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Assessment of Two Solid Anaerobic Digestate Soil Amendments for Effects on Soil Quality and Biosolarization Efficacy

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Supporting Information

ABSTRACT: Anaerobic digestion is an organic waste bioconversion process that produces biofuel and digestates. Digestates have potential to be applied as soil amendment to improve properties for crop production including phytonutrient content and pest load. Our objective was to assess the impact of solid anaerobic digestates on weed seed inactivation and soil quality upon soil biosolarization (a pest control technique that combines solar heating and amendment-induced microbial activity). Two solid digestates from thermophilic (TD) and mesophilic (MD) digesters were tested. The solarized TD-amended samples presented significantly higher mortality of *Brassica nigra* (71%, $P = 0.032$) than its equivalent incubated at room temperature. However, biosolarization with digestate amendment led to decreased weed seed mortality in certain treatments. The plant-available water, total C, and extractable P and K were significantly increased ($P < 0.05$) in the incubated amended soils. The results confirm the potential of digestates as beneficial soil amendments. Further studies are needed to elucidate the impacts of digestate stability on biosolarization efficacy and soil properties.

KEYWORDS: *soil biosolarization, pest control, anaerobic digestates, soil amendment, weeds inactivation, volatile fatty acids*

INTRODUCTION

Anaerobic digestion (AD) is a process to convert organic wastes into two economically useful byproducts: biogas, a renewable energy source, and digestate, a potential soil amendment. The use of AD has expanded significantly in the past decade, mainly in Europe.[1,2] During AD, most of the labile organic fraction of the feedstock is degraded, leaving behind a more stable organic matter residue. Fluctuations in feedstock availability or biogas demand may reduce the residence time of organic matter in anaerobic digesters, resulting in less stabilized digestates.[3] Therefore, managing these digestates via soil application may differentially affect soil properties based on carry-over of anaerobic digestion metabolites and the potential for continued biological activity in the soil.

Digestates from AD have potential as fertilizers because AD may promote the preservation and accumulation of inorganic nutrients such as P, K, and N.[4] However, prior studies report conflicting outcomes for the direct application of digestates as soil amendments.[5,6] For instance, it is suspected that the elevated N concentration of digestates can enhance carbon mineralization (priming effect).[7] Moreover, continued application of pig slurry in soils increased the salinity of the soil and decreased the total organic carbon (OC).[8] Other studies have indicated that carbon from AD digestates was more stable than other organic wastes and that digestates had great potential to increase carbon sequestration in the soil.[9] Digestates have also shown a high fertilizing potential, associated mainly with their NH_4-N content.[3,10] With the very few exceptions of cases involving feedstocks with very high C/N ratios, short-term studies have shown that soil amendment with anaerobic digestates improved soil quality by increasing microbial biomass and N and P contents.[5] Nonetheless, in the long term, land application of digestates may be restricted by the risk of accumulation of metal elements, increased salinity, biodegradability, phytotoxicity, and health considerations associated with some of the materials.[3]

Although the variable stability of AD digestates can create challenges for conventionally amending soil, integrated pest management practices exist that may capitalize on digestate instability. Soil biosolarization is a relatively recent disinfestation technique developed as a fumigation alternative.

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Table 1. Chemical Contents on Dry Weight Basis of the Soil and the Thermophilic (TD) and Mesophilic (MD) Digestates

digestate	total N (%)	total C (%)	C/N	NH_4-N (ppm)	NO_3-N (ppm)	K (ppm)	PO_4-P (ppm)
soil	0.04	0.38	8.62		18.77	84	14.90
TD	1.48	47.10	31.75	373.33	<10	7500	8363.33
MD	1.03	41.53	40.19	150.00	<10	12200	760.00

Biosolarization builds upon conventional soil solarization, a method that induces thermal inactivation of soil pests by covering moist soil with clear plastic tarp to promote passive solar heating.[11,12] However, the pesticidal efficacy of solarization may be limited by factors including climate, time of year, treatment duration, soil depth, susceptibility of target pest organisms, and other factors.[12] To address this, biosolarization combines organic soil amendments with solarization to increase pesticidal activity. Enhanced pest inactivation may be due to multiple effects, including (i) additional heat generation from biological activity in soil[13,14] and (ii) the production or release of (biotoxic) compounds, such as volatile fatty acids (VFAs) or ammonia[15−17] from the amendments; (iii) competition with the microbial community introduced through soil amendment, and (iv) colonization of pest organisms by fungi and/or bacteria introduced through soil amendment.[16] Additional research is needed to better resolve the interactions between soil amendments and passive solar heating with respect to biosolarization efficacy and the impact on soil quality.

The use of digestates as soil amendments for soil biosolarization could influence biosolarization performance. Conversely, biosolarization may affect changes in soil quality afforded by digestate amendment. These effects must be elucidated to develop soil amendment and biosolarization strategies that can serve as a post-treatment process for anaerobic digester residues. To this end, the objectives of this study were to assess soil biosolarization using solid digestates from anaerobic digesters operating under different conditions for induction of pest-inactivating soil conditions and to evaluate the impact of these digestates on soil quality via measurement of several physicochemical properties.

MATERIALS AND METHODS

Soil and Digestate. Dry topsoil (Hanford sandy loam) was collected from the 0−15 cm depth range at the University of California Kearney Agricultural Research and Extension Center (KARE) in Parlier, CA, USA (36.6° N; 119.5° W; elevation 97 m asl), sieved through a 2 mm screen, and stored at room temperature. The contents of organic matter, sand, silt, and clay were 0.015, 0.41, 0.37, and 0.22 g g^{-1}, respectively.

