KSÜ Tarım ve Doğa Derg 25 (2): 374-379, 2022
KSU J. Agric Nat 25 (2): 374-379, 2022
https://doi.org/10.18016/ksutarimdoga.vi.898314.

Effects of Gyttja Applications on Some Chemical Properties of Acidic Soils

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ABSTRACT

Acidic soils need to be improved of pH in order to maintian sustainable agricultural production. In order to ameliorate the pH, lime, available Ca and some other properties of acidic soils, materials that increase the soil pH value are needed. One of these organic substances is gyttja. Gyttja contains 30-40% $CaCO_3$ and 40-50% organic matter, which is generated as waste in the Afşin Elbistan thermal power plant and its reserve is estimated to be 4.8 billion tons. The aim of this research was to determine the effects of applying different amounts of gyttja on soil pH, macro (Ca, Mg, K) and micronutrient (Fe, Mn, Zn, Cu) elements. A pot experiment was conducted as a comletely randomized design with four different doses of the gyttja (0, 1, 2 and 4%) and three replications. After 6 months of incubation period under greenhouse conditions, soil samples were taken from the pots. The chemical properties such as pH, lime, organic matter, exchangeable Ca, Mg, K, DTPA-extractable Fe, Cu, Zn and Mn contents were analyzed. Soil pH, lime, organic matter and exchangeable Ca significantly ($p<0.001$) increased, but DTPA-extraxteable Fe and Mn contents decreased depending on the application doses. Application of gyttja to acid soils has improved the soil properties mentioned above. Therefore, gyttja can be suggested to be used for amelioration the acid soils.

Research Article

Article History
Received : 16.03.2021
Accepted : 26.05.2021

Keywords
Acid soil
Gyttja
Lime
pH
Available elements

Gidya Uygulamasinin Asit Karekterli Topraklarin Bazi Kimyasal Özellikleri Üzerine Etkisi

ÖZET

Asidik topraklarda tarımsal üretimin sürdürülebilirliği için pH'nın iyileştirilmesi gerekmektedir. Asit karakterli toprakların pH, kireç, alınabilir Ca ve diğer bazı özelliklerini iyileştirmek için, toprak pH değerini artıran materyallere ihtiyaç vardır. Bu materyallerden birisi de gidyadır. Gidya; Afşin-Elbistan termik santralinde atık madde olarak açığa çıkmakta olup %30-40 kireç ve %40-50 organik madde içermektedir. Gidyanın bölgedeki rezervinin 4.8 milyar ton olduğu tahmin edilmektedir. Bu araştırmanın amacı, farklı miktarlarda uygulanan gidyanın toprağın pH, makro (Ca, Mg, K) ve mikro besin (Fe, Mn, Zn, Cu) elementleri üzerindeki etkilerini belirlemektir. Araştırma tesadüf parselleri deneme desenine kurulmuş olup saksılara %0, 1, 2, 4 dozlarında gidya uygulanarak üç tekerrürlü olarak sera koşullarında yürütülmüştür. Altı aylık inkubasyon süresi sonunda saksılardan toprak örnekleri alınarak, toprakların pH, kireç, organik madde, değişebilir Ca, Mg, K, DTPA ile ekstrakte edilebilir Fe, Cu, Zn ve Mn içerikleri analiz edilmiştir. Uygulama dozlarına bağlı olarak toprak pH'sı, kireç, organik madde ve değişebilir Ca içeriği istatistiksel olarak önemli düzeyde ($p<0.001$) artarken, DTPA'da ekstrakte edilebilir Fe ve Mn içerikleri ise azalmıştır. Asit topraklara gidya uygulaması ile yukarıda belirtilen toprak özelliklerinin iyileştiği görülmektedir. Bu nedenle, gidya'nın asit toprakların iyileştirilmesinde kullanımı önerilebilir.

Araştırma Makalesi

Makale Tarihçesi
Geliş Tarihi : 16.03.2021
Kabul Tarihi : 26.05.2021

Anahtar Kelimeler
Asit toprak
Gidya
Kireç
pH
Yarayışlı elementler

To Cite : Saltalı K, Kara Z. 2022. Effects of Gyttja Applications on Some Chemical Properties Of Acidic Soils. KSU J. Agric Nat 25 (2): 374-379. https://doi.org/10.18016/ksutarimdoga.vi.898314.

