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CO_2 Emission and Change in the Fertility Parameters of a Calcareous Soil Following Annual Applications of Deinking Paper Sludge (The Case of Tunisia)

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Abstract: The use of deinking paper sludge (DPS) as a fertilizer instead of sending it to landfill could play a role in reducing greenhouse gases and improving soil properties. The objectives of this study were (1) to evaluate the changes in the physical (permeability and structural stability), chemical (particularly soil pH), and biological (microbial metabolic quotient (qCO_2), microbial biomass soil CO_2 emissions) of a calcareous agricultural soil following two successive annual amendments with three treatments (0, 30, and 60 Mg DPS ha^{-1}—control, DPS30, and DPS60, respectively); and (2) to determine whether the addition of N-fertilizer to these treatments (controlF, DPS30F, and DPS60F, respectively) causes changes to soil fertility. The DPS application increased soil organic matter (+0.80%: DPS60 vs. control; and +0.35%: controlF vs. DPS60F), available phosphorus (+23.14 mg kg^{-1}: DPS60 vs. control; and +14.34 mg kg^{-1}: DPS60F vs. controlF), potassium (+0.6 g kg^{-1}: controlF vs. DPS30F), and calcium (+0.28 g kg^{-1}: DPS60 vs. control). The 60 Mg DPS ha^{-1} rate improved permeability and structural stability, regardless of the presence or absence of N-fertilizer. On the other hand, the 60 Mg DPS ha^{-1} rate without N-fertilizer lead to a decrease in total mineralization rate and qCO_2, thereby indicating a reduction in CO_2 emissions. The rate of 60 Mg ha^{-1} DPS could be effectively used to enhance the permeability and stability (soil restoration) and mitigate CO_2 emissions, whereas the 30 Mg ha^{-1} rate could be used as fertilizer to improve the fertility of calcareous soils.

Keywords: deinking paper sludge; permeability; stability index; soil fertility; biomass; CO_2 emissions; fluvisols

1. Introduction

The intensification of agricultural activities has led to serious environmental problems and one of the main issues is related to the maintenance of soil fertility at different levels [1]. Generally, the use of organic amendments (OA) instead of chemical ones improves soil fertility by slowly releasing nutrients to support soil quality and productivity [2]. The incorporation of OA also leads to an increase in carbon dioxide (CO_2) emissions from the soil as a result of rapid soil organic matter decomposition [3].

In recent years, biosolids were proposed as a novel solution to mitigate greenhouse gases (GHGs), especially in agriculture (which is responsible for 70% of N_2O emissions) and forestry [4–6]. N_2O is a part of the global nitrogen cycle and is bound to other forms of N (organic N, ammonia, nitrate). In the soil, N_2O is generated by the microbial transformation of organic and inorganic N and is enhanced under wet conditions [7]. Nunes et al. [8] showed that the addition of deinking sludge as an organic amendment with a very high C/N ratio in alkaline soil can cause N immobilization and reduce yield. Rashid et al. [9] also showed that adding deinking paper sludge (DPS) on acidic soil for one-year results in total N immobilization. In this context, the use of pre-existing agricultural, forestry, or pulp waste (biosolids) is more interesting to mitigate climate change than using chemical fertilizers [10]. Moreover, the use of biosolids such as DPS or pulp paper sludge as soil amendments instead of landfilling them considerably reduces GHG emissions. DPSs, however, contain organic matter (OM) that is mainly lignocellulosic (cellulose, hemicelluloses, and lignin) and are characterized by neutral to basic pH, high carbon and calcium contents and low nutrient (N, P, K) levels [11,12] compared to other sources of organic matter and can be used as a soil amendment or as a fertilizer residual (RFM). Based on the study by Beauchamp et al. [13], DPSs contain relatively low levels of metals, and the risk of contamination, if any, is organic rather than metallic. However, the composition of DPS varies from one industry to another depending on the pulping and deinking process [12], hence the importance of redoing the characterization and pre-treatment steps for each industry. The purpose of detailing the deinking process is to identify the sources of contamination and the composition of the deinking sludge. The deinking process is carried out in several stages [13]: The first stage is pulping, during which the wastepaper is suspended, and ink particles are removed due to the addition of certain chemicals such as fatty acids and soda. The second stage is flotation, during which the fibers are recovered following a separation of the various constituents by injecting air bubbles into the flotation cell. The third stage is washing, during which there is a dispersion of ink particles made hydrophilic by the surfactants that contain clay. In the fourth step, clarification, a flocculation polymer agglomerates the dispersed ink particles. The final step is the removal of excess water under mechanical pressure to facilitate handling. The sludge comes mainly from the flotation, washing, and clarification stages. DPS accounts for about 95% of the volume of discharges from paper recycling plants [14]. Characterization of the DPS and understanding the deinking process is a key step in determining whether trace elements and contaminant levels exceed the limits set for RFM. DPSs contain fatty and resinous acids from the wood or chemicals added during the deinking process and may contain polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds such as dioxins from the chlorine products used in pulp bleaching. Hébert et al. [12] established limits for these contaminants and DPSs can be applied in practice depending on their composition.

DPS has a high carbon (C)-to-nitrogen (N) ratio (C: N = 70–150) [9,11], and N supplement was required to avoid N immobilization [15,16]. According to the Kyoto protocol, the reduction of GHGs through waste management and the use of residual fertilizing matter (RFM) can help to mitigate climate change [12,14].

Tian et al. [17] describe that the use of de-inking biosolids significantly increases carbon sequestration in agricultural soils decreasing CO_2 emissions. Indeed, the concentration of soil organic carbon increases with the addition of biosolids, and several factors come into play: temperature, soil moisture, and initial composition of the introduced material [18–21]. For example, the use of lignocellulosic products in agricultural soils can constitute new carbon reservoirs other than forests references added [17,20]. To better understand the role of lignocellulosic material in carbon sequestration, it is essential to understand the processes of mineralization and humification. The fate of soil organic matter depends on its composition; the higher the lignin content, the slower it decomposes [22–24]. According to the theory of Waksman and Hutchings [25], humic substances, mainly humic acids, are derived from lignin. Some lignin-rich wood by-products such as de-inking biosolids are said to be recalcitrant and their residence time in the soil is important with a slow decomposition rate. The use of this material in the soil would have benefits comparable to those of no-till, which would promote carbon sequestration in the soil [16–18]. This use of materials of lignocellulosic origin seems interesting and deserves to be further developed in new research work.

Carbon storage in the soil depends on intrinsic soil factors such as pH, mineralogy, microbiology, aggregation, microclimate [25], and extrinsic factors or quality of organic matter [26]. Organic matter forms, together with soil minerals, a clay-humic complex, which confers stability and protection to the soil organic matter.

In Canada, DPS has been used as an RFM for crop fertilization and to increase yield [14] in species such as alder and aspen [15], as well as for soil restoration and land management [17,18] because of the various nutrients that DPS contains [9,18]. For example, in Quebec where the norms are considered to be the most strict, DPS was used according to the regulations of the *Bureau de normalisation du Québec* (BNQ), BNQ 0419-090, and BNQ 0419-200 which covers liming residues [11,12].