Two solid digestates from two anaerobic digesters with different operational conditions and different original feedstocks were used in the experiment. A thermophilic digestate (TD) was acquired from the anaerobic digester located on the University of California—Davis (UC Davis) campus in Davis, CA, USA. The UC Davis digester processes mixed organic waste (food, agriculture, and green wastes). The digester utilizes sequential thermophilic hydrolysis and methanogenesis (55 °C) with a low solids loading (5−10% of total solids). The solid digestate was periodically separated from the liquid phase and dewatered by pressing. The Yolo County Landfill (Woodland, CA, USA) provided a mesophilic digestate (MD) from anaerobic digestion of food, animal, and green wastes. Digestion occurred under high solids loading (40−60% of moisture content) and mesophilic conditions (35 °C). Both digestates were air-dried, ground, and sieved (<2 mm) after sampling. The properties of both digestates are summarized in Table 1.

Soil Mesocosm Preparation. Soil mesocosms served as experimental units in field studies. Soil mixtures for mesocosms were prepared by amending dry soil with dry thermophilic (STD) or mesophilic digestate (SMD) to achieve 1.5% loading (dry weight basis). Soil without amendment was used as a control (S). Soil mixtures were wetted to their respective field capacities and allowed to equilibrate overnight at 4 °C. Equilibrated soil mixtures were packed into 3.8 L black plastic grow bags (17.8 cm diameter and 22.5 cm height, neHydro, Southampton, MA, USA) with drainage holes to facilitate moisture and gas exchange with the surrounding soil. Compact temperature sensors and data loggers (Thermochron iButtons model 1922L, Embedded Data Systems, Lawrenceburg, KY, USA) were embedded in the center of each microcosm at a 15 cm depth. Two permeable nylon mesh packets of weed seeds were also placed at this depth within each mesocosm, each containing either 30 seeds of *Brassica nigra* (black mustard) or 50 seeds of *Solanum nigrum* (black nightshade) and 2.46 mL of the appropriate soil mixture to provide direct contact with seeds.[18] The baseline germination rates of the seed stocks were 75 and 43% for *B. nigra* and *S. nigrum*, respectively.

Field Experiment. Field preparations and plot arrangements at the KARE Center (Parlier, CA, USA) followed a previously described protocol.[14] Each field plot contained one mesocosm from each treatment randomized. Five replicate plots were prepared. Mesocosms were buried in field plots, sprinkler irrigated, and then covered with clear plastic tarp (Huskey Film Sheeting, Poly-America, Inc., Grand Prairie, TX, USA) to initiate biosolarization. An identical set of mesocosms without temperature loggers was prepared and incubated in parallel at room temperature (RT, 22−27 °C). They were loosely covered with plastic tarp to avoid water loss. After 8 days of treatment, the mesocosms were extracted from the field and divided into three sections representing different soil depths (H = 0−7.5 cm, M = 7.5−15 cm, and L = 15−22.5 cm depth). Incubation of control mesocosms at RT ceased at the same time. The contents of control mesocosms were thoroughly mixed as no depth effect was expected due to the absence of solar heating. Samples were stored at −20 °C for further analysis.

Weed Inactivation Analysis. *B. nigra* and *S. nigrum* were selected as cool- and warm-season weedy forbs, respectively. After biosolarization, weed seed packets were removed from the mesocosms, and the weed seed inactivation was analyzed by measuring germination and uptake of tetrazolium chloride vital dye as previously described.[19]

Stability Measurements. The stability of the digestates in the soil was determined by measuring microbial respiration in amended soils. A previously described bioreactor-based respirometry method was used.[14,20] Briefly, 250 mL aerated bioreactors (20 mL air min^{-1}) filled with 100 g (dry weight) of nonamended or digestate-amended soils were incubated at 55 °C for 60−190 h. Incubations were ended once CO_2 production ceased. CO_2 content in the gaseous effluent of each reactor was continuously monitored, permitting calculation of the CO_2 evolution rate (CER, mg day^{-1} g $soil^{-1}$) as previously described.[14,20] Cumulative CO_2 evolution (cCER, g CO_2 g $soil^{-1}$) was determined by integrating CER over time and fitting the observed data to a saturation model.[21]

Analysis of Electrical Conductivity, pH, and Volatile Fatty Acids. The electrical conductivity (EC) of soil was determined by creating 1:1 (w/w) mixtures of soil and distilled water, equilibrating for 15 min, and then using a conductivity meter (Mettler Toledo, Columbus, OH, USA) to measure the EC value according to the manufacturer's guidelines. For pH and VFA analyses, extracts were prepared by combining soil and water (1:4, w/w), thoroughly mixing by vortexing for 30 s, and then centrifuging for 10 min at 10000*g*. The pH was measured in the supernatant with a pH meter (Mettler Toledo) calibrated according to manufacturer guidelines. For VFA analysis, an aliquot of the supernatant was filtered through a 0.2 μm

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filter (Titan-3, 17 mm filter blue 0.2 μm PTFE membrane, Thermo Fisher Scientific Inc., San Diego, CA, USA) into an HPLC vial. Acetic, propionic, formic, butyric, and isobutyric acids were measured using an HPLC-UFLC-10Ai (Shimadzu, Columbia, MD, USA) equipped with an Aminex HPX-87H (300 × 7.8 mm) column (Life Science Research, Education, Process Separations, Food Science, Hercules, CA, USA) and an SPD-M20A diode array detector set at 210 nm. The HPLC conditions are described elsewhere.[22]

Water Retention Capacity. The water retention capacity of soil was measured at the UC Davis Analytical Laboratory (University of California, Davis, CA, USA) using a previously described moisture retention method.[23] The original soil and the solarized amended samples (SMD and STD) from the medial 7.5−15 cm layer were analyzed. Samples were saturated with water and then allowed to equilibrate on porous plates under a constant-pressure differential in a pressure plate apparatus. The magnitude of the pressure differential was varied to estimate the field capacity (FC, moisture of the soil after applying pressure of 0.33 atm) and the wilting point (WP, moisture of the soil after applying a pressure of 15 atm). Moisture content in the equilibrated soils was measured by measuring the weight difference between the wet soil and the soil dried at 105 °C. The plant-available water (PAW) was estimated as the difference between the FC and the WP.

