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Gyttja as a Soil Conditioner: Changes in Some Properties of Agricultural Soils Formed on Different Parent Materials

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Abstract: Organic matter is essential in improving the physical, chemical and biological properties of soils. Thus, the organic matter is widely considered a crucial indicator of environmental quality and biodiversity. In this study, the effect of gyttja addition as a soil conditioner on some physical and chemical properties of soils formed on volcanic and serpentine parent materials was investigated. The layout of the incubation study was randomized plots with 3 replications and the study lasted for 8 months to determine the value of gyttja in improving soil quality in two different parent materials. The results showed that pH, EC, total $CaCO_3$, soil organic matter (SOM), wet aggregate stability (WSA), structural stability index (SSI), Ca-ex, Mg-ex, Fe-ex and P-av values of volcanic soils were significantly increased with increasing gyttja addition rates, while dispersion ratio (DR), Cu-ex and Cd-ex values were decreased. Likewise, pH, total $CaCO_3$, SOM, WSA, SSI, Ca-ex and P-av values of serpentine soils were increased with increasing gyttja rates, while DR, Mg-ex, Fe-ex, Cd-ex, Ni-ex, Mn-ex, Cu-ex and Zn-ex values were decreased. The changes in the values of soil properties were statistically significant. The results demonstrated that gyttja addition overall decreased the erosion susceptibility and heavy metal contents of serpentine and volcanic soils. Moreover, the gyttja addition ameliorated some of the chemical soil properties. Therefore, gyttja could be suggested as a soil conditioner in the remediation of problematic soils.

Keywords: heavy metal; plant nutrient; serpentine; structural stability; sustainable agriculture; volcanic parent material

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1. Introduction

The most important agricultural issues of the 21st century are the increase in atmospheric CO_2 concentration, food security threats, human-induced soil degradation, the increase in energy demands for crop production and the gradual decrease in arable land and fresh water resources per capita [1]. These issues arise from population growth as well as changes in living behaviors and the short-sighted global policies of countries. Although modern advanced technology may be a powerful means of addressing such problems from many different perspectives, the demand of the increasing population and the desire to benefit more from nature reduce the benefits of technology. An understanding of the problems arising from the unsustainable use of natural resources has led to the emergence of new concepts such as sustainable land management, land use and agriculture.

One of the main conditions of sustainable agriculture is to keep soil organic matter (SOM) level at a certain level. The multifaceted benefits of SOM have been described in many previous studies [2–6]. The soil conditioner effects of organic materials obtained from many different sources have been investigated, considering the importance of SOM on soil quality [7–12].

Gyttja is one of the many substances studied as a soil conditioner in agricultural lands. Gyttja, which is a layer that must be removed to reach coal for coal power plants, was first described by Swedish scientist Hampus von Post in 1862 [13]. Gyttja is a light gray to brown-black sediment consisting of plankton particles, mollusk shells, insect shells, high plant content, pollen spores and mineral particles in eutrophic waters [14]. Gyttja is an organo-mineral material containing 30–40% lime and 35–50% organic matter. It is low cost, having a current price of 2.5 USD ton^{-1}, and considerably abundant, with an estimated reserve of 4.8 billion tons in the Afşin–Elbistan (Turkey) coal basin [15]. Its relatively high organic matter content has motivated researchers to apply gyttja as a soil conditioner. The high organic matter content, low concentration of toxic elements, high humic acid content and structural compliance with organic fertilizer regulations make gyttja suitable to be used as a soil conditioner [16]. The effects of gyttja on physical [17,18], chemical [19–21] and biological [22,23] soil properties and on the plants grown with it [24–27] have been investigated in different studies. The effect of composted gyttja on soil properties has not been studied [13]. Moreover, the effect of gyttja on soils with different properties has not been comparatively discussed in previous studies. The effect of gyttja on soils developed over parent materials with different properties, such as serpentine and volcanic ash, may be different due to their relatively high lime and organic matter content.

Soils formed on volcanic parent materials contain compounds such as Al–humus complexes, minerals such as allophone and imogolite and a high ferrihydrite and volcanic glass ratio and these properties are called Andic soil properties. These characteristics lead the soils to acquire properties such as low bulk density, high water-holding capacity and a high phosphorus-holding capacity [28]. Andisols are characterized by a low phosphorus concentration, high phosphorus adsorption capacity, variable moisture-holding capacity, occasional Al^{+++} and Mn^{++} phytotoxicity symptoms and a high acidity level. The clay fraction of volcanic soils contains significant quantities of allophane, silicate and iron and aluminum oxides together with allophane-like secondary minerals [29]. Soils formed on volcanic parent material in Turkey have low organic matter content, and farmers' use of organic fertilizers or organic materials has not reached the expected level [30]. In addition, studies carried out on some volcanic origin soils from Turkey have indicated that cadmium and lead concentrations are higher than the threshold values [31]. A study conducted on the soils formed on volcanic parent materials around Erciyes Mountain showed that cadmium, chromium and nickel concentrations in soils formed on ignimbrite parent materials were high, and Co, Cu, Mn, Hg and Zn levels in soils formed on volcanic ash parent material were high. The heavy metal content of soils formed on volcanic ash and andesite parent materials was reported as higher than that of soils formed on basalt, ignimbrite and dacite parent materials. In the same study, heavy metal concentrations in fruit, vegetable and water samples and heavy metals in blood and tissue samples from animals had a statistically significant correlation [32,33].