In developing countries, especially those in North Africa, waste management is a major problem, as is the deterioration of soil properties, while organic matter (OM) sources are limited. In Tunisia, for example, soils have very low OM content (less than 2%) so OM is required to improve soil fertility [21]. DPS could be used as an OM source for the restoration of calcareous agricultural soils [22]. Agricultural areas in the semi-arid regions have silty clay soils, which are characterized by high $CaCO_3$ and low organic matter content [3,21]. After COP21 (Paris Climate Conference), Tunisia's reduction target was estimated to be 40% of total emissions, whereas the recycling rate for paper residues such as DPS is around 0%; this lack of recycling represents a big loss of organic matter (OM) [11]. However, DPS can be used as RFM.

The pulp industry generates a large amount of lignocellulosic waste that needs to be managed [11,23]. The use of DPS as an amendment may improve the biological, physical, and chemical properties of calcareous soils. However, most studies have focused on the effects of DPS (an alkaline agent) on the chemical and biological properties of acidic or slightly acidic soils. The work of Nunes et al. [8] on secondary sludge showed that paper sludge is a good potential source of OM, nitrogen (N), phosphorus (P), and potassium (K), while it is a potential liming agent for acidic soils, especially when an appropriate fertilizer is also used. The absence of studies evaluating CO_2 emissions and the effects of DPS as a source of OM for low fertility calcareous soils in Tunisia led us to propose the present line of research. Much research is needed to provide data for determining the effects of DPS on soil properties under such conditions.

The objectives of this research were (1) to study the effects of increasing application rates of DPS (0, 30, and 60 Mg ha^{-1}) on the change in the physical (permeability and structural stability), chemical (particularly soil pH), biological (microbial biomass and microbial metabolic quotient—qCO_2) and CO_2-C emissions of a calcareous soil following two successive annual applications and (2) to determine whether the addition of N fertilizer induces changes in these agricultural parameters.

2. Materials and Methods

2.1. Experimental Design

The study was conducted on a representative Mediterranean agricultural soil in Tunisia: a silty clay Calcaric Fluvisol (FLc) [26]. The experiment was carried out over two years in an experimental field (819 m^2) belonging to the National Agronomic Institute of Tunisia (INAT) located in the Mornag region of Ben Arous Governorate in northern Tunisia (36°41'33.09" N, 10°15'32.89" E). The soil used is calcareous, with little evolution of alluvial input, a silty-clayey texture, 1.08% OM and an apparent density of 1.43. The climate is of the upper semi-arid type, characterized by an irregular distribution of rainfall throughout the year, with an annual average of 500 mm. The average annual temperature is 18 °C [26]. The crop was durum wheat (Karim variety) amended with sewage sludge in November during two growing seasons (2013–2014 and 2014–2015) and then plowed and sown for harvesting in June 2014 and 2015. The present work focuses only on the effects on soil properties and CO_2 emissions. The DPS used was obtained from pulp and paper of the Tunisie Ouate paper company (Enfidha, Sousse, Tunisia). Three different doses of dry DPS (0, 30, and 60 Mg ha^{-1}) were used either with or without a 150-kg ha^{-1} rate of N fertilizer applied as ammonium nitrate (NH_4NO_3) (34-0-0). Six treatments were used: control, DPS at 30 Mg ha^{-1} (DPS30), DPS at 60 Mg ha^{-1} (DPS60), control with fertilizer (controlF), DPS at 30 Mg ha^{-1} with fertilizer (DPS30F), and DPS at 60 Mg ha^{-1} with fertilizer (DPS60F). The application of raw DPS rates was followed by shallow tillage to incorporate the sludge into the soil. The study was conducted using four completely randomized blocks; each block was composed of six plots and each plot had a surface area of 4 m^2 and was 2.5 m distance separated from adjacent plots. Soil samples were collected at a 0–20-cm depth in June 2015 after the wheat harvest, air-dried, sieved, and ground (2 mm) for all the analyses except the microbial content (for which fresh soil samples were used). For physical analyses, the preparation of soil samples included air drying, crumbling of clods, and 2 mm sieving. The reduction of aggregates into fragments using a mortar to obtain fine soil with a diameter of 2 mm or less was used for chemical analyses. For the four replicates of treatment, each treatment was mixed into a composite sample for the analyses.

2.2. Characterization of DPS

The DPS amendment was generated at the deinking station of a Tunisian paper plant (Enfidha, Tunisia). A sampling of the DPS for analyses was carried out in accordance with the sampling protocol for residual materials used as the fertilizer of the accredited *Centre d'expertise en analyse environnementale du Québec* (CEAEQ) and following the *Bureau de normalisation du Québec* (BNQ) standard for calcium (Ca) and magnesium (Mg) amendments (BNQ 0419-090), which covers liming residues, deinking residues, and composts. Most of these analyses were previously reported by Marouani et al. [11]. The moisture content of the DPS was calculated from weight loss after oven-drying to a constant weight at 105 °C and OM content was determined by loss on ignition at 450 °C for 4 h. The Na, Ca, and Mg contents were determined after dry-ashing at 500 °C for 3 h [27]. Total P was extracted using wet acid digestion according to the method of Parkinson and Allen [27]. Concentrations of P were measured in digests or extracts by the colorimetric blue method [28]. Total trace elements were determined by inductively coupled plasma (ICP) spectrometry following acid digestion [29,30].

Fourier-transform infrared (FTIR) spectroscopy was used to identify the functional groups present in the DPS. The FTIR was conducted using a Shimadzu IRTracer-100 spectrometer (Kyoto, Japan) in diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) mode at the Biomaterials Laboratory at the University of Quebec in Abitibi-Témiscamingue [11]. The DRIFTS method has been widely used in soil quantitative analysis and is especially useful for OM analysis [31]. For each sample, spectra were recorded by collecting 128 scans in the range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. For accurate analysis, the spectra were baseline-corrected and normalized in absorbance mode [11].

2.3. Soil Analyses

2.3.1. Soil Physical and Chemical Analyses

All chemical and physical analyses were performed according to Pauwels et al., [29]. The soil pH values were measured at 25 °C in a sample suspended in distilled water (1:2.5; w: w), using a Consort C860 multi-parameter analyzer (Global Test, Turnhout, Belgium). Total organic C was determined using the Walkley and Black method based on potassium dichromate oxidation. Total N was determined using the Kjeldahl method [30]. Available P was extracted using the Olsen method [30] and measured with the ascorbic acid–molybdate reaction [32]. The determination of the content of exchangeable K, Ca, and Na in soil was based on the principle of extracting the exchangeable bases with a 1 N solution of ammonium acetate ($C_2H_7NO_2$). The extract was passed to the flame photometer to measure K, Ca, and Na concentrations [33]. The determination of the percentage of clays and silts was based on the principle of sedimentation. The proportion of sand was determined by dry sifting [30]. Structural stability was assessed according to Hénin [34]. To determine structural stability, Henin [34] proposed two complementary tests. The principle adopted consists of subjecting a soil sample to the degrading action of water under specific operating conditions. The first test, known as the aggregate analysis test, provides an index of structural instability "Is" which essentially considers the effects of organic matter.