Fertility Parameters. To determine the impact of digestate amendment and biosolarization on soil fertility, total carbon and nitrogen along with extractable NH_4-N, NO_3-N, potassium, and phosphate were measured. These parameters were also analyzed at the UC Davis Analytical Laboratory. Total nitrogen and carbon were analyzed using the combustion method.[24] Briefly, samples were combusted with a dynamic flash combustion system producing a complete and instantaneous oxidation of the sample converting all organic and inorganic substances into combustion gases (N_2, NO_x, CO_2, and H_2O). Then, the gases were separated by gas chromatographic separation system and detected by a thermal conductivity detection system. The extractable NH_4-N and NO_3-N were estimated by the flow injection analyzer method.[25,26] Briefly, NO_3-N and NH_4-N were extracted from soils using a 2.0 N KCl solution. NO_3-N was determined by reduction to nitrite via a copperized cadmium column. The nitrite was then determined by diazotizing with sulfanilamide followed by coupling with *N*-(1-naphthyl)ethylenediamine dihydrochloride. The concentration was determined at an absorbance wavelength of 520 nm. NH_4-N was determined by heating the samples with salicylate and hypochlorite in an alkaline phosphate buffer. The concentration of NH_4-N was then estimated from the absorbance of the reaction product at 660 nm. The extractable phosphorus was estimated using the Olsen method, which determines the bioavailability of inorganic orthophosphate (PO_4-P).[27] Finally, the exchangeable K was measured by using the sulfuric acid extraction method.[27,28]

Degree of Humification. The UV absorption of soil extracts was used to assess the degree of condensation of humic aromatic compounds following an adapted method.[29] A mixture of 1 g of air-dried sample and 50 mL of 0.5 M NaOH was shaken for 2 h and then centrifuged at 1238*g*. An aliquot of the extract was combined with distilled water to achieve a 1/10 dilution for analysis. The absorbance spectrum between 200 and 830 nm was recorded on an Eppendorf BioSpectrometer (Eppendorf, NY, USA). The absorbance (E) of the solution at wavelengths of 664 nm (E_6), 472 nm (E_4), and 280 nm (E_2) was measured. The absorbance at 280 nm corresponds to the aromatic C.[30] The absorbance at 472 nm relates to the depolymerization of organic macromolecules through microbial decomposition. The absorbance at 664 nm is characteristic of compounds with high oxygen content and aromatic compounds produced in the stabilization phase.[29]

The ratios E_2/E_4, E_2/E_6, and E_4/E_6 were calculated to describe various humifaction phenomena. The ratio E_2/E_4 was used as an indicator of the relative amounts of lignin at the beginning of humification. The ratio E_2/E_6 was employed to relate nonhumified and highly humified material.[29,31] Finally, the E_4/E_6 ratio was used to assess humification degree.

Statistical Analysis. Degree-day values were calculated by using the trapezoidal rule to approximate the integral of soil temperature versus time data using 0 °C as baseline in R-studio (version 0.98.1103, RStudio, Boston, MA, USA). Factorial analyses, ANOVA, and Tukey's honest significant difference (HSD) post hoc test were used to compare means at a significance level of 0.05. Statistical analyses were performed using JMP-IN software (version Pro 12, SAS, Cary, NC, USA).

RESULTS

Weed Inactivation Analysis. Analysis of *B. nigra* seed inactivation by two-way ANOVA revealed that the only significant effect was the main effect of amendment type (P = 0.009). This was evidenced by soils amended with MD showing decreased seed inactivation compared to nonamended and TD-amended soils under both RT and solar heating conditions. One-way ANOVA indicated that seed mortality was significantly (P < 0.05) greater in solar-heated STD soil compared to STD soil incubated at RT and MD-amended soils (Figure 1).

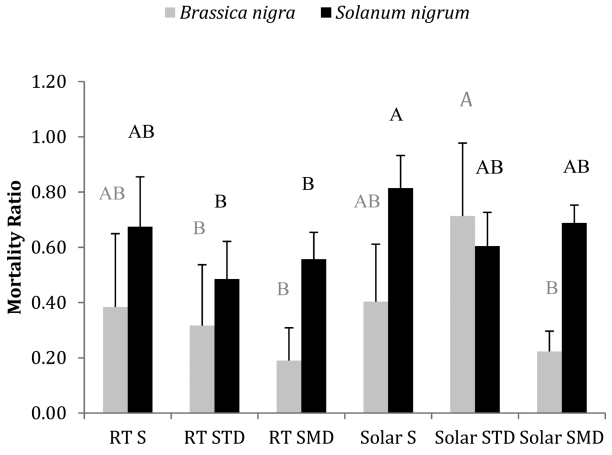

Figure 1. Seed mortality fraction of *B. nigra* and *S. nigrum* in the nonamended soil (S), the TD-amended soil (STD), the MD-amended soils (SMD), and soils incubated at room temperature (RT) or solarized (Solar). Error bars represent the standard deviation of the mean (n = 5). Different letters indicate significant differences between the samples for the same weed (gray bars for *B. nigra* and black bars for *S. nigrum*).