Serpentine rock, which attracts particular interest due to its specific geochemical and mineralogical properties, is a hydrothermally modified ultramafic rock from the upper mantle exposed in orogenic zones and containing less than 45% silica (SiO_2), Ca or K and low levels of P. Serpentine also contains high levels of Mg, Cr, Ni and Co [34]. One study [35], investigating some properties of soils formed on serpentine parent material, concluded that such soils have high Fe, Mn, Co, Cr and Ni contents. Therefore, the researchers claimed that high heavy metal content in soils may disrupt enzyme activity and many other metabolic processes due to their toxic effects. Serpentines are characterized by their low water-holding capacity [36]. Yılmaz et al. [37] reported that soils formed on the serpentine parent material have a coarse texture and large macro-porosity and thus have high hydraulic conductivity.

Soils developed on serpentine and volcanic parent material have different characteristics, and these soils need reclamation at different levels. The productivity of these soils is reduced, especially when containing toxic heavy metals, and the agricultural activities carried out in these soils pose a serious threat to human health. Furthermore, these soils may suffer from serious erosion and degradation problems when these soils are managed without considering the inherent dynamic characteristics of the soils. In addition, materials containing $CaCO_3$ can reduce the uptake of heavy metals in the soil by plant roots. This study will also give an idea of whether gyttja containing 53.2% $CaCO_3$ affects extractable metal content by using diethylenetriaminepentaacetic acid (DTPA), which is an indicator of metal content that can be taken up by plant roots. The objective of this study was to investigate the effects of gyttja applied to agricultural soils formed on serpentine and volcanic parent material on their structural stability, cation concentration and heavy metal contents.

2. Materials and Methods

2.1. Soils

The incubation studies were carried out using surface soils (0–30 cm) developed over volcanic (4267536 N, 733970 E, UTM; 1662 m asl) and serpentine parent material (4134782 N, 322667 E, UTM; 568 m) in Turkey (Figure 1). Volcanic soil was taken from the vicinity of Erciyes Mountain in the Tomarza District of Kayseri Province. The soil formed over serpentine was taken from the vicinity of Kadioglu Farm in the Turkoglu District of Kahramanmaras Province.

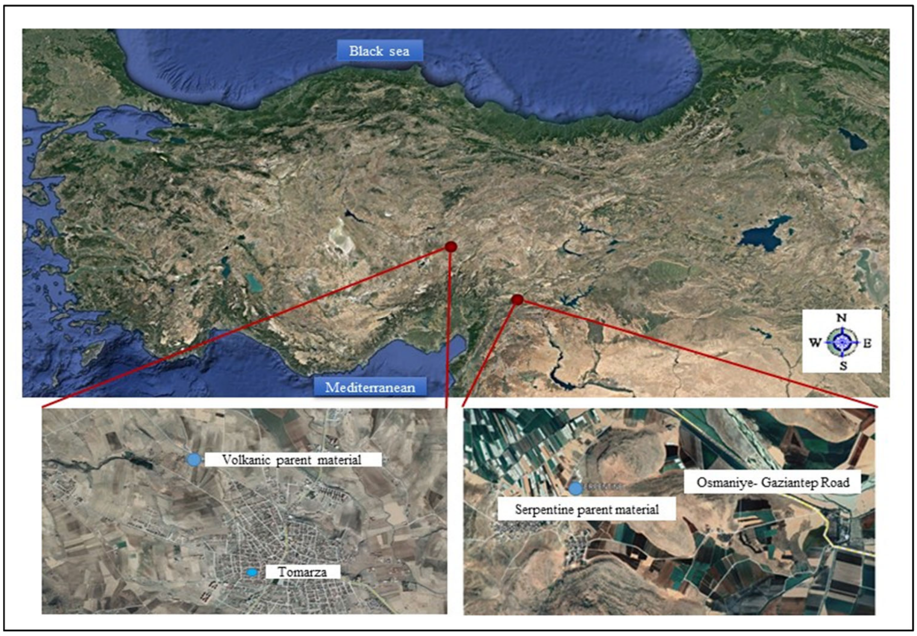

Figure 1. Location of experimental soils (Copyright © Google).

Some physical and chemical properties of soils are given in Table 1. Both soils were low in organic matter and salt content and slightly acidic. The soil developed on volcanic material had a coarser texture and lower structural strength than the soil developed on serpentine. The total lime content of both soils was very low. The available phosphorus of the serpentine soil was twice that of the volcanic soil. In addition, the serpentine soil had a very high magnesium and nickel contents.

Table 1. Some of the physical and chemical properties of soils used in the experiment [38,39].

Soil Property	Parent Material	
	Volcanic	Serpentine
Sand, %	54.5	38.0
Silt, %	27.2	23.6
Clay, %	18.3	38.4
Textural class	SL	CL

Table 1. *Cont.*

Soil Property	Parent Material	
	Volcanic	Serpentine
WSA, %	36.0	65.6
SSI	15.2	60.1
DR	72.1	11.0
pH	6.60	6.75
EC, dSm^{-1}	0.802	0.971
SOM, %	0.66	2.26
$CaCO_3$, %	1.18	0.70
P-av, μgg^{-1}	8.3	16.4
Ca-ex, μgg^{-1}	559.7	2189
Mg-ex, μgg^{-1}	95.9	3578
K-ex, μgg^{-1}	217.8	209
Fe-ex, μgg^{-1}	5.41	12.4
Cu-ex, μgg^{-1}	0.48	1.30
Zn-ex, μgg^{-1}	0.88	0.60
Mn-ex, μgg^{-1}	6.8	22.40
Ni-ex, μgg^{-1}	0.41	29.6
Cd-ex, μgg^{-1}	0.052	0.080

2.2. Gyttja

Gyttja, an organo-mineral material [15], was taken from the lignite basin of Afşin–Elbistan Coal Power Plant. Images of gyttja layers in the sampling location and the gyttja used in the experiments are shown in Figure 2. The physical properties and mineral composition of gyttja change depending on the depth of excavation [13]. The general properties of the gyttja used in the experiment are given in Table 2. The gyttja was slightly alkaline and its salt concentration was very low. Its organic matter content was 41.3% and its total lime content was remarkably high (53.2%). Its extractable calcium and magnesium contents were also high. Its heavy metal content was low; therefore, the use of gyttja is recommended for the improvement of soils [24] and for the production of organomineral fertilizers [27].

