



SOIL STUDIES

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Overview

"Soil Studies (SoilSt)" is the successor to the "Soil Water Journal (Toprak Su Dergisi)" which has been published since 2012. Based on the experience and strengths of its predecessor, SoilSt has been developed to create a truly international forum for the communication of research in soil science. SoilSt is a refereed academic journal has been published free of charge and open accessed by Soil, Fertilizer and Water Resources Central Research Institute. The journal will be published 2 issues (July & December) starting from 2022. It covers research and requirements of all works within the areas of soil.

Aims and Scope

Soil Studies is an international peer reviewed journal that aims to rapidly publish high-quality, novel research of studies on fertility, management, conservation, and remediation, physics, chemistry, biology, genesis, and geography of soils. In addition, the main purpose of Soil Studies is to reveal the influences of environmental and climate changes on agroecosystems and agricultural production. In this context, Soil Studies publishes international studies address these impact factors through interdisciplinary studies. In the journal, articles on hypothesis-based experimental observation of the interactions of all components of agricultural ecosystems, field trials, greenhouse or laboratory-based studies, economic impact assessments, agricultural technologies, and natural resources management will be accepted within the peer-reviewed process. Topics include, but are not limited to:

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- Environmental soil physics and biophysics
- Soil microbiology, biodiversity and biotechnology
- Soil mineralogy and micromorphology
- Soil ecology and agroecosystems
- Soil degradation and conservation/restoration
- Organic farming, conservation agriculture and sustainability
- Best management practices in agricultural production
- Soil-water-plant relations and agricultural water management
- Cop water relations, crop yields and water productivity
- Soil and society
- Climate/environmental changes and sustainable agriculture
- Digital soil mapping
- Soil economy and agricultural production-environment policies
- Conservation agriculture systems and its impacts on soil
- Soil regeneration
- Land management
- Environmental stress on soil and plants
- Physiology and metabolism of plants
- Diversity and sustainability of agricultural systems
- Organic and inorganic fertilization in relation to their impact on yields
- Quality of plants and ecological systems

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RESEARCH PAPER

H₂O₂ and NO mitigate salt stress by regulating antioxidant enzymes in two genotypes of eggplant (*Solanum melongena* L.)

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Abstract

H₂O₂ and NO are the key molecules of plant signaling and perception. In this study, we aimed at the antioxidant capacity of foliar-applied eggplant genotypes which shows different responses to salinity (Artvin: salt-sensitive; Mardin: salt-tolerant). For this purpose, H₂O₂ and NO donor (SNP) were sprayed on the leaves of the seedlings for 2 days and then exposed to 100 mM NaCl for 10 days. The amount of Malondialdehyde (MDA), which increased with salt application and is the most important indicator of lipid peroxidation, decreased significantly with individual or combined pretreatments of H₂O₂ and NO donors. SOD and CAT enzyme activities are affected by foliar spraying of donors. While CAT enzyme activity increased significantly with salt application in both genotypes, it showed a significant increase again with individual or combined application of donors. SOD enzyme activity, on the other hand, showed a minor increase in both genotypes with the application of salt stress, while it was significantly increased with the application of donors individually or together.

Introduction

H₂O₂ and NO are biologically active molecules involved in the signaling pathways in plants (Uchida et al., 2002; Azevedo-Neto et al., 2005; Hung et al., 2005; Li et al., 2011; Wahid et al., 2022). Both molecules show a dose-dependent manner, at the high concentrations they have deleterious effects on the plant body, and at the low concentrations play an important role as “signaling molecules” (Gechev & Hille, 2005; Quan et al., 2008). Especially under stress conditions, these molecules play important roles in inducing acclimation (Hayat et al., 2013).

Among the environmental stresses, salt stress is one of the most important factor that limits yield productivity and food security. High salt concentrations cause osmotic, ionic, and oxidative stresses that affect plant metabolism negatively

(Munns & Tester, 2008). Plants have developed different mechanisms to cope with these multiple stress factors, the most important of which is activating the plant's antioxidant systems. Possible mechanisms of the positive effects of externally applied H₂O₂ and NO to plants on salt tolerance have been investigated in several studies (Uchida et al., 2002; Tanou et al., 2009a; Tanou et al., 2009b; Qiao et al., 2009; Gohari et al., 2020; Hasanuzzaman et al., 2018; Niu & Liao, 2016; Hajjhashemi & Pavla, 2020). Thus, the negative effects of salt stress were eliminated and the salt tolerance was increased.

Under normal respiratory conditions, the production of ROS takes place due to the leakage of electrons to oxygen. Under stress conditions, this process intensifies and excess ROS production takes place. Plants possess various antioxidant systems keeping ROS at low levels but if ROS production

exceeds the capacity of antioxidant systems, then ROS becomes deleterious, causing damage to proteins, lipids, and nucleic acids (Gupta & Igamberdiev, 2015).

In this study, under salt stress conditions, the effects of pretreatment of H₂O₂ and NO on the antioxidant metabolism of eggplant were investigated.

Materials and Methods

Plant material

The eggplant (*Solanum melongena* L.) seeds of the Artvin (susceptible) and Mardin (tolerant) genotypes (Yaşar, 2003) were obtained and grown in a climate chamber under controlled conditions until 4-5 leaf stage. All studies covering the germination and growth cycle were carried out under controlled conditions in the "Digi-Tech Growth Chamber PG34-3" climate chamber. The temperature was set to 25 °C and the humidity was 60-70%.

Pretreatments

After the plants reached a 4-5 leave-stage, 50 days after seed sowing, their leaves were sprayed with chemicals (H₂O₂ and NO) every 6 hours for 48 hours. Accordingly, a total of 5 applications were composed. These; are Control, Salt, H₂O₂ (Hydrogen peroxide, Sigma-Aldrich, 1.08600) SNP (Sodium nitroprusside dihydrate, Sigma-Aldrich, puriss. p.a., ACS reagent, reag. Ph. Eur., ≥99%), H₂O₂ +SNP. The leaves of the seedlings were harvested, submerged in liquid nitrogen, and stored in a refrigerator at -80°C for analysis. The independent sampling process was made with 3 repetitions.

MDA Analysis

The amount of Malondialdehyde (MDA) in leaf tissues was measured based on the work done by (Lutts et al., 1996). According to this method; a fresh leaf sample, trichloroacetic acid (TCA) was added and homogenized by crushing in a mortar. The homogenate was centrifuged and thiobarbituric acid (TBA) was added. The mixture, which was kept in a water bath, was read at 532 and 600 nm in the spectrophotometer, and the results were obtained.

CAT Analysis

Catalase activity (CAT) was measured (Cakmak & Marschner, 1992) based on the degradation rate of H₂O₂ at 240 nm (E=39.4 mM cm⁻¹).

SOD Analysis.

Superoxide dismutase (SOD) activity was measured by the method of reduction of NBT (nitro blue tetrazolium chloride) by O₂⁻ under light (Giannopolis & Ries, 1977).

Statistical Analysis

The experiment was set up according to a random plot design and was carried out in 3 replications. The

obtained numerical data were evaluated with the GraphPad Prism 8. program. First of all, the data belonging to both genotypes were evaluated separately and whether the changes within each genotype were significant or not was examined by analysis of variance (One-way-ANOVA), and the significance of the differences between the applications was checked with the Duncan test ($p < 0.05$). Then, the mean values of all replications were also evaluated with the t-test, so the importance of the difference between genotypes was checked.

Results

Effects of H₂O₂ and SNP pre-treatments on Malondialdehyde (MDA) Amount

100mM NaCl treatment significantly increased the lipid peroxidation in both genotypes ($p < 0.05$). H₂O₂ pretreatment slightly reduced the MDA amount in the Artvin genotype, but had no change in Mardin genotype, SNP-pretreatment did not affect the MDA amount in Artvin genotype compared to the salt-stressed group but reduced the MDA amount in Mardin genotype. The combined H₂O₂+NO application group significantly reduced the MDA amount in both genotypes compared to the salt-stressed group (Figure 1).

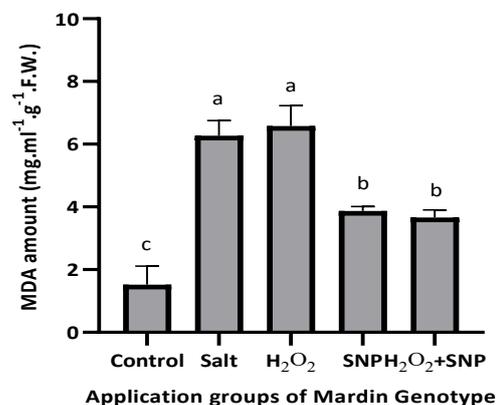
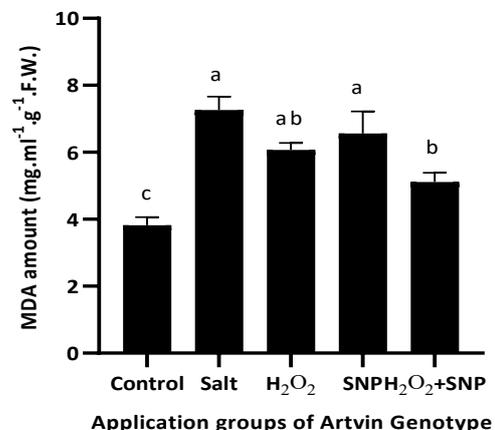


Figure 1. MDA amount in eggplant genotypes.

Effects of H₂O₂ and NO applications on CAT Enzyme Activity

Salt stress significantly increased CAT activity in both genotypes ($p < 0.05$). The H₂O₂ application significantly increased the CAT Activity ($p < 0.05$). SNP pre-treatment increased the CAT activity compared to the salt-stressed group. H₂O₂+SNP pretreated seedlings were significantly increased in both genotypes compared to the salt-stressed group (Figure 2).

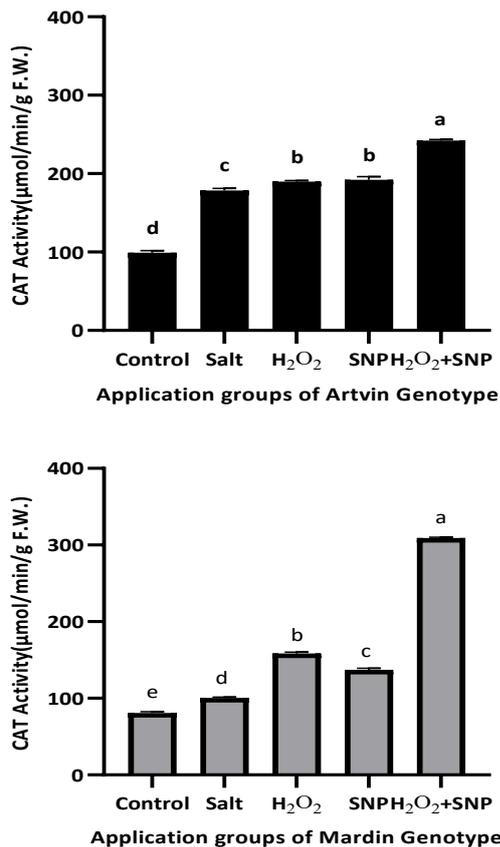


Figure 2. CAT enzyme activity in eggplant genotypes

Effects of H₂O₂ and NO applications on SOD Enzyme Activity

In the Artvin genotype, there was no significant alteration in SOD activity in the H₂O₂ pretreatment group, but SNP pre-treatment markedly increased the SOD activity ($p < 0.05$). H₂O₂+SNP group had the highest value of SOD-enzyme activity in the Artvin genotype.

In Mardin genotype, salt stress increased the SOD activity ($p < 0.05$). While H₂O₂ pretreatment significantly increased the SOD activity, SNP pretreatment significantly decreased the SOD activity compared to the salt-stressed group ($p < 0.05$). H₂O₂ combined with the SNP application group significantly increased the SOD activity (Figure 3).

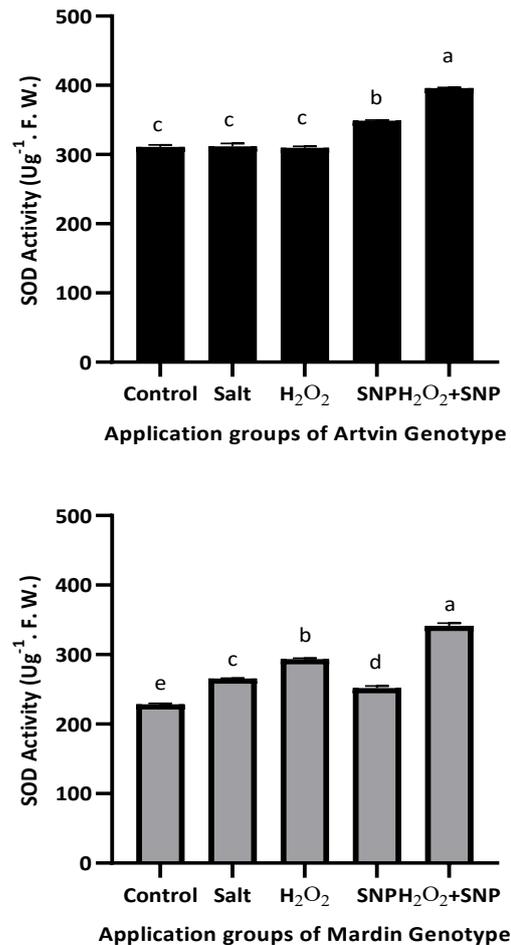


Figure 3. SOD enzyme activity in eggplant genotype

Discussion

Ion toxicity and osmotic stress resulting from salinity inhibit the plant photosystem, leading to excessive ROS production (Hasanuzzaman et al., 2017; Hajhashemi & Pavla, 2020; Wahid et al., 2022). It is known that the increased amount of ROS in the cell increases the amount of MDA by causing lipid peroxidation (Mishra & Choudhuri, 1999). In our study, salt treatment significantly increased the MDA amount in both genotypes. Alone or together both pretreatments decreased the MDA amount but these applications had never as few as the Control group (Figure 1).

Similar to our results, externally applied H₂O₂ in corn (Chen & Li, 2002), mung bean (Saleh, 2007), wheat (Li et al., 2008), barley (Kim et al., 2013), and Panax ginseng (Sathiyaraj et al., 2014) has been reported to prevent the increase in MDA amount by reducing electrolyte leakage, which increases with stress. In cucumber (Hasanuzzaman et al., 2017), soybean (Güler & Pehlivan, 2016), and canola (Gao et al., 2010), H₂O₂ application did not cause any change in the amount of MDA.

It was observed that MDA amounts remained

close to the control group in plants where H₂O₂ and SNP were applied together. Thus, it can be said that H₂O₂ and SNP act in the direction of reducing the lipid peroxidation occurring in the cells by controlling the sudden increases in MDA that occurred in the salt-treated group. Similar to our results, in rice ([Uchida et al., 2002](#)) and citrus fruits ([Tanou et al., 2009a](#)), externally applied H₂O₂+SNP decreased the amount of MDA and this was achieved by reducing the amount of ROS in the cell by stimulating the antioxidant enzyme activity has been reported.

In various studies, it has been reported that CAT activity either increases ([Baysal Furtana & Tipirdamaz, 2010](#)) or does not change ([Nohar et al., 2015](#)) or decreases ([Hasanuzzaman & Fujita, 2012](#)) in plants grown under salt stress conditions. In our study, it was determined that CAT activity increased in plants treated with H₂O₂ alone compared to the only salt-applied group. This increase was found higher and more significant in Mardin genotype. Similar to our study, it has been reported by de ([Azevedo Neto et al., 2005](#)) and ([Gechev et al., 2002](#)) that H₂O₂ applied through leaf increased CAT activity in corn and tobacco. In a different study, it has been reported that the increase in CAT enzyme activity in corn plants treated with H₂O₂ occurs by a complex mechanism including CAT gene regulation ([Gondim et al., 2012](#)). In addition, unlike other enzymes that sweep H₂O₂, it has been reported by ([Mhamdi et al., 2010](#)) that CAT has more affinity for H₂O₂. In addition, CAT transcripts have been reported by researchers to increase in plants treated with H₂O₂ ([Gondim et al., 2012](#); [Mhamdi et al., 2010](#)). In our study, salt stress significantly increased CAT activity in both genotypes. The pretreatments applied alone or together increased the enzyme activity in both genotypes compared to the salt-stressed group (Figure 2). In plants treated with H₂O₂ +SNP, CAT activity reached the highest value among all groups in both genotypes.

In plants treated with NO donor SNP, SOD activity increased in Artvin genotype compared to Control and salt-stressed groups, while it increased compared to the control group in Mardin genotype and decreased compared to the salt-stressed group. NO is thought to be a molecule that regulates ROS metabolism through stimulation of the cellular antioxidant system in stress tolerance. Similar to our results, externally applied NO donor SNP has been reported to increase CAT and SOD activity ([Fan et al., 2007](#)). The SOD enzyme is a powerful antioxidant enzyme whose primary activity causes the change of O₂^{•-} reagent to H₂O₂ and O₂ ([Fridovich, 1986](#)). In our study, under the salt-stressed conditions, SOD enzyme activity did not show a significant increase in the susceptible Artvin genotype, however, increased significantly in the tolerant Mardin genotype. In plants treated with H₂O₂, SOD activity increased in both genotypes compared to Control and only-salt applied groups. H₂O₂+SNP application group significantly increased the SOD activity.