Although greater seed inactivation was observed in the solar-heated STD soil compared to the nonamended control soils subjected to RT or solar heating conditions, the difference was not significant.

Two-way ANOVA analysis of the amendment type, temperature of incubation, and their interaction on *S. nigrum* inactivation showed significant main effects for both solar heating (P = 0.011) and the amendment type (P = 0.007) on *S. nigrum* seed inactivation. There was no significant interaction effect between the two factors. Generally greater inactivation was observed in the solar-heated treatments. Additionally, greater inactivation was observed in nonamended soil under both RT and solar-heating conditions. One-way ANOVA showed that digestate-amended soils incubated at RT had significantly lower inactivation relative to solar-heated nonamended soil (P < 0.05, Figure 1).

Temperature Evolution. For the nonamended soil and the TD- and MD-amended soils, similar trends in temperature evolution were observed at 15 cm depth (Figure 2). Temperature fluctuated daily with increasing daily peak

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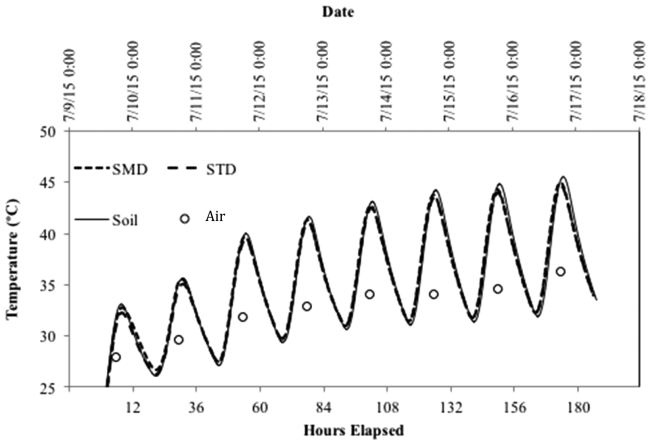

Figure 2. Mean temperature evolution (°C) for solarized mesocosms. Points are related to the maximum air temperature registered at the closest meteorological station (n = 5 for S and SMD, n = 4 for STD).

temperatures during the treatment period. This was attributed to the initially (and uncharacteristically) cool weather conditions at the onset of the experiment followed by a warming trend over the duration of the experiment. On the last day of treatment, the maximum mean temperatures observed at 15 cm depth were 9 °C higher than the air temperature (36.11 °C[32]). The cumulative temperature of the samples in degree-days reached 273 °C-day in all of the samples (Table S1). No significant differences (P > 0.05) in degree-days between the unamended and the digestate-amended samples were observed.

Analysis of the Soil pH and VFA Accumulation. When the pH values of the original nonamended soil (S) and the STD samples were compared, the pH was only significantly higher (P = 0.029) in the samples incubated at RT (Table 2). With regard to the SMD samples, the pH of the samples incubated at RT and solarized at layers 0−7.5 and 15−22 cm were significantly higher (P < 0.05) than those of the control and the 7.5−15 cm solarized layer.

VFAs were detected in two of the analyzed samples. The lowest layer of the solarized soil amended with TD (15−22.5 cm) indicated acetic acid and propionic acid accumulation (160.98 ± 85.78 and 13.24 ± 10.03 μg/g of soil, respectively).

Soil amended with MD incubated at RT also presented quantifiable amounts of acetic, propionic, and butyric acid production (153.98 ± 8.63, 110.30 ± 6.56, and 77.35 ± 9.40 μg/g of soil), respectively.

Stability of the Amended Soil. The laboratory incubation of the nonamended soil in bioreactors at 55 °C for 60 h showed cCER values of 0.20 ± 0.01 mg CO_2 g $soil^{-1}$. After 190 h of incubation, the cumulative CO_2 released by the STD and SMD soils was 2.87 ± 0.31 and 1.83 ± 0.41 mg CO_2 g $soil^{-1}$ (Figure 3). When the results were fitted to the saturation model, the

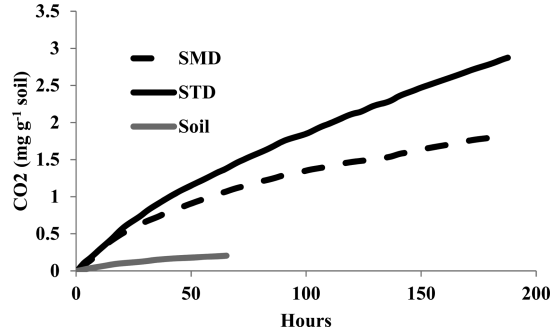

Figure 3. Mean cumulative CO_2 evolution in soil amended with mesophilic (MD) and thermophilic (TD) digestates in aerobic conditions at 55 °C (n = 3).

$cCER_{max}$ values in the STD samples (5.69 ± 2.19 mg of CO_2 g $soil^{-1}$) were significantly (P < 0.05) higher than SMD soil (2.59 ± 0.65 mg of CO_2 g $soil^{-1}$). The amended soils had significantly higher (P < 0.05) values for $cCER_{max}$ compared to the nonamended soils (0.37 ± 0.04 mg of CO_2 g $soil^{-1}$).