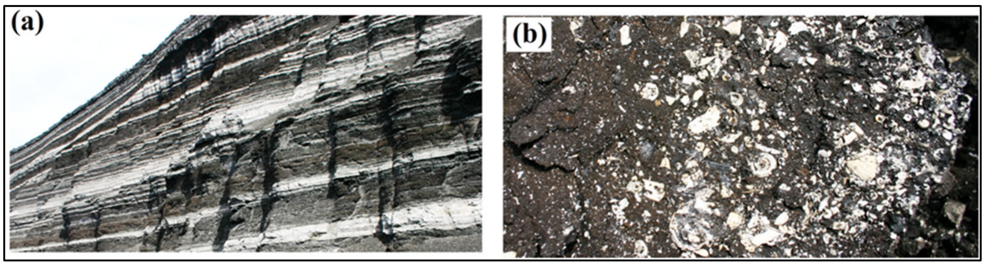

Figure 2. Afşin–Elbistan Coal Power Plant site: (**a**) gyttja layers, (**b**) dislodged gyttja block.

Table 2. General properties of the gyttja material used in the experiments [38,39].

Property	Value
pH	7.22
EC, dSm^{-1}	1.13
OM, %	41.3
$CaCO_3$, %	53.2
P-av, μgg^{-1}	12.0
Ca-ex, μgg^{-1}	6697
Mg-ex, μgg^{-1}	745

Table 2. *Cont.*

Property	Value
K-ex, $\mu g g^{-1}$	103
Fe-ex, $\mu g g^{-1}$	128
Cu-ex, $\mu g g^{-1}$	0.24
Zn-ex, $\mu g g^{-1}$	1.58
Mn-ex, $\mu g g^{-1}$	3.74
Ni-ex, $\mu g g^{-1}$	1.32
Cd-ex, $\mu g g^{-1}$	0.38

2.3. Experimental

Soil samples were dried under shade, ground with a wooden hammer and passed through a 2 mm sieve. The gyttja was mixed with 1000 g soil at ratios of 1%, 2% and 4% and placed into 1.1 L pots. In addition, soil samples without gyttja were used as control treatments.

The layout of the experiment was a randomized plot with 3 replications (Figure 3). The pots were kept under controlled conditions (at 22 °C and 65% relative humidity) in a glass greenhouse for 8 months. The pots were irrigated when moisture content decreased to 50% of field capacity and the moisture content was brought back to field capacity. The experiment was terminated at the end of the 8-month incubation period.

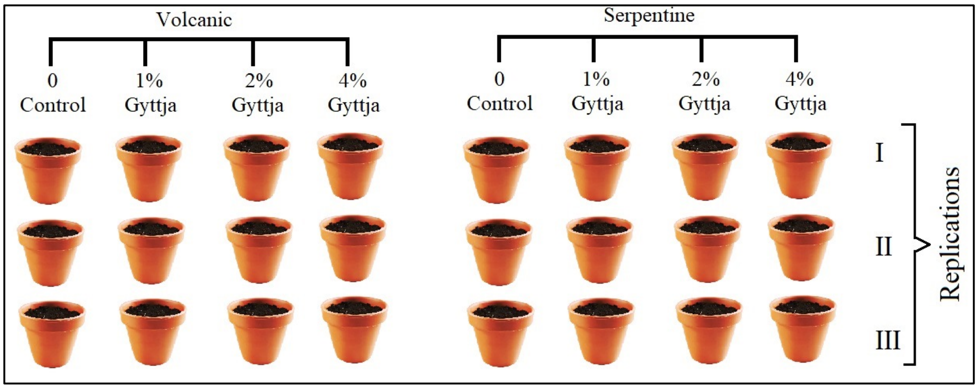

Figure 3. Experimental design.

2.4. Analyses

Soil pH was determined in a 1:2.5 soil–water suspension (w:v) using a pH meter. Electrical conductivity (EC) was measured in the same suspension using an EC meter. Organic matter content (SOM) was determined by a modified Walkley–Black method, total lime ($CaCO_3$) content by the Scheibler calcimeter method and available phosphorus (P-av) content of soil samples by the Olsen method using $NaHCO_3$ extractions. The exchangeable cation (Ca-ex, Mg-ex and K-ex) levels of the soil samples were determined by the 1N NH_4OAc extraction method and the exchangeable metal (Fe-ex, Cu-ex, Zn-ex, Mn-ex, Ni-ex and Cd-ex) levels by diethylenetriaminepentaacetic acid (DTPA) extraction [40]. Three different indices were used to evaluate the structural strength of the soils. Soil wet aggregate stability (WSA) was determined by the wet sieving method [41]. Dispersion ratio (DR) and structural stability index (SSI) were determined by using the percentages of silt and clay dispersed in water and measured in texture analysis [42].