INTRODUCTION

Soil acidity is formed by leaching the basic cations (Mg, Ca, Na and K) from the soil profile in regions with high precipitation and the increase of acidic cations (H^+ Al and Fe etc.) in the soils. Soil acidity affects the physico-chemical and biological properties of the soil and thus plant growth in direct or indirect manner (Chintala et al., 2012a). The acidification of soils, that is, the decrease in soil pH value, causes Ca, Mg and K deficiency in soils due to leaching of basic cations; while elements such as Fe, Al and Mn increase towards toxic levels (Cosgrove, 1967; Bayraklı, 1975; Foy, 1984; Aydemir, 1985). Lime is widely used to rehabilitate acid soils and increase soil pH. With the application of lime to acidic soils, plant nutrients such as Ca and Mg are also provided, it neutralizes the active H^+ and H^+ ions generated by hydrolysis of Al, Fe and Mn which can be at toxic levels and the soil pH increases (Van Zwieten et al., 2009; Namlı et al., 2017). Optimum pH value for tea which grown in acidic soils is 4.5-6.0. The pH value of 86.26% of the soils where tea is cultivated is below the optimum pH value recommended for tea (Özyazıcı et al., 2013). The recommended pH value for hazelnuts is around 6.0 (Özyazıcı, 2014), so it is recommended to apply 2-5 ton ha^{-1} of lime in every 3-5 years in order to increase the pH and maintain sustainability of acid soils (Usta, 1995).

Lime material is obtained from solid limestone rocks and there is a certain cost for operations such as burning and/or grinding the solid limestone rock to obtain agricultural lime. However, it is suggested that gyttja can be an alternative to conventional lime material in correcting the soil acidity (Saltalı and Korkmaz, 2015). The gyttja reserve is estimated to be 1.8 billion tons in A + B units in the Afşin-Elbistan Thermal Power Plant basin, and approximately 4.8 billion tons with the newly planned units (C + D + E) (Kadıoğlu et al., 2015). Gyttja is an organomineral material formed by a mixture of organic and mineral materials on the old lake floors, varying in colour from light gray to brownish-black, containing fossils of the organisms that used to live in the lake. The organic matter and lime contents of gyttja varies between 40-50% and 30-40%, respectively (Saltalı and Korkmaz, 2015). It has been suggested that gyttja may contain fossils of the organisms that used to live in the lake to improve fertility of acid soils, which are located on the lignite layer in the Afşin-Elbistan thermal power basin, that are not suitable for energy production in thermal power plants due to their low calories. Gyttja materials are excavated and then used as filling material (Saltalı and Korkmaz, 2015).

The aim of this study was to investigate the effect of gyttja application on the chemical properties of soils taken from the Black Sea region and having a pH value of 5,12 by applying different amounts of gyttja. Based on the data to be obtained, it is to be determined whether the gyttja would be suitable for the improvement of acid soils.

MATERIAL and METHOD

In the study, acidic soil samples taken from Gülyalı-Alibeyköy (X:421353 and Y:4534600) district of Ordu, and gyttja samples were taken from Afşin-Elbistan Thermal Power Plant coal basin (X: 559221 and Y: 4245394).

Experimental Design

The experiment was established by mixing the gyttja material homogeneously with the soils at the rate of 0, 1, 2 and 4%. The experiment was conducted in a completely randomized design with three replications. The prepared soil and gyttja mixtures were incubated under greenhouse conditions. Dried soil-gyttja mixtures were placed in pots and irrigated with deionized water to field capacity. Soils were brought to field capacity in every 3-week. Soil samples were taken at the end of the 6th month of the experiment. The collected soil samples were dried and prepared for analysis.