Soil Salinity. TD addition to soil did not significantly increase the EC compared to the nonamended soil (Table 2). Likewise, a significantly lower EC was observed at the top layers (0−15 cm) of the TD-amended solarized soil compared to the initial and RT-incubated samples (P < 0.007). The addition of the MD amendment significantly increased the EC to almost twice the initial value of the nonamended soil (P < 0.001, Table 2). Incubation at RT decreased the EC, but it was still significantly higher than that of the nonamended soil (P = 0.002). After solarization, these MD-amended soils presented no significant differences in the EC values in comparison with the nonamended soil.

Soil Water Retention Capacity. Water retention of samples at field capacity (FC), the wilting point (WP), and the plant-available water (PAW) were compared in the original nonamended soil and the middle layer of the digestate-amended soil mesocosms after solarization (Table 3). The FC and PAW significantly increased (P < 0.001) in both amended soils after solarization. Particularly, the soil amended with MD increased PAW by 11%, whereas TD increased it by 17%.

Total C and N. The total N was similar for almost all treatments, showing a significant difference (P = 0.027, Figure 4; Table S2 presents a summary of the statistical results) only between the control nonamended soil and the lower layer of the TD-amended soil (STD-L). Amendment with TD

Table 2. Mean and Standard Deviation (n = 5) of the EC and pH of Initial Nonamended Soil (S) and Soil Amended with Thermophilic Solid Digestate (STD) and Mesophilic Solid Digestate (SMD) prior to Biosolarization (T = 0), after Incubation at Room Temperature (RT), and after Solarization at Three Different Depths[a]

	sample	pH	EC (μS/cm)
S	control	7.21b ± 0.03	308.33abc ± 20.40
STD	T = 0	7.69ab ± 0.03	337.00ab ± 15.28
	RT	7.92a ± 0.05	347.60a ± 24.45
	0−7.5 cm	7.75ab ± 0.39	263.40c ± 20.51
	7.5−15 cm	7.29ab ± 0.06	261.80c ± 15.12
	15−22 cm	7.27ab ± 0.75	301.20bc ± 34.63
S	control	7.21b ± 0.03	308.33c ± 20.40
SMD	T = 0	7.13b ± 0.11	594.20a ± 28.05
	RT	7.77a ± 0.07	385.40b ± 30.88
	0−7.5 cm	7.67a ± 0.10	306.00c ± 11.25
	7.5−15 cm	7.31b ± 0.31	325.80c ± 21.53
	15−22 cm	7.79a ± 0.16	324.60c ± 22.41

[a]Values represent the mean ± standard deviation. Different letters indicate significant differences within the control nonamended soil and the same amendment group STD or SMD (P < 0.05).

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Table 3. Water Retention Characteristics of the Nonamended Soil and the Medium Layer (7.5−15 cm depth) of Soil Amended with Thermophilic Solid Digestate (STD) and Mesophilic Solid Digestate (SMD) after Solarization[a]

	FC (%)	WP (%)	PAW (%)
S	10.8a ± 0.3	2.7a ± 0.2	8.0a ± 0.2
STD	12.6c ± 0.2	3.2b ± 0.1	9.4c ± 0.3
SMD	11.9b ± 0.3	3.1b ± 0.1	8.8b ± 0.3

[a]Values represent the mean and standard deviation (n = 5) of the percent of water (g of water/g of wet soil) observed at field capacity (FC), wilting point (WP), and plant-available water (PAW). Different letters indicate significant differences (p < 0.05).

significantly increased (P < 0.001) the C level from 0.38 ± 0.01% in the nonamended soil to 1.07 ± 0.24% in the amended soil. The C level decreased in the samples incubated at RT and solarized, but this decrease was only significant for the upper layer of the solarized soil (P < 0.001). The C/N ratio of the nonamended soil increased due to TD addition (Figure 4, right axis). The significant decrease in C in the upper solarized layer also resulted in a significant decrease in the C/N.

The addition of the mesophilic digestate did not significantly affect the total N of the soil, and no significant differences were observed due to incubation at RT or solarization. The total C contribution of the mesophilic digestates significantly (P < 0.001) increased the C level. As for the solarized soil amended with TD, these values decreased during solarization and incubation at RT. Again, this decrease was significant only for the upper layer of the solarized soil (0.66 ± 0.09%, P = 0.001). Finally, the C/N ratio of the MD-amended soil was 19.49 ± 0.52 initially, and it decreased significantly to 14.28 ± 1.89 only for the upper layer of the solarized mesocosms (P = 0.003).

Extractable NH_4-N, NO_3-N, P, and K. The nonamended soil presented a NO_3-N level of 18.77 ± 0.47 μg g^{-1} (Figure 5; Table S2 presents a summary of the statistical results). The addition of the thermophilic digestate significantly decreased this level to 2.77 ± 0.95 μg g^{-1} (P < 0.001). After solarization or incubation at RT, this concentration dropped to <1 μg g^{-1}. The nonamended soil presented a NH_4-N level of 3.96 ± 0.03 μg g^{-1}. The addition of the thermophilic digestate did not significantly change this level. After incubation at RT, the NH_4-N level did not change significantly, whereas after solarization a significant accumulation of NH_4-N was observed in both upper and lower layers of the TD-amended soil (P < 0.001). With regard to extractable P, the TD amendment showed a significant increase from 14.90 ± 0.24 μg g^{-1} in the nonamended soil to 27.14 ± 0.55 μg g^{-1} in the TD-amended sample (P < 0.001). After incubation at RT and solarization, it significantly dropped (P < 0.001) only in the upper layer of the solarized microcosm (STD-H, Figure 5). With regard to extractable K, a slight significant increase due to the TD addition was observed from 84.67 ± 9.99 μg g^{-1} in the original soil to 98.60 ± 2.30 μg g^{-1} after TD addition (P = 0.006). After the experiment, this difference increased for the samples incubated at RT and the bottom (STD-L) layer of the solarized mesocosms (P < 0.05, Figure 5). On the other hand, the K concentration at the top layer of the solarized soil decreased to similar levels of the control soil.

