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Possibilities of Use Fertilizer Industry Waste Gypsum Material of Improve Sodic and Boron Soils

Barış BAHÇECİ[a*], Ali Fuat TARI[b], İdris BAHÇECİ[b]

[a]*Çukurova University, Faculty of Agriculture, Department of Agricultural Structures and Irrigation, Adana, TURKEY*

[b]*Harran University, Faculty of Agriculture, Department of Agricultural Structures and Irrigation, Şanlıurfa, TURKEY*

[b]*Harran University, Faculty of Agriculture, Department of Agricultural Structures and Irrigation (Retired), Şanlıurfa, TURKEY*

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Corresponding Author: Barış BAHÇECİ, E-mail: baris_bahceci@hotmail.com

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ABSTRACT

The effect of the Fertilizer Industry Waste Gypsum Material (FIWGM) on the rehabilitation of barren soils has been investigated with this research. The soil improvement tests were carried out in randomized blocks with three replications and 0, 20, 40 and 60 tons ha^{-1} of FIWGM have been applied. By the intermittent ponding method, a total of 360 cm of water has been given, including 30 cm at each time. At the end of the trial, the application of FIWGM has showed positive effect on the physical and chemical properties of the soil. As the dose of FIWGM increased, soil infiltration rates increased, and soil sodium and boron concentrations decreased significantly. 360 cm of leaching water provided the removal of exchangeable sodium equivalent to 33.7 and 42.9 tons of gypsum for 100 cm of soil depth, with 20 and 40 tons per hectare of FWIGM applied to the test plots. The statistically significant correlation coefficient (R^2=0.921**) has been determined between the leaching water depth (Dlw)/soil depth (Ds) and the boron/initial boron remaining (B/Bo) in the soil (B/Bo = 0.622-0.168Ln Dlw/Ds).

Keywords: Sodic soils, Industrial gypsum, Waste material, Leaching water, Boron leaching, FIWGM

1. Introduction

Salt-affected soils are considered to be one of the main problems affecting agriculture, as well as a global environmental problem (Martinez-Beltran & Manzur 2005). According to the FAO/UNESCO soil map (1970-1980), the global total area of saline soils was 397 million hectares, while the total area of sodic soils 434 million hectares (FAO 2019).

A number of studies have been conducted for a long time on the use of different industrial wastes containing gypsum in the improvement and use of sodic soils (Hussain et al. 2001). For example, the addition of organic bio-ameliorants into sodic-soils has significantly increased root growth and yield of wheat (Gill et al. 2009). The application of gypsum, as well as organic fertilizer which reduces the sodicity of the soil, improves physicochemical properties by reducing pH, exchangeable sodium percentage (ESP) and bulk density and, as a result, improves the availability of nutrients in the soil (Singh et al. 2013). Matured municipal solid waste compost effectively recovered degraded soils with high soluble salt content and exchangeable sodium content (Hanay et al. 2013). In recent years, researchers have used different substances to properly treat barren lands. It was quite effective; mixtures of fly ash and sewage sludge were applied to saline-sodic soils for the purpose of soil recovery and environmentally friendly waste recycling (Örs et al. 2014). Recycled sewage sludge and fly ash allowed for cheap saline-sodic soil reclamation. The use of gypsum with biological modifications provided is more beneficial for the recovery of sodic and saline-sodic soils than for gypsum alone (Sisoday &Vaghani 2016), the combination of farmyard manure (FYM) and gypsum has increased physiological growth (Haque et al. 2015). Gypsum and calcium chloride provided direct source of Ca^{2+} to replace Na^{+}, while sulphuric acid increases the calcite dissolution (Gupta & Abrol 1990; Mace et al. 1999; Qadir et al. 2001). Gharaibeh et al. (2010) have demonstrated that phosphoric acid can be used to reclaim saline-sodic soils, and the use of organic modification by Diacono & Montemurro (2015) must be considered an effective measure to restore soil quality in salt-affected soils. On the other hand, with the application of domestic solid waste and farm waste, soil pH was lowered and the bulk density and seepage properties of the soil (Singh et al. 2017).