It varies from 0.1 for soils rich in organic matter, which are very stable, to over 100 for very unstable sodium soils. The second test, carried out on another part of the sample, consists of measuring the filtration rate "K". The important disintegration of the aggregates during the water flow reduces the permeability. This test considers the action of the cations, calcium, and sodium. "K" varies from zero for low-filtration soils to 60 for highly permeable soils [34].

Henin and Monnier (1956) estimated that by applying standard "aggregate" analyses in water to samples pretreated with alcohol, either benzene or untreated, the structural stability of several samples can be compared. After agitation in water, the fraction >0.2 mm was collected by sieving, and the fraction <0.02 mm determined by sedimentation. The permeability of soil noted K, expresses the power of soil to allow the flow of any fluid. It depends on the structure and texture of the soil. Soil permeability was measured by Darcy's method.

Darcy's method was used to determine the amount of water that percolates through the soil during a time *t*. The soil was introduced into a Henin tube. A constant load of water was applied to the surface of the tube. After one hour, the volume of water percolating through the tube, the height of the soil and the height of the water at the tube were measured. Permeability was determined in cm/hour according to Darcy's law [34].

$$K\,(\mathrm{cm/h}) = \frac{V \times L}{H \times S}$$

where, V is the volume of water percolated from the tube in cm after one hour; H is: the water load in cm; L is the height of the sample in cm and S is the cross-section of the tube in cm^2.

2.3.2. Soil Biological Analysis

Determination of Microbial Biomass

The soil biological parameters described in this study were determined using fresh soil samples that had been sieved to 5 mm and stored for three days at 4 °C. The results are presented on a soil dry-weight basis. The fumigation–extraction method was applied to estimate the microbial biomass C (MBC) and N (MBN) content of the different soil treatments. Microbial biomass determination consisted of cell lysis with chloroform ($CHCl_3$) and the subsequent release (potassium sulfate (K_2SO_4)–extractable) of C and N from microorganisms without other OM in the soil being solubilized. Microbial biomass was determined by the difference in values between the fumigated and the non- fumigated soil samples [35–38]. The amount of C was determined by the potassium dichromate oxidation method [35]. The two extractable C (C_{ext}) of microbial origin were calculated on a 10-mL test sample of K_2SO_4 filtrate from fumigated and non-fumigated samples.

The amount of extractable C (C_{ext}) was converted to microbial biomass (expressed in mg C kg^{-1} soil) using a proportionality coefficient (K_{Cext}) of 0.35; according to [37]. The MBC was calculated by dividing the C extraction of microbial biomass by K_{Cext}, as follows:

$$MBC = C_{ext}/K_{Cext} \tag{1}$$

Nitrogen in the microbial biomass was determined using a 10-mL test sample of the K_2SO_4 filtrate from fumigated and non-fumigated samples. After that, total N was quantified according to the Kjeldahl digestion method. The calculation of MBN was performed according to Equation (2) [33]:

$$MBN = [NF - NNF]/k_{EN} \tag{2}$$

where NF is total N in the K_2SO_4 filtrate from fumigated soil; NNF is total N in the K_2SO_4 filtrate from non-fumigated soil, and k_{EN} is the extraction efficiency coefficient for microbial organic N and inorganic N from the soil. A value of 0.68 was reported for k_{EN} by [37].

Carbon Mineralization of DPS-Amended Soil

At the end of the two agricultural years of wheat amended to DPS, the surface soil (0–20 cm) was taken for mineralization tests in the laboratory. Soil incubations were carried out under controlled conditions at humidity close to field capacity and a constant temperature (30 °C) in the dark for 95 days so that the soil respiration of the DPS-amended soil could be quantified and compared to that of the control. CO_2 emissions during the incubation period were trapped in 1 mol L^{-1} NaOH and the excess NaOH was titrated with 0.1 mol L^{-1} H_2SO_4 after the addition of 2 mL of $BaCl_2$ [38]. The CO_2-C released by mineralization was expressed as mg CO_2 kg soil^{-1} using Equation (3) [38]:

$$CO_2\text{-C emission rate} = [(T - V) - (T - B)\ (NE/W)\ d] \tag{3}$$

where T is the total volume (mL) of NaOH at the start of incubation; V is the volume (mL) of H_2SO_4 required to titrate the NaOH in treatments; B = volume of H_2SO_4 used to titrate NaOH in blanks; N is the normality of the H_2SO_4 to titrate NaOH; E (E = 6) is the equivalent weight of carbon; W is the soil weight and d is the days between every two sampling times. To study the kinetics of organic matter mineralization, the exponential model form was used [36]:

$$C_t = C_0\ (1 - e^{-(kt)}) \tag{4}$$

where C_t is cumulative carbon mineralized at time t expressed in mg C kg^{-1}; C_0 is mineralizable carbon potential expressed in mg C kg^{-1}; k is the mineralization constant expressed in day^{-1} and t is incubation time expressed in days. The data was also tested using Curve Expert software and the kinetics parameters were calculated.

2.3.3. Microbial Metabolic Quotient

The qCO_2, which is used as an indicator of the ecosystem and microbial stresses [39], was calculated for each DPS dose according to the equation [39]:

$$qCO_2 = SR/MBC \tag{5}$$

where SR is soil respiration in mg CO_2-C kg soil^{-1} evolved over the 95 days of incubation and MBC is the microbial biomass C expressed in milligrams of C per kilogram of dry matter.

2.4. Statistical Analyses

The soil chemical parameters (pH, OM, total N, available P, K, Na, and Ca), trace elements and soil physical parameters (permeability and structural stability) were subjected to variance analysis (ANOVA) using a mixed model approach. A two-way ANOVA was applied to determine the effect of the type of treatment (control, DPS30, DPS60, controlF, DPS30F, and DPS60F) and fertilization (a 150-kg ha^{-1} rate of N fertilizer applied as ammonium nitrate (NH_4NO_3)), and their interactions, on the chemical and physical properties of the soil. Statistical analyses were performed using the SAS statistical package, version 9.4 [40]. The statistical significance was determined using *F*-tests at $p < 0.05$. The mean and the coefficient of variation for each parameter were calculated for each treatment. Least significant differences (LSD) were used to test significant statistical differences in soil chemical variables between the six treatments.

3. Results

3.1. Characterization of DPS

The DPS has an alkaline pH and contains large quantities of nutrients, especially C, P, Ca, and Mg which are derived from wood chips (rich in nutrients) and/or products used during the pulping process or pulp bleaching, whereas the C:N was high, showing the importance of N supply in maintaining soil fertility (Table 1). Using FTIR analysis, Marouani et al. [11] observed peaks at 3350, 2920, 2850, 1740, 1650, 1460, 1158, and 1030 cm^{-1}, indicating that the DPS is rich in aromatic, phenolic, aliphatic, and polysaccharide structures. Inorganic bands such as quartz (800–770 cm^{-1}), kaolinite and smectite (3620, 3650, and 3690 cm^{-1}), and carbonate (875 and 2520 cm^{-1}) are also present in the DPS (Figure 1). According to Table 6 and the results of Marouani et al. [11], which compared the trace elements content of the same DPS used in this study with BNQ 0419-090 norms, there is no risk of soil contamination by trace elements, pathogens or organic pollutants and the DPS can be used as RFM [11,12].