The addition of the mesophilic digestate also significantly decreased the level of NO_3-N (P < 0.001), although to a lesser extent than for the TD-amended soil. Again, incubation at RT and solarization led to a decrease in NO_3-N, with final levels being <1 μg g^{-1}. Similar to the TD-amended soils, MD addition did not significantly change the levels of NH_4-N. The incubation at RT did not affect these levels; however, an accumulation of NH_4-N was observed at the lower layer of the solarized samples that was significantly higher that the ammonium level at RT (P = 0.002). MD amendment also increased the extractable P, but to a lower extent than the TD. This level did not change significantly during the experiment in the top solarized layer. Finally, the contribution of MD digestate to the extractable K was larger than that observed for TD. This value significantly decreased during solarization, and this decrease was more significant in the upper layer of the solarized soil (P < 0.001).

Humification Degree of the Soil. Figure 6 shows the UV absorption results of the humic substances of the amended soils during the experiment. With regard to the initial values (T = 0),

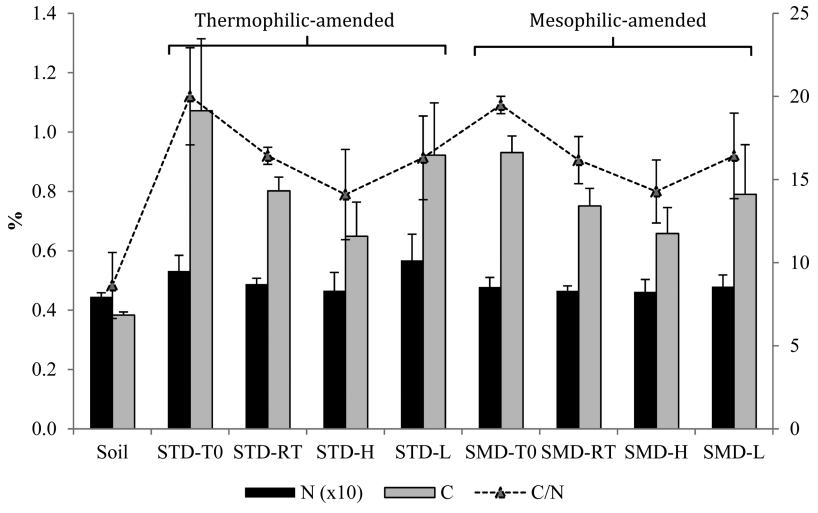

Figure 4. Total C and N contents and C/N ratio of the nonamended soil and soil samples amended with thermophilic (STD) and mesophilic (SMD) digestates at the beginning of the experiment (T0), after incubation at room temperature (RT), and after solarization at different depth (S-H = 0−7.5 cm and S-L = 15−22 cm). Error bars represent the standard deviation of the mean (n = 5). For visual reasons the total N values in the figure are 10 times higher than the measured value.

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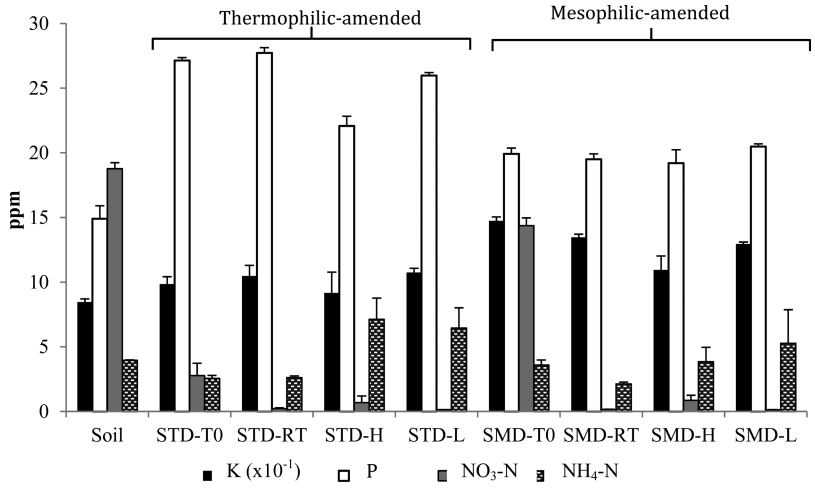

Figure 5. Extractable NH_4-N, NO_3-N, P, and K contents of the nonamended soil and the amended samples with thermophilic (STD) and mesophilic (SMD) digestates at the beginning of the experiment (T0), after incubation at room temperature (RT), and after solarization at different depths (S-H = 0−7.5 cm and S-L = 15−22 cm). Error bars represent the standard deviation of the mean (n = 5). For visual reasons the K values in the figure are 10 times lower than the measured value.