Global studies have demonstrated that the most reliable method to determine the reclamation criteria for saline-sodic soils with high boron content improvement is to carry out experimental trials in the problematic areas. Therefore, this study presents a paper on soil and land reclamation in the Ereğli Plain, which is located in the Center Anatolia in Turkey. The objective of the study was to determine reclamation criteria like required Fertilizer Industry Waste Gypsum Material (FIWGM), amount of leaching water, reclamation time, and the effect of the difference FIWGM dosages on the exchangeable sodium removal and infiltration rate of the soil for the sodic and boron soils in the area.

2. Material and Methods

1.1. Trial site

The test area is located in the Ereğli Plain, 1044 m above sea level, and it is a closed basin, with no outlet to discharge its waters into the sea, therefore its water is discharged to Lake Akgöl. The plain, which is the research area, has an agricultural land area of approximately 95 000 ha (Figure 1).

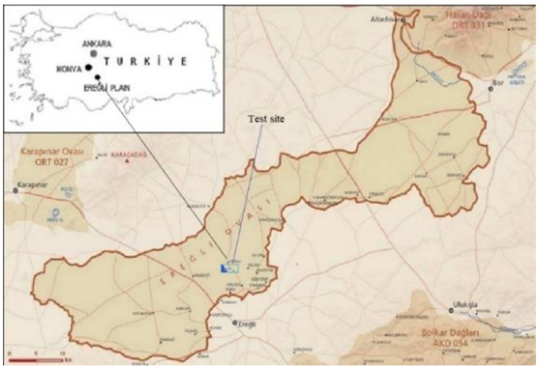

Figure 1- Geographic location of the trial

2.2. Climate characteristics

The region wherein the research is conducted has a semi-arid, continental climate conditions. The average annual precipitation is 320 mm, 10% of which falls in the summer, while the rest falls approximately equally in the other season. Summer is hot and dry, and it is cold in winter.

2.3. Soil characteristics

Research site soils have clay textures and a high amount of lime content (30–40%) and cation exchange capacity (CEC) is low, sodium exchangeable and soil salinity is high and the dominant salt type is sulphate, while soil pH varies from 8.0 to 8.4 (Table 1).

Table 1- Soil chemical and physical properties of experimental plots before treatment

Depth cm	*pH*	*Saturation %*	*EC_e dS m^{-1}*	*CEC $cmol^+kg^{-1}$*	*Exc. Na $cmol^+kg^{-1}$*	*ESP %*	*SAR*	*Lime %*	*BD g cm^{-3}*
0-20	8.0	92.2	16.12	20.10	14.3	73.4	77	35.3	1.26
20-40	8.3	87.0	5.45	14.10	6.4	45.6	30	35.3	1.39
40-60	8.3	79.2	2.98	11.45	3.8	33.5	17	37.0	1.40
60-80	8.4	71.8	1.88	8.63	1.9	22.5	14	41.6	1.56
80-100	8.3	69.0	1.33	10.28	1.6	15.3	7	41.1	1.58

EC_e: electrical conductivity of the saturation extract; CEC: Exchangeable Sodium Percentage; SAR: Sodium Adsorption Ratio; Exc. Na: Exchangeable Sodium; BD: Bulk Density

2.4. Leaching water

The electrical conductivity of the leaching water used in this experiment is 0.520 dS m^{-1} and the SAR value is approximately 0.45. The groundwater salinity is 1.72 dS m^{-1} and the SAR value is 8.2. (Table 2).

Table 2- Chemical properties of the leaching water and groundwater

Water resource	*pH*	*EC dS m^{-1}*	*Cations, meq L^{-1}*				*Anions, meq L^{-1}*			*Total*	*SAR*
			Na	*K*	*Ca*	*Mg*	***HCO_3***	***Cl***	***SO_4***		
Leaching water	8.2	0.52	0.83	0.1	1.52	5.30	3.80	0.30	3.60	7.74	0.45
Groundwater	8.2	1.72	11.3	0.2	2.39	11.86	8.20	1.40	16.19	25.79	8.2

FIWGM is the waste generated during the phosphorus fertilizer production in Mersin fertilizer factory. It is in powder form and its purity level is between 85% and 90%. FIWGM has been applied by hand spread to the soil surface and mechanically mixed with shovels approximately within the 30-40 cm of soil depth.