Table 1. Physical and chemical characteristics of the soil in the plots prior to the amendment and the deinking paper sludge (DPS) used for this study.

	DPS	FLc Soil
Texture	-	Clayey silt
Sand (%)	-	6.2
Clay (%)	-	51.6
Loam (%)	-	42.2
pH-water	7.9	7.8
EC (µS cm^{-1})	204.3	175.6
OM (%)	60.0	1.1
TOC (%)	31.5	0.6
Total nitrogen (%)	0.29	0.16
C:N	108.6	3.8
Potassium (mg kg^{-1})	400.9	1.4
Calcium (g kg^{-1})	270.0	5.11
Magnesium (g kg^{-1})	4.5	-
Total phosphorus (mg kg^{-1})	350.2	-
Available phosphorus (mg kg^{-1})	56.8	18.7
C:P	900.0	-
Ca:Mg	60.1	
θcc	-	26.1
Total $CaCO_3$	-	25.5

Abbreviations: FLc, Calcaric Fluvisols; EC, electrical conductivity; OM, organic matter; TOC, total organic carbon; "C:N", carbon-to-nitrogen ratio; "C:P", carbon-to-phosphorus ratio; "Ca:Mg", calcium-to-magnesium ratio, θcc, Moisture content at field capacity; $CaCO_3$, calcium carbonate.

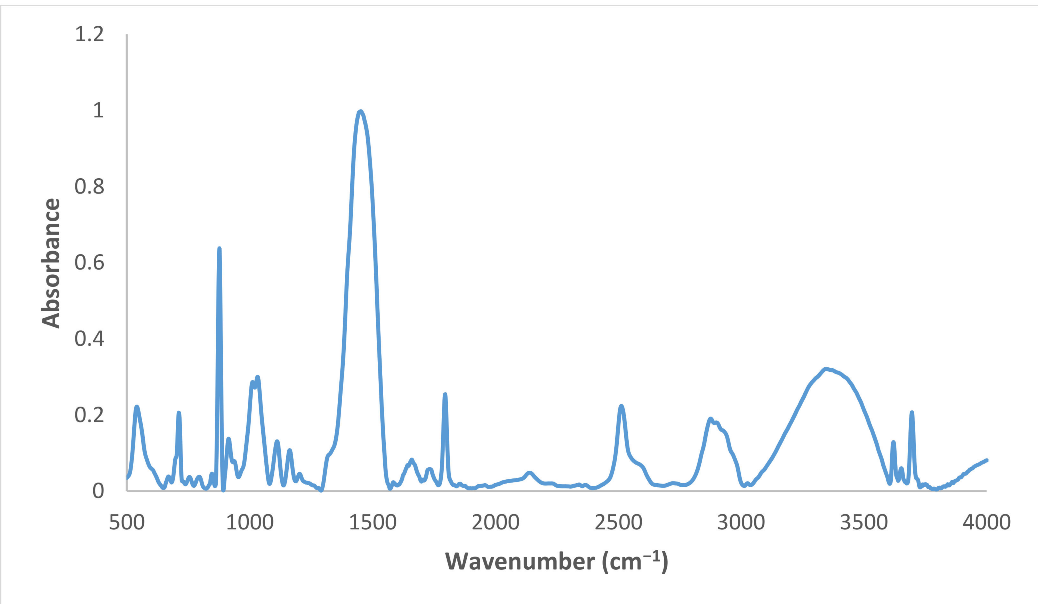

Figure 1. Fourier-transform infrared spectra of the deinking paper sludge (DPS).

3.2. Effect of DPS Application on Soil Chemical Properties

3.2.1. Effect on Soil pH

The DPS application rate and the presence of N fertilizer were closely related to the change in soil pH (*F*-value = 3.58; $p < 0.05$) (Table 2). After two successive annual DPS amendments, the pH of the control soil increased from 7.78 to 7.92 and the pH increased with the increase in DPS dosage rate, from 7.78 to 8.01 for unfertilized soil and from 7.70 to 7.90 for fertilized soil (Table 2). The addition of different rates (30 and 60 Mg ha^{-1}) of DPS to the soil had a significant effect ($p < 0.05$) on soil pH, regardless of the presence or absence of ammonium nitrate fertilizer.

Table 2. Means and standard deviations (italicized and in parentheses) for the analysis of variance of soil chemical properties as related to treatment with deinking paper sludge (DPS) at 0, 30, and 60 Mg ha^{-1} after two annual DPS applications (with ammonium nitrate fertilizer F or without).

Treatments	pH	EC (µS cm^{-1})	OM (%)	Total N (g kg^{-1})	P (mg kg^{-1})	K^+ (g kg^{-1})	Ca^{2+} (g kg^{-1})	Na^+ (mg kg^{-1})
Control	7.8 ^{bc} *(0.1)*	204.3 ^{d} *(7.9)*	1.1 ^{c} *(0.2)*	1.6 ^{ab} *(0.1)*	40.0 ^{d} *(2.7)*	1.3 ^{b} *(0.01)*	5.1 ^{d} *(0.1)*	620.0 ^{a} *(20)*
DPS30	7.9 ^{ab} *(0.1)*	209.5 ^{d} *(2.7)*	1.5 ^{b} *(0.2)*	1.4 ^{b} *(0.1)*	51.7 ^{bc} *(3.4)*	1.3 ^{b} *(0.01)*	5.3 ^{b} *(0.02)*	633.3 ^{a} *(30.6)*
DPS60	8.0 ^{a} *(0.1)*	217.3 ^{d} *(3.6)*	1.9 ^{a} *(0.2)*	1.2 ^{c} *(0.1)*	63.1 ^{a} *(10.3)*	1.3 ^{b} *(0.01)*	5.4 ^{a} *(0.03)*	640.0 ^{a} *(34.6)*
ControlF	7.7 ^{c} *(0.2)*	247.8 ^{b} *(4.3)*	1.1 ^{c} *(0.1)*	1.7 ^{a} *(0.1)*	40.7 ^{cd} *(6.5)*	1.3 ^{b} *(0.04)*	5.2 ^{d} *(0.03)*	213.3 ^{c} *(11.6)*
DPS30F	7.9 ^{ab} *(0.0)*	260.3 ^{a} *(29.7)*	1.3 ^{bc} *(0.1)*	1.5 ^{ab} *(0.0)*	49.9 ^{bc} *(3.3)*	1.4 ^{a} *(0.01)*	5.3 ^{b} *(0.06)*	293.3 ^{b} *(3.1)*
DPS60F	7.9 ^{ab} *(0.0)*	231.7 ^{c} *(4.0)*	1.5 ^{b} *(0.1)*	1.5 ^{ab} *(0.0)*	55.1 ^{ab} *(1.3)*	1.4 ^{a} *(0.01)*	5.2 ^{c} *(0.02)*	320.0 ^{b} *(34.6)*

For each sampling date, means ($n = 4$) labeled with different letters are significantly different according to Tukey's test at $p < 0.05$. Bars show standard errors (±SE) of means. EC, electrical conductivity; OM, organic matter; N, nitrogen; P, phosphorus; K^+, potassium ion; Ca^{2+}, calcium ion; Na^+, sodium ion. Treatments: control, no DPS; DPS30, DPS at 30 Mg ha^{-1}; DPS60, DPS at 60 Mg ha^{-1}; controlF, control with fertilizer; DPS30F, DPS30 with fertilizer; DPS60F, DPS60 with fertilizer.