Chemical analysis of samples

Soil pH and EC were measured with a pH meter (Thomas, 1996) and electrical conductivity instrument (Rhoades, 1996) in saturation paste, respectively. Calcium carbonate content of soils and gyttja were determined by Scheibler calcimeter method (Allison and Moodie, 1965). Organic carbon content of soils and gyttja were performed employing a carbon/sulphur analyser equipment (Eltra CS-580) after inorganic carbon (Carbonate-C) removal with 0.1 N HCl and drying (Eltra GmbH, 2009). The obtained organic C value was multiplied by 1.724 and given as the organic matter value (Allison,1965). The exchangeable Ca, Mg and K content of the soil and gyttja were analysed according to NH_4OAc method (Helmke and Sparks, 1996). Micro element contents (Fe, Cu, Zn and Mn) in the soils and gyttja were extracted by DTPA+$CaCl_2$+TEA solution (Lindsay and Norvell, 1978) and analysed by means of Atomic absorption spectroscopy (Agilent 200 Series AA).

Statistical Analysis

The data-sets were subjected to one-way ANOVA and the mean separation between the gyttja doses was made by the Duncan Multiple Range test at $p<0.05$ significance level using SPSS 18.00 (SPSS, Inc., Chicago, USA).

RESULTS and DISCUSSION

Some physicochemical properties of soil and gyttja

Some physico-chemical properties of the experimental soil and gyttja were given in Table 1. The results for gyttja showed that it is a lime and organic matter rich material, therefore it is a useful material to correct the deleterious effect of acidity as well as to improve organic matter content of soils. Potentially readily available amounts of basic cations such as Ca, Mg and K were also high which was indication of it as possible improver of acidic soils.

The soil used in the experiment was classified as moderate acid, its Ca and K concentration was deficient, Mg concentration was sufficient, and Fe and Mn concentration was high (Alparslan et al., 1998).

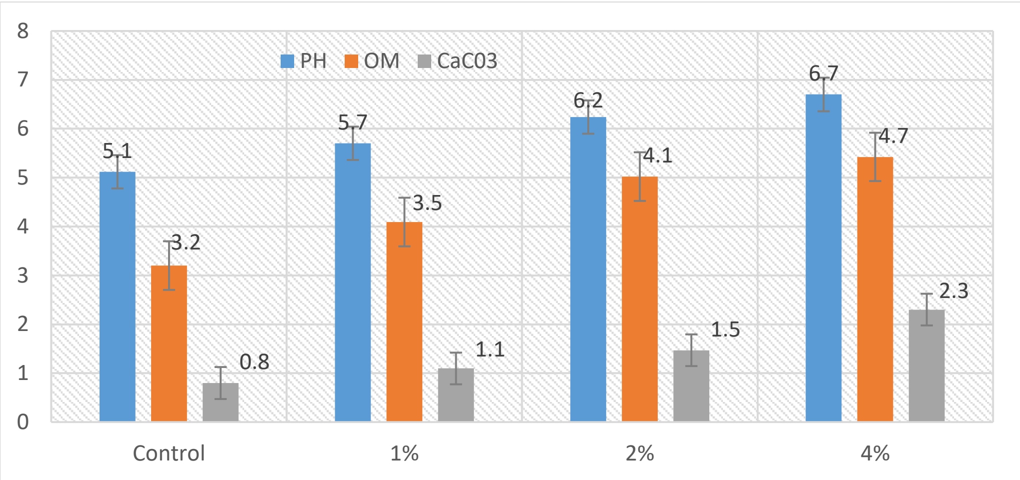
Table 1. Physico-chemical analysis results of soil and gyttja samples
Çizelge1.Toprak ve gidya örneklerinin fiziko-kimyasal analiz sonuçları

	pH	EC	Texture	OM	$CaC0_3$	Ca	Mg	K	P	Fe	Zn	Cu	Mn
		dSm^{-1}		%	%	…	…	…	µg/g	…	…	…	…
Gyttja	7.24	1.15	….	45	52	6701	755	110	10	32	1.04	0.23	3.80
Soil	5.12	0.92	Loam	3.2	0.8	1020	274	105	8	60	0.79	1.2	75

The effect of gyttja on pH, organic matter and lime content

The effects of gyttja on pH, lime and organic matter contents of the soils are given in Figure 1. The highest pH, organic matter and lime contents were obtained in 4% gyttja treatments, while the lowest was found at the control application.