2.5. Experimental set-up

The research has been designed for remediation trials; data on infiltration have also been provided for these trials. The research was developed with the design of a randomized block of four FIWGM dosage treatments and three replications. The dimensions of the plot are arranged as 3 m x 5 m= 15 m^2.

The soil has been plowed deep with the plow to increase the water permeability at the research site and to ensure that the breeding agent blends well into the soil. In order to prevent leakage to the sides, the edges of the parcel have been covered by a plastic cover, approximately 40-50 cm deep.

2.6. Procedures

Leaching water has been given in 30 cm portions. When the water was infiltrated, the plots were expected to dry for about three days. After soil samples have been taken from the middle of the plots, the holes were filled with soil and the sampling points were marked with a wooden stake.

Soil and water samples analyzed using the methods described by Richards (1954) and the hydrometer texture (Bouyoucos 1951). Carbonates analyzed by calcimeter, salinity (EC_e) analyzed by conductivity meter, CEC and exchangeable sodium (NaX) were determined using a flame photometer (Tüzüner 1990).

2.7. Assessment of data

The time of application of water and infiltration has been recorded for each 30 cm of water depth and for each plot. The infiltration capacity of each treatment has been determined separately. Consequently, the average of these values for each FIWGM treatment has been calculated. Cumulative infiltrated (Z) has been determined using the mean values and infiltration equation (Kostiakov 1932) as follows:

$$Z = KT^n \tag{1}$$

Where: K, constant; T; time (h) and n, exponent.

2.8. Exchangeable Na removal

The theoretical gypsum requirement for each soil depth was calculated using the following equations, taking into account the ESP value below 10:

$$GR = EW \times 10^{-5} \times A \times BD \times D_S \times ((ESP_i - ESP_f)/100) \times CEC \tag{2}$$

$$ESP = (NaX / CEC) \times 100 \tag{3}$$

The following abbreviations have been used in equation; GR; gypsum requirement ($cmol^+ kg^{-1}$ dry weight), EW, the equivalent weight of gypsum ($cmol^+ kg^{-1}$ dry weight), ESP; exchangeable sodium percentage (%), ESP_i and ESP_f; initial and final ESP value (%), CEC; cation exchange capacity ($cmol^+ kg^{-1}$), BD; bulk density of the soil ($g\ cm^{-3}$), A; area m^2 and D_s; soil depth m, NaX; exchangeable sodium, $cmol^+ kg^{-1}$ dry weight.

First, a certain amount of leaching water for each FIWGM, and for each soil layer using the GR equation, and how much gypsum equivalent of the exchangeable sodium removed from the soil profile has been calculated.

2.9. Boron leaching

The arithmetic average of three plots was used in all assessments. The remaining boron (B) after leaching was divided by the initial boron value (B_0) and therefore the values of B/B_0 were obtained by each leaching water depth. For each FIWGM dose, the ratio of leaching water (D_{lw}) to soil depth (D_s) has been calculated. Thus, the depth of the leaching water and the boron has been removed independently of the soil depth, and the boron leaching curve and function were obtained as reported by Boumans et al. (1963).

3. Results and Discussion

3.1. Change of hydraulic properties of soil

The infiltration rate is a rather sensitive indicator of soil physical conditions. Sodium disrupts the soil structure, disperses soil particles, blocks pores, and slows down the flow of water. When a calcium source is used for soil rehabilitation, the process is reversed and the soil coagulation is regenerated, leading to a noticeable increase in soil porosity.