3.2.2. Effect on Soil Electrical Conductivity

No significant effect on soil electrical conductivity (EC) was noted in comparison with the control following two successive annual amendments with different doses of DPS (Table 2). However, when N fertilizer was added, EC increased significantly ($p < 0.001$) in all treatments in comparison with the control.

3.2.3. Effect on Soil OM Content

Soil amended with DPS (OM = 60%) had significantly greater ($p < 0.0001$) OM content in the 0–20-cm layer. There was a significant difference between the DPS doses (Table 2). The OM content increased (+0.80%) after two years of DPS application from the control to DPS60 and increased (+0.35%) from controlF to DPS60F.

The addition of fertilizer (ammonium nitrate at 150 kg ha^{-1}) to the control soil had no significant effect on OM. In contrast, for the soil amended with DPS, there was a decrease in OM in the presence of N fertilizer in comparison with the DPS-amended soil without fertilizer (Table 1).

3.2.4. Effect on the Total Soil N Content

The DPS had a negative effect on the total N content in the soil owing to the amendment's high C:N ratio (Table 2). Total soil N content decreased significantly ($p < 0.01$) with increasing DPS dose. The addition of fertilizer (ammonium nitrate at 150 kg ha^{-1}) significantly increased total N from 1.4 to 1.5 g kg^{-1} of soil, for 30 Mg ha^{-1} rate; and from 1.2 to 1.5 g kg^{-1} of soil for the 60-Mg ha^{-1} rate. The combination of DPS with ammonium nitrate as a source of mineral nitrogen made it possible to maintain and increase the total nitrogen content of the soil and avoid the deficiency that would occur if DPS were added alone (Table 2).

3.2.5. Effect on Soil Available P

Soil available P significantly increased ($p < 0.05$) with the addition of DPS both with N fertilizer (+14.3 mg kg^{-1}: DPS60F vs. controlF) and without (+23.1 mg kg^{-1}: control vs. DPS60) (Table 2).

3.2.6. Effect on Soil Exchangeable Bases (K^+, Ca^{2+}, and Na^+)

Soil amended with DPS in combination with N fertilizer significantly increased ($p < 0.001$) the exchangeable K content in comparison with the same treatments without N fertilizer (+0.6 mg kg^{-1}: DPS30 vs. DPS30F) (Table 2). The application of different rates of DPS to the soil had a highly significant positive effect ($p < 0.001$) on the Ca^{2+} content in the soil, which was 5.1 g kg^{-1} of soil in the control, but was estimated at 5.3 and 5.4 g kg^{-1} for the DPS30 and DPS60 soils, respectively. The effect of adding 150 kg ha^{-1} of ammonium nitrate with the DPS treatments was significant ($p < 0.001$) for both DPS rates. After two years of DPS amendment, no significant effect on the Na^+ content was observed in the soil for either dose of DPS (Table 2). The application of DPS with N fertilizer significantly ($p < 0.001$) increased Na^+ levels (Table 2).

3.3. Effect of DPS on Soil Physical Properties

3.3.1. Effect on Soil Permeability

Following two successive annual applications of different doses of DPS, a highly significant increase ($p < 0.001$) in permeability was noted, especially for the 60-Mg ha^{-1} rate, where permeability was more than four times higher than it was for the 30-Mg ha^{-1} rate (Figure 2).

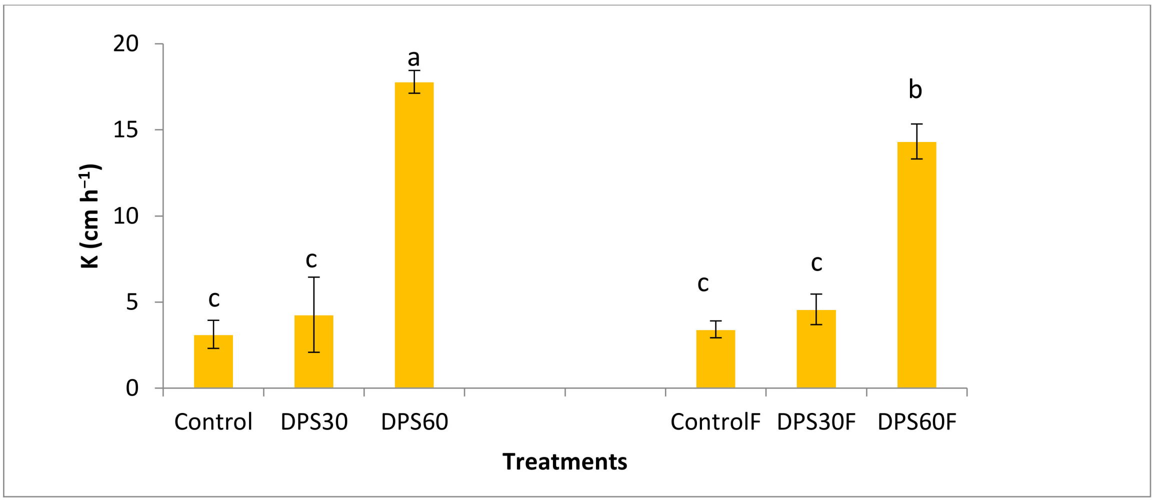

Figure 2. Effect of the application at different rates (0, 30, and 60 Mg ha^{-1}) of deinking paper sludge (DPS) on the permeability (K) of the calcareous soil (in the presence or absence of nitrogen fertilizer (ammonium nitrate at 150 kg ha^{-1})). Bars with different letters are statistically different at $p < 0.001$. Treatments: control, no DPS; DPS30, DPS at 30 Mg ha^{-1}; DPS60, DPS at 60 Mg ha^{-1}; controlF, control with fertilizer; DPS30F, DPS30 with fertilizer; DPS60F, DPS60 with fertilizer.

3.3.2. Effect on Structural Stability

To make an overall assessment of the effect of the DPS amendment on soil structural stability, we combined two parameters, instability index (Is) and permeability (k), as shown in Figure 3. For the two soil controls and the 30-Mg ha^{-1} rate, the structural stability was satisfactory, since $1 < \log(10\ \mathrm{Is}) < 1.3$. Therefore, the enrichment of the soil with the 30-Mg ha^{-1} rate of DPS slightly increased the soil's structural stability, although stability remained in the satisfactory zone for the 60-Mg ha^{-1} rate.