The differences between the application doses were found to be statistically different for pH, OM and lime ($p < 0.01$) as shown Table 2.



Şekil 1. Gidya uygulamasının toprakların pH, OM ve kireç içeriğine etkisi
Figure 1. Effects of gyttja applications on soil pH, OM and lime content

Table 2. Effects of the application of gyttja on soil properties
Çizelge 2. Toprak özellikleri üzerine gidya uygulamasının etkisi

Application	OM	$CaCO_3$	pH	Ca	Mg	K	Mn	Fe	Cu	Zn
Control	3.20**a**$^{\pm0.05}$	0.80**a**$^{\pm0.09}$	5.12**a**$^{\pm0.06}$	1020**a**$^{\pm15}$	274$^{\pm6}$	105$^{\pm3.8}$	75**a**$^{\pm1.2}$	60**a**$^{\pm1.1}$	1.20$^{\pm0.06}$	0.79$^{\pm0.04}$
1%	3.55**b**$^{\pm0.08}$	1.11**b**$^{\pm0.08}$	5.70**b**$^{\pm0.05}$	1850**b**$^{\pm18}$	275$^{\pm4}$	108$^{\pm4.5}$	64**b**$^{\pm1.1}$	50**b**$^{\pm1.4}$	1.10$^{\pm0.05}$	0.76$^{\pm0.03}$
2%	4.08**c**$^{\pm0.08}$	1.46**c**$^{\pm0.08}$	6.24**c**$^{\pm0.07}$	2221**c**$^{\pm20}$	275$^{\pm5}$	110$^{\pm4.1}$	44**c**$^{\pm1.0}$	40**c**$^{\pm1.2}$	1.08$^{\pm0.05}$	0.75$^{\pm0.04}$
4%	4.71**d**$^{\pm0.06}$	2.27**d**$^{\pm0.09}$	6.73**d**$^{\pm0.05}$	2902**d**$^{\pm18}$	278$^{\pm5}$	109$^{\pm3.9}$	32**d**$^{\pm1.1}$	35**d**$^{\pm1.3}$	1.11$^{\pm0.04}$	0.79$^{\pm0.03}$
P	**	**	**	**	nd	nd	**	**	nd	nd

Values shown with the same symbol in the same column are not statistically different from each other at the $p \leq 0.05$ level according to the Duncan test. OM; organic matter, P; probability, nd; non differences, **$p<0.01$, *$p<0.05$

The increase in pH, and organic matter and lime contents of acid soils can be attributed to the 52% lime and 45% OM contents of the gyttja used in the experiment. When gyttja containing lime is applied to acid soils, it reacts with water in the soil (reaction 1) to form Ca^{+2}, HCO_3^- and OH^- ions.

$$CaCO_3 + H_2O \rightarrow Ca^{+2} + HCO_3^- + OH^- \quad (1)$$

The formed OH^- and HCO_3^- ions reacts with H_3O^+ (H^+), and causes a decrease in H ion concentrations in the soil solution, thus increasing the pH of acid soils (reaction 2 and 3).

$OH^- + H_3O^+ \rightarrow 2H_2O$ (2)
$HCO_3^- + H_3O^+ \leftrightarrow CO_2 + 2H_2O$ (3)