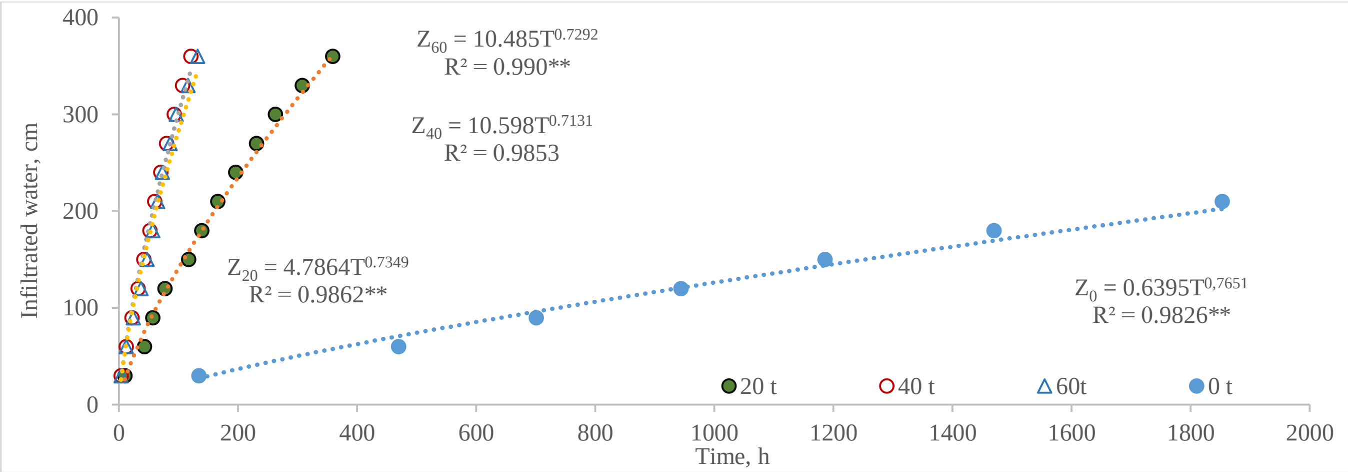

Figure 2- Effect of different doses of FIWGM on infiltration capacity of soil

The passage of water through the soil profile is, therefore, easier and the hydraulic conductivity increases significantly (Qadir & Scuhbert 2002). These research findings are consistent with the above-mentioned hypothesis. The soil infiltration rate increased as the dose of FIWGM applied increased (Figure 2).

Initially, while the infiltration rate (I) in the plot without FIGWM has been 0.22 cm h^{-1}, when 20, 40 and 60 tons of FIWGM have been applied per hectare, the infiltration rates increased to 3.0, 8.57, and 8.57 cm h^{-1}, respectively (Table 3, Figure 2).

Table 3- Effect of different doses of industrial gypsum on infiltration capacity

Applied water depth, cm	*FIWMG, t ha^{-1}*											
	0	*20*	*40*	*60*	*0*	*20*	*40*	*60*	*0*	*20*	*40*	*60*
	Time, h				*I, cm h^{-1}*				*Average I, cm h^{-1}*			
0	134	10	3.5	3.5	0.22	3.00	8.57	8.57	0.22	3.00	8.57	8.57
210	1853	166	65	60	0.08	1.11	3.75	3.75	0.11	0.18	3.23	3.50
330	-	308	116	107		0.67	1.50	2.14		0.10	2.84	3.08
360	-	359	132	121		0.59	1.88	2.14		0.08	2.73	2.98

As can be seen, the FIWGM application has enabled significant increases in infiltration rates. In plots where FIWGM was applied, 360 cm of leaching water has been infiltrated, while in plots without FIWGM, only 210 cm of leaching water could be infiltrated. In plots where 20, 40 and 60 tons of treatment material have been used, the infiltration rates at the end of the test have been 1.11, 3.75 and 3.75 cm h^{-1}, respectively. Exponential relationships with high correlation coefficients have been identified between cumulative infiltration and time for different FIWGM doses (Figure 2).