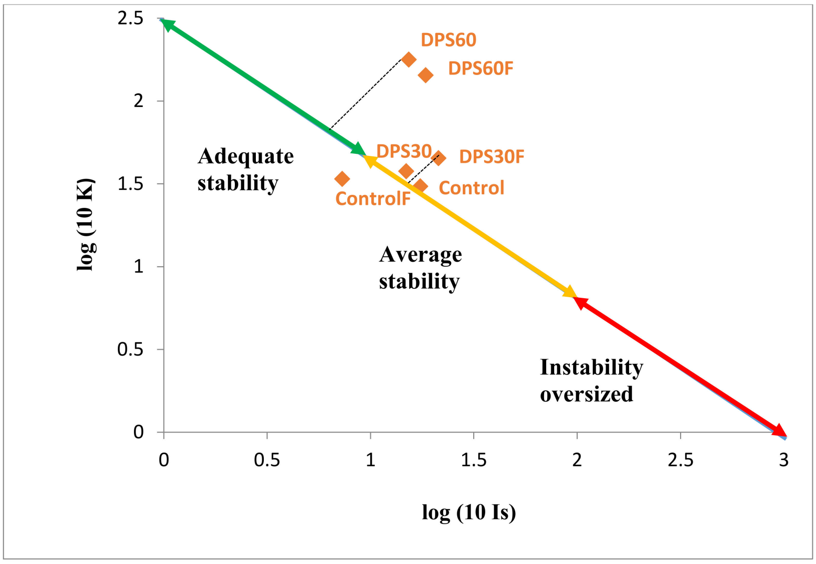

Figure 3. Effect of different rates of deinking paper sludge (DPS) on the structural stability of a Calcaric Fluvisol soil in the presence or absence of nitrogen fertilizer (ammonium nitrate at 150 kg ha^{-1}) after two successive annual amendments. Treatments: control, no DPS; DPS30, DPS at 30 Mg ha^{-1}; DPS60, DPS at 60 Mg ha^{-1}; controlF, control with fertilizer; DPS30F, DPS30 with fertilizer; DPS60F, DPS60 with fertilizer.

3.4. Effect on Soil Biological Parameters

3.4.1. Effect on Mineralization Parameters

Following the addition of DPS, supplemental C mineralization occurred for all the treatments in comparison with the control. For both doses of DPS (30 and 60 Mg ha^{-1}), the mineralization curves were almost the same during the first phase of mineralization, with a slight increase in CO_2 release for the 60-Mg ha^{-1} dose. The second phase of mineralization showed a net increase in CO_2 release for the 30-Mg ha^{-1} dose in comparison with the 60-Mg ha^{-1} dose (Figure 4, Table 3). The kinetic study indicated that the exponential form used by Jedidi [41] (Ct = C_0 (1 − $e^{(-kt)}$) was the suitable model for describing soil cumulative C mineralization after DPS application (R = 0.99) (Table 4). The rate of DPS added affected the resulting parameters (Table 4).

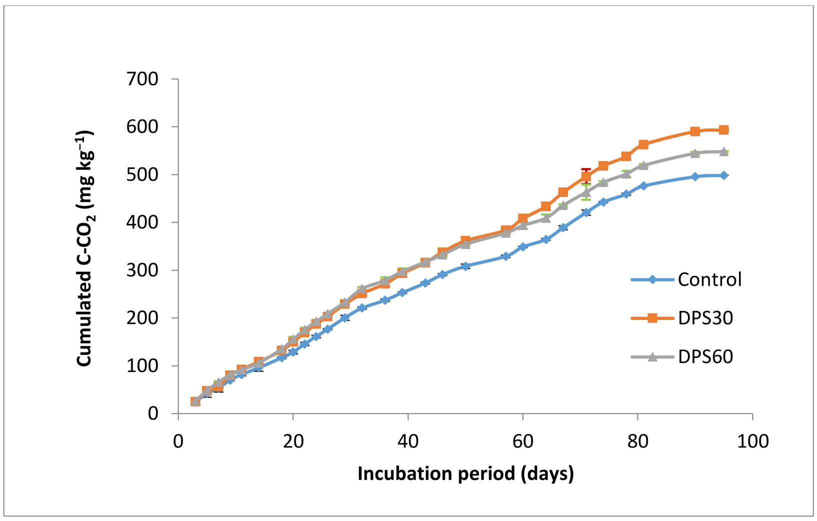

Figure 4. Cumulated carbon-carbon dioxide (C-CO_2) following two successive annual deinking paper sludge (DPS) amendments at two rates, 30 and 60 Mg ha^{-1} (DPS30 and DPS60, respectively).

Table 3. Analysis of variance (ANOVA) of the effects of the addition of deinking paper sludge on physical and chemical calcaric soil properties after two annual DPS applications. [1] Treatments: control, DPS at 30 Mg ha^{-1} (DPS30), DPS at 60 Mg ha^{-1} (DPS60), control with fertilizer (controlF), DPS at 30 Mg ha^{-1} with fertilizer (DPS30F), and DPS at 60 Mg ha^{-1} with fertilizer (DPS60F). [2] Fertilization: a 150-kg ha^{-1} rate of N fertilizer applied as ammonium nitrate (NH_4NO_3). [3] SS: Soil Stability.

Effect	*p*-Value											
	DF	pH	CE	OM	Total		Na	Ca	K	Available	Permeability	SS [3]
					N	C				P		
Treatments [1]	2	0.09	0.0002	0.007	0.04	0.007	0.039	0.002	0.01	0.009	<0.0001	0.001
Fertilization [2]	1	0.03	<0.0001	0.029	0.03	0.029	<0.0001	0.039	0.32	0.40	0.12	0.87
Interaction T × F	2	0.33	<0.0001	0.11	0.21	0.11	0.08	0.009	0.29	0.24	0.04	0.52

Table 4. Kinetic parameters of carbon (C) mineralization according to the exponential model calculated as $Ct = C_0 (1 - e^{(-kt)})$ by the CurveExpert Professional software program.

Treatment (1)	C_0 (2) (mg C kg^{-1})	k (3) (day^{-1})	C_0 * k	R	TMR (4) (%)
Control	1234.4	0.00578	7.1	0.99	4.3
PS30	1774.1	0.00454	8.1	0.99	4.6
DPS60	985.4	0.00890	8.7	0.99	4.1

(1) Treatments: control, no deinking paper sludge (DPS); DPS30, DPS at 30 Mg kg^{-1}; DPS60, DPS at 60 Mg kg^{-1}.
(2) Mineralizable C potential. (3) Mineralization coefficient. (4) Total mineralization rate.

3.4.2. Effect on Microbial Biomass

The addition of DPS to the soil had a significant positive effect on microbial biomass, with DPS60 increasing MBC and MBN, but no significant difference occurred for DPS30 compared to the control.

Furthermore, the addition of DPS decreased the qCO_2 for DPS60, but no significant difference was observed between DPS30 and the control (Table 5). The double rate of DPS leads to more microbial biomass production, consuming minerals, and decreasing CO_2 release in the soil. In this study, the responses of qCO_2 seemed to be strongly affected by the rate used.

Table 5. Effect of different deinking paper sludge (DPS) doses on microbial metabolic quotient (qCO_2), microbial biomass carbon (MBC) and nitrogen (MBN), and the MBC:MBN ratio in a calcareous soil after 95 days of incubation.

Treatment [1]	qCO_2 [2]	MBC (mg kg^{-1})	MBN (mg kg^{-1})	MBC: MBN
Control	3.3 a	152.4 b	16.5 b	10.2 b
DPS30	3.5 a	167.6 b	19.1 b	8.9 b
DPS60	0.6 b	914.3 a	30.2 a	19.4 a

[1] Treatments: control, no DPS; DPS30, DPS at 30 Mg ha^{-1}; DPS60, DPS at 60 Mg ha^{-1}. [2] qCO_2 = mg CO_2-C/mg microbial biomass C. Averages that are not followed by the same letter are significantly different at the 5% risk threshold.