In recent studies, it has been shown that the increase in antioxidant enzyme activity in plants with H₂O₂ and NO pre-treatment is due to the increase in the expression of the genes encoding these enzymes by H₂O₂ and NO ([Beligni & Lamattina, 2001](#); [Neill et al., 2002](#); [de Pinto et al., 2006](#); [Zhang et al., 2007](#)).

Conclusion

In this study, the possible effects of H₂O₂ and NO pretreatment under salt stress on two genotypes of eggplant were studied. 100mM NaCl-stress significantly increased MDA content and CAT activity in both genotypes. H₂O₂ pretreatment slightly reduced the lipid peroxidation in the Artvin genotype and significantly increased the CAT Activity in two genotypes.

H₂O₂ combined with the NO application group significantly reduced the MDA amount in both genotypes compared to the salt-stressed group, this pretreatment also increased the CAT and SOD activity in both genotypes compared the salt-stressed group. H₂O₂ combined with the SNP application group significantly increased the SOD activity in two genotypes.

Author contributions

FOO: Investigation, data curation, visualization, writing and reviewing; **HD and RT:** supervision, conceptualization, administration and reviewing, **GBF** helped to design the analysis and reviewed the paper. All authors have read and agreed to the published version of the manuscript.

Credit

This work was based on the Ph.D thesis studies of the first author Fahriye Öcal Özdamar.

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The effect of different germination times on some nutritional and anti-nutritional properties of green lentil sprouts

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Abstract

In the developing, changing and constantly renewing food and beverage sector, different nutrition trends are becoming more important day by day. One of these is the consumption of germinated legumes, which has attracted attention in the world recently and has many practitioners. The germination process is an effective process on the nutritional values of legumes and can make them even more valuable. The aim of this study was to determine the effects of germination time (3, 6, 9 days) on some nutritional and anti-nutritional contents contained in green lentils sprouts. Both sprouting period and cultivars significantly influenced the nutritional quality of lentil sprouts. The values of protein, starch, phytic acid, condensed tannins, total phenolic, total flavonoid, free radical scavenging activity contents of sprouting periods ranged between 26.4 (Raw) to 27.8% (9 day), 48.8 (raw) to 45.5% (9 day), 0.59 (6 days) to 1.09% (raw), 0.60 (3 days) to 0.77% (9 days), 3.97 (raw) to 10.24 mg GA/g (9 days), 0.55 (raw) 4.58 mg QE/g (9 days), 9.32 (raw) to 13.50% (9 day), respectively. The highest ash, Fe, Cu, Mn and Zn contents were obtained from raw grains with 2.76%, 5.96 mg/100g, 0.95 mg/100g, 1.34 mg/100g and 4.09 mg/100g values. Germination process improved quality of lentils by enhancing the nutritive value and digestibility of nutrients and reducing the anti-nutrients.

Introduction

Lentil (*Lens culinaris* Medic.), which is grown in temperate and sub-tropical climates between 58° North and 40° South latitudes in the world (Alghamdi et al., 2014), is grown in almost every region of Turkey. Lentil is produced 5.7 million tons in the world. It is produced 353 thousand tons in Turkey and with this value, it ranks 3rd in the world's lentil production (FAO, 2019). Lentils, as a pulse crop, are a very important component of agriculture especially in developing countries and nutritional rich-food. Lentil is widely used in human nutrition because of its high protein content, rich vitamin and mineral content, low level of nutrition-hindering factors and shorter cooking (Yadav et al., 2007).

Today, healthy life and healthy food consumption have particularly become the lifestyle of people with

high-income levels. While searching for new sources of functional and healthy foods, special attention has been paid to sprouts from the pulses which are more and more frequently used in human diets worldwide (Ghumman et al., 2016). Ready-to-eat seedlings, commonly known as sprouted seeds that are harvested at the earliest and earliest plant growth stages, play a special role in healthy living (Benincasa et al., 2019).

Sprouted seeds (germinated seeds), which have been known for centuries in many cultures, are widely used because it is technologically can be done without advanced equipment, cheap, has a quick production cycle, simple processing technique, and provides fairly high yields (Delian et al., 2015). This practice is reported to be associated with improvements in the nutritive value of seeds. Sprouted seeds have owned by higher contents of nutrients (amino acids, protein, vitamins, and minerals), and lower levels of non-

nutrients (trypsin inhibitors, tannins, phytates, and lectins) (Troszyńska et al., 2011). Therefore, the sprouts may thus become a potential source of nutritious food or food ingredients. Lentil sprouts contain many functional and health-promoting components. Therefore, its consumption reduces the risk of many diseases such as cardiovascular diseases, diabetes, obesity, inflammation and cancer (Świeca et al., 2013).

The aim of this study was to determine the effects of germination time on some nutritional and anti-nutritional contents contained in green lentils sprouts.

Materials and Methods

Plant materials and germination

Raw green lentil seeds of the Ceren and Ankara Yesili cultivars were provided from Field Crops Central Research Institute in Ankara, Turkey. While the Ankara yesili is a coarse-grained cultivar with a thousand-grain weight of 55.8 g, the Ceren is a small-grained cultivar with a thousand-seed weight of 31.3 g.

In the study, three different germination times (3, 6, 9 days) were applied on two green lentil cultivars. Germination experiments were carried out the factorial arrangement of completely randomized design with 4 replications. For the purpose of surface sterilization of lentil seeds, they were first kept in 1% sodium hypochlorite solution for 15 minutes and then washed several times with distilled water. 200 g of surface-sterilized seeds were placed in separate containers and 1000 ml of distilled water was added to them and kept at room temperature for 6 h. Then the seeds were filtered and kept on blotting paper at room temperature for 2 h. The seeds that are kept to drain the water were placed in germination containers with two layers of filter paper in a way that they would not overlap. They were watered with fresh distilled water when necessary.

The study was carried out at 20°C in the temperature, light and humidity controlled Climate Room of Bilecik Seyh Edebali University Faculty of Agriculture and Natural Sciences. The seeds were germinated in dark conditions for 3, 6, and 9 days. The sprouted seed samples were harvested. During this time, the radicle of the seed came out, and the seed coat was torn. Sprouted seeds were frozen for 12 h to stop the germination process. After thawing at room temperature, then raw and sprouted seeds were dried in a draught oven at 40 °C. The dried samples were ground to pass through a 0.5 mm sieve. Samples were preserved in at +4 °C until analysis. All analyses were performed in 3 replicates.

Chemical analysis

The raw and sprouted samples were analyzed for crude protein (N × 6.25) and ash as described in AOAC, 2000. Total starch and phytic acid was determined enzymatically using a Megazyme Total Starch Assay kit and phytic acid Assay Kit (Megazyme International,

Ireland), respectively. The total flavonoid content was determined by using Arvouet-Grand et al. (1994) with some modifications. The effect of each sample on 2,2-diphenyl-1-picryl-hydrazylhydrate (DPPH) radical was identified according to Gezer et al. (2006) and Yildirim et al. (2021). Total condensed tannin: A 6 ml of tannin solution was added to 0.01 g of ground seed then placed in a tube and mixed on a vortex. The tubes were tightly capped and kept at 100 ° C for 1 hour, and the samples were allowed to cool. Then, they were read at a spectrophotometer at the absorbance value of 550 nm (Bate-Smith, 1975). Condensed tannins were calculated by the following formula: Absorbance (550 nm x 156.5 x dilution factor) / Dry weight (%) (Yildiz et al., 2021). Mineral element concentrations of grain were measured using inductively coupled plasma - mass spectrometry (ICP - MS). All samples were analyzed in duplicate and the mean was used for the statistical analysis (Başaran et al., 2021). The following minerals were quantified: iron (Fe), copper (Cu), manganese (Mn) and zinc (Zn).

Statistical analysis

All experimental results were subjected to two-way analysis of variance (ANOVA) using Minitab Statistical Software. Duncan test was employed to draw the comparison between means and the significance was accepted at $p < 0.05$.

Results and Discussion

The mean of squares and significance for cultivars, sprouting periods, and their interactions of all experiments are given in Table 1. Both sprouting period and cultivars significantly influenced the nutritional quality of lentil sprouts.

Table 1. Mean squares of investigated experiments of two green lentils on raw and different sprouted period

Parameter	Source (DF)			
	Cultivar (C) (1)	Sprouting period (SP) (3)	Rep (3)	C × SP (3)
Protein	17.13**	2.88**	0.07 ^{ns}	0.03 ^{ns}
Starch	18.98**	16.18**	0.06 ^{ns}	1.35*
Phytic acid	0.009 ^{ns}	0.369**	0.003 ^{ns}	0.026**
Condensed tannin	0.005 ^{ns}	0.062**	0.0026 ^{ns}	0.027**
Total polyphenols	3.09**	61.31**	0.10 ^{ns}	2.92**
DPPH radical scavenging	25.45**	30.74**	1.92 ^{ns}	5.37**
Total Flavonoids	0.45*	23.88**	0.09 ^{ns}	0.33*
Ash	1.18**	1.72**	0.03 ^{ns}	0.02 ^{ns}
Iron (Fe)	0.004 ^{ns}	1.53**	0.02 ^{ns}	0.13*
Copper (Cu)	0.0007 ^{ns}	0.005 ^{ns}	0.002 ^{ns}	0.0004 ^{ns}
Manganese (Mn)	0.35**	0.08**	0.002 ^{ns}	0.011*
Zinc (Zn)	1.24**	3.93**	0.004 ^{ns}	0.32**

*: Significant at the $p < 0.05$ probability level, **: Significant at the $p < 0.01$ probability level, DF: Degree of Freedom

The mean value for cultivars, sprouting periods, and their interactions of all experiments are given in Table 2, Table 3 and Figure 1. Protein content varied between 26.4 (Raw) to 27.8% (9 day) with an average

value of 26.9%. Sprouting time caused significant increases in protein content. Ankara Yesili cultivar (27.67%) had higher protein content than Ceren cultivar (26.20%) (Table 2). The increase in protein content is thought to be due to losses in dry weight, especially carbohydrates, along with respiration during germination. The increase of crude protein content during lentil germination has been reported by other researchers ([Fouad & Rehab, 2015](#); [Xu et al., 2019](#)).

Table 2. Some quality experiments of lentil sprouts grown under different germination times

Experiments	PC	SC	PA	CT	TP	TF
Sprouting period						
Raw	26.4b	48.8a	1.09a	0.75a	3.97d	0.55d
3 day	26.5b	47.3b	0.80b	0.60b	8.66c	3.29c
6 day	27.0b	46.5c	0.59d	0.62b	9.13b	3.63b
9 day	27.8a	45.5d	0.70c	0.77a	10.24a	4.58a
Cultivars						
Ceren	26.20 b	46.3b	0.78	0.69	8.31a	3.13a
Ankarayesili	27.67 a	47.8a	0.81	0.68	7.69b	2.89b
Mean	26.9	47.0	0.80	0.69	8.00	3.01

PC: protein content (%), SC: starch content (%), PA: phytic acid (%), CT: Condensed tannin (%), TP: total phenolic (mg GA/g), TF: total flavonoid (mg QE/g)

Table 3. Some quality experiments of lentil sprouts grown under different germination times

Experiments	DPPH	AC	Fe	Cu	Mn	Zn
Sprouting period						
Raw	9.32c	2.76a	5.96a	0.95	1.34a	4.09a
3 day	12.32b	2.43b	5.81b	0.93	1.24b	3.22b
6 day	13.34a	2.17c	5.37c	0.90	1.17c	2.89c
9 day	13.50a	1.66d	5.16d	0.89	1.11d	2.43d
Cultivars						
Ceren	12.95a	2.06 b	5.59	0.92	1.11 b	3.36 a
Ankarayesili	11.29b	2.45 a	5.56	0.91	1.32 a	2.96 b
Mean	12.12	2.30	5.58	0.92	1.21	3.16

DPPH: Free radical scavenging activity (%), AC: ash content (%), Fe: iron content (mg/100g), Cu: copper content (mg/100g), Mn: manganese content (mg/100g), Zn: zinc content (mg/100g)

Starch content in raw grain and in samples obtained at germination times of raw, 3, 6 and 9 days was 48.8%, 47.3%, 46.5%, and 45.5%, respectively. Ankara Yesili cultivar (47.8%) had higher starch content than Ceren cultivar (46.3%) (Table 2). According to C X SP interaction, the highest starch content was obtained in raw seed of Ankara Yesili cultivar with 49.1% (Figure 1). Although the reduction in starch varied due to different species and germination conditions, these decreasing trends are close with the previous studies in lentils ([Ghavidel & Prakash, 2007](#); [Fouad & Rehab, 2015](#)). Some enzymes activated during the germination of legumes seeds are responsible for the conversion of starch into oligosaccharides or monosaccharides resulting in reduction ([Olaerts et al., 2015](#)). It is thought that this situation causes significant decreases in starch

content during sprouting time, as in our study.

According to germination time, phytic acid and tannins content of genotypes ranged from 0.59 (6 days) to 1.09% (raw) and 0.60 (3 days) to 0.77% (9 days), respectively. The sprouting process caused significant decreases in phytic acid and tannins content up to day 6 of germination (Table 2). According to C X SP interaction, the highest phytic acid content was obtained in raw seed of Ceren and Ankara Yesili cultivars with 1.10% and 1.08%, respectively. The highest tannins content was obtained in raw seed of Ceren cultivar with 0.83% (Figure 1). Antinutrients, extensively found in plant part, have both health advantages and disadvantages. For example, phytic acid binds some minerals and forms insoluble complexes. Germination significantly reduced the phytic and tannin contents as previously observed by [Fouad & Rehab \(2015\)](#) in lentil seeds. [Khattak et al., \(2007\)](#) indicated that the decrease in phytate content in lentil seeds during germination is associated with an increase in phytase activity. [Shimelis & Rakshit \(2007\)](#) and [Saharan et al. \(2002\)](#) reported that the decrease in tannins of seeds during the germination process may be due to the leaching of tannins into water and binding of polyphenols with other organic materials.

As germination days progressed, a significant increase in the total phenolic and flavonoids content of lentil seeds were observed. According to germination time, total phenolic and flavonoid contents of genotypes ranged from 3.97 (raw) to 10.24 mg GA/g⁻¹ (9 days) and 0.55 (raw) 4.58 mg QE/g (9 days), respectively. For both experiments, higher values were determined in Ceren cultivar than in Ankara Yesili cultivar. According to C × SP interaction, the highest total phenolic (11.12 mg GA/g⁻¹) and flavonoid contents (4.71 mg QE/g⁻¹) were obtained in the 9-day seed of Ceren cultivar (Figure 1).

[Randhir et al. \(2004\)](#) reported that these increases that occur in total phenolic with the germination process could be due to the biosynthesis and bioaccumulation of phenolic compounds as a defensive mechanism to survive under environmental stresses. After germination, diverse changes in the phenolic compounds happen which are depending on many factors like the type of seeds, germination time, etc [Fouad & Rehab, \(2015\)](#). Flavonoids are prevalent in plant parts. In the study by [Fouad & Rehab, \(2015\)](#), the total phenolic and flavonoids of raw lentil seeds were significantly lower than sprouted seeds.

Sprouted seeds had significantly higher DPPH compared to raw seeds. The highest DPPH was determined in the 9-day sprout period (13.50%), while the lowest was in the raw seed (9.32%) (Table 3). According to C X SP interaction, the highest DPPH content was obtained in 9-day of Ceren cultivar with 15.5% (Figure 1). Ceren cultivar (12.95%) had higher DPPH content than Ankara Yesili cultivar (11.29%) (Table 3). DPPH is one of the most important methods to evaluate the antioxidant properties of plants and is

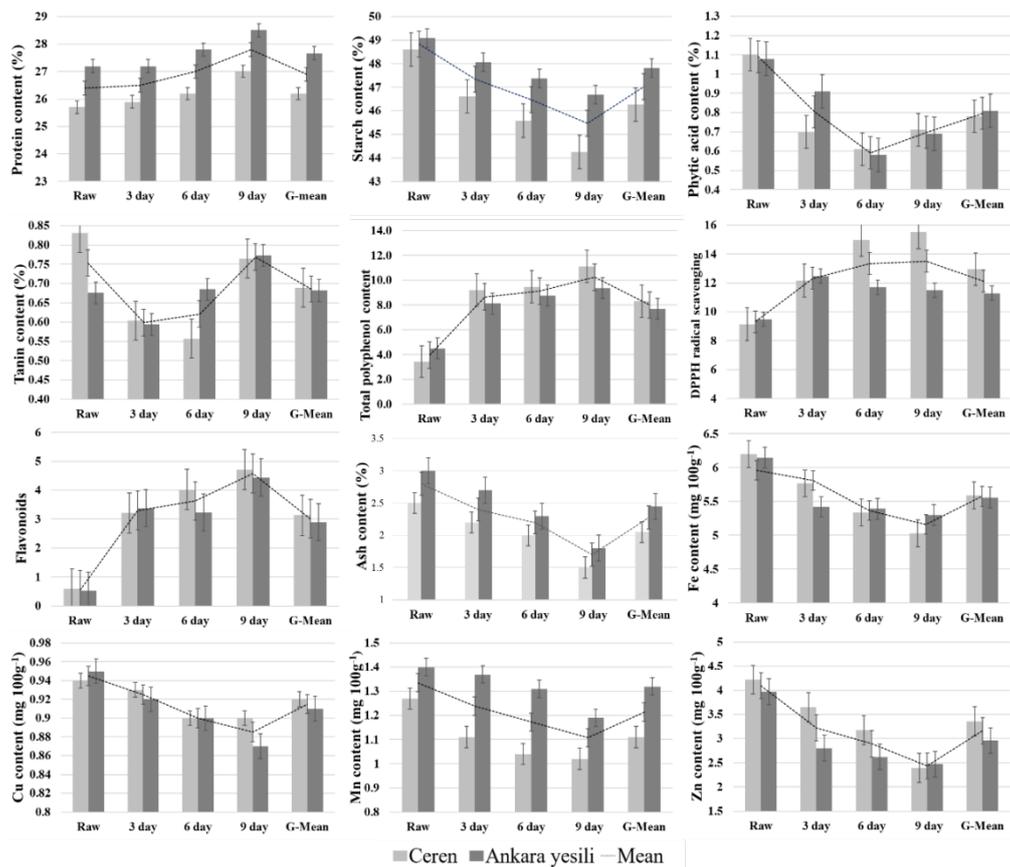


Figure 1. Cultivar \times sprout period interaction for all experiments

desirable to be high. Phytochemicals have high DPPH, which helps to reduce the risk of some diseases (chronic diseases and cancer etc.,) (Lako et al., 2007).