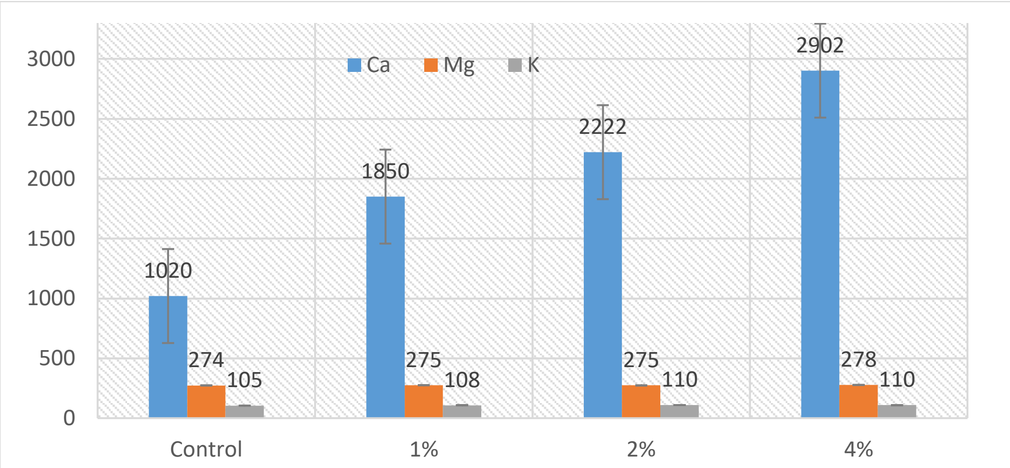
At the same time, Ca ions formed by dissolving lime in acid soils can replace with exchangeable Al, Fe and H adsorbed on the surface of colloids (reaction 4), these acidic cations form different compounds with OH^- ions (reaction 5).

Colloid]-Fe, -Al, -H + $Ca^{2+} \leftrightarrow$ Colloid]-Ca + Al^{3+} + Fe^{3+} + H^+ (4)
$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3$; $Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3$; $OH^- + H^+ \leftrightarrow H_2O \leftrightarrow$ (5)

As seen in the above reactions, the application of gyttja containing high amounts of lime to acidic soils not only contributes to neutralization of active acidity, but also to neutralization of potential acidity. At the same time, organic compounds in gyttja contribute to the buffering and neutralization of acidic cations such as Fe, Al and H. The application of different types of organic residues to acid soils caused significant increases in soil pH and reduced the exchangeable acidity levels (Thakuria et al., 2016). Saltalı and Yıldırım (2016) pointed out that the gyttja application to the alkaline soils caused an increase in lime and OM content of soils. Korkmaz et al. (2017) observed that the pH value and lime content of acid soils increased with gyttja application. Hence, gyttja could be considered as one of the alternative materials for amelioration of soil acidity.

The effect of gyttja on calcium, magnesiun and potassiun availability

The effects of gyttja application to acidic soils on the exchangeable Ca, Mg and K contents of soils were given in Table 1. Depending on the application dose of gyttja, the exchangeable Ca content of the soils increased and this increase was significant ($p < 0.001$). If the available Ca contents in soils is between 1150-3500 mg kg^{-1}, it is considered sufficient (Alpaslan et al.,1998). With the application of gyttja, the available Ca contents of the soils reached sufficient levels (Table 2 and Figure 2). However, the effect of the gyttja application on the available Mg and K was found to be non-significant. This situation can be attributed to the fact that the gyttja does not contain too much Mg and K (Table 2).



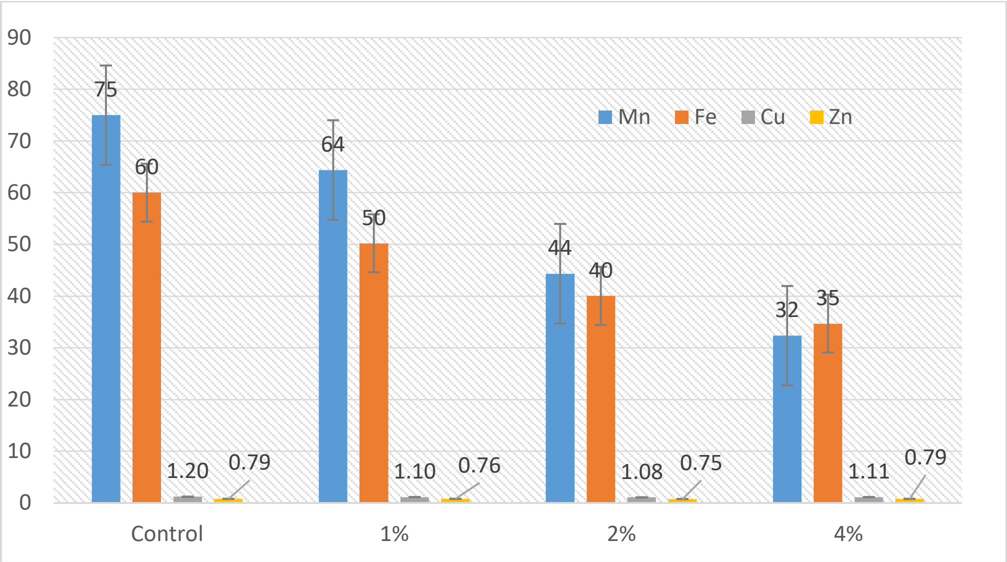
Şekil 2. Gidya uygulamarının değişebilir Ca, Mg ve K içeriğine etkisi
Figure 2. Effects of gyttja applications on exchangeable Ca, Mg and K contents