3.5. Soil Trace Element Content

Despite the relative abundance of trace elements (STE) in the soil (Table 6), no significant increases in STE were observed compared to the control, expect for Cd at the 60 Mg ha^{-1} rate, but the amount was still below acceptable standards (Table 6). According to Bejaoui [42], STE are not very available in calcareous soils due to their high pH.

Table 6. Trace element concentrations (mg/kg) after two annual DPS applications. Treatments: control, no deinking paper sludge (DPS); DPS30, DPS at 30 Mg ha^{-1}; DPS60, DPS at 60 Mg ha^{-1}.

Parameters	Control	DPS30	DPS60	Regulations CCME and EN13650
Cd	2.2 b *	2.2 b	2.4 a	3
Co	10.2 a	10.1 a	9.9 b	40
Cu	51.9 a	49.7 b	49.4 b	63
Fe	16,646.4 a	16,584.7 a	16,317.3 b	
Mn	293.2 a	287.8 a	284.9 b	
Mo	85.7 a	85.0 a	85.2 a	
Pb	27.1 a	25.6 ab	26.1 ab	180

* Averages followed by different letters are significantly different according to Tukey's test at $p < 0.05$.

4. Discussion

The DPS contained mainly lignocellulosic OM (cellulose, hemicellulose, and lignin) (Figure 1) and formed a clay-humic complex after incorporation into the soil. The presence of the typical lignin peaks at 1600 to 1650 cm^{-1} and at 1460 cm^{-1} is proof of the presence of lignin-derivative products in DPS (Figure 1) [43]. The C:N ratio was very high (Table 1), whereas the suitable C:N ratio had previously been established at between 20 and 30, and the C:P ratio had been established at between 40 and 50 [8]. The Ca: Mg ratio is another measure of the suitability of organic residues as a nutrient source for plant growth [8,44–46]. This ratio was estimated at 60.13. Difficult mobilization of N, P, and Mg may be expected when DPS is added to the soil.

The addition of N fertilizer had a positive and highly significant effect ($p < 0.001$) on EC in comparison to the control. This salt enrichment of the soil was due to the salts in the fertilizer. Comparing the two fertilized doses with the fertilized control, we noted a decrease in EC for the DPS60F treatment (247.8 to 231.6 µS cm^{-1}) and a significant increase in EC for DPS30F (from 247.8 to 260.3 µS cm^{-1}) (Table 2). It should be noted that the effect of ammonium nitrate on soil EC was greater in DPS30F than in DPS60F. This decrease in EC for the 60-Mg ha^{-1} treatment may be correlated with the effect of this rate on the improvement in soil permeability. To avoid an EC increase resulting from the salts in chemical fertilizer, an organic N source can be recommended.

The DPS amendment significantly ($p < 0.05$) increased soil pH for the 30 and 60-Mg ha^{-1} doses (Table 2). However, this soil pH change, either with an acidic or a basic amendment, is temporary, and the soil returns to its original pH after a certain period. This principle is very important when calculating the dose needed to be incorporated into acidic soils to correct the pH. It can be concluded that the soil returned to its initial pH after a period longer than one year and that the pH remained unchanged until a new amendment was applied. These results are in accordance with other studies reporting a close relationship between paper sludge application rate and pH in Mediterranean soils [8,47]. Soils with high initial pHs are expected to be more strongly buffered than soils with low pHs [8,47]. Indeed, following a limestone amendment, the Ca^{2+} ions replace the H^{+} ions on the clay-humic complex and the acidity thus decreases. After a period, however, the soil buffering capacity plays a role in regulating the pH to reach values close to those before the amendment [47,48]. A slight decrease in pH (−0.11 units) was observed in the 60-Mg ha^{-1} treatment without added ammonium nitrate in comparison with the same rate with fertilizer. This decrease highlights the acidifying effect of this fertilizer since it was characterized by an acidic pH. However, few studies have reported the effect of ammonium nitrate in combination with DPS on soil properties [15]. Buffer capacity of calcareous soil is mainly attributed to calcium carbonate. Then the buffering capacity potential of DPS is not expected to be effective in such soils.

The decrease in OM content for the soil amended with ammonium nitrate in combination with DPS (Table 2). is due to the acceleration of the mineralization process, which increased the availability of N to the plant; a positive effect on crop yield is expected [15,20]. Based on the results below, if the objective of adding DPS to the soil is to increase the soil organic C, the 60-Mg ha^{-1} rate is recommended for a calcareous soil.

Studies have reported that amending soils with high C:N paper sludge caused a net immobilization of soil N [5] and reduced plant growth [8], whereas low C:N sludge increased plant- available N and biomass production in N-limited ecosystems [44]. This effect can be explained by the rapid mineralization of organic N following the addition of mineral N in the form of chemical fertilizer [5]. This suggests that the mineral N could have been immobilized during the degradation of labile C constituents in the DPS and that the organic N mineralized very slowly when high levels of sludge were applied to the FLc soil. The DPS amendment improved acidic soil properties, but at the same time induced N immobilization, which was the major cause of yield loss in a barley crop seeded shortly after DPS application [44]. This result highlights the importance of integrating organic N with DPS (i.e., sewage sludge, poultry manure, or secondary sludge) in the future [11]. Thus, the choice of N supplement is important; one could believe that an organic form of an N supplement would lead to slower OM mineralization compared to a mineral form because the OM creates humic complexes with soil clay [2].

The results for available P (Table 2) suggest that DPS with or without N fertilizer led to a better mobilization of available P. The use of DPS can constitute a valuable means for enhancing soil available P for crops [20]. As for the effect of ammonium nitrate, the dose-effect persists in both cases, but P levels were lower in the soil amended with a combination of DPS and ammonium nitrate than in the soil without N supplementation, owing to OM mineralization. This result can be explained by the fixation of P on soil complexes via Ca^{2+} cations or by the few positive charges on the edges of the clay particles.

The DPS combined with N fertilizer increased K^+ and Ca^{2+} following two successive annual applications of DPS (Table 2).

In calcareous soils, Ca^{2+} cations are found in large quantities and there is thus the possibility of an antagonistic effect between P and Ca through the formation of insoluble compounds [49]. This effect could explain the slight decrease in Ca^{2+} content in the DPS60F treatment.

According to our previous study [11], the composted DPS does not contain high concentrations of Na^+. No significant effect on soil Na^+ content was observed when the DPS dose increased ($p < 0.0001$), whereas the study of [50] noted that the addition of ammonium nitrate at a rate of 150 kg ha^{-1} to the control or DPS-amended soil led to a significant decrease in Na^+. However, few studies have considered the effect of ammonium nitrate in combination with DPS and more research is therefore needed to confirm whether the Na^+ migrates to the plants and/or whether DPS can be used as an effective amendment to help desalinate soil. According to our previous study [11], the composted DPS does not contain high concentrations of Na^+. No significant effect on soil Na^+ content was observed when the DPS dose increased ($p < 0.0001$), whereas the study of [51] noted that the addition of ammonium nitrate at a rate of 150 kg ha^{-1} to the control or DPS-amended soil led to a significant decrease in Na^+. However, although many studies have described decreased salinity effect of organic amendments [50,51], few studies have considered the effect of ammonium nitrate in combination with DPS and more research is therefore needed to confirm whether the Na+ migrates to the plants and/or whether DPS can be used as an effective amendment to help desalinate soil.