As germination days progressed, a significant (except for Cu) decrease in the ash, Fe, Cu, Mn and Zn of lentil seeds were observed. The highest crude ash, Fe, Cu, Mn and Zn contents were obtained from raw grains with as 2.76%, 5.96 mg/100g⁻¹, 0.95 mg/100g⁻¹, 1.34 mg/100g and 4.09 mg/100g values. The lowest values for all of these experiments were obtained after 9 days of germination (Table 3). It was determined that the G \times SP interactions of Fe, Mn and Zn contents were important (Table 1 and Figure 1). In the study conducted by Ghavidel & Prakash, (2007) on some legume seeds, they found that some minerals such as Fe, Ca and P contents decreased with the germination process, but the biological availability of these minerals increased. In addition, the same investigator also determined a decrease in ash content with germination.

Conclusion

Lentil sprouts have become a highly desirable food product in recent years due to their nutritional content and health benefits. In this study, it was determined that the nutrient content of green lentil varieties changed with the germination process. On the

9-day of germination, the protein content increased while the tannin content decreased. The cultivars responded differently to the investigated experiments. The germination process improved the quality of lentils by enhancing the nutritive value and digestibility of nutrients and reducing the antinutrients.

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Author Contributions

The authors contributed equally to this work.

Conflict of Interest

The author(s) declare that they have no known competing financial or non-financial, professional, or personal conflicts that could have appeared to influence the work reported in this paper.

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Determination of the working performance of a new fertigation system developed for hose reel irrigation machine

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Abstract

The aim of this study is determining of the working performance of the a new fertigation system (TURPO CLK FS) that developed for hose reel irrigation machines (HRIM). As a liquid fertilizers nitrogen and phosphorus were used. The HRIM was operated under two different irrigation water pressures (5 and 2.5 bar) conditions. The dosing pump was operated for two different frequencies (150 and 300 pulse/min). Field experiments were realised by using two different liquid chemical fertilizers and measured of pH, electrical conductivity (EC), and total dissolved solids (TDS) values. According to evaluation when using nitrogen fertilizer pH values ranged between 8.40 - 8.59, EC values 602.92 - 915.83 $\mu\text{S}/\text{cm}$, and the TDS values 294.17 - 451.25 mg/L at all sets. When using phosphorus fertilizer, pH values ranged between 7.13 - 8.03, EC values 485.42 - 519.58 $\mu\text{S}/\text{cm}$, and TDS values 236.25 - 252.92 mg/L. And then the Christiansen Coefficient of Uniformity (CCU) was calculated over 24 samples in each set. The CCU values were founded between 95.02% - 99.95%. As the result it has been concluded that the TURPO CLK FS could be used together with HRIM during fertigation applications.

Introduction

Irrigation is one of the two critical cultural processes and the other is fertilization, aimed at reducing the unit product cost by increasing yield and quality in crop production. In a general definition, irrigation and fertilization is the application of water and plant nutrients that plants need and cannot be met naturally to the plant root zone or directly to the plant (Cetin & Tolay, 2020). While fertigation was used in horticulture and greenhouse agriculture in the past, it has started to be used in field agriculture as a result of technological developments in irrigation machines in recent years. Due to the synergy created by the use of fertilizer and water, there is an increase in yield and quality in plant production where fertigation is applied (Imas, 1999). The use of HRIMs has become quite common in recent years. Water usage efficiency is high

and application methods are easy. In this study, an HRIM with fertigation system developed by us was used. Here, the function of the dosing pump is to mix the fertilizer into the irrigation water line in a uniform and homogeneous phase. The mixing of the fertilizer with the irrigation water is done according to a predetermined ratio. Dosing pumps are manufactured in many different types and powers and are generally used with a control unit. In this study, a dosing pump was used together with an electronic control unit

The amount of fertilizer to be mixed into the irrigation water is determined by controlling the frequency of the dosing pumps. In the fertigation technique, synergy is achieved by applying irrigation water and fertilizer together to the plants. Thus, required labor costs of fertilizer distribution are also reduced. Chemical or organic fertilizers used in fertigation systems should be either in liquid form or

dissolved in water. There are problems the supplying of electricity to the electronic control units during the fertigation in the field. For this reason, it is important that feeding of dosing system by a source independent of the grid, such as solar energy. Thus, dosing pump that fed by photovoltaic panel system was used in the study.

Materials and Method

Materials

Study field

The field experiments of this study was done in research area belonging to the Field Crops Central Research Institute- İkişce Research and Application Farm of Agriculture and Forest Ministry. This research area is a field has barley stubble and no slope.

In order to finish the experiments related to irrigation water mixed with fertilizer in a short time, attention was paid to the fact that the selected field was close to the laboratory where the measurements would be made. A hydrant was used to feed HRIM on the field where the study was carried out. The pressure can be adjusted by different values through valve of hydrant. Another reason why the study was carried out on a field with stubble is transporting easily the water collection containers (WCC) placed in the machine work area are from the mud formed after irrigation to the field without stubble. The field where the study was done is shown in Figure 1.



Figure 1. Study field

Hose reel irrigation machine

HRIM is trailed type agricultural machine that makes sprinkler irrigation and works with pressurized water. Its main components consist of a trailer, bodywork, drum, polyethylene pipe with a length of 400 m and a diameter of up to 125 mm, turbine-gear box mechanism and water distributor (boom or gun). The use of machine is simple and its water use efficiency is extremely high.

The “turbine-gearbox combined mechanism” on the HRIM converts the kinetic energy of the pressurized irrigation water to the work and moves the water distributor carrier and provides conveying water with

the polyethylene pipe.

In our study, an equipment with a fertigation system named TURPO CLK FS with a boom designed for HRIMs and a 400 m long PE water pipe was used (Figure 1). The TURPO CLK FS, which has a photovoltaic panel, can fertilize independently from the electricity grid in field conditions (Figure 2).



Figure 2. HRIM equipped TURPO CLK FS with PV

Portable pH, EC, TDS, and temperature meter (HI9811-5)

A multifunctional portable measuring device HI9811-5, which can measure four values (pH, EC, TDS, temperature), is used. The aforementioned device is easy to use and has the ability to measure with high precision. Measurements were made using a combined probe connected to the device with an 8-pin DIN connector (from the User's Manual). The measured values were read on the liquid crystal display of the device as EC $\mu\text{S}/\text{cm}$ and TDS mg/L . The accuracy of the instrument is $\pm 2\%$ for EC, $\pm 2\%$ for TDS and ± 0.1 for pH. Figure 3 shows the portable HI9811-5.



Figure 3. Portable HI9811-5

Dosing pump and liquid chemical fertilizers

In the TURPO CLK FS built on HRIM, there is an ENELSA-ANTECH brand NOVA-D model volumetric dosing pump with 0.555 ml stroke. The pump has a solenoid coil and a teflon diaphragm. Suction and discharge pipes with an outer diameter of 8 mm and an inner diameter of 6 mm were used to connect the dosing pump to the fertilizer tank and the pressurized irrigation water pipe. Since the cross-sectional areas of the pipes used are small, liquid fertilizers were

preferred in order to avoid clogging in the system during operation. The dosing pump can be operated at different frequencies by using the adjustment buttons on the electronic control unit integrated into the pump.

In the experiments, UAN 32 fertilizer containing 32% nitrogen (8% NH_4 , 8% NO_3 , 16% NH_2) and micronutrients (boron, copper, iron, manganese, zinc and molybdenum) and phosphorous fertilizer containing 61% phosphorus pentoxide (P_2O_5) in acidic character (CLEANPHOS) was used. One of the reasons why the aforementioned fertilizers are preferred is that no clogging occurs in the nozzles. Figure 4 shows photographs of the dosing pump used in this study.



Figure 4. Dosing pump

Water collection containers

In the study, a boom with nozzles, which is an organ of HRIM, was used. There are 34 nozzles with 8 mm hole diameter and impact plate placed at 140 cm intervals on the lower part of the boom, which has a working width of approximately 50 m. During irrigation, samples were taken from the outlet of the nozzles with water collection containers placed in the field under the nozzles. While placing the water collection containers (WCC) under the boom, care was taken to have them both directly under and between the nozzles. The samples taken contain a mixture of water and fertilizer. 6 WCC with a cross-sectional area of 1200 cm^2 and a volume of 30 L were used. After the boom had passed through the sampling points, the lids of the WCC were quickly closed to prevent evaporation losses. Figure 5 shows the WCC lined up under the boom.



Figure 5. WCC lined up under the boom

Method

In the arrangement of the experiment plots, 6 plots with 4 replications were created with 2 different fertilizers. Samples were obtained from each of the 8 experimental sets with the help of 24 WCCs with lockable lids. According to the experiment plan, HRIM was operated at two different pressures, the first being 5 bar and the second being 2.5 bar. Adjustment is made using the slider of the hydrant valve. Two different liquid chemical fertilizers (UAN 32 and CLEANPHOS) containing nitrogen and phosphorus were given to the pressurized water line at two different frequencies, 150 pulses/min and 300 pulses/min, with a 0.555 mL stroke volume dosing pump. The dosing pump can be operated at different frequencies by using the adjustment buttons on the electronic control unit integrated into the pump. Repeated experiments were made by opening the 200 m irrigation pipe of the HRIM placed in the study area. In order to collect the samples mixing fertilizer into the irrigation water, 6 WCC were placed under the boom.

In order to transmit the water-fertilizer mixture to the boom at a distance of 400 meters at the first time start-up of the HRIM, the hydrant valve was opened until the machine was supplied with water, and the pressure value of 5 bar was read from the manometer on the machine. It was observed that after the valve was opened, water sprayed from the nozzles in 120 seconds for a pipe length of 400 m. Thus, it has been determined that the velocity of the water in the pipe can reach up to 12 km/h.

The turbine gearbox mechanism, which is the main part of HRIM, converts the kinetic energy of water into mechanical energy. The peripheral speed of the drum can be adjusted by changing the cross-sectional area where the water enters the turbine. The adjusted speed value can be easily read from the speedometer on the HRIM. Drum circumferential speed, which is a linear speed, also determines the speed of the boom in the field during irrigation. Thus, in all sets and repetitions of the experiment, it was ensured that the boom passed over the WCCs in the field at a constant speed of 30 m/h. The images of the manometer and speedometer on the HRIM during operation are shown in Figure 6.



Figure 6. Manometer and speed meter on the HRIM

After measuring the instantaneous and average wind speed with an anemometer on the boom, the experiments were started. In order to make accurate measurements, the work was suspended on windy and rainy days. HRIM with TURPO CLK FS was placed next to the hydrant and 6 WCC were placed 8 m back from the boom. The boom with a feed rate of 30 m/h reached the WCC lined axis after about 15 minutes. The boom then completed its passage over the WCC and the lockable covers of the WCC were immediately closed.

For each set, 24 WCCs were placed in the experiment area. Measurements were made using the calibrated portable HI9811-5 and recorded in the pre-prepared observation log. Immediately after the measurements in one set were completed, the WCC and its lids were cleaned by flushing with adequate tap water. In this way, erroneous measurements that may occur due to WCC contamination of liquid chemical fertilizers applied at different doses in different sets are prevented.

Result and Discussion

Working performance of TURPO CLK FS was determined by measuring the pH, EC, and TDS values of the irrigation water mixed fertilizer in WCC in different sets and making the CCU calculation. Irrigation water samples taken without fertilizer mixing were used to determine the mean values of pH, EC and TDS before fertigation and were determined as 8.7, 560 $\mu\text{S}/\text{cm}$ and 270 mg/L, respectively. After nitrogen fertilizer application, average pH values for different dosage pump frequencies at different irrigation water pressures are between 8.40 and 8.59, EC values were between 602.92 and 915.83 $\mu\text{S}/\text{cm}$, and TDS values are between 294.17 and 451.25 mg/L. After using phosphorus fertilizer, pH values were between 7.13 and 8.03, EC values were between 485.42 and 519.58 $\mu\text{S}/\text{cm}$, and TDS values were between 236.25 and 252.92 mg/L for different dosage pump frequencies at different irrigation water pressures.

HRIM is a turbine driven, automatic rewind and water saving irrigation equipment. In order to use the kinetic energy of the water, the pressurized water coming from the hydrant comes to the turbine-gear box mechanism. The rotation of the water turbine-gearbox mechanism realizes the rotation of the drum that pulls the PE pipe and the boom carrier car. In the meantime, pressurized water is transmitted through the PE pipe to the nozzles on the boom and sprinkler is carried out. The system can be used in different areas of irrigation projects for water saving purposes.

Plant nutrients to be used in fertilization should be mixed homogeneously into the irrigation water. For this reason, the working performance of the systems that mix fertilizer into the irrigation water in fertigation applications is extremely important. The performance of the systems is determined by measuring whether the fertilizer-water mixture is homogeneous. In

addition, the phase of the fertilizer to be mixed with the irrigation water also affects the homogeneity of the fertilizer-water mixture. More homogeneous fertilizer-water mixtures are obtained by mixing liquid fertilizers with irrigation water instead of solid fertilizers.

In a study, the nitrogen ratio taken from the fertilizer applied with the drip irrigation method in tomato production was determined and compared with other fertilizer application methods. In the aforementioned study, drip and furrow irrigation method was applied by applying 6 different sets of fertilizer to the irrigation water and plant row during planting and flowering periods. In the soil analyzes made after the study, it was seen that most of the nitrogen fertilizer applied in the application with the drip irrigation method was removed from the plant and fertilizer was given to the plant row, but if nitrogen fertilizer was mixed with the irrigation water, such a problem did not occur. It has been shown that the efficiency of fertilizer use in nitrogen applications made by adding fertilizer to the irrigation water with the drip irrigation method is higher than the nitrogen applications made by adding fertilizer to the plant row with the furrow irrigation method ([Miller et al., 1976](#)).

In a study comparing the sprinkler irrigation method and irrigation with a gun, the water distribution in the soil and on the surface during and after irrigation was investigated. As a result of the study, it was determined that the distribution of the amount of water entering the soil at the sampling points showed unacceptably large differences. Since the amount of water entering the soil is less than the amount of water applied, it has been stated that ponds occur on the soil surface and in small and inclined areas of surface runoff. The CCU equation was used to calculate the uniformity of the distribution of water distributed over the soil surface and entering the soil. In the calculation made using the amount of water applied and the amount of water collected, it was seen that the irrigation efficiency was 80%. It has been reported that both the amount of water per unit area and the water uptake rate of the soil should be taken into account in systems where components that apply water only once through the area where it acts, such as a movable sprinkler gun, will be used ([Cook, 1983](#)).

In an article published on the future of the irrigation industry, it is reported that in the systems to be designed in the future, advanced equipment that mixes plant nutrients into irrigation water according to the need to increase crop yield will be available and applications called fertigation technique will become widespread ([Burt, 1995](#)).

In a study, the effects of wind speed and operating pressure on the water distribution uniformity of linear irrigation motion systems were investigated. It is stated that circular and linear irrigation systems have become widespread in Southeastern America in recent years. It has been pointed out that mobile irrigation systems are used in large areas and it is stated that there is a need

for measurable information about the performance of sprinkler equipment in working conditions. Two types of sprinkler nozzles were tested in the study. One of these nozzles is a fixed rib plate LDN (low drag nozzle), and the other is IWOB (rotating plate nozzles and swinging diffuser nozzles), allowing the water to diffuse away from the center by shaking it. It has been stated that LDN nozzles are designed to prevent droplet drift by producing large droplets in irrigation works carried out in low pressure and windy conditions. In LDN nozzles used to prevent droplets from entrainment, irrigation water is distributed through a fixed plate with a certain number of grooves on it. It has been stated that the design of IWOB nozzles is to provide high water distribution homogeneity regardless of the pressure and flow rate of the water. It has been explained that a movable distributor rotates around a center in IWOB nozzles, which are used to provide high water distribution homogeneity. It is stated that the use of both LDN and IWOB sprinkler nozzles in linear and circular motion irrigation systems has become widespread ([Dukes, 2006](#)).

In the study conducted for the distribution of cattle manure used in corn production, the feasibility of the fertigation system, which is a new technique because it is more environmentally friendly, was evaluated. Thus, conventional fertilizer distribution systems and fertigation systems used with HRIM were compared. It was noted that nitrogen losses in the form of nitrates were less in the water and air samples taken from the fertigation application area. It has been reported that the unused nitrogen lost due to low-efficiency practices in agricultural areas increases the algae density in water resources such as lakes, ponds, estuaries, and rivers, reducing oxygen, and as a result, it causes the death of many microorganisms. This oxygen reduction leads to eutrophication. In order to prevent the pollution that occurs in this way, it has been explained that fertilizers should be given when the plants need it, in the right amount and with the right technique ([Bortolini & Bisol, 2008](#)).