The distribution of data was checked for normality. All soil properties had normal distributions. Variance analysis (ANOVA) was carried out to assess the effect of gyttja treatments on soil properties. Duncan's multiple comparison test ($\alpha < 0.05$) was used to compare gyttja rates when the ANOVA result indicated a significant difference between the treatments. Statistical evaluations were carried out using the IBM SPSS 22.0 software program.

3. Results

The results of ANOVA are given in Table 3. The effect of gyttja on the pH and $CaCO_3$ values of volcanic soil was statistically significant ($p < 0.01$), and the effect on EC value was significant at $p < 0.05$. The effect of the gyttja on SOM content was significant at $p < 0.001$. Gyttja addition significantly changed the structural strength of volcanic soil. The changes to P-av, Ca-ex, Cu-ex and Cd-ex contents in volcanic soil were statistically significant at $p < 0.05$, while they were highly significant ($p < 0.01$) significant for Mg-ex and Fe-ex contents. The gyttja had no significant effect on the K-ex, Zn-ex, Mn-ex and Ni-ex contents of volcanic soil.

Table 3. The results of ANOVA.

Parent Material	Soil Properties								
Volcanic	pH **	EC *	$CaCO_3$ **	SOM ***	WSA ***	SSI *	DR *	K-ex ns	Ca-ex *
	Mg-ex **	P-av *	Fe-ex **	Zn-ex ns	Cu-ex *	Mn-ex ns	Ni-ex ns	Cd-ex *	
Serpentine	pH **	EC ns	$CaCO_3$ *	SOM ***	WSA **	SSI *	DR *	K-ex ns	Ca-ex ***
	Mg-ex **	P-av *	Fe-ex **	Zn-ex **	Cu-ex **	Mn-ex **	Ni-ex *	Cd-ex *	

* F is significant at $p < 0.05$, ** F is significant at $p < 0.01$, *** F is significant at $p < 0.001$, ns: not significant statistically.

The addition of gyttja to the serpentine soil had a significant effect on all measured variables except EC and K-ex content. The changes in the SOM and Ca-ex contents of the serpentine soil were highly significant ($p < 0.001$). The changes in pH, Mg-ex, Fe-ex, Zn-ex, Cu-ex and Mn-ex were significant at $p < 0.01$. The changes in $CaCO_3$, P-av, Ni-ex and Cd-ex concentrations were significant at $p < 0.05$. The erodibility of the experimental soil also changed significantly with the addition of gyttja. The change in WSA was significant at $p < 0.01$ and the changes in SSI and DR were significant at $p < 0.05$.

The pH value of untreated volcanic soil was 6.60 at the start of experiment, and it increased to 7.54 in 4% gyttja rate at its end. However, the effects of gyttja on soil pH were not statistically significant. Similar to pH values, the effect of gyttja on EC was also significant (Figure 4). $CaCO_3$ content increased from 1.18 to 1.86% in the 2% gyttja rate and to 2.09% in the 4% gyttja rate. The organic matter content of the volcanic soil (0.66%) increased to 1.69%, 2.13% and 2.53% in the 1, 2 and 4% gyttja rate, respectively. The effects of the two highest percentages on SOM were statistically the same. The SOM levels in the soil with the two highest gyttja content were 3 times higher than the control. The WSA of the volcanic soil was 36.0% and increased to 57.5% and 64.1% in the 1 and 2% gyttja rates, respectively. The highest WSA (67.1%) was obtained in the 4% gyttja rate, which was significantly different from the other rates. The change in SSI of volcanic soil was similar to the WSA. The DR in the control soil was 72.1% and gradually decreased with the increase in gyttja content. The lowest DR (61.0%) was recorded in the 4% gyttja rate. The P-av content was 8.3 $\mu g g^{-1}$ in the control soil and increased to 12 $\mu g g^{-1}$ in the 1 and 2% gyttja rates (Figure 4). The most effective treatment level in increasing P-av was 4%, which brought it to 13.9 $\mu g g^{-1}$. The Mg-ex content in the control was 95.9 $\mu g g^{-1}$ and increased to 124.2 $\mu g g^{-1}$ in the 4% gyttja rate. The Ca-ex contents of soils receiving different gyttja rates were statistically different from each other. Ca-ex content was 530 $\mu g g^{-1}$ in the control and increased to 1857 $\mu g g^{-1}$ in the 4% gyttja rate. The DTPA-extractable Fe content significantly increased with the increase in gyttja percentage. The Fe-ex content in the control was 5.4 $\mu g g^{-1}$ and increased to 10.0 $\mu g g^{-1}$ in the 4% gyttja rate. The DTPA-extracted Cu-ex and Cd-ex contents of soils decreased with gyttja. The Cu-ex content was significantly reduced in the 1 and 2% gyttja application rates. The Cu-ex content in the control soil was 0.48 μgg^{-1}, and reduced to 0.35 μgg^{-1} and 0.32 μgg^{-1} with 2 and 4% rates, respectively.