As a lignocellulosic matter, DPS incorporated into the soil is expected to form a clay-humic complex, which could explain the positive dose effect on soil permeability as well as the better soil structure, confirming the results of [52]. The addition of ammonium nitrate at 150 kg ha^{-1} did not affect permeability in the control soil or the amended soil. However, there was a slight decrease in permeability, from 17.79 to 14.33 cm h^{-1}, for the DPS60F treatment in comparison with DPS60, but permeability was still very high. The 60-Mg ha^{-1} dose seems to be the recommended dose for ensuring better soil permeability. The presence of clay in the amendment could play a role in modifying the permeability and structural stability of soil by enhancing particle adhesion. Physical soil tests may invalidate or confirm the hypothesis that the clay in the DPS modifies soil physical properties.

Cations near the negatively charged clay surfaces are subject to electrostatic attraction towards the surface as well as a tendency to diffuse into the bulk solution. As a result, the concentration of cations diminishes exponentially as the distance from the clay surfaces increases [47]. Dispersion and flocculation phenomena are important factors determining the effects of liming on soil physical properties [48].

The positive effects of direct liming on soil structure can be ascribed to the flocculating and cementing actions of calcium carbonate ($CaCO_3$) itself and of newly precipitated iron and aluminum oxides and hydroxides [48,49]. However, for the 60-Mg ha^{-1} rate, structural stability was close to the adequate stability zone. Therefore, after two successive annual DPS applications, there was no significant effect in terms of improving soil stability. Applying a high dose of DPS (>60 Mg ha^{-1}) may not improve soil stability. The studies of Trépanier et al. and Nemati et al. [51,52] established that the addition of DPS did not significantly increase structural stability until two years later. Based on the results of the FTIR spectra (Figure 1), which showed the richness in the clay of the DPS, there may be settling and compaction problems in the soil, as well as a decrease in soil stability. In this case, 60 Mg ha^{-1} would be the recommended dose for ensuring better soil stability (Figure 3).

A previous study also concluded that the application of high rates of DPS (≥45 Mg ha^{-1}) should be avoided if the land is to be used for grain or cereal crops immediately afterwards, because of the yield loss that will occur with such rates [44].

The short-term effects of DPS on soil biological properties following two successive annual DPS amendments were a decrease in the soil respiration rate (CO_2 evolution) and significant increases in MBN and in the MBC:MBN ratio for the DPS60 treatment in comparison with the control and DPS30. A significant effect on MBC was observed. A previous study of Chan and Heenan [53] found that the beneficial effect of liming on aggregate stability was evident only after two successive annual amendments, whereas other authors reported that an increase in MBC content was observed in the first year after application [51]. Soil treatment with de-inking sludge for durum wheat cultivation showed that the higher the rate (data not shown, work in progress), the lower the yield in the absence of nitrogen fertilizer. The added DPS, due to its high carbon content, would not be sufficiently mineralized to be available and assimilated by the plant. Soil nitrogen would be consumed by the plant in the control treatment, whereas it would be used by soil microorganisms for DPS mineralization in the other treatments. Moreover, the addition of organic fertilizer (pig slurry) to the soil amended with paper sludge increased straw and ear yields [5,10,15]. These results show that DPS amendment increases or decreases soil biological activity depending on the N content and form of the raw amendment and on the N soil content, which is a good index of the mineralization process. It depends whether the objective is soil sequestration or plant growth. The increase of soil respiration expresses less C sequestration but can traduce mineralization that leads to more nutrients for crops.

According to the literature, the short-term effects of liming, in terms of causing a flush of microbial activity, will affect soil aggregation by increasing aggregate stability. The microbial biomass produces gelatinous extracellular polysaccharides that act as binding agents in soils and fungal hyphae by forming a network that also promotes aggregation [54].

Soil fumigation by chloroform vapors denatures the cell membranes of microorganisms and releases MBN and organic C. Thanks to its high cellulose content, DPS is an important energy source for microorganisms [54]. The qCO_2 was used as an indicator of the ecosystem and microbial stresses [55]. Therefore, for the 30 Mg ha^{-1} rate, there was no microbial stress in comparison with the control, whereas for 60 Mg ha^{-1}, there was a significant difference. The kinetics C_o parameter values in the model used were much higher in the DPS30 than in DPS60 or the control. This could be explained by higher cumulative CO_2-C emissions and thus higher microbial activity after mineralization of the fresh OM. Generally, increasing the application rate led to increases in the C_o values [52], whereas for DPS, there was a decrease (Table 4). The values of total mineralization rate and qCO_2 (Tables 4 and 5) showed a reduction in CO_2 emissions when the 60 Mg ha^{-1} rate was used. In fact, the soil microbial community represents a sensitive indicator of the effect and changes produced by agricultural management practices on soil quality [1]. Soils can act as a source of C during organic matter decomposition after the organic matter amendment or as a sink of C by enhancing carbon sequestration into the soil [1].

Results showed that the application of 60 Mg ha^{-1} of DPS to calcareous soil is an effective strategy to reduce atmospheric soil C losses. According to Verdi et al. [1], soil CO_2 emissions represent the main cause of soil C losses and may be used as an early indicator for the estimation of soil organic C level in the short-term.

Further research is needed to establish the exact relationship between the short-and long-term effects of the DPS amendment on microbial activity and soil stability. Moreover, studying the effects of repeated DPS amendments on the bioavailability of metallic trace elements would make it possible to assess one of the essential environmental impacts of such amendments in calcareous soils.

5. Conclusions

Significant improvements in soil permeability and structural stability were obtained when DPS was applied at a rate of 60 Mg ha^{-1} for two successive years. The application of DPS can play a role in soil restoration (i.e., mined or degraded soils).

Improvements in the contents of OM, nutrients, available P, K, and Ca and a decrease in total N in the soil were observed. There was also an increase in soil pH for both DPS doses. In terms of salinity, there was no significant effect on the EC of the soil following the application of the highest dose of DPS (60 Mg ha^{-1}), but an increase in salinity was observed after N fertilizer was applied. Short-term effects of DPS on soil biological properties were reported. A decrease in soil respiration (CO_2 evolution) and significant increases in MBN content and the MBC: MBN ratio for the DPS60 treatment in comparison with DPS30 were shown.

Although DPS improves some physical, biological, and chemical properties of the soil, leading to better conservation of the soil and the environment, it is still necessary to assess the risk of plant contamination by various contaminants such as heavy metals or organic pollutants. It is important to evaluate the rate of sludge to be applied depending on the soil texture and the application period to improve the physical and chemical properties of the soil. The 60 Mg ha^{-1} DPS rate could be used to enhance the permeability and stability of the soil and as a fertilizer for calcareous soil with a CO_2 mitigation potential. However, long-term studies must be carried out to assess the soil properties effect of different soil textures. The co-application of the DPS with N fertilizer increases the mobilization of the nutrients therefore we recommend either compost or to mix DPS with N organic sources such as poultry manure or sewage sludge.

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