In a study conducted in field conditions, it was stated that the fertigation technique was an effective method and was recommended to farmers. It has been claimed that, thanks to fertigation in many plants, an increase in efficiency between 20% and 60% is achieved, and a savings of between 20% and 70% can be achieved in water use. It has been stated that fertigation is a useful technique that increases the efficiency of water and fertilizer use, has a high technological level and cost, but is beneficial. It has been explained that solid fertilizers and liquid fertilizers can be used in fertigation application. It is reported that fertigation is important for the effective use of fertilizer and water, especially in arid and semi-arid regions ([Biswas, 2010](#)).

In a study conducted in soilless environment (hydroponic farming) in two different modern greenhouses equipped with NMC-PRO and DARES

brand fertigation systems. Equipment costs and water and fertilizer use efficiency were compared in different fertilization systems. It has been reported that the cost and water use efficiency of the NMC PRO fertilization system is higher than the DARES fertilization system. It has been stated that the fertilizer use efficiency is equal in both systems ([Chen et al., 2014](#)).

In a study, fertigation equipment used in drip irrigation systems was tested in gardens and the advantages of fertigation application were explained. These advantages are savings in water and energy and fertilizer application labor, reduction of possible pollution in both soil and groundwater due to not washing the pesticides and fertilizers used, the fertilizer use efficiency being up to 80%, and the reduction of water and fertilizer losses in sloping and uneven lands. In addition, after fertilization, it is another advantage to use irrigation systems that only address the root zone by reducing the density of weeds without the need to spare time for irrigation, adding some fertilizing equipment to the old irrigation systems ([Sovaiala et al., 2017](#)).

In a study conducted with HRIM for fertigation, an external system was designed using a pump that does not need electrical energy and works with the proportional dosing principle. In order to determine the working performance of the system, food coloring was mixed into the irrigation water instead of fertilizer. Then laboratory and field experiments were carried out. In the experiments, the amount of residue on the filter papers placed in the HRIM study area during irrigation was measured by colorimetric method and statistical analyzes were made. It has been suggested that the use of HRIM and dosing pumps can increase the fertilizer use efficiency. It has been claimed that when the fertilizer is mixed with the irrigation water by dosing pump, the coefficient of variation (CV) of the fertilization distribution homogeneity is between 21-38% and is at an acceptable value ([Demircioğlu & Çelen, 2020](#)).

The uniformity of HRIM's water distribution is important to the performance of fertigation applications. The reason for this is that the amount of fertilizer applied per unit area in fertigation applications is a function of the amount of irrigation water mixed with fertilizer per unit area. In this study, it was tried to determine whether the fertilizer mixed with irrigation water was uniform or not.

In this study, a set was formed with the samples taken with the help of 24 water collection containers placed in the HRIM study area. CCU values were calculated using pH, EC and TDS values as percentages. CCU values, which are an indicator of fertilization performance of the TURPO CLK FS. At the end of the calculations, it was found that each of the 8 sets of CCU values for pH, EC and TDS varied between 95.97% and 99.95%, between 95.02% and 98.71%, and between 95.12% and 98.87%, respectively.

The average pH, EC and TDS values obtained by

using the TURPO CLK FS for nitrogen fertilizer at different irrigation water pressures and different dosing pump frequencies are given in Table 1.

Table 1. Average pH, EC, and TDS values in nitrogen fertilizer use

Irrigation water pressure (bar)	Dosing pump frequency (pulse/min)	Average pH	Average EC ($\mu\text{S/cm}$)	Average TDS (mg/L)
5	150	8.58	602.92	294.17
	300	8.58	690.42	339.17
2.5	150	8.59	694.17	341.67
	300	8.40	915.83	451.25

EC: Electrical conductivity, TDS: Total dissolved solids

The average pH, EC and TDS values obtained by using the TURPO CLK FS for phosphorus fertilizer at different irrigation water pressures and different dosing pump frequencies are given in Table 2. The experiment was carried out by measuring the average values of pH, EC and TDS measured in irrigation water mixed with liquid chemical fertilizer. The experiment plan consists of 8 sets and two different irrigation water pressures, two different fertilizers and two different dosing pump frequencies were used as factors. While pH, EC and TDS values differ between sets, they show high homogeneity in 24 irrigation water samples mixed with liquid fertilizer in the same set.

Table 2. Average pH, EC, and TDS values in phosphorus fertilizer use

Irrigation Water Pressure (bar)	Dosing Pump Frequency (pulse/min)	Average pH	Average EC ($\mu\text{S/cm}$)	Average TDS (mg/L)
5	150	8.03	519.58	252.92
	300	7.53	503.75	244.17
2.5	150	7.58	504.58	244.17
	300	7.13	485.42	236.25

EC: Electrical conductivity, TDS: Total dissolved solids

In Table 3, the pH, EC and TDS values measured in 24 irrigation water samples mixed with nitrogen fertilizer in each set are given together with the calculated CCU values. In Table 4, the pH, EC and TDS values measured in 24 irrigation water samples mixed with phosphorus fertilizer in each set are given together with the calculated CCU values.

Table 3. CCU values for pH, EC, and TDS in nitrogen fertilizer use

Irrigation Water Pressure (bar)	Dosing Pump Frequency (pulse/min)	CCU Values for pH (%)	CCU Values for EC (%)	CCU Values for TDS (%)
5	150	99.95**	97.36	97.05
	300	99.62	98.71	98.87
2.5	150	99.72	95.02*	95.12
	300	99.95	96.57	96.65

CCU: Christiansen Coefficient of Uniformity, EC: Electrical conductivity, TDS: Total dissolved solids

Table 4. CCU values for pH, EC, and TDS in phosphorus fertilizer use

Irrigation Water Pressure (bar)	Dosing Pump Frequency (pulse/min)	CCU Values for pH (%)	CCU Values for EC (%)	CCU Values for TDS (%)
5	150	95.97	96.87	96.72
	300	99.09	98.61	97.72
2.5	150	98.24	97.62	97.67
	300	99.10	98.18	97.80

CCU: Christiansen Coefficient of Uniformity, EC: Electrical conductivity, TDS: Total dissolved solids

Another factor affecting the working performance of the developed TURPO CLK FS is HRIM water distribution homogeneity. In this study, both nitrogen and phosphorus liquid chemical fertilizers were used together with irrigation water. The amount of nitrogen mixed with irrigation water (ANWCC- kg) and the amount of phosphorus (APWCC- kg) were obtained from the samples collected in the water collection cups placed under the boom. The average values calculated for the CCU for HRIM water distribution homogeneity in all sets where the operation is performed at different irrigation water pressures and different dosing pump frequencies are given in Table 5. When Table 5 is examined, it is seen that the HRIM water distribution homogeneity used in the study is at least 80.06% and at most 88.91%.

Table 5. Average and CCU values for ANWCC and APWCC

Measurements	5 bar	5 bar	2.5 bar	2.5 bar
	150 pulse/min	300 pulse/min	150 pulse/min	300 pulse/min
ANWCC				
Average (kg)	5.40	5.39	4.35	4.27
CCU (%)	88.91	85.30	83.88	84.95
APWCC				
Average (kg)	5.75	5.69	4.41	4.43
CCU (%)	85.35	88.38	86.69	80.06

ANWCC: The amount of nitrogen mixed with irrigation water (kg), APWCC: The amount of phosphorus mixed with irrigation water (kg), CCU: Christiansen Coefficient of Uniformity, EC: Electrical conductivity, TDS: Total dissolved solids

Conclusion

In the study, the working performance of the TURPO CLK FS developed for HRIM was determined. The main component of the TURPO CLK FS is a dosing pump fed from a photovoltaic panel. The pump was operated at different frequencies. With the help of the developed system, liquid chemical fertilizers can be applied to irrigation water in field conditions, independently of the electricity network. The homogeneity of the fertilizer mixed irrigation water was determined by calculating the CCU. 24 different CCU values were calculated for pH, EC and TDS values in 8 sets of experiments. Calculations showed that the the lowest CCU value was 95.02% and the highest CCU value was 99.95%. In the TURPO CLK fertigation system, there is no mixing component (mixer, etc.) for homogeneous mixing of liquid chemical fertilizers with irrigation water, that is turbulence. Although it is not a mixing component, the CCU values calculated to determine the operating performance of TURPO CLK FS revealed that the fertilizer-water mixture showed a high level of homogeneity.

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Author Contributions

TP: Conceptualization, Data Curation, Formal Analysis, Funding Acquisition, Investigation, Methodology, Project Administration, Resources, Supervision, Validation, Visualization, Writing-Original Drafting, Writing-Review and Editing; **AÇ:** Theoretical Management of Thesis, Conceptualization, Data Curation, Formal Analysis, Funding, Review, Methodology, Project Consulting, Resources, Audit, Verification, Visualization, Writing-Original Drafting, Writing-Reviewing and Editing; **MAD:** Formal Analysis, Methodology, Visualization and Writing-Examination, Orientation and Arrangement; **HA:** Formal Analysis, Methodology, Visualization and Writing-Examination, Direction and Editing.

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Effects of soil conditioner and humic acid applications on the development of some soil quality parameters

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Abstract

This study was conducted under greenhouse conditions in order to determine the effects of polyvinyl alcohol (PVA), polyacrylamide (PAM) and humic acid (HA) applications on the improvement of some soil quality (erosion ratio and coefficient of linear extensibility) parameters. Surface soil samples with three different textures (clay, loam and sandy loam) were used in the study. In the greenhouse, PVA, PAM and HA were applied to soil samples at doses of 500, 100 and 500 ppm, respectively, and incubated in four different periods (0, 15, 30 and 45 days). During the incubation, irrigation was performed when 50% of the available moisture in the soil samples was decreases. As a result of the analysis and evaluation made on the soil samples after the incubation, it was determined that PVA, PAM and HA applications reduced the erosion ratio and linear extensibility values in all three soil groups and that the conditioners were more effective in the soil in clay texture category. It was observed that the conditioners were ranked as PVA>PAM>HA in terms of the said effectiveness. It was observed that PVA's first period applications were more effective on erosion resistance and PVA's second period applications were more effective on coefficient of linear extensibility.

Introduction

The demands created by the increasing population and developing economies and the widespread use of inappropriate production techniques in agricultural systems cause degradation of soil quality, the emergence of certain environmental problems and a decrease in the crop production (Verhulst et al., 2010; Martinez-Blanco et al., 2011). Soil conservation has traditionally emphasized the processes involved in keeping soil in place for agricultural production (Blanco & Lal, 2008). Development of agricultural practices and management of soil resources should take into account land use models, cultivation practices, and consequences on the environment (Dickinson, 2015). Accelerated erosion caused mainly by human activities in nature is the most important factor of soil

degradation. Erosion causes a decrease in yield in soils and the loss of soil's organic matter, clay content, plant nutrients, soil water, and fertile topsoil to be cultivated, and significantly restricts plant development (Özdemir, 2013).

Soils are subjected to shrinkage and expansion processes as a result of successive drying and wetting processes depending on their basic properties such as mechanical composition, clay content, clay type, and organic matter content. Cracks that occur due to swelling and shrinkage events cause damage to plant roots and young seedlings, negatively affect the water and air balance of the soil, increase moisture loss, decrease the effectiveness of irrigation water, and cause deterioration of the soil structure (Sönmez & Öztaş, 1988; Dengiz & Gürsoy, 2019). Therefore, revealing the swelling and shrinkage potentials of soils is very important in terms of applications related to soil

management. In the studies conducted, it has been found that it is possible to apply organic polymers to improve the structural stability of the soil ([Harris et al., 1966](#)), and that artificial polymers can be used to improve the physical properties of soils in a short time ([Levy, 1996](#)). To this end, in recent years, studies on various soil stabilizers of organic origin such as polyvinyl alcohol (PVA), polyacrylamide (PAM) and humic acid (HA) have been intensified. Most of these studies show that the application of synthetic organic polymers and humic acid to the soil surface even at very low concentrations has positive effects on the structural properties of the soil ([De Boodt, 1993](#); [Sojka & Lentz, 1994](#); [Zhao & Xu, 1995](#); [Nadler et al., 1996](#); [Imbufe et al., 2005](#); [Gizgin, 2020](#); [Civelek, 2021](#); [Fahramand et al., 2014](#)).

Synthetic polymers are effective in increasing hydraulic conductivity and porosity, improving water-holding capacity ([Shanmuganathan & Oades, 1982](#)), and increasing resistance to erosion ([Wood & Oster, 1985](#)). In the studies conducted in this respect, polymers such as ammonium lauryl sulphate, liquefied humic substance ([Ritchey et al., 2012](#)), polyvinyl alcohol and polyacrylamide ([Yilmaz & Uysal, 2010](#); [Yönter, 2010](#)) are focused on. ([Cochrane et al., 2005](#)) found that phosphogypsum (PG), polyacrylamide (PAM) and (PG + PAM) applications under simulated rainfall conditions significantly reduced soil losses in splash erosion, while Sinkpehoun and ([Yönter, 2018](#)) found that liquefied humic substance applications did the same thing. In their study, ([Piccolo et al., 1997](#)) reported that the application of humic acid to the soil reduced soil loss by 36% and increased aggregate stability and water-holding capacity.

The determination of the degrees of contribution or effect of the components affecting the swelling and shrinkage potential or the susceptibility to erosion in the soil is very important in terms of creating an ideal plant development medium, reducing water losses, controlling erosion, and planning an appropriate land management. This study was conducted to determine the effects of polyvinyl alcohol (PVA), polyacrylamide (PAM) and humic acid (HA) applications on the erosion ratio and coefficient of linear extensibility (COLE-bar) parameters for soils with clay (C), loam (L) and sandy loam (SL) texture.

Materials and Methods

The research was carried out on surface (0-20 cm) soil samples taken from Ondokuz Mayıs University Faculty of Agriculture, experiment area (41°36'-36°18' N) and Ondokuz Mayıs University, Bafra application field (41°55'-35°86'; 41°50'-35°82' E). In the greenhouse experiment, three different soil conditioners were used: humic acid, polyvinyl alcohol and polyacrylamide. As humic acid, commercially-available material containing 15% humic matter was used. Fluka-labeled material, which is insoluble in organic solvents and especially soluble in hot water, is used as polyvinylalcohol. As polyacrylamide, water-soluble PAM obtained from the company ACROS was used.

Surface soil samples taken from the land were dried in the shade and then passed through a 4.75-mm sieve ([ASTM, 1974](#)) and used in the experiment. Soil samples were weighed on the basis of their oven dried weights and transferred to 1-kg pots. PVA, PAM and HA were applied to the labelled pots at doses of 500, 100 and 500 ppm, respectively ([Özdemir et al., 2015](#); [Yakupoğlu & Öztaş, 2016](#); [Aksakal & Öztaş, 2010](#)), by mixing PAM and HA with pure water, and by turning PVA into a solution at 80 °C in pure water. The study, which is based on four different periods (0, 15, 30, and 45 days), was set up on 30 September 2020 in the greenhouse of the Department of Soil Science and Plant Nutrition. During the experiment, irrigation was done when 50% of the available moisture in the soil was decreases. After the end of each period, soil samples were dried in the air and crushed by hand and made ready for analysis.

Soil texture was determined by Bouyoucos hydrometer method ([Demiralay, 1993](#)); soil reaction (pH) by pH meter in soil-water mixture of 1:2.5 ([Kacar, 2016](#)); electrical conductivity value by a glass-electrode electrical conductivity tool in soil-water mixture of 1:2.5 ([Kacar, 2016](#)); lime content of soils by Scheibler calcimeter method ([Kacar, 2016](#)); soil organic matter by Walkley-Black method ([Kacar, 2016](#)); field capacity ([Demiralay, 1993](#)); cation exchange capacity by Bower method ([Kacar, 2016](#)). The coefficient of linear extensibility values of the soils were determined from the change in the size of the rods with a diameter of approximately 1 cm and a length of 10 cm prepared with the help of a syringe after the soil samples were turned into paste ([Schafer & Singer, 1976](#)); erosion ratio values were determined using some physical analysis results of the soil ([Özdemir, 2013](#)).

Statistical evaluation of the data obtained as a result of the research was made using SPSS computer package program. Duncan test was used for multiple comparisons (IBM SPSS statistics 21.0).

Some of the physical and chemical properties of the soil samples used in the study conducted under greenhouse conditions, determined before the experiment, are given in Table 1.

As can be seen from the examination of this table, the soil sample (sample no. 1) taken from the Ondokuz Mayıs University Faculty of Agriculture experiment area is a soil with clay texture, neutral reaction, low lime and medium organic matter content; the soil sample taken from Ondokuz Mayıs University Bafra Application field (sample no. 2) is a soil with loamy texture, slightly-alkaline reaction, medium lime and high organic matter content; and the other soil sample taken from Ondokuz Mayıs University Bafra Application field (sample no. 3) is a soil with sandy loam texture, moderate alkaline reaction, moderate lime and low organic matter content. The pH values of the soils are below 8.5 and there is no alkalinity problem in the soils ([Soil Survey Staff, 1993](#)).