The use of gypsum on the soil surface has been commonly used for a long time in California to reclamation sodic soils and improve infiltration rates (Oster et al. 1996). The application of gypsum spread to soil has increased the rate of infiltration by 152% (Raza et al. 2001). The use of gypsum in sodium-affected soils is commonly used to increase aggregate stability and infiltration rates (Agassi et al. 1981; Keren & Shainberg 1981). Soluble salts promote flocculation in the soil (Keren & Shainberg 1984) as well as a decrease in the relative sodium content and an increase in the salt content of the water influence the rate of infiltration (Ayers & Westcott 1985). In this trial, the applying FIWGM developed the physical properties of the soil and provided a significant level of an increase in the rate of infiltration. It was understood that test area soils could not be recovered without the use of any reclamation material due to very low infiltration capacity. Considering the gypsum content of FIWGM, it has been concluded that the expected results of this study had been achieved.

3.2. Leaching of exchangeable sodium

In this research, the fertilizer industry waste gypsum material (FIWGM) containing approximately 85-90% gypsum has been used as a reclamation material.

While 360 cm of water has been infiltrated which passes through the profile in the plots where FIWGM is applied, in the plots without FIWGM application, only 210 cm of water could be infiltrated during the whole phase. Without FIWGM, NaX decreased significantly only in the upper soil. Infiltration capacity was very low in these plots, and the amount of NaX removed was very small and, finally, the soil could not be rehabilitated.

In the FIWGM applied plots, the soil analysis revealed that the exchangeable sodium was removed from the topsoil layers and accumulated in the lower soil layers following the completion of the leaching (Table 4, Figure 3a).

At the end of 20 tons per hectare, FIWGM and 240, 300 and 360 cm of leaching water applications, the ESP values in the upper layer (20 cm) decreased to 6, 8 and 2, respectively (Figure 3b). No more NaX has been leached from the lower layers after 240 and 300 cm of leaching water. Whereas, at the end of 360 cm of leaching water, the ESP values decreased below 15 in 100 cm of the soil profile and ranged between 2-12 % across the entire profile (Table 4).

Table 4 - Average exchangeable sodium (NaX) and exchangeable sodium percentage (ESP) of soils prior to and after leaching with 240, 300 and 360 cm water

FIWGM applied t ha^{-1}	*Soil depth cm*	*Bulk density g cm^{-3}*	*Leaching water, NaX, cmol$^+$kg^{-1},* 0	240	300	360	*CEC cmol$^+$kg^{-1}*	*Leaching water ESP* 0	240	300	360
	0-20	1.26	11.51	9.47	-	-	18.41	62	51	-	-
0	20-40	1.39	5.57	9.56	-	-	12.65	44	52	-	-
	40-60	1.40	2.20	4.50	-	-	10.00	22	45	-	-
	0-20	1.26	11.07	1.04	1.35	0.36	17.37	64	6	8	2
20	20-40	1.39	3.69	2.59	4.55	1.2	12.72	29	21	38	9
	40-60	1.40	2.01	2.60	3.6	0.67	10.48	19	25	34	12
	0-20	1.26	11.79	1.45	1.13	0.67	17.96	65	8	6	4
40	20-40	1.39	5.36	1.63	1.5	1.61	12.94	41	13	12	12
	40-60	1.40	3.37	2.65	1.62	1.55	10.56	32	25	15	15
	0-20	1.26	10.23	1.17	0.98	0.68	17.51	58	7	6	4
60	20-40	1.39	5.19	1.43	1.99	2.24	12.18	43	12	16	18
	40-60	1.40	2.34	2.06	1.86	2.67	10.73	22	19	17	25

However, even when 40 tons per hectare of industrial gypsum and 240 cm of leaching water have been used, the ESP values in the 40 cm soil profile dropped to safe values. When the water depth of the leaching is 300 cm, the ESP values in the 100 cm profile have dropped below 15%, except for the soil depth of 60-80 cm. When 360 cm of leaching water has been applied, the ESP values have been lower than 15% in the entire profile (Figure 3c).

However, the application of 60 t ha^{-1} of FIWGM could not provide for further sodium removal in all leaching waters (Figure 3d). From this point on, it has been concluded that the applied irrigation water was not sufficient to dissolve more FIWGM.