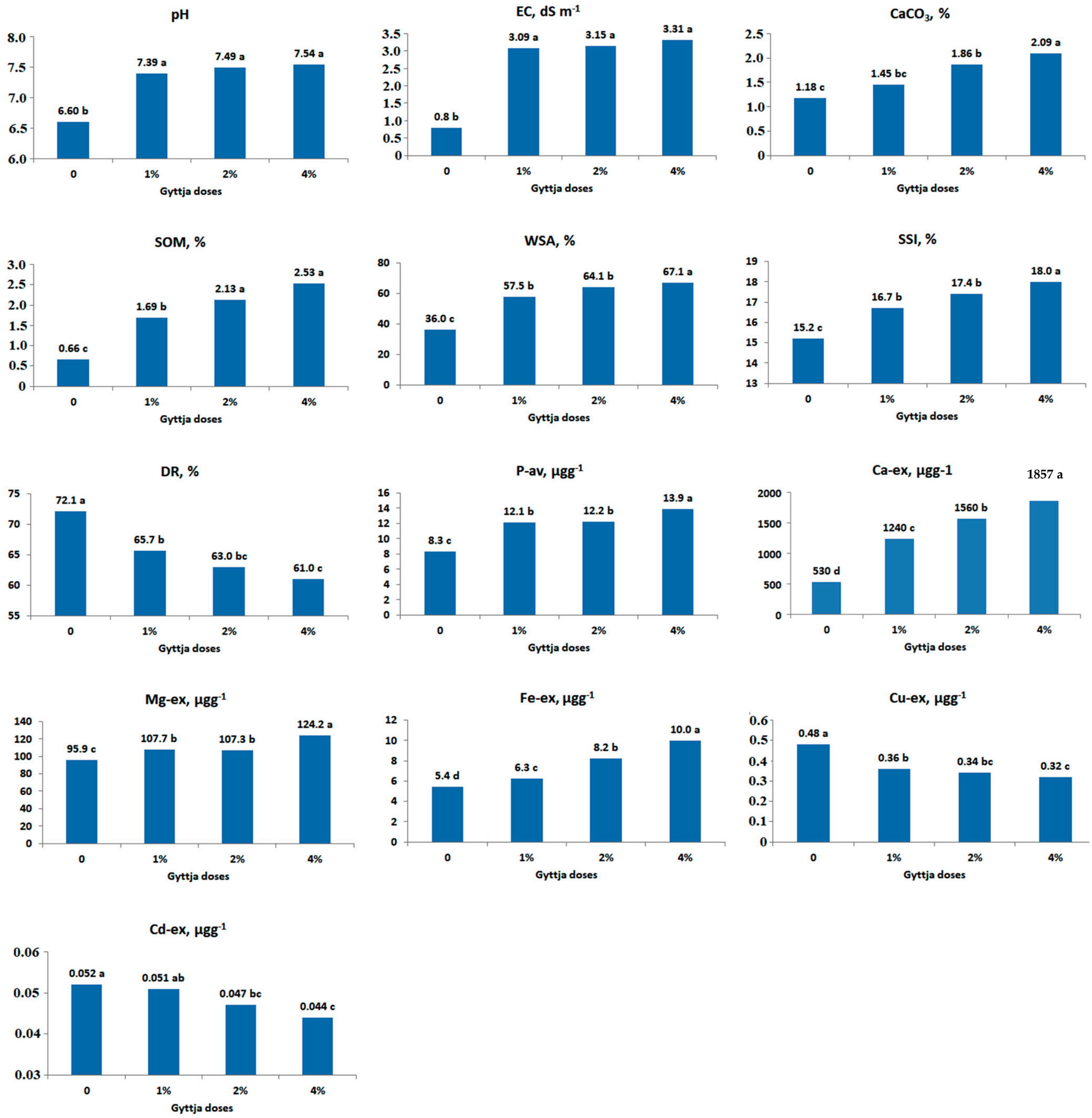

Figure 4. Changes in properties of volcanic soil and Duncan test results ($\alpha < 0.05$). The different lowercase letters indicate significant differences ($p < 0.05$) among different stands.

The Cd-ex content of the control soil was 0.052 μgg^{-1}. The smallest gyttja addition (1%) did not make a statistical difference in Cd-ex content. The Cd-ex content decreased to 0.047 and 0.044 μgg^{-1} in the 2 and 4% gyttja application rates, respectively. The Cd-ex content in the soil with the two highest gyttja levels was statistically similar.

The pH values of serpentine soil increased with the addition of gyttja compared to the control (Figure 5). The pH value was 6.75 in the control and increased to over 7.50 with the addition of gyttja. The highest pH (7.62) was obtained from the 4% gyttja application rate, while the pH difference between the three levels of gyttja was not statistically significant.

The $CaCO_3$ content increased with the increase in gyttja levels. The lowest $CaCO_3$ content was 0.70% in the control, while the highest $CaCO_3$ content was measured in the 4% gyttja application (1.70%). The addition of 1% gyttja to serpentine soil significantly increased SOM (from 2.26% in control to 3.70%). The additions of 2 and 4% gyttja further increased the SOM (4.60% in 2% gyttja and 5.10% in 4% gyttja). The WSA and SSI values of serpentine soil increased and the DR decreased with the increase in gyttja level. The WSA was 65.6% in the control soil and increased to 68.8%, 72.0% and 75.6% in the 1, 2 and 4% gyttja application rates, respectively. The effect of gyttja level on the SSI was similar to the effect on WSA. The most efficient levels for reducing the DR were 2 and 4%, which were not statistically different from each other. The DR was 11.0% in the control soil and decreased to 9% in the 2 and 4% application rates. All gyttja application rates significantly increased P-av content (over 17 μgg^{-1}) compared to the control (16.4 μgg^{-1}); however, the difference between the gyttja levels was not statistically significant. The Ca-ex content was 2189 μgg^{-1} in the control and increased to 2897, 3391 and 3834 μgg^{-1} in the 1, 2 and 4% gyttja application rates, respectively. The Mg-ex concentration in the control soil was 3578 μgg^{-1} and decreased with the addition of gyttja.