Table 1. Some of the physical and chemical properties of the soils used in the research

Sources	Degrees of freedom	Sum of squares	Mean of squares	F value	Level of significance
Soils (A)	2	53034.745	26517.372	12591.002	0.000
Conditioners (B)	2	1637.414	818.707	388.739	0.000
Periods (C)	3	1581.905	527.302	250.374	0.000
A*B	4	42.460	10.615	5.040	0.001
A*C	6	1720.307	286.718	136.140	0.000
B*C	6	125.868	20.978	9.961	0.000
A*B*C	12	650.118	54.177	25.724	0.000
Error	72	151.636	2.106		
General	108	188009.537			

The erosion ratio values of the soils vary between 9.73% and 64.65%, and sample 1 in the clay texture class has the lowest (9.73%) erosion ratio value and sample 3 in the sandy loam texture class has the highest (64.65%) erosion ratio value. It was determined that the coefficient of linear extensibility (COLE-bar) values of the soils varied between 0.010% and 0.212%, the highest value being in sample 1 in the clay texture class, and the lowest values being in sample 3 with the sandy loam texture class.

Results and Discussion

Erosion Ratio

The results of the variance analysis of the erosion ratio values determined after the soil samples in the experiment were subjected to incubation in four different periods by mixing polyvinyl alcohol, polyacrylamide and humic acid are provided in Table 2, and the average changes in the erosion ratio values (mean of the three values) and the results of the multiple comparison (Duncan) test are provided in Table 3. As can be seen from the examination of the variance analysis results in Table 2, the mean of squares ($p < 0.01$) of the erosion ratio values of the tested soils were found to be significant. In other words, the soils differed in terms of their erosion ratio values at the end of the experiment.

Again, from the same table, the mean of squares ($p < 0.01$) of the conditioners and the applied periods were found to be significant. This result emphasizes that the effects of the conditioners such as polyvinyl alcohol, polyacrylamide and humic acid used in the experiment and the applied periods, on the erosion ratio are different. From the results of the variance analysis, it was determined that soil x conditioner, soil x period, conditioner x period and soil x conditioner x period interaction were also significant.

When the effects of conditioner applications (Table 1 and 3) are examined, it is seen that all three conditioners provide significant decreases in the erosion ratio values of soils depending on the application periods and soil texture. Given the changes, it was determined that the conditioners used were more effective in the soil number 1 in the clay texture class.

Upon examination of Duncan's multiple comparison test results (Table 3) applied to the data for the comparison of the tested soils, applied conditioners and application periods according to the mean of erosion ratio values at the end of the experiment, it is determined that the soils, the conditioners used in the application, and the application periods are ranked as given in Table 3 in terms of the effect they have on the mean of the erosion ratio values. In this grouping, the differences between soils and periods ($p < 0.01$) were found to be significant (Values shown with separate letters are significant at 1% level on the basis of the mentioned test).

The average decreases (%) found in the erosion ratio value according to the controls are presented in Figure 1. In all three soils, the decreases occurred with polyvinyl alcohol were much higher.

The mean decreases (%) caused by the applications of polyvinyl alcohol, polyacrylamide and humic acid in the erosion ratio of the soils showed significant differences between the said conditioners. The decreases (%) caused by the periods related to these three conditioners in the erosion ratio of the soils are given in Figure 2. As it can be understood from these data, the efficiency of the conditioners decreases as the period time increases.

Erosion ratio value is a parameter used to evaluate the resistance of soils to erosion, and soils of which this ratio value is below 10 are considered to be resistant to erosion while those of which this ratio value is higher than that are considered to be susceptible to erosion (Morgan, 2009; Özdemir, 2013). When the tested soils are evaluated in this respect, it can be initially considered that sample 1 is resistant to erosion and samples 2 and 3 are susceptible to erosion. The applied conditioners decreased the ratio value depending on the application periods and increased the resistance of the soils to erosion, but they could not be sufficient in soil no. 2 and 3 in terms of causing a decrease below the limit value (< 10) given for resilience. On the other hand, when the test findings are examined accordingly, it can be stated that the erosion ratio values are affected by the type of conditioner used (as $PVA > PAM > HA$) and the

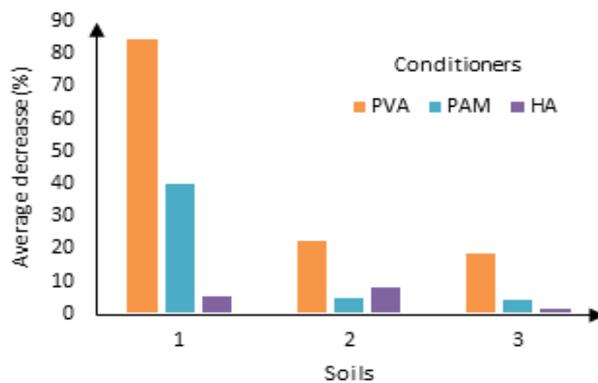
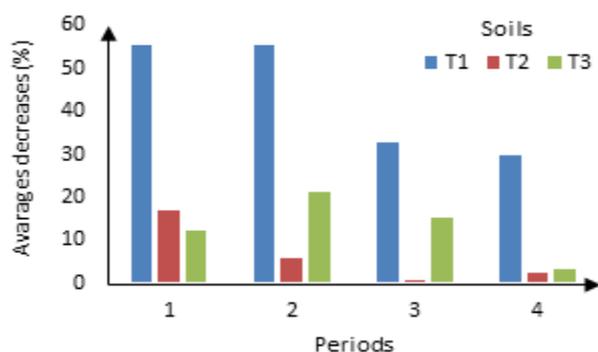
Table 2. The results of the variance analysis of the erosion ratio values of the soils

Soil number	Soil properties								
	Sand, %	Silt, %	Clay, %	Texture class	pH (1:2.5)	EC dS/m	CaCO ₃ , %	OM, %	CEC me/100g
1	31.70	23.14	45.16	C	6.97	0.1497	2.22	1.54	65.48
2	36.18	41.57	22.25	L	7.40	0.4924	8.47	3.02	38.26
3	58.91	29.34	11.75	SL	7.92	0.1173	8.26	0.77	31.66
Soil number	Parameters								
	ER, %	COLE							
1	9.73	0.212							
2	42.41	0.024							
3	64.65	0.010							

Table 3. The mean erosion ratio values of the soils and Duncan multiple comparison test results

Soils	Conditioners	Periods				Soil averages
		1	2	3	4	
1	PVA	2.01	0.65	1.39	2.00	5.53c
	PAM	3.95	4.64	7.49	7.42	
	HA	7.14	7.76	9.79	11.14	
2	PVA	28.33	34.24	34.85	34.87	38.89b
	PAM	40.17	41.43	41.63	38.44	
	HA	37.05	44.27	50.67	50.8	
3	PVA	55.66	40.49	70.12	44.42	59.29a
	PAM	51.49	57.52	78.57	82.08	
	HA	63.26	54.87	74.95	61.57	
Periods averages		32.38cd	31.80d	41.16a	32.93bc	
Conditioner Averages	PVA	29.33c				
	PAM	35.74b				
	HA	38.65a				

The averages shown in separate letters are different from Duncan multiple comparison test

**Figure 1.** Average decreases (%) determined in the erosion ratio value on the basis of conditioners**Figure 2.** Average decreases determined in the erosion ratio value over the periods on the basis of control (%)

application periods as $2 > 1 > 4 > 3$ (Table 3). In their study, (Yılmaz & Uysal, 2010) examined the effects of polyvinyl alcohol and polyacrylamide applications on runoff and soil loss. As a result of the research conducted on 3 soil samples with sandy loam textures with PVA and PAM solution, the researchers found that the mentioned polymers significantly reduced the runoff and soil loss, but that PVA was more effective than PAM. (Tümsavaş, 2005), who investigated the effects of different doses of PVA application in agricultural soils, found that PVA application at a dose of 500 mg/L was an effective dose in protecting the soils against erosion.

Coefficient of Linear Extensibility (COLE-bar)

Variance analysis results of the COLE-bar values determined after the incubation of the tested soils over four different periods by mixing polyvinyl alcohol, polyacrylamide and humic acid are given in Table 4, and the average changes in COLE-bar values (average of three values) and multiple comparison (Duncan) test results are given in Table 5. As can be seen from the examination of the variance analysis results in Table 4, the mean of squares ($p < 0.01$) of the COLE-bar values of the tested soils was significant. In other words, the soils differed in terms of their COLE-bar values at the end of the experiment.

From the same table, it is seen that the mean of squares ($p < 0.01$) of the conditioners and the applied

Table 4. The results of the variance analysis on the coefficient of linear extensibility values of the soils

Sources	Degrees of freedom	Sum of squares	Mean of squares	F value	Level of significance
Soils (A)	2	0.446	0.223	53037.205	0.000
Conditioners(B)	2	0.001	0.000	86.502	0.000
Periods (C)	3	0.019	0.006	1521.654	0.000
A*B	4	0.000	0.000	29.097	0.000
A*C	6	0.006	0.001	227.794	0.000
B*C	6	0.000	8.169E-05	19.418	0.000
A*B*C	12	0.001	0.000	24.903	0.000
Error	72	0.000	4.207E-06		
General	108	0.993			

Table 5. Coefficient of linear extensibility values of soils (mean) and Duncan multiple comparison test results

Soils	Conditioners	Periods				Soil averages
		1	2	3	4	
1	PVA	0.13	0.11	0.17	0.18	0.156a
	PAM	0.16	0.13	0.17	0.18	
	HA	0.15	0.13	0.18	0.18	
2	PVA	0.02	0.01	0.03	0.03	0.028b
	PAM	0.02	0.02	0.04	0.03	
	HA	0.02	0.01	0.03	0.03	
3	PVA	0.01	0.00	0.02	0.01	0.012c
	PAM	0.01	0.01	0.02	0.02	
	HA	0.00	0.00	0.01	0.01	
Periods average		0.058c	0.047d	0.080a	0.076b	
Conditioner Average	PVA	0.062c				
	PAM	0.067ab				
	HA	0.067b				

The averages shown in separate letters are different from Duncan multiple comparison test

periods were also found to be significant. This result indicates that the effects of the conditioners such as polyvinyl alcohol, polyacrylamide and humic acid used in the experiment and the applied periods, on the COLE-bar are different. From the results of the variance analysis, it was found that soil x conditioner, soil x period, conditioner x period and soil x conditioner x period interaction were also significant.

As can be seen from the examination of the average changes in the COLE-bar values (Table 1 and 5), all three conditioners applied caused significant changes in the coefficient of linear extensibility values of the soils depending on the periods. The change in question occurred at a higher level in the soil number 1 with clay texture class.

Upon examination of Duncan's multiple comparison test results (Table 5) applied to the data for the comparison of soils, applied conditioners, and application periods according to the COLE-bar value averages at the end of the experiment, it is seen that the soils differ in terms of their COLE-bar averages at the end of the experiment. Again, according to the aforementioned

test, it was seen that the conditioners used differed also in terms of the effect they had on the mean COLE-bar values at the end of the experiment.

On the other hand, the differences between the periods were also found to be significant in the same grouping (The values shown in separate letters are significant at 1% level on the basis of the mentioned test).

The mean changes (%) in the coefficient of linear extensibility value on the basis of the controls are provided in Figure 3. As can be seen from these data, the change (decrease) obtained with polyvinyl alcohol in soil no. 1, which has clay texture class, was at a higher level. While there was a decrease in the samples treated with only polyvinyl alcohol and humic acid in the soil no. 2, only the humic acid provided an effective decrease in the soil no. 3.

The average changes (%) caused by polyvinyl alcohol, polyacrylamide and humic acid applications in the coefficient of linear extensibility of the soils showed significant differences among the mentioned conditioners. The changes (%) caused by the periods related to these three conditioners on the coefficient of linear extensibility of the soils are presented in Figure 4.

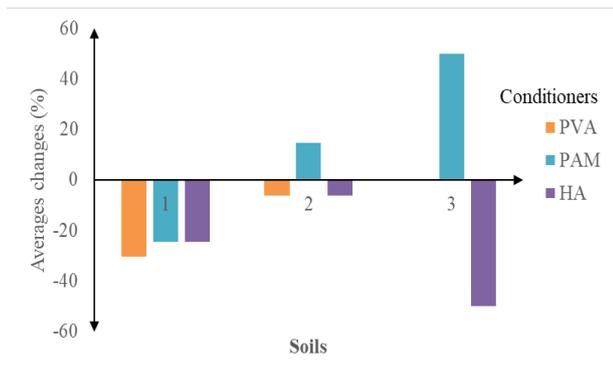


Figure 3. Average changes in COLE-bar value determined on the basis of conditioners (%)

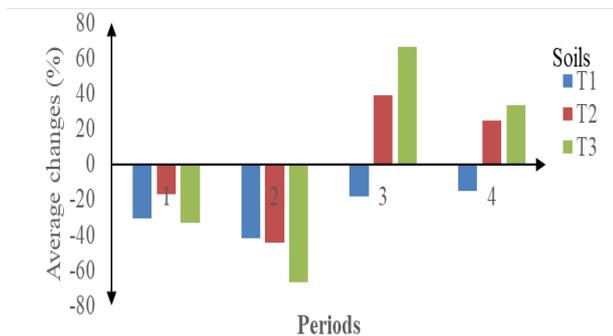


Figure 4. Average changes in COLE-bar value determined over periods on the basis of the control (%)

As it can be understood from these data, the effectiveness of the conditioners decreases after the second period (15 days).

As can be seen from the examination of the test findings, it can be stated that COLE-bar values are affected by the type of the applied conditioners (PVA>HA>PAM) and the application periods (2 > 1 > 4>3), that PVA is the most effective conditioner on COLE bar value, and that period 2 is the most effective period in terms of conditioner effectiveness (Table 3). In other words, it can be said that as the period time increases, the conditioner effectiveness decreases. On the other hand, when the COLE-bar values of the tested soils are examined, it can be stated that there is a significant risk of swelling and shrinkage in the soil number 1 in the clay texture class and that PVA, HA and PAM have significant effects in terms of mitigating this risk.

Özdemir et al. (2016) found in their study that garbage compost, tobacco processing waste and paddy husk compost applied to soils with acid, neutral and alkaline reactions improved the mechanical properties and decreased the COLE-bar values. In the study examining the effects of wheat straw, hazelnut sludge, humic acid and PAM conditioners on the coefficient of linear extensibility of soils, COLE-bar values, (Civelek, 2021) found that COLE-bar values decreased with the application of the conditioners and that there were statistically significant negative correlations between the COLE-bar values and the organic matter content.

Conclusions

As a result of this study that was conducted under greenhouse conditions in order to determine the effects of polyvinyl alcohol, polyacrylamide and humic acid applications on the improvement of erosion susceptibility and coefficient of linear extensibility (COLE-bar) parameters in the soils;

From among the tested soils, soil no. 1 with clay texture was found to be resistant to erosion ($ER < 10$) and soils no. 2 and 3 with loam and sandy loam texture ($EO > 10$) were found to be susceptible to erosion. PVA, PAM and HA applications increased the resistance of soils to erosion by causing significant decreases in the ratio values depending on the application periods and soil texture. Given the changes in the erosion ratio value in soil no. 2 and 3, the conditioners could not be sufficient in terms of causing a decrease below the limit value given for resistance to erosion. It was observed that the applied conditioners were effective as $PVA > PAM > HA$ and the application periods were effective as $1 > 2 > 3 > 4$.

PVA, PAM and HA applications used in the test decreased the COLE-bar values; the conditioner effectiveness was $PVA > HA > PAM$ and the application period effectiveness was as $2 > 1 > 4 > 3$; in other words, it can be said that PVA was the most effective conditioner on the COLE bar value and that period 2 was the most effective period in terms of conditioner effectiveness. On the other hand, when the COLE-bar values of the tested soils are examined, it can be stated that there is a significant risk of swelling and shrinkage in the soil number 1 in the clay texture class and that PVA, HA and PAM have significant effects in terms of mitigating this risk.

As a result, it was determined that polyvinyl alcohol, polyacrylamide and humic acid applications increased resistance to erosion in the soils and decreased the swelling-shrinkage feature. It was also determined that the effectiveness depends on the characteristics of the conditioners, soil texture class, and the period duration. It would be helpful to pay attention to this issue in practice.

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Author Contribution

NÖ: Funding, project administration, conceptualization, supervision, writing, revised editing; **HK:** Formal analysis, investigation, methodology, writing original draft, resources.

Conflict of Interest

The authors declare that they have known

competing financial or non-financial, professional, or personal conflicts that could have supported to influence the work reported in this paper.

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Field scale variability in soil properties and silage corn yield

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Abstract

Field scale spatial variability of soil properties, crop quality parameters and yield are needed to evaluate the efficiency of management practices in crop production. The purpose of this study was to determine the magnitude of field variability in soil properties, silage yield of corn (*Zea mays* L.) varieties, and to characterize their spatial structures, and map the stated attributes. The experiment was conducted in an alluvial flood plain of lower Kazova watershed in Tokat province of Turkey. Several physical and chemical soil properties and silage corn yield were determined. Coefficient of variation (CV%) varied from 1.0% (pH) to 38.1% (P₂O₅) in herbicide not applied plots and from 0.9% (pH) to exchangeable Na (55.1%) in herbicide applied plots. Calcium carbonate, organic matter and clay displayed well defined spatial structure. Sand, pH and electrical conductivity (EC) showed moderate spatial dependency. However, silt, moisture content, bulk density, plant available phosphorus and potassium had weak spatial structure. Silage corn yield distribution map successfully distinguished the three corn hybrids planted. The difference in vegetation period among three corn hybrids was effective in distinguishing the location of hybrids within the field. However, the variability in each of the hybrids blocks was assumed to occur due to the difference in short range soil properties. The longest range values were obtained for silage corn yield at both herbicide applied and herbicide unapplied plots.

