastewater [32]. This fact have a positive effect over soil aeration which is related with the microbial activity and growth yield according to different authors [31, 33] that have demonstrated as organic matter improves soil structure, infiltration rate, aggregate stability to raindrop impact and water holding capacity of the soil reducing soil loss and runoff.

Previous studies have showed that thermal analysis is an interesting tool to follow the evolution state of the organic matter [34, 35]. Figure 3 shows DTA of amended soils in air atmosphere. The oxidation of organic matter is produced between 250 and 550 °C and two main areas could be distinguished. A comparative study of thermal behaviour of samples reveals that generally, the increment of DPS:SL dosage produces an increase in the intensity of the first exothermic peak due to the addition of immature organic matter. In addition, the second peak enlarges and moves to highest temperatures with the increment of DPS:SL dosage, especially with amended soil SA according to the increment in C$_{THS}$ values.

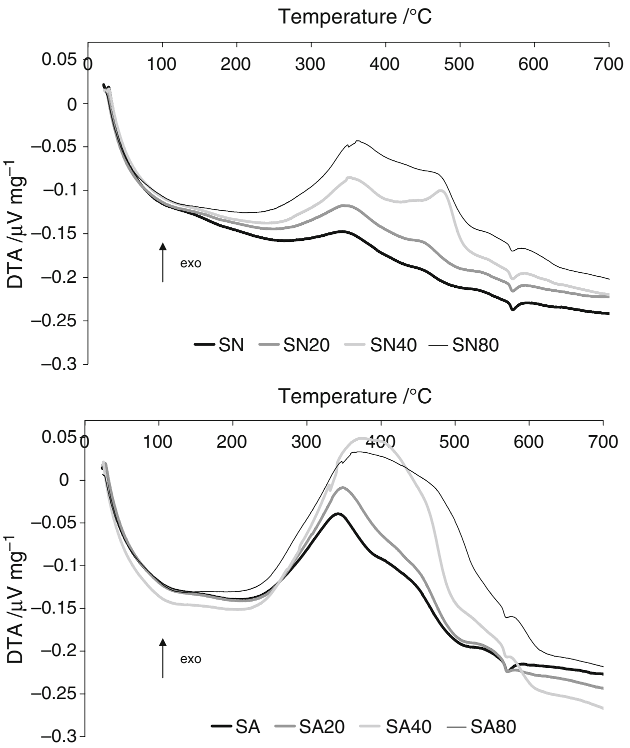

Fig. 3 DTA of amended soils after incubation experiments

Conclusions

(1) Addition of DPS:SL (1:1 in mass) increases the biological activity of soils as shown the CO_2 evolved and the total humified substances content. Moreover, the highest dosages leads to lowest humification index due to the addition of immature organic matter from DPS:SL.

(2) Addition of DPS:SL improved the physical soil conditions as shown the increment of water stability of soil aggregates and soil porosity.

(3) Differential thermal analysis is an interesting tool to evaluate the organic matter evolution of amended soils during incubation process. Two peaks between 250 and 550 °C could be observed due to oxidation of organic matter. The increment of the dosage increased the first exothermic peak due to the addition of immature organic matter from DPS:SL. In addition, the second peak enlarges and moves to highest temperatures with the increment of DPS:SL dosage according to the increment in C$_{THS}$ values.

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