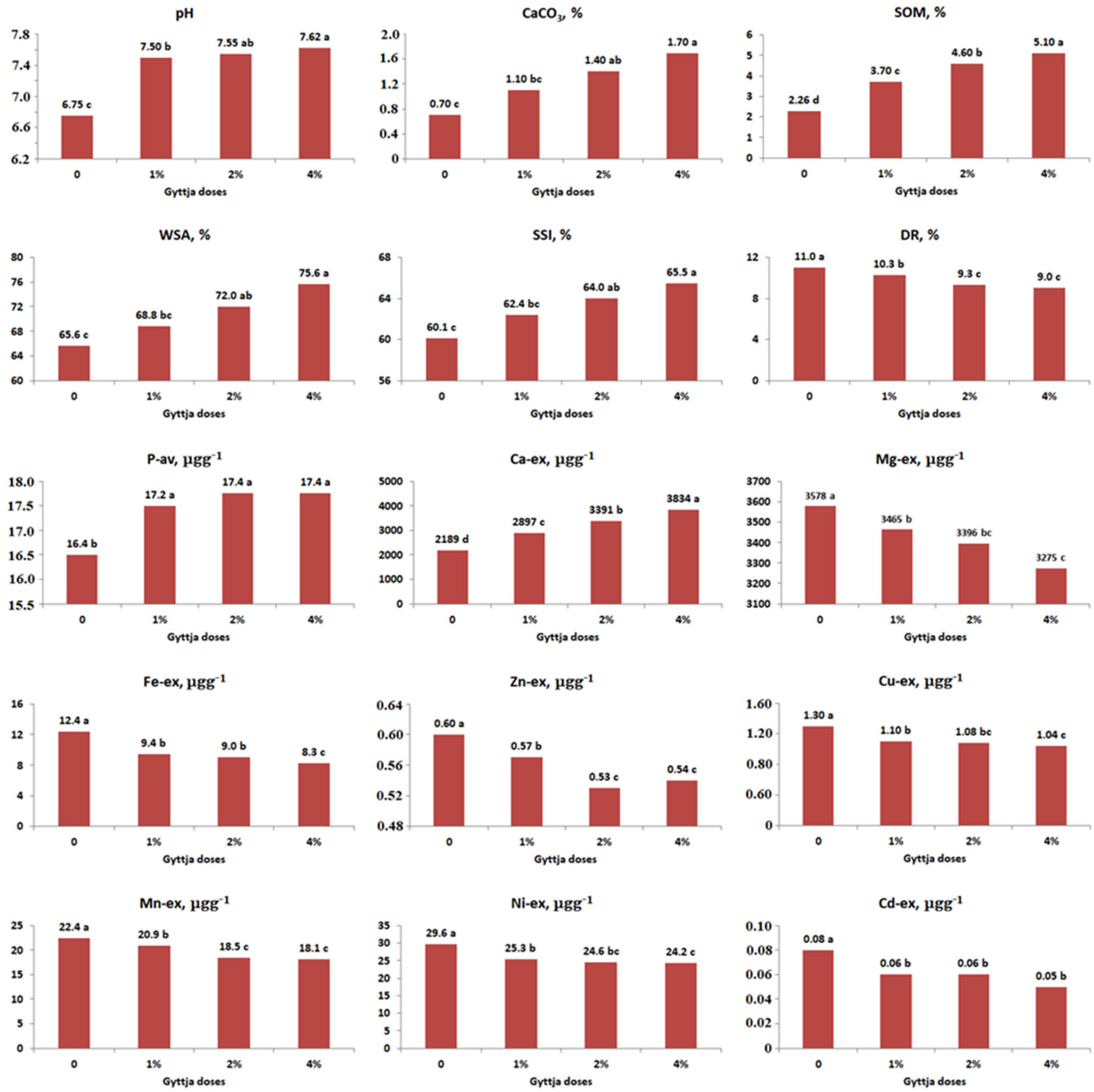

Figure 5. Changes in properties of serpentine soil and Duncan test results ($\alpha < 0.05$). The different lowercase letters indicate significant differences ($p < 0.05$) among different stands.

The Mg-ex content in the 4% gyttja application was 3275 μgg^{-1}. All extractable heavy metal values tended to decrease with the addition of gyttja to serpentine soil. The lowest gyttja application rate (1%) was statistically efficient in reducing heavy metal contents. The Fe-ex content in the control was 12.4 μgg^{-1} and decreased to 9.4 μgg^{-1} in the 1% gyttja application rate, Zn-ex content decreased from 0.60 to 0.57 μgg^{-1}, Cu-ex content wents from 1.30 to 1.10 μgg^{-1}, Mn-ex content went from 22.4 μgg^{-1} to 20.9 μgg^{-1}, Ni-ex content went from 29.6 to 25.3 μgg^{-1} and Cd-ex content went from 0.08 to 0.06 μgg^{-1}. The concentrations of extractable Fe, Cu and Ni in the 1 and 2% gyttja rates were statistically similar. Three gyttja application rates had the same effect on reducing the Cd-ex content of the soil. The lowest extractable heavy metal values were obtained in the 4% gyttja rate (Fe-ex was 8.3 μgg^{-1}, Zn-ex was 0.54 μgg^{-1}, Cu-ex was 1.04 μgg^{-1}, Mn-ex was 18.1 μgg^{-1}, Ni-ex was 24.2 μgg^{-1}, Cd-ex was 0.05 μgg^{-1}). The differences in DTPA extractable Zn, Cu, Mn and Ni between the 2 and 4% gyttja application rates were similar.