Introduction

Spatial variability in soil properties, agricultural practices (tillage, irrigation, fertilizer application etc.) and pest and pathogen damage cause significant spatial and temporal changes in crop yield within a field (Al-Gaadi et al., 2018). However, small-scale variability in soil properties or even in yield is not often taken into account by farmers (Hausherr-Lüder et al., 2019). However, monitoring soil and yield variability within a field can help farmers to make right decisions to improve crop yield and to prevent environmental pollution (Kayad et al., 2019). Variable-rate application of fertilizers within a field improves nutrient use efficiency and also decreases water pollution (Tagarakis & Ketterings, 2018).

Precision agriculture can be defined as site-specific management of inputs within a field to obtain

the desired crop yield. Adoption of precision farming is needed to optimize crop production and to reduce environmental pollution risks caused by over application of agrochemicals (Roy & George, 2020). Plant nutrients in soils are usually provided by application of either a mineral fertilizer or animal manure. When nutrients are applied at rates higher than the crop removal, concentration of particular nutrient is elevated to levels that sometimes may hinder the availability of other nutrients. Some of nutrients such as nitrate and phosphorus may leach to ground/surface water, and create serious problems for ecosystem or human health (Al Tawaha et al., 2022). The budget of farmers will also be negatively affected by the application of excess amount of fertilizers. Therefore, the requirement and the amount of inputs should precisely be determined to sustain the productivity and profitability of agricultural production.

In order to apply appropriate amounts of agrochemicals, it is important therefore, to determine and map the spatial pattern of soil properties. Spatial variability of soil properties within a single field is needed to design a site-specific crop management and to delineate management zones (Bogunovic et al., 2017; Hausherr-Lüder et al., 2018). In this context, Piotrowska-Długosz et al. (2016) considered spatial variability of phosphorus (P) to improve the management decision. Considering the within field spatial variability of P helps to develop a more productive and efficient crop management system. Goulding (2016) used the variability of soil pH within a field to organize the variable-rate lime application for reclamation of an acidic soil. In a recent study, Günel (2021) used the information on spatial variability of salinity and sodicity in a field to determine the amount of chemicals and water needed to reclaim saline-sodic soils in Turkmenistan.

Internal (soil forming factors such as parent material, topography etc.) and external factors (management related such as fertilization, soil tillage etc.) contribute to the spatial distribution of the soil properties (Barton et al., 2004; Atreya et al., 2008). (Cambardella et al., 1994) attributed strong spatial dependence of a soil property to the internal factors and weak spatial dependence to management related external factors. The interaction between soil characteristics, position of the landscape and climate should be taken into account when yield has significant changes from year to year. Therefore, soil properties and position of a landscape have been reported as the main cause of spatial variability of yield within a field (Maestrini & Basso, (2018). In addition, tillage practices and the management of crop residues significantly affect the small-scale variability in plant growth, crop yield, soil properties, distribution of weeds, pests and diseases (Qiu et al., 2016).

Quantifying spatial variability is fundamental for understanding the underlying the factors affecting variation in productivity throughout a field (Leroux & Tisseyre, 2019). Classical statistics, geostatistics and fractal theory are the most common methods to define spatial variability. Geostatistics in soil science has been used to determine the spatial variability of soil properties (Surucu et al., 2013; Günel et al., 2012). The purpose of this study was to determine spatial variability of soil characteristics silage yield in a field where three corn hybrids grown under five different soil tillage systems.

Material and Methods

Study area

The experiment was conducted in Kazova Plain located at Tokat province of Turkey. Soils in study area were formed over alluvium and the slope was nearly level. Long term (1929-2021) annual average total precipitation of study area is 446 mm and the

temperature is 12.4 °C (Anonymous, 2022). Based on meteorological data, soil moisture regime is Ustic and soil temperature regime is Mesic (Soil Survey Staff, 1999).

Methods

The experiment was conducted in a complete randomized block design with three replicates and continued three years. The experiment consisted of three block for each corn hybrid and a total of 45 plots. The size of individual plots was 6.5 m x 20 m (130 m²). Corn seeds were sown at 70 cm interrow and 20 cm intra-row spacings. Three corn hybrids (Girona, Borja and Mataro) have been grown under 2 conventional, 2 reduced and a no-till tillage systems (Figure 1). Tillage practices used in the experiment were; 1.) Irrigation + moldboard plow + Disc harrow, 2.) moldboard plow + rotovator, 3.) Rotovator, 4.) Chisel+Disc Harrow, and 5.) No-till (direct sowing). The vegetation period of corn hybrids used in the experiment were different.

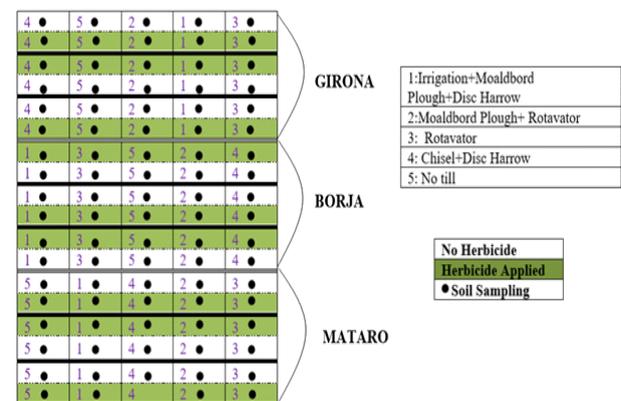


Figure 1. Experimental design and the treatments

Hybrid 1 (Girona, FAO 450): This is a single hybrid variety and an average of 100-105 days needed for the harvest maturity. The Girona is known with a high harvest index. Hybrid 2 (Borja, FAO 500): This is a single hybrid variety that reaches grain harvest maturity in average of 105-110 days and is recommended for silage production. The Borja is known with a high harvest index. Hybrid 3 (Mataro, FAO 550): This is known as a single hybrid variety with a high harvest index, and reaches the harvest maturity in average of 110-115 days (Anonymous, 2006).

Soil samples from 0-10 cm, 10-20 cm and 20-30 cm depths were sampled both from herbicide applied and non-herbicide plots. Total of 45 soil samples from each of soil layers for herbicide and non-herbicide plots were collected. All soil samples have been analyzed for some of physical and chemical characteristics. The data obtained for each layer at a particular sampling point have been averaged for 0-30 cm depth.

Soil Analyses

Particle size distribution was determined using the hydrometer method in a sedimentation cylinder; with

sodium hexametaphosphate as the dispersing agent [Gee & Boudier \(1986\)](#). Bulk density and water content were determined using a soil core method ([Blake & Hartge, 1986](#)). Soil reaction (pH) and electrical conductivity (EC) were measured in 1:2 soil–water suspensions ([Rhoades, 1982](#)). Part of each sample was analyzed for organic matter by using the Walkley–Black dichromate oxidation procedure ([Nelson & Sommer, 1982](#)). Available phosphorus was extracted with 0.5M sodium bicarbonate (NaHCO_3) ([Olsen et al., 1954](#)) and determined by spectrophotometry. Total nitrogen was determined with ([Bremner, 1965](#)), available potassium with ([Thomas, 1982](#)) and calcium carbonate with ([Allison & Moodie \(1965\)](#)) methods. Exchangeable Na and Ca was extracted with ammonium acetate determined by flame spectrometry ([Soil Survey Laboratory, 1992](#)).

Silage Yield

Plants on randomly selected six strips with 6 m length were harvested 5 cm above the soil surface and weighed. Based on the results obtained from harvested corn plants, the silage yield for herbicide applied and not applied blocks have been calculated as kg ha^{-1} . In this study, silage yield determined at the end of third year have been presented.

Statistical and Spatial Analyses

Descriptive statistics of the analyzed data viz., minimum, maximum, mean, standard deviation, coefficient of variation, and skewness were computed using SPSS 21.0 statistical software. The spatial structural analysis of soil properties and silage corn yield and mapping were carried out using GS⁺ (version 7.0) software. Spherical, exponential or linear models were fitted to the semivariograms and the model used was selected based on visual best fit and the corresponding coefficient of determination (R^2) for the regression. In addition, residual sum of squares (RSS) was used to choose the best variogram model. Cross-validation was used to validate the accuracy of model by eliminating one observation at a time, and estimating the value at that location with the remaining data. Then the difference between the actual and estimated value for each data location was calculated ([Li et al., 2011](#)).

The semivariogram for each variable was calculated using a measure of variability between pairs of points at various distances. The distance between pairs at which the variogram was calculated is called lag distance. Model parameters (nugget variance (C_0), range (A) and sill (C_0+C)) were calculated for each of the variable. Nugget semivariance shows the variance at zero distance, and represents variability that is not detectable at the sampling scale of the study or variability caused due to or sampling and analytical error. Lag distance between measurements at which one value for a variable does not influence neighboring values is described as sill. The range is the distance at

which the points have no longer spatially independent ([Trangmar et al., 1986](#)). The nugget to sill ratio is defined as spatial dependency. The spatial dependence of variables was classified into three classes based on the nugget to sill ratio value ([Cambardella et al., 1994](#)). The variable is considered to have strong spatial dependence if the ratio is <0.25 , the variable is considered to have moderate spatial dependence if the ratio is between 0.25 and 0.75, and the variable is considered to have weak spatial dependence, if the ratio is >0.75 .

Results and Discussion

Clay content ranges from 34.4 to 56.7% with an average of 44.0%. Silt content ranges from 32.8 to 46.7% with an average of 41.2 (Table 1). High silt content of experimental site caused a formation of hard and impermeable surface crust in some places (Figure 2). [Yang et al. \(2020\)](#) indicated that rain drop impact breaks down the weak aggregates and clogs soil pores, which further leads to firm packing of particles particularly in soils with high silt content. Surface crust prevents the infiltration of water as well as emergence of plants. The nonhomogeneous distribution of moisture and crop yield within the field can be associated with the non-permeable layer observed on soil surface especially during germination stage of the plant growth. [Aubert et al. \(2011\)](#) also stated that silty soil disperses especially in the depressed parts of the field, and resulting in the formation of surface crust up to 7 cm thick following dry conditions.



Figure 2. Surface crust in high silty locations of the experimental site

Organic matter (OM) content within non-herbicide plots ranged from 1.24 to 2.12% and the average OM was 1.71% (Table 1). The OM content in herbicide applied plots was between 1.40 and 2.27% with a mean value of 1.66% (Table 2). Weeds almost completely covered the soil surface in non-herbicide plots, and competed with corn plants for nutrients, water and sunlight (Figure 3). Therefore, average silage yield in herbicide applied plots ($36987.0 \text{ kg ha}^{-1}$) was 8.5% lower compared to the silage yield ($40152.4 \text{ kg ha}^{-1}$) recorded in non-herbicide plots (Table 1 and 2). The

nutrients and water have been highly used by weeds in almost everywhere of the plots. [Kaur et al. \(2018\)](#) indicated that weeds are more aggressive, easily adapt to new environment, and persist longer than the main crops in the field. Low silage yield in weedy plots is related to the ability of weeds to extract more water and nutrients from the soil compared to the corn. Higher concentrations of P and K in herbicide applied plots, where weeds have been controlled both mechanically and chemically can be attributed to the consumption of nutrient. The variability of data among the sampling locations was evaluated with the coefficient of variation (CV) value. The CV values were interpreted using the criteria introduced by [Wilding \(1985\)](#), who defined the CV in the most (CV>35%), moderate (CV:15-35%) and least (CV<15%) variable classes. The variability of P (CV: 45.7%) and K (CV: 37.3%) content in herbicide applied plots was higher than those in non-herbicide plots (Table 1 and 2). In contrast to the findings of [Sylvester-Bradley et al. \(1999\)](#) and [Goulding, 2016](#) who reported a high heterogeneity of soil pH within a field, the variability of soil pH indicated by the CV values in both plots was very low (CV: 0.9 and 1.0% for herbicide applied and not applied plots). The variability of lime, EC, OM, N, exchangeable Ca, bulk density and moisture content were low in both experimental plots (Table 1 and 2).



Figure 3. Weed density in non-herbicide and herbicide applied plots from the experiment

Within Field Variability of Soil Characteristics and Silage Corn Yield

The experiment has been designed as a complete randomized block. Considering the spatial variability of soil properties, the blocks have been randomly placed within the experimental site. Data on soil characteristics and silage yield for herbicide applied and not applied plots have been separately analyzed for spatial variability. Two different maps were produced from each of the data set for the experimental site (Figure 4 and 5).

Reliable models for silt, lime, organic matter, EC, P and N concentrations could not be obtained by using the data from weedy plots. The longest range (168.4 m) value of weedy plots was obtained for K content and the shortest range value (4.7 m) was obtained for P content (Table 3). The range value of P content in herbicide applied plots was 17.2 m, while in contrast to weedy plots the range value of K content in herbicide applied plots was shorter (23.4 m) (Table 4). Low range value of P concentration in weedy plots compared to herbicide applied plots could be attributed to the high density of weeds between the rows in weedy plots. The patchy distribution of weeds within the plots caused a decrease in the range value of P content. In non-herbicide plots, available K and exchangeable Ca contents of soils had contrasting pattern with the silage yield. The highest K and exchangeable Ca concentration in non-herbicide applied block was on the northern part of the study area and gradually decreased towards the south. In contrast to K and exchangeable Ca contents, silage yield in herbicide applied plots was at the highest level on the south and decreased towards the north section of the study area (Figure 4). [Hausherr-Lüder et al. \(2019\)](#) who investigated the effects of tillage intensity on small-scale spatial variability of soil and winter wheat parameters in three different location stated that spatial relationships between soil properties and winter wheat parameters

Table 1. Descriptive statistics of soil characteristics and silage yield in non-herbicide plots

Attribute	Unit	Min	Max.	Mean	Std. Dev.	CV	Skewness
Clay	%	32.4	56.7	44.0	5.48	12.5	0.08
Sand	%	7.6	25.0	14.7	4.69	31.9	0.55
Silt	%	32.8	46.7	41.2	2.76	6.7	-0.71
Lime	%	6.13	8.13	7.15	0.40	5.6	0.11
pH	1:2	8.28	8.64	8.43	0.09	1.0	0.54
EC	mmhos cm ⁻¹	261.7	526.0	330.0	48.61	14.7	2.07
P ₂ O ₅	kg ha ⁻¹	193.4	900.4	459.0	175.2	38.2	0.48
OM	%	1.24	2.12	1.71	0.19	11.2	-0.01
N	%	0.10	0.16	0.13	0.01	9.6	-0.17
K ₂ O	kg ha ⁻¹	207.3	881.2	327.5	100.2	30.6	3.92
Ca	me 100g ⁻¹	13.63	19.84	17.36	1.24	7.2	-0.48
Na	me 100g ⁻¹	0.33	0.71	0.47	0.09	19.3	1.04
Moisture	%	23.28	29.14	26.33	1.21	4.6	-0.12
Bulk Density	g cm ⁻³	1.34	1.53	1.43	0.05	3.6	-0.06
Silage Yield	kg ha ⁻¹	15857.1	59083.3	36987.0	10757.3	29.1	0.26

CV: Coefficient of variability

Table 2. Descriptive statistics of soil characteristics and silage yield in herbicide applied plots

Attribute	Unit	Min	Max.	Mean	Std. Dev.	CV	Skewness
Lime	%	6.50	8.25	7.30	0.43	5.9	0.15
pH	1:2	8.21	8.60	8.43	0.07	0.9	-0.68
EC	mmhos cm ⁻¹	275.3	489.3	336.3	46.37	13.8	1.97
P ₂ O ₅	kg ha ⁻¹	174.4	1205.3	477.4	218.2	45.7	1.62
OM	%	1.40	2.27	1.66	0.18	10.8	0.78
N	%	0.10	0.18	0.13	0.02	13.2	0.45
K ₂ O	kg ha ⁻¹	184.3	886.6	347.5	129.7	37.3	2.58
Ca	me 100g ⁻¹	14.93	19.46	17.88	0.97	5.4	-0.89
Na	me 100g ⁻¹	0.25	2.22	0.50	0.27	55.1	5.92
Moisture	%	22.31	28.06	25.53	1.30	5.1	-0.15
Bulk Density	g cm ⁻³	1.31	1.52	1.45	0.04	2.9	-1.18
Silage Yield	kg ha ⁻¹	23178.6	62631.0	40152.4	9929.6	24.7	0.08

CV: Coefficient of variability

Table 3. Parameters of semivariance models for soil characteristics and silage yield of non-herbicide plots

Attribute	Model ^a	A ^b (m)	Co ^c	Sill (Co+C) ^d	Spatial Dep	R ² ^e	RSS ^f
Clay	Sph	102	6.4	42.80	14.95	0.918	30.2
Sand	Sph	134	5.8	37.40	15.51	0.933	18.2
Silt	Sph	37	4.28	9.47	45.20	0.484	16
CaCO ₃	Sph	12.2	0.0086	0.16	5.24	0.212	8.048E-03
pH	Sph	41.6	0.0027	0.01	32.93	0.668	1.11 E-05
EC	Exp	10.7	959	2432.00	39.43	0.141	3.918 E+06
P ₂ O ₅	Exp	4.7	54.6	329.30	16.58	0.069	13033
OM	Exp	4.7	0.008	0.04	21.80	0.049	7.332 E-04
N	Not modelled						
K ₂ O	Exp	168.4	15.8	52.60	30.04	0.632	126
Ca	Exp	147.5	0.839	2.46	34.13	0.672	0.212
Na	Sph	20.1	0.0012	0.01	12.77	0.648	5.012 E-06
Moisture	Sph	128.2	0.829	2.18	38.10	0.744	0.52
Bulk Density	Sph	135.5	0.0016	0.00	34.04	0.941	1.323E-07
Silage Yield	Exp	224.2	719000	1866000	38.5	0.628	5.44E+11

a: Model, sph: Spherical, exp: Exponential, b: A, Range, Spatial Correlation Distance, c: Co, Nugget Variance, d: Sill (Co+C): Structural Variance, e: R² Value of Semivariance Model, f: RSS, Residual Sum of Squares

were in the herbicide applied plots, the shortest range distance (8.9 m) was obtained for pH and the longest range distance (211.9 m) was obtained for moisture content, followed by silage yield (210.9 m) and organic matter (176.2 m). Moisture content, pH, P and exchangeable Ca contents had strong spatial dependency and all other characteristics had a moderate level spatial dependency (Table 4). All soil characteristics other than pH and Ca had similar spatial distribution patterns (Figure 4).