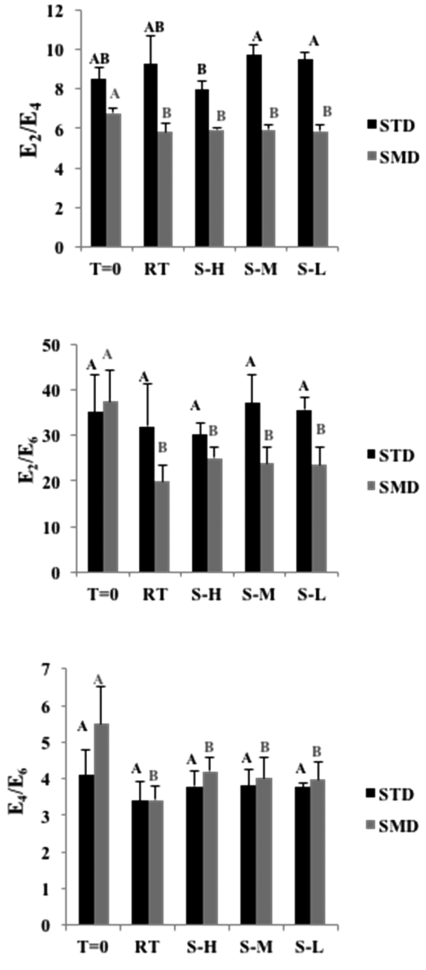

Figure 6. UV analysis of the soil amended with thermophilic (STD) and mesophilic (SMD) digestates at the beginning of solarization (T = 0) and after incubation at room temperature (RT) and at three different depths (S-H = 0−7.5 cm, S-M = 7.5−15 cm, and S-L = 15−22 cm) after solarization. Error bars represent the standard deviation of the mean (n = 5). Different letters indicate significant differences between the samples for the same amendment (gray bars for SMD and black bars for STD).

the soil amended with the TD presented higher E_2/E_4 values after incubation at RT and at lower depths (<7.5 cm depth). The upper layer of the solarized soil showed a slight decrease. This sample was only significantly lower than the other solarized soil layers (P = 0.012 and P = 0.037 for 7.5−15 and 15−22 cm, respectively). The E_2/E_6 and E_4/E_6 ratios presented similar values across all of the samples without any significant trend.

The MD-amended soils presented a similar trend for the E_2/E_4, E_2/E_6, and E_4/E_6 ratios. Thus, the highest values for every ratio were recorded at the beginning of the experiment. Incubation at RT and solarization significantly decreased these ratios (P < 0.05) for all of the samples. No significant differences were observed between the samples incubated at RT and the solarized samples.

DISCUSSION

Soil Biosolarization Weed Seed Inactivation. The soil temperatures reached in our study were relatively mild, and we found a significant increase in inactivation of *B. nigra* seeds only when TD amendment and solarization were combined. There are several possible explanations for the lack of inactivation. First, temperatures were mild during the first days of the experiment. A thunderstorm occurred in the area on the first day of the experiment and caused the maximal air temperature to drop from 32 to 27 °C.[32] Moreover, the digestate-amended mesocosms did not show higher temperatures associated with biological heating from soil microbial activity. Previous laboratory studies incubating soil amended with 2% of compost plus 5% of tomato pomace or 5% of white wine grape wastes showed values for cCER of 40 and 10 mg of C-CO_2 g soil^{-1} after 10 days. This produced an increase in the temperature in the bioreactors of up to 2 °C.[20] The laboratory incubation of our samples showed a lower respiration rate compared to the tomato pomace study (Figure 3), indicating too little metabolic heating to result in a temperature increase during the experiment. Laboratory studies have shown that seeds of *B. nigra* were inactivated when they were exposed to 50 °C for 16 h,[33] but the maximum temperature recorded during the experiment was 45.57 °C (Table S1). A significant temperature effect was observed for *S. nigrum* as mortality in the solarized

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samples was significantly higher than in the samples incubated at RT. *S. nigrum* has been shown to be completely inactivated after 16 days of incubation at 42 °C.[34]

Second, the slight change in pH and the low concentration of VFAs detected in the amended soils may also explain the lack of weed seed inactivation in many of the amendment treatments. For instance, it has been observed that immature compost extracts with acetic acid concentrations of between 2474 and 1776 mg kg^{-1} delayed and reduced the germination percentage of important economic weed species.[35] In a companion study using tomato pomace as a source of unstable organic carbon and compost microorganisms as inoculum, a significant correlation was shown between soil VFA levels and inactivation of *B. nigra* and *S. nigrum*.[19]

The different properties of the digestates could be related to the variable inactivation of *B. nigra*. For instance, the thermophilic digestate was more unstable and showed higher respiration and, therefore, higher metabolic activity. This could have contributed to the appearance of VFAs at a similar depth as the weed seeds, supporting the higher weed inactivation observed. However, the applied digestates did not seem to be unstable enough to produce VFAs at a sufficient level to produce complete weed inactivation as observed in other studies.[19] Other factors such as different microbial communities[16] harbored by each digestate could also have affected weed inactivation. Considering that amendment type was a significant determinant of weed seed inactivation for both weed species alongside the finding that SMD amendment decreased weed mortality, caution must be used in biosolarization with digestate amendments. Additional research is needed to understand and enhance the weed inactivation efficacy of solid anaerobic digestates in biosolarization, perhaps by using additional labile coamendments as has been successful with mature compost.