4. Discussion

In this study, soils formed on volcanic and serpentine parent materials with very different wet aggregate stability (WSA) values were used. The WSA of untreated volcanic and serpentine soils was 36.0 and 65.6%, respectively. In general, kaolinite is dominant in volcanic soils and smectite group clay minerals are dominant in serpentine soils [33] The results can be attributed to particle size distribution and soil organic matter, which are very important in the aggregation compared to the clay mineralogy. The texture class of serpentine soil was CL and the clay content was 38%, which was almost twice as high (18.3%) as in the volcanic soil. In addition, the SOM of serpentine soil was significantly higher, more than 4 times that of volcanic soil (Table 1). The WSA of volcanic soil was very low compared to serpentine soil; therefore, the effect of gyttja was higher in volcanic soil. The increase in WSA with a 2% addition of gyttja to serpentine soil was 9.7% (from 65.6% to 72.0%) and this increase was 15.2% with a 4% gyttja addition. The increase in WSA was more pronounced in volcanic soil. Even a 1% addition of gyttja was sufficient to increase WSA by 60% (from 36% to 57.5%). The 4% gyttja addition increased the WSA by 86% compared to the control. WSA is the leading indicator used to evaluate soil degradation [43]; WSA of soils is affected by clay mineralogy, SOM, Fe-Al complexes, clay content, microbial activity and plant roots [44], which determine the strength of bonds in aggregate formation mechanisms. Previous studies clearly stated that organic soil conditioner forms organo-mineral complexes increase aggregate stability, depending on the origin of the applied material, soil properties, climate characteristics and exposure time [45–49]. However, studies utilizing gyttja as an organic soil conditioner are rather scarce. The WSA of soils in 3% gyttja application significantly increased and the aggregate stability increased even more when gyttja was added after composting [13]. The gyttja used in this study had an organic matter content of 41.3% (Table 2); therefore, it had a positive effect on the stability of soil aggregates. The results obtained are in accordance with the above-mentioned studies.

The structural stability of a soil largely determines how much a soil can resist wind or water erosion, breakage, fragmentation or puddles during mechanical manipulation [50]. Many indices have been developed to evaluate soil erodibility. Dispersion ratio (DR) and structural stability index (SSI) are two of the most commonly used indices. The DR value is used to define the tendency of soils to disperse in water and the SSI is used to evaluate their resistance to mechanical forces. The threshold value for DR is accepted as 15% and a DR below 15% indicates high resistance to erosion [42]. The threshold value for the SSI as an erosion indicator is 40%. Soils with a SSI value below 40% are highly susceptible to erosion [51,52]. The results showed that volcanic soil is highly susceptible to erosion compared to serpentine soil (Table 1). Even the highest gyttja addition could not bring the erosivity indexes closer to the threshold values in volcanic soil. The result can be attributed to the particle size distribution of volcanic soil (sand content: 54.5%). The DR of serpentine soil was less than 15% and the SSI was higher than 40% at the beginning. In contrast to the volcanic soil, serpentine soil's high resistance to erosion is probably related to its high clay fraction content (clay content: 38%). The gyttja additions improved the SSI and decreased the erodibility of soils. The decrease in susceptibility to erosion can be attributed to the formation of clay–humus complexes during the incubation period. The organo-mineral structures increased the soil's resistance to dispersion in water and dispersion under mechanical forces. Singh et al. [53] concluded that the organic matter content and DR of soils are closely related. Soil organic matter is the most important binding agent [54]. The addition of gyttja increased the structural stability of the soils due to its high organic matter content. The effect of gyttja on stability was dependent on gyttja quantity and soil type.

Soil pH is affected by both acid- and base-forming ions and materials. The increase in soil pH, $CaCO_3$ and organic matter contents is related to the properties of the added material. The pH value and $CaCO_3$ content of the gyttja material were higher compared to the pH value and $CaCO_3$ content of the soils. When $CaCO_3$-containing material is added to acidic soils, $CaCO_3$ is dissolved by reacting with water in the soil and creating basic ions such as OH^-, HCO_3^- and Ca^{++}, thus increasing the soil pH value. Saltalı and Kara [21] reported that soil pH, total $CaCO_3$ and organic matter contents increased with the addition of gyttja to acidic soils (pH = 5.12) and suggested the use of gyttja for the reclamation of acidic soils. The addition of different organic materials to acid soils caused an increase in soil pH and organic matter content and a decrease in exchangeable acidity [55,56]. A similar approach can be put forward for $CaCO_3$ and organic matter content as well. The $CaCO_3$ and organic content of the gyttja used were 53% and 41.3%, respectively. The $CaCO_3$ and organic matter contents of the soils increased with the addition of gyttja to the soils. The pH value, $CaCO_3$ and organic matter contents of the soils increased with the addition of gyttja to the acid soils (pH; 5.1) where hazelnut cultivation was carried out [57].