Spatial distribution of silage corn yield clearly differentiated the location of silage varieties used in the experiment (Figure 4g and 5g). The main reason to distinguish the three corn varieties was the length of vegetation period for each of corn varieties required to be matured. The corn with FA0450 code was enough mature when harvested, whereas the harvest was little early for the corn with FA0550 code. Therefore, the

differences in silage yield of different corn hybrids can be attributed to the differences in the maturation period. Another reason in variability of silage corn yield was spatial variability of soil properties within the blocks in which the corn hybrids grown. The variation of clay and sand content in the study area will significantly affect the cation exchange capacity, water holding capacity and some of other important soil characteristics, which have a significant impact on plant growth. High variability of P and N content indicated the need for variable rate application of nutrients. The variable-rate fertilizer application will cause an increase in silage yield compared to the uniform application of N and P. In a two-year study, (Yang et al., 2001) obtained significantly higher grain yields in variable rate application of nutrients compared to the uniform applications.

Table 4. Parameters of semivariance models for soil characteristics and silage yield of herbicide applied plots

Attribute	Model ^a	A ^b (m)	Co ^c	Sill (Co+C) ^d	Spatial Dep	R ² ^e	RSS ^f
CaCO ₃	Exp	32	0.1221	0.25	49.80	0.661	4.226 E-03
pH	Sph	8.9	0.0004	0.01	7.27	0	4.274 E-05
EC	Exp	125.6	1736	4242.00	40.92	0.566	1.28 E+06
P ₂ O ₅	Sph	17.2	22.6	230.20	9.82	0.271	7918
OM	Sph	176.2	0.0166	0.04	38.88	0.499	1.063 E-04
N	Not modelled						
K ₂ O	Sph	23.4	18.1	57.68	31.38	0.449	344
Ca	Sph	9.5	0.106	1.01	10.45	0	0.386
Na	Sph	20.9	0.0023	0.01	35.94	0.289	5.033 E-06
Bulk Density	Sph	20.2	0.0005	0.00	29.41	0.319	8.096 E-07
Moisture	Sph	211.9	0.679	3.47	19.58	0.901	0.279
Silage Yield	Sph	210.9	281000	2527000	11.12	0.87	1.604 E+11

a: Model, sph: Spherical, exp: Exponential, b: A, Range, Spatial Correlation Distance, c: Co, Nugget Variance, d: Sill (Co+C): Structural Variance, e: R² Value of Semivariance Model, f: RSS, Residual Sum of Squares

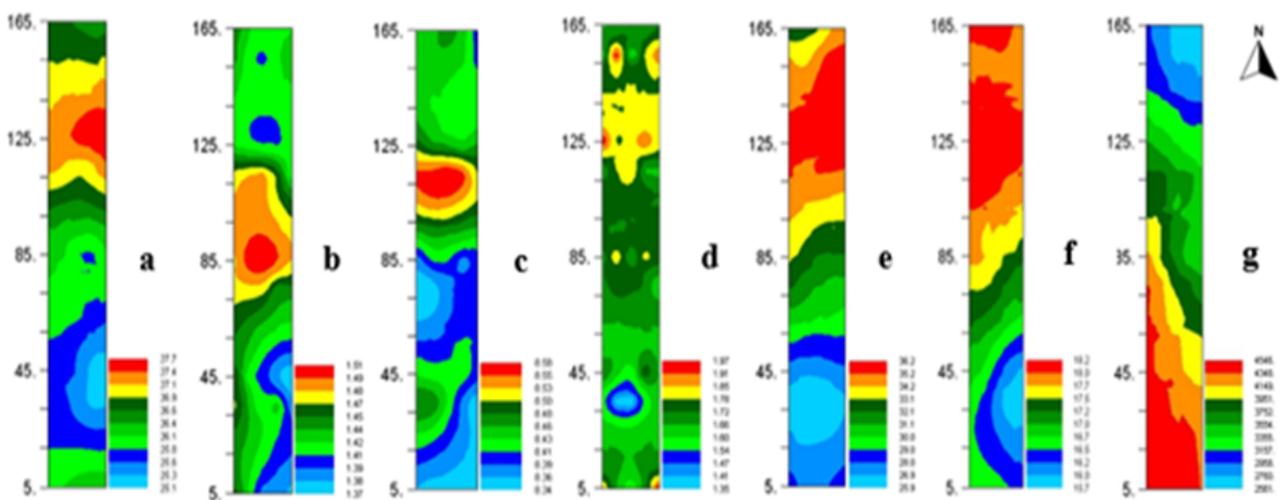


Figure 4. Spatial distribution of some of soil characteristics and yield for non-herbicide plots (a: moisture (%), b: bulk density (g cm⁻³), c: pH, d: organic matter (%), e: available potassium (K₂O, kg ha⁻¹), f: exchangeable calcium (me 100g⁻¹), g: silage yield (kg ha⁻¹))

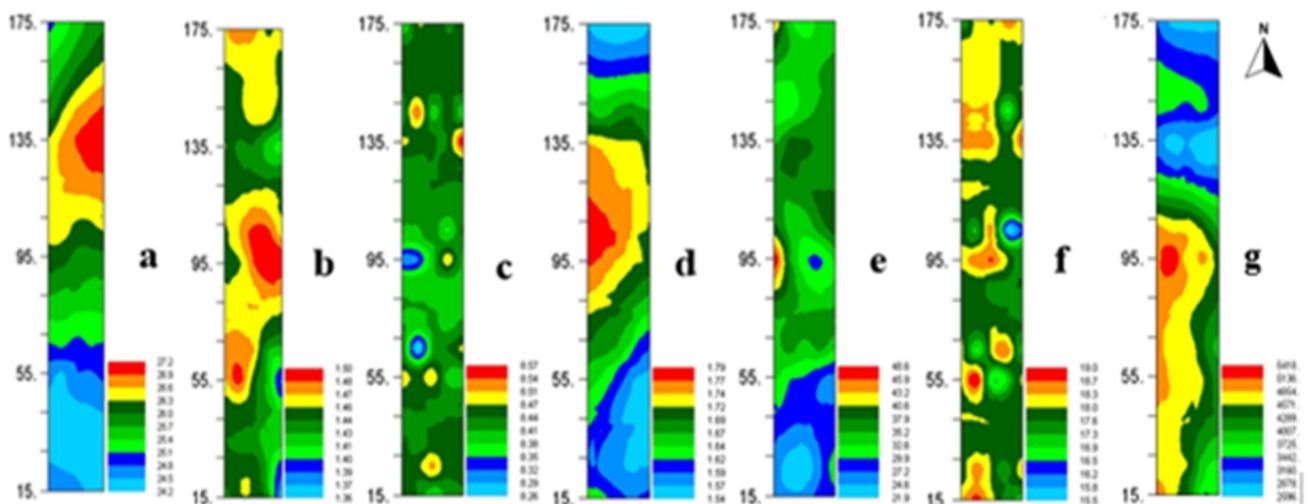


Figure 5. Spatial distribution of some of soil characteristics and yield for herbicide applied plots (a: moisture (%), b: bulk density (g cm⁻³), c: pH, d: organic matter (%), e: available potassium (K₂O, kg ha⁻¹), f: exchangeable calcium (me 100g⁻¹), g: silage yield (kg ha⁻¹))

Conclusion

In this study, variability of soil properties and silage yield of three corn hybrids grown under five different tillage systems with and without weed control was investigated. Within field variability of soil characteristics especially available phosphorus and potassium affected the silage yield of corn hybrids. High content of silt in some parts of the field caused formation of surface crust, which inhibited homogenous germination of corn seeds. Farmers should take variability in soil properties and crop yield within and between fields into account to adopt precision farming techniques, such as site-specific nutrient management, in order to increase productivity. Indeed, not only for the nutrient management, many of the agricultural practices such as soil tillage, irrigation and reclamation activities should be accomplished considering the spatial variability to improve economic returns and reduce the impacts on the environment. New technologies in variable rate application help to reduce the environmental impacts of agricultural production, while maintaining, or even improving, current levels of soil quality and crop productivity.

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Conflict of Interest

The authors declare that they have no known competing financial or non-financial, professional, or personal conflict that could have appeared to influence the work reported in this paper.

Author Contributions

MB: Data Curation, Formal Analysis, Investigation, Methodology, Writing Original Draft; **HG:** Supervision, Review and Editing.

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Contaminant removal processes from soil

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Abstract

Soil pollution of numerous inorganic and organic chemicals has resulted to the destruction of vast amounts of arable and urban land around the world. Toxic pollutants pose a serious health danger to individuals as well as other biological processes. Dispersed literature is used to scientifically examine the numerous physical and anthropogenic causes and probable risks to determine the remediation solutions for a variety of toxins and heavy metals. This review discusses the remediation approaches such as phytoremediation as well as the chemical strategies. Chemical remediation methods like soil cleaning or verification are comparatively extensive and environmentally harmful, making them unsuitable for big-scale soil remediation operations. Phytoremediation, on the other hand, has arisen as an environmentally sustainable and viable technique for restoring the polluted soils, but relatively little attempts have been made to demonstrate this technique in the region. Heavy metal-polluted soil remediation is needed to decrease the related dangers, increase the land requirements for agricultural cultivation, improve food security, as well as reduce land tenure issues caused by changing land-use patterns.

Introduction

A contaminant is a substance that doesn't occur naturally in the environment but is incorporated into the earth by physical activities as well as anthropogenic actions and changes the structure of the soil. It could be classified as physical, biological, chemical, or radiological substances that, in high enough quantities and harm living organisms through air, soil, food, and water. A pollutant causes damage to people or animals (Verma et al., 2022). For example, in the environment chlorine gas does not naturally exist, so it is a pollutant; but, once it is introduced into the air as a result of human-induced action, it will be a pollutant due to its adverse impacts on homo sapiens as well as wildlife. Pollutants enter soils from both natural phenomenon and human activities, which are discussed further below.

Contaminants are naturally introduced into soils by volcanic activity and breaking down of soil parent material. Large amount of aerosol from mineral dust, is a natural source of metals. Cadmium (Cd), mercury (Hg), cobalt (Co), vanadium (V), chromium (Cr), nickel (Ni), copper (Cu), Iron (Fe), manganese (Mn), zinc (Zn), and lead (Pb) are the main trace elements in crustal dust in order of concentration, but their amounts differ widely across the earth's surface. Metal concentrations also has been discovered to improve with diminishing constituent portion, particularly in wind-eroded as well as highly weathered soil (Dardouri & Sghaier, 2018).

Anthropogenic processes are the most significant cause of toxins in soils and liquids. Fertilizers, herbicides, and pesticides are major agricultural contaminants as other pollutants from heavy mechanical industries, mining and smelting practices, and leather tanning firms. These practices introduce a

variety of organic and inorganic toxins into the soil, making it unhealthy for microorganisms, wildlife, humans, and plants ([Jones et al., 2011](#)).

On the grounds of their source and types of pollution, each of these origins could be classified into two types: point sources and nonpoint sources. Each noticeable, restricted, as well as separate transmission, together with but not confined to any drain, trench, canal, rolling stock, container, fissure, discrete, well, conduit, tunnel, other floating craft, vessel, or concentrated animal feeding activity, from which pollutants are or may be released, is referred to as a "point source" ([Kalbitz et al., 2000](#)). This definition excludes agricultural rainwater outflows and irrigated irrigation return flows. Unprocessed company waste, sanitation facilities, waste treatment plants, wastes from agronomic ranch house, solid waste collection places, plant growth regulator application sites, and pesticide processing sites are the main point origins of pollutants emitted into soils ([Ahmad and Rahman, 2009](#)).

The chief water pollution which causes in waterways is polluted runoff (also known as nonpoint source of pollution) from wetlands operations, hydromodification, marinas, forestry and recreational boating, urban development, and agriculture.

The aim of the study is to describe the contaminant removal methods from the soil and to present comparative discussions between each other. In this context, contaminant classification and remediation methods were emphasized. Some comments were also made in terms of future perspectives.

Classification of Contaminants

Organic Contaminants

The main chemicals cluster consists of aromatic hydrocarbons such as grease, tar and phthalate esters, polychlorinated biphenyls (PCBs), halogenated aliphatic, polynuclear hydrocarbons (PAHs), petroleum hydrocarbons, benzenes, and organochlorine pesticides, which come from a variation of nonpoint as well as point o-rigins ([Borja et al., 2005](#)). Organic contaminant penetration into plant parts is usually poor, with volatilization from the surface of the ground serving as the primary pathway, supplemented by aboveground vegetation uptake of infected air.

Inorganic Contaminants

This category includes a wide range of contaminants from both point and nonpoint origins, such as products formed as a result of contacts with other components in soil, toxic gases, heavy metal (loid)s, and ion pair or ion complexes in the form of compounds. Strong metalloids / metals (e.g., As, Cr, Pb, Ni, Cd, Zn, Cu) are the most common inorganic pollutants, originating mostly from industrial discharges and domestic grey water, as well as leakage

from Pb also Cu tubing also Zn from household items (deodorants, skin creams, etc.) ([Alvarez et al., 2009](#)).

Innovations for Remediation of Contaminated Soils

Adsorption/Biosorption

Addition of such materials to soils are likely to make soil-applied contaminants less bio-available due to increased adsorption. This could reduce their leaching. Adsorption is a quick and changeable mechanism that mimics in some situations ion exchange for the removal of harmful anions or cations from wastewater by effective adsorbents. Adsorption provides a solution to industrial effluent treatment as well as soil remediation. Using organic amendments to remediate soil will increase adsorption of pesticides, reducing their bio-availability and efficacy, but also reducing their tendency to leach into root zones of deep-rooted crops and into groundwater ([James et al., 2019](#)).

Biosorbents are made from physically abundant biomass and/or waste biomass. Biosorption is a step forward to a prospective process owing to its large absorption capability and low cost of raw material. It has been shown that both living and non-living biomass should be used in biosorptive processes because they also have a high tolerance for metals and other harmful conditions. Based on the bacterial strain and environmental factors, metal ions may attach to cells through various physiochemical pathways. Because of this heterogeneity, current understanding of these processes is limited.

Bacterial cell walls, in particular, are polyelectrolytes that bind with ions in solution to preserve electroneutrality. Extracellular precipitation, redox interactions, covalent bonding, van der Waals forces, and electrostatic interactions are possibly pathways by which metal ions attach to the cell surface, or a mixture of these processes since it uses algal biomass, which is often called waste from certain biotechnological activities or merely because of its high abundance in coastal areas, biosorption of heavy metals by algal biomass is an advantageous option, an effective and commercially viable approach used for drainage and waste cleanup.

Immobilization

Immobilization systems are intended to reduce contaminant volatility by altering the physical or leaching properties of the polluted system. Movement is typically reduced by either physically limiting interaction between the pollutant and the ambient groundwater or chemically changing the pollutant to render it more suitable for groundwater dissolution. Metals' solid-phase as well as aqueous chemistry lends itself to immobilization through these strategies. Metal pollutants can be immobilized using a number of approaches, comprising those that utilize thermal

therapy and/or chemical reagents to directly attach the polluted soil or slurry. The majority of immobilization approaches could be done either in situ or ex situ. In situ methods are favored because they require less manpower and resources, but their execution would be dependent on complex site situations.

Stabilization / Solidification

Stabilization/solidification, also known as waste fixation, is a process that limits the movement of toxic compounds and chemicals in the atmosphere by using both physical and chemical means (Fu et al., 2021). Stabilization is the process of transforming a pollutant into an immobile or low soluble state in order to reduce the danger presented by the waste (Fu et al., 2021). The in-situ solidification as well as stabilization process consists of three constituents: (1) a method for mixing the polluted soil in place, (2) a collection of reagents, groundwork, as well as system feed, and (3) a method for delivering to the soil-mixing zone reagent. In most cases, ex situ as well as in situ solidification/stabilization techniques are used on soils polluted with other inorganic compounds as well as heavy metals. That being said, also for reactive organics, stability of soils with low amounts of organic components is possible. Most solidification/stabilization methods have minimal effectiveness against organics and pesticides, with the exception of asphalt batching and confirmation, which remove most organic pollutants (Gao et al., 2021).