Effect of Biosolarization with Solid Digestate on Soil Quality. Despite the low application rate used in this experiment, the positive effect of both digestates on soil quality was evident. Their increase of the PAW is of great importance for crops of arid regions. The addition of liquid digestates from agricultural waste to soil has already been shown to provide a long-term increase in the moisture retention capacity of soil.[36] In addition, this study shows that soil solarization alone does not affect PAW. Another concern about the application of amendment is their phytotoxicity due to soluble salts.[3,17] The EC was used as an indirect method to measure soluble salts. Only the addition of the MD presented a significant increase in EC at the beginning of the experiment; nonetheless, the levels were reduced to those observed in nonamended soil levels after the experiment. The higher decrease of the EC level on the top layer of the solarized samples could be attributed to downward transport of some salts from this layer due to irrigation prior solarization. A higher microbial activity at this level would also consume organic acids or nutrients, which contribute to EC. This is supported by the significant decrease in total C observed at the top layer of both amended-solarized soils (Figure 4).

The selected digestates had an initial C/N ratio higher than usual values (5−20) typical for stable organic materials.[29,37] The higher C/N ratio of solid digestates is attributed to the liquid−solid separation step, where most of the available N remains in the liquid fraction.[38] Therefore, the solid digestate addition had a greater impact on the C content of the soil and a lower impact on the total N. The primary available form of N in the digestate was NH_4-N (Table 1). Contrary to the accumulation of NO_3-N found in other solarization and biosolarization studies,[39] the lack of NO_3-N during the experiment indicates that nitrification was inhibited during the experiment. This may have been due to a lack of nitrifying bacteria and/or their sensitivity to high temperatures.[40] In addition, the disappearance of N-NO_3 may be related to immobilizing inorganic N via sequestration in microbial biomass.[41] Despite their high N-NH_4 content, the addition of the amendments did not increase N-NH_4 significantly. The solarization process has also been reported to promote the accumulation of N-NH_4.[40] This accumulation was significant only for the TD-amended samples and may have contributed to the higher inactivation observed in the TD-amended soil.[17,40,42,43] As N-NO_3 is the preferred N form for plants, it is critical to perform further studies to understand how nitrifying/denitrifying bacteria recover after biosolarization and affect the fate of N in biosolarized soil.

Solarization studies have also reported an increase in extractable P and no impact on the extractable K after solarization without amendments.[44] The high K and P contents of the solid digestates provide opportunities for digestates to serve as fertilizers suitable for crops that require relatively high amounts of P and K, such as leguminous plants or crops at the reproductive or blooming phase.[5] These elements seem to be depleted during solarization at the top layer. As for the decrease of the EC, a possible explanation could be biological fixation due to the higher microbial activity in this layer.

The ratio of optical densities of E_4/E_6 has been considered a traditional parameter to estimate the degree of humification and/or the molecular size of the humic substances.[45] More unstable organic matter presents a larger E_4/E_6 ratio, associated with the presence of smaller size organic molecules or more aliphatic structures and usually with a higher content of functional groups.[29] With time, the E_4/E_6 ratio decreases significantly, suggesting the mineralization of carbohydrates and quinones, the oxidation of phenolic compounds, and the bonding to methoxyl groups and/or aliphatic side chains in humic substances.[46] The lower E_4/E_6 value for TD compared to MD (Figure 6) indicates a higher humification degree. This higher humification degree agrees with the slight changes after incubation at RT and solarization for TD-amended samples. On the other hand, MD-amended soil presented a lower humification degree (higher E_4/E_6 values), and a significant decrease of E_4/E_6 was observed after the experiment, which suggests polycondensation of the organic matter.[47] Similarly, high values of E_2/E_6 of solarized MD samples provide evidence of the significant participation of weakly humified compounds in the structure, typical for lignins.[48] This is in agreement with the feedstocks used to generate the MD, which were partially composed of lignocellulosic green waste. The significant decreases of E_2/E_6 and E_2/E_4 after incubation at RT and solarization also are related to microbial activity, characterized by rapid loss of readily decomposable organic substances leading to CO_2, NH_3, H_2S, organic acids, and other incompletely oxidized substances.[29]

In summary, the amended soils showed significant positive effects on the PAW, nutrient (P and K) availability, and amendment properties such as total C content and humification degree. Biosolarization using digestates did not have a negative impact on soil properties or on the humification rate. The lack of NO_3-N and the accumulation of NH_4-N may pose a toxicity risk or lack of available N for crop growing subsequent to soil biosolarization. Further studies are needed to assess the long-term effect on nitrifying/denitrying bacteria

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after soil biosolarization. The microbial activity from these amendments was not sufficient to induce drastic biological heating of the soil distinguishable from the passive solar heating. Nevertheless, TD amendment showed a significant positive interaction with solar heating to enhance the mortality of *B. nigra* seeds compared to TD-amended soil without solar heating. However, MD amendment may decrease the efficacy of solarization, indicating that certain digestates can be detrimental to weed seed inactivation during biosolarization. Additional research is needed to determine if weed seed mortality can be improved through adjustments to the amendment strategy or via addition of coamendments. Similarly, future work should elucidate the individual and synergistic contributions of volatile fatty acid and ammonia production on weed seed inactivation in addition to exploring other potential inactivation mechanisms such as the introduction of seed coat-degrading microorganisms.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.6b04816.

Maximal temperature and degree-day values recorded in the nonamended soil, mesophilic, and thermophilic amended soils; statistical analysis of the total C and N contents, C/N ratio, and extractable NH_4-N, NO_3-N, P, and K contents of the nonamended soil and soil samples amended with thermophilic and mesophilic digestates (PDF)

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Notes

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■ ABBREVIATIONS USED

AD, anaerobic digestates; CER, CO_2 evolution rate; EC, electrical conductivity; FC, field capacity; MD, mesophilic digestate; PAW, plant-available water; RT, room temperature; S, soil; TD, thermophilic digestate; WP, wilting point

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