The K-ex content of soils was not significantly changed with gyttja addition. This may be related to the higher K-ex content of the soils than the applied material and the incubation period. The Ca and Mg are alkaline earth metals and have different stability and solubility properties in soils. In general, the solubility of Ca salts is lower than that of Mg salts. In volcanic and serpentine soils, the amount of Ca-ex significantly increased with the addition of gyttja. This increase can be attributed to the $CaCO_3$ content of the gyttja The Mg-ex content of volcanic soils increased significantly with gyttja addition, while it decreased significantly in serpentine soils. The Ca-ex and Mg-ex content in serpentine soil were 2189 and 3578 $\mu g g^{-1}$, respectively. The amount of Mg-ex decreased with the addition of gyttja, which is 53% $CaCO_3$. The decrease in Mg-ex content may be due to gyttja as well as the balance and solubility properties of Mg in soils. The Ca-ex and Al-ex content increased with $CaCO_3$ addition to Oxisol soils, while Mg-ex content decreased [58]. Miyazawa et al. [59] suggested that Mg-ex content decreased with $CaCO_3$ addition and soil pH increased and the decrease in Mg-ex content was due to the Mg adsorption of different Al compounds.

The P-av contents of volcanic soil, serpentine soil and gyttja were 8.3, 16.4 and 12 $\mu g g^{-1}$, respectively. The P-av content of volcanic soil increased compared to control soils. The increase could be attributed to the higher P-av content of gyttja than of volcanic soils and the conversion of phosphorus adsorbed by Al-Fe hydro-oxides in volcanic soils into an available form by gyttja addition. Gyttja serves as a source of both P and organic acid compounds. Phosphorus sorption surfaces in soils could be masked by organic acids and compounds, thus reducing phosphorus adsorption and increasing the P-av contents of soils. The addition of organic matter to calcareous and Al-Fe oxide-rich soils causes an increase in phosphorus mobilization by masking the P adsorption surfaces of soil components [60–62].

The Fe-ex contents of volcanic soil, serpentine soil and gyttja were 5.41, 12.4 and 128 $\mu g g^{-1}$, respectively. The Fe-ex content of volcanic soils significantly ($p < 0.01$) increased; conversely, the Fe-ex content of serpentine soils decreased ($p < 0.01$). Kılıç et al. [33] determined that the dominant clay minerals in the area where the volcanic soils were taken are kaolinite, allophane, imogolite, ferrihydrite (poorly crystalline Fe oxide) and illite and soils were classified as Andisols. The clay fraction of serpentine soil was dominated by smectite (68.8–72.4%) and kaolinite (9.46–19.2%) [63]. Allophane and imogolite have large surface areas and variable loads [64]. Ferrihydrites, which are abundant in Andisols, show similar characteristics. Carbon dioxide and reducing compounds formed during the decomposition of organic matter in gyttja may cause a reduction of Fe (III) in ferrihydrites and an increase in the Fe-ex content of volcanic soils. The ferrihydrite compounds can be reduced ($F^{+3} \rightarrow Fe^{+2}$) by the reaction of organic matter with ferrihydrites [65], so Fe-ex can also increase with the reduction of ferrihydrite. Smectite, being the dominant clay mineral in serpentine soils and formation of clay–humus complexes with organic compounds combined with gyttja, may cause a decrease in Fe-ex content.

The DTPA-extractable Cu, Zn, Mn, Ni and Cd contents in serpentine soils were significantly decreased with gyttja addition. In volcanic soils, Cu-ex and Cd-ex contents significantly decreased, while Zn-ex, Mn-ex and Ni-ex contents did not significantly change (Table 3). The pH values of serpentine soil (pH = 6.60) and volcanic soil (pH = 6.75) were very close to each other (Figures 4 and 5). The increases in pH values were close to each other with the gyttja addition. However, the clay content of serpentine soils was two times higher than that of volcanic soils (Table 1). In addition, the dominant clay mineral in serpentine soil was smectite [63], whereas kaolinite was the dominant clay mineral in volcanic soil [33], resulting in higher metal adsorption in serpentine soils. In general, smectite clay minerals adsorb more metals compared to kaolinite [66,67]. The Cu-ex and Cd-ex contents of both soils decreased significantly with gyttja addition. Sorption of Cu by gyttja was almost taken place by chemisorption [68] and Cu ions and organic materials (such as peat) form strong and stable complexes [69]. The cadmium was successfully immobilized by oxide compounds, $CaCO_3$, biosolids and clays [67].

5. Conclusions

The addition of gyttja to soils formed on the volcanic and serpentine parent materials statistically significantly affected the physical (WSA, SSI and DR), chemical (pH and $CaCO_3$, available nutrient and heavy metal contents in DTPA extractable) and organic matter contents of the soils. The favorable impacts of the gyttja related to the addition quantity, and the effect varied for volcanic and serpentine soils. Soil properties should be taken into consideration in gyttja addition and the appropriate rate should be determined considering the properties of gyttja and soil. The results of this study showed that gyttja can be successfully added as a soil conditioner to agricultural soils formed on volcanic and serpentine parent materials. In order to obtain more detailed information on the effects of gyttja on agricultural soils, field experiments with different crops and soils should be conducted.

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Abbreviations

pH	soil reaction
EC	electrical conductivity
$CaCO_3$	total lime
SOM	soil organic matter
WSA	wet stability of aggregates
SSI	structural stability index
DR	dispersion ratio
K-ex	Potassium that can be extracted by 1N Ammonium acetate
Ca-ex	Calcium that can be extracted by 1N Ammonium acetate
Mg-ex	Magnesium that can be extracted by 1N Ammonium acetate
P-av	available phosphorus content extracted by $NaHCO_3$ extraction
Fe-ex	Iron that can be extracted by DTPA
Zn-ex	Zinc that can be extracted by DTPA
Cu-ex	Cupper that can be extracted by DTPA
Mn-ex	Manganese that can be extracted by DTPA
Ni-ex	Nickel that can be extracted by DTPA
Cd-ex	Cadmium that can be extracted by DTPA

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