Tarmac Batching

Tarmac batching is a hydrocarbon-contaminated soil solidification/stabilization technique that integrates petroleum-laden soils into steamy tarmac combinations as a fractional replacement for pebble collective; the blend could be used for paving. Diggings of polluted soils is supplemented by injection of the treated and an initial thermal treatment soil into asphalt collective. Heating the blend all through the amalgamation progression causes the more toxic hydrocarbon components to volatilize. During cooling, the leftover substances are integrated into an asphalt matrix, reducing contingent migration. Since ample time has passed for it to fix as well as recover, the ensuing tarmac solid has the waste evenly spread in it and is insoluble in water (Jiang et al., 2018).

Vitrification

Vitrification, also known as liquefied glass utilization, is a solidification/ stabilization process that utilizes a formidable energy source to dissolve earthen or other soil components at incredibly great temperatures (1,600–2,000°C), removing organic and immobilizing most inorganics pollutants by heating (Lin et al., 2021). The bulk of chemicals subsequently found in the earth are volatilized during this phase, whereas the remnants are processed into crystalline products, solid glass, and chemically inert materials (Navia et al.,

2005). Since the high temperatures destroy any organic components, there are several by-products. Radionuclides and heavy metals, for example, are built into a goblet matrix that is typically solid, stable, and resistant to leaching (Shi et al., 2018).

Chemical Oxidation

For at least 20 years, chemical oxidation innovation has been used as a in situ remediation method of groundwater and soil. Chemical oxidation has been utilized extensively to strip large amounts of pollutant mass from soils and streams at a number of locations (Smaranda et al., 2017). The bulk of the chemicals of concern have been successfully removed utilizing a combination of oxidants such as permanganate, ozone (COCs), percarbonate, hydrogen peroxide, and persulfate.

Soil Cleansing

Soil cleansing in in situ is a novel remediation technique that involves flooding polluted soils with a solution that carries the pollutants to a safe location (Terbouche et al., 2011). The method of soil flushing is achieved by injecting or infiltrating an extraction solvent into the soil. Using normal groundwater storage wells, polluted extraction fluids as well as groundwater are collected and drained to the surface. Until being discharged or recycled to state, openly maintained receiving streams or wastewater treatment works, adsorbed pollutants in recovered groundwater and extraction fluids can require treatment to meet sufficient discharge requirements (Wang et al., 2021a).

Phytoremediation

Plants are used in phytoremediation to clear up polluted soils (Cabral et al., 2015). The capability of vegetation to amass, degrades, or/and remove pollutants found in soil and water ecosystems is included in this process. Both plants derive necessary elements from polluted soil, along with heavy metals and nutrients (Appenroth, 2010). Hyperaccumulators are plants that have the capacity to accumulate vast quantities of heavy metals that they cannot need in their digestive processes. Crops have also been observed to absorb different organics and reduce or refine them for utilization in physical processes (Wang et al., 2021b; Xie et al., 2011) provided an excellent description of polluted soils phytoremediation. It primarily covers the six fundamental strategies of phytoremediation: Phytostabilization, phytotransformation, phytostimulation, phytoextraction, phytovolatilization and rhizofiltration.

Phytostabilization

Perhaps metal-polluted areas are not crucial for cleaning up, also because the liable organizations no longer operate or because the locations are not on the remediation agenda's high list of priorities. Metal toxicity can be reduce by in situ inactivation in a

conventional way, a mitigation procedure that utilizes the use of soil additives to stabilize or immobilize soils that has metals in it. While movement of metal from soil to plants is reduced, soils are still prone to wearing away also create a danger to other animals as well as humans. Phytoremediation also identified as phytostabilization, is a plant-based mitigation innovation that equalizes pollutants as well as avoids revealing trails through water as well as wind removing top soil; gives hydraulic power, preventing contaminants from migrating vertically into water in the ground; also, chemically as well as physically immobilizes pollutants via adsorption to complexation or stems with exudates of stems ([Zhang et al., 2021](#)). This approach is an updated form of in situ inactivation, in which crops primary role is to modify soils. Not like phytoextraction, the aim of phytostabilization is to normalize metals in soils and reduce risk to human health as well as the environment.

[Dardouri & Sghaier, \(2018\)](#) described the phytostabilization mechanism in depth. The polluted soil is rammed before planting to add lime as well as to make a seed bed, other amendments, or fertilizer to inactivate metal pollutants. Metals must be fixed quickly after integration and chemical modification in soil amendments, ideally for a long time if not permanently. The most promising fertilizers are manganese oxyhydroxides or iron, artificial clay or natural minerals, biosolids, phosphate fertilizers, organic matter (OM), or a combination of these modifications. Crops selected for phytostabilization may be destitute emissors of metal pollutants into plant tissues aboveground that humans and animals may consume. Since there are no measurable metals in shoots, there is no need to evaluate harvested shoot residue as toxic waste. The plants chosen must be simple to develop as well grow rapidly as, thought for, have thick domes as well as stem systems, and be resistant to metal pollutants and other site circumstances that might restrict crop development. The study of [Dardouri & Sghaier, \(2018\)](#) contributed to the production of one of *Festuca rubra* L as well as two cultivars of *Agrostis tenuis* Sibth which are now commercially viable for Zn, Cu, and Pb phytostabilization of polluted soils.

Phytostabilization works well in fine-coarse soils with astronomical OM content, but it can be used to treat a variety of soils in degraded areas ([Fu et al., 2021](#)). Plant performance and survival are not feasible in certain heavily polluted sites, so phytostabilization is not an option ([Fu et al., 2021](#)). At plant growth sites, battle managers must be vigilant about the movement of infected plant filtrates off-site, as well as insect issues and malady that bounds plant lifespan. Price, environmental effects, ease of application, and aesthetic appeal are only a few of the advantages of phytostabilization over other soil treatment methods ([Fu et al., 2021](#)). When disinfection methods are used regardless of the proportions of the polluted zone or a

shortage of funding, phytostabilization has benefits. It might also be used as a stopgap solution to minimize danger in situations where using the right solution for the job isn't possible.

Phytotransformation

A few organic and inorganic pollutants in nature might be biochemically attached to tissues cellular (biotransformed) less active or indolent forms until absorbed within the root ([Shi et al., 2018](#)). Phytotransformation is metabolization organic toxins in crops and recombination reactions, accompanied by product inculcation in their tissues. Trichloroethylene is transformed in soil and groundwater by poplar trees (*Populus* species).

Plants have the requisite device to decontaminate cyanides found in wastes from silver (Ag) and gold (Au) mining. The leach component of selection for Ag as well as Au removal is cyanide (ammonium thiocyanate) ([Shi et al., 2018](#)). Plants are exposed to cyanide as a by-product of breakdown throughout certain biochemical processes. This happens most often throughout the formation of "ethylene" in fully grown tissues, when "hydrogen cyanide" (HCN) is generated as a by-product. As a result, vascular plants have developed efficient enzyme-based detoxification mechanisms for the toxic cyanide. *Salix* spp. and *Sorghum* spp. have been linked to cyanide detoxification. Plants could only withstand cyanide toxicity to the extent that they can remove it. The "beta-cyano-alanine synthase" enzyme pathway detoxifies cyanide by connecting free cysteine to cyanoalanine and cyanide. Asparagines, a harmless basic amino acid in crops, are the last metabolic product ([Smaranda et al., 2017](#)).

Phytostimulation

Soil microorganisms have been shown to be useful in enhancing the bioavailability of metals for phytoextraction and increasing plant phytoremediation capacity in a variety of ways. Chemical pollutants may be degraded by soil microbes into simpler organic compounds, which plants may use as a fertilizer for improved phytoremediation of polluted sites. In the production of microbial, rhizosphere of plants is many times greater than the bulk soil. In the rhizosphere, the inhabitants of microflora are significantly larger than in soil with less vegetation. This is because the presence of nutrients from plant root exudates. Bacteria, actinomycetes, and fungi make up the average microbial community found in the rhizosphere per gram of air-dried soil. The inner rhizosphere at the root surface and the outer rhizosphere directly next to soil are the two main regions of the rhizosphere in plants. In the inner region, where root exudates are localized, the microbial population is greater. Exudates in the kind of basic vitamins, sugars, as well as amino acids are secreted from roots in a wide number of forms.

Benzene, esters, Acetates and derivatives can also be found in root exudates. In the rhizosphere enzymes

are also found, also could serve as food for the contagious community. Esterases and various oxidoreductases are among the secreted enzymes by microbial population or root system in the rhizosphere (phenoloxidases and peroxidases). Any members of the Solanaceae, Fabaceae, and Gramineae families secrete plant peroxidases. "Peroxidase" is secreted by horseradish (*Armoracia rusticana*) and white radish (*Raphanus sativus*), whereas "laccase" is secreted by the marine green algae *Nitella* and *Chara*. ([Lin et al., 2021](#)).

Metal abundance has been shown to be improved by chemolithotrophic bacteria. So many *Pseudomonas* and *Bacillus* strains have been shown to improve *B. juncea*'s Cd aggregation. Rhizobacteria present in wetlands have been set up to induce Hg as well as Se crops bioaccumulation. When organic composts are introduced to the soil, these bacteria thrive. Biodegradations of principal microbial in the rhizosphere may aid in the accumulation of larger hydrophobic xenobiotics. 2,3,7,8-tetrachlorodibenzo-pdioxin (TCDD) and PCDD/Fs, both hydrophobic recurrent organic pollutants with current log Kow values beyond 4, have been confirmed to be picked up by stems also transferred to sprouts in *Cucurbita pepo* ([Navia et al., 2005](#); [Cajthaml et al., 2006](#)).

Exudates from the roots, which are chemically identical to the chemicals used by microorganisms, will increase bacterial development in the rhizosphere, speeding up the breaking down phase. Some phenolic compounds found in root exudates have been shown to aid the growth of PCB-degrading bacteria and serve as structural analogs for PCB degradation ([Navia et al., 2005](#)). The phyto-degradation of organic contaminants in the soil can also be improved by inoculating plant soil with microbes. After being inoculated with *Pseudomonas* strain SR 3 in the soil where it was growing, the prosomillet accelerated the deterioration of "pentachlorophenol" (PCP).

Phytoextraction

Phytoextraction is the furthestmost well-known of all methods of phytoremediation. The method of phytoextraction employs plants to aid in the separation of metals from polluted soils. Metals from the soil and transported to the shoots through plant roots accumulation. If soil metal supply is insufficient for adequate plant absorption, mineral nutrients (such as phosphate to increase arsenate obtainability), chelates, or acidifying agents could be utilized to extract them into soil solution. After adequate crop development as well as deposition of metal, the aboveground part of the seedling is processed, removing metals from the site completely. The processed metal-containing plant biomass poses a secondary pollution risk. According to some researchers, gasification of processed plant material significantly reduces the amount of plant material that must be disposed of at a landfill site. In certain situations, precious metals may be mined from

metal-rich ash and used to generate income, offsetting the cost of remediation. Furthermore, the big proportion of biomass obtained could be utilize as a raw material for the manufacture of biofuel to generate energy from bio. Phytoextraction can be treated as a lengthy-tenure mitigation exertion that would necessitate multiple harvesting phases to lower metal concentrations to sufficient heights ([Yang et al., 2020](#)).

Phytovolatilization

Some metal pollutants, such as Se, As, and Hg, occur in the atmosphere as gaseous species. Researchers have recently been looking for genetically engineered plants or innately arising able to absorb rudimentary sources of certain metals from soils, biologically turning them to steamy classes within the crop, also then introducing them into the environment. This procedure is known as phytovolatilization, and it is the greatest contentious of all the phytoremediation methods. Se, CN, As, Cr, as well as Mercury are poisonous and it is unclear if volatilization of these components into the environment is healthy ([Cabrejo & Philips, 2010](#)). Because selenium phytovolatilization is a significant issue in several parts of the globe, it has received the most attention. Nevertheless, extensive attempts have been made to introduce bacterial Hg ion reductase genes into plants for the intent of Hg phytovolatilization. While no attempts to genetically modify plants that volatilize As have been made, it is likely that scientists will explore this option in the coming years. According to ([Gao et al., 2021](#); [Lewis et al., 1966](#)) became the first to announce the launch of volatile Se compounds from higher plants. Representatives of the Brassicaceae family will release up to Se of 40 g/ha/day as differing gaseous compounds, according to ([Gao et al., 2021](#)). Cattails and other aquatic plants may help with Se phytovolatilization ([Jiang et al., 2018](#)). Plants that volatilize Hg, in contrast to those that volatilize Se, are genetically modified organisms.

The bacterial mercuric reductase (Mer A) and organomercurial lyase (Mer B) genes have been inserted into *Arabidopsis thaliana* L. and tobacco. These plants captivate elemental mercury (II) and methylmercury from the soil and emit reactive mercury (O) into the environment through their leaves. The inorganic type of Se present in soil is 1/600 to 1/500 as toxic as volatile Se compounds including dimethylselenide. The elimination of inorganic components of these elements as well as gases are unable to redeposit at or close the surface, volatilization of Hg and Se is also a stable spot solution. Furthermore, after the initial planting, sites that use this innovation might not even need much monitoring. This form of mitigation has the additional advantages of causing minimum site disruption, reducing erosion, and eliminating the need to dispose of polluted plant material. According to ([Zhang et al., 2021](#)), adding HgO

to the atmosphere would have no major impact on the atmospheric pole. Those that favor the procedure, though, accepted that it would not be appropriate to use phytovolatilization near population centers or in areas with special metrological circumstances that encourage the fast deposition of unstable composites ([Jiang et al., 2018](#)).

Rhizofiltration

Rhizofiltration is the adsorption or precipitation of dissolved compounds onto plant roots. Plants are grown hydroponically before being transplanted into metal-polluted water, where they ingest and accumulate metals in their roots and shoots. Metals precipitated onto the root surface as a result of root exudates and variations in rhizosphere pH. Roots or entire plants are collected for recycling when they become contaminated with metal toxins. The majority of scientists agree that plants used for phytoremediation can only absorb metals in their roots ([Terbouche et al., 2011](#)). According to ([Wang et al., 2021a](#)), metal transmission to shoots reduces the effectiveness of rhizofiltration by increasing the volume of polluted plant debris that must be disposed of ([Wang et al., 2021b](#)), on the other hand, proposed that the efficiency of this procedure could be improved by using plants that can consume and migrate metals inside the plant. Despite these disparities, it is clear that proper plant evaluation is critical to rhizofiltration's effectiveness as a water cleanup strategy.

The attributes of a suitable plant for rhizofiltration were identified by ([Wang et al., 2021a](#)). Crops ought to be able to absorb as well as withstand a massive proportion of bull's eye metal(s) while still being stress-free to handle, minimal repairs, and producing minimal secondary waste. It's also a plus whether plants can grow a lot of root biomass or root surface area. Water hyacinth, pennwort, and duckweed are among the marine plants that can extract metals from water ([Xie et al., 2011](#)). Nevertheless, because of their minor and slow-growing roots, these plants have little capacity for rhizofiltration because they are ineffective at metal removal ([Xie et al., 2011](#)). These writers also point out that aquatic plants' high-water content makes drying, composting, and incineration more difficult. Despite these drawbacks, ([Yang et al., 2020](#)) found that trace elements from wastewater could be removed by water hyacinth. Earthly crops are considered to be more suited to rhizofiltration because they create a larger, fibrous root system with a greater surface area for metal adsorption. The greatest viable earthly contenders for metal elimination from water are sunflower and Indian mustard. The roots of Indian sunflower extract lead from hydroponic solutions.

Rhizofiltration is a price-effective innovation for treating surface water or groundwater having small but important amounts of metals such as Zn, Cr, and Pb. The commercialization of this innovation is being

motivated by finances and technological advantages such as appropriateness to numerous issue metals, capability to handle large quantities, less need for hazardous materials, recycling opportunity, lower amount of secondary leftover, as well as probability of legislative also community approval ([Zhang et al., 2021](#)). Nevertheless, the deployment of this plant-based innovation could be more difficult and prone to errors than other technologies or at a comparable expense. The processing of hydroponically grown transfusions and the upkeep of a viable hydroponic system in a field would necessitate the expertise of trained staff, and the conveniences and specialist equipment needed will raise overhead costs. Possibly the most significant advantage of this remediation approach is attributable to positive public understanding. The utilization of the plants in a contaminated area conveys ideals of cleanliness and improvement to a population who would otherwise view the area as contaminated.

Conclusions

To choose appropriate remedial alternatives, a thorough understanding of the source, chemistry, and potential health as well as ecological effects of pollutants from contaminated soils is needed. To minimize the associated health risk, make land resources available for agricultural production, increase food security, and reduce land tenancy problems, contaminated soils must be remedied. Chemical mitigation processes, as mentioned earlier in this chapter, are comparatively extensive as well as environmentally dangerous. Phytoremediation utilizing toxic element amassing crops organisms, on the other hand, has arisen as an ecologically sustainable and viable innovation for washing up polluted soils, but has yet to be tested technically in the region, with the exclusion of insufficient field trials. Researchers and commercial/government organizations must pay attention to the request of phytoremediation (predominantly phytostabilization as well as phytoextraction) to the field scale, so novel crop class will be investigated for their phytoremediation capability. While the biggest barrier to phytoremediation adoption is the long mitigation period, future studies on approaches and strategies to improve crop biomass productivity as well as pollutant elimination capacity of crops from polluted soils is urgently needed.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationship that could be construed as a potential conflict of interest.

Author Contributions

SR: conceived and designed the review. **ADA** and **SR:** wrote and edit the review. All authors contributed to the article and approved the submitted version.

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