Increase in available Ca content of soils, a seen in reaction 1, it can be attributed to the formation of Ca ions by dissolving lime in an acidic environment. Demir (2014) reported that the application of gyttja to the soils with varied pH values formed on different parent materials significantly increased the amount of exchangeable Ca in the soils.

The effect of gyttja on available iron, copper, zinc and manganese contents

The effect of different dose of gyttja application to acidic soils on available Fe, Cu, Zn and Mn contents of soils are given in Table 2 and Figure 3. The available Fe and Mn contents decreased depending on the gyttja application dose, and this decrease was significant at $p < 0.01$. However, Zn and Cu contents were not influenced by the treatments. This sitiation can be attributed to the fact that the concentrations of these elements are very low compared to the Fe and Mn contents, and their chemisorption on the Fe and Mn oxides. The plant uptake of these micronutrients can affect each other antagonistically in soils. Thus, micro elements with high concentrations in soils reduce the uptake by plant roots of nutrients with low concentrations (Mengel and Kirby, 2001).

The avaliable concentrations of micro nutrients (Fe, Mn) of soils are largely dependent on the soil pH, lime and organic matter content. High pH value and lime content in soils increase the micronutrients adsorption by soil colloidal surfaces (Sparks, 1995), and reduce their solubility reactions by leading precipitation of hydroxide and carbonate compounds (Lindsay, 1979).



Şekil 3. Gidya uygulamalarının değişebilir Mn, Fe, Cu ve Zn içeriğine etkisi
Figure 3. Effects of gyttja applications on exchangeable Mn, Fe, Cu and Zn contents

The lime content of the gyttja material used in this research is 52 % and the pH is 7.24. Many studies reported that with the addition of lime to acid soils, the available Fe and Mn contents decreased and their toxicity moderated as a function of treatment (Cumming, 1990; Aydın et al., 1997; Turan et al., 2002). If the available Fe concentration is much higher than 4.5 mg kg^{-1}, which is accepted as the higher value (Lindsay and Norwell, 1978; FAO, 1990) differing degrees of toxic symptoms and/or nutritional disorders regarding the balance with the other elements may occur. The acid soils' available Fe concentrations is much higher than the recommended value (Tablo 2). It can be said that a similar situation is valid for the available Mn. Although the available Zn concentrations are sufficient in the studied soils, there may be a possibility of Zn deficiency in plants due to high Fe and Mn concentrations (Mengel and Kirby, 2001; Clark and Baligar, 2000; Rengel, 2015). Therefore, the reduction of the high Fe and Mn concentrations of the soils with the application of the gyttja can be considered as a good agricultural practice.

CONCLUSIONS and RECOMMENDATIONS

Gyttja is a waste product which generated in the Afşin-Elbistan Thermal Power Plant. It has high organic matter and lime content. The application of gyttja to acid soils significantly enhanced pH, organic matter, lime and exchangeable Ca content of soils. At the same time, the DTPA extractable Fe and Mn contents, which was high for many plants grown on acid soils, decreased depending on the application doses of gyttja. The improvement of these soil properties is important in terms of the physico-chemical properties of the acid soils. These results suggested that gyttja would be considered as economically feasible and environmental friendly alternative material for amelioration of soil acidity. Moreover, gyttja could be included into the "Regulation on organic, mineral and microbial sourced fertilizers used in agriculture" as an amelioration material for acid soils.

Author's Contributions

The authors declare that they have contributed equally to the article.

Statement of Conflict of Interest

Authors have declared no conflict of interest.

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