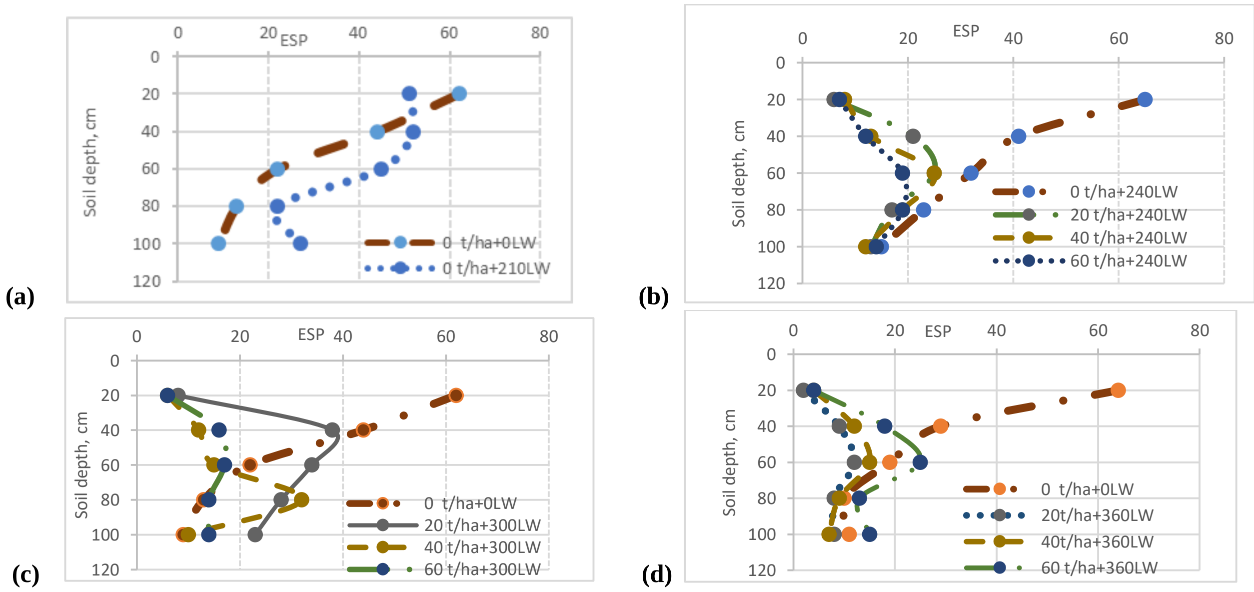

Figure 3- Effect of different leaching water (LW) at different FIWGM dosages on change ESP at the soil profile

A similar situation has also been observed in some studies, and it has been observed that the administered FIWGM dose increases and the sodium removed for each mined gypsum unit decreases (Beyce 1977, Bahçeci 2008).

Overall, the results have shown that favorable leaching of interchangeable sodium at the site of the test site is not possible without some kind of reclaimed chemical material. Therefore, in recent years, lower doses have been recommended instead of the theoretically calculated amount of gypsum.

3.3 Gypsum calibration curves for sodic soils reclamation

Table 5 shows the quantities of theoretical gypsum calculated for the removal of the exchangeable Na at different soil depths and at two leaching water levels. As can be seen, in plots where FIWGM has not been applied, sodium leached is approximately 4.420 tons per hectare equivalent to gypsum.

Table 5- Theoretical amounts of gypsum calculated for the replaced exchangeable Na with amendments in different doses on the sodic soils

FIWGM applied t ha^{-1}	*Soil Depth, (cm)*	*Leaching water, (cm)* Theoretical gypsum calculated for removed NaX, (t ha^{-1}) — *300*	*360*	*Soil Depth, (cm)*	*Leaching water, (cm)* Cumulative removed, NaX (t ha^{-1}) — *300*	*360*
0	0-20	4.420	4.420	20	4.420	4.420
	0-20	21.07	23.21	20	21.07	23.21
20	20-40		5.95	40	21.06	29.16
	0-20	23.10	24.10	20	23.10	24.10
	20-40	9.23	8.97	40	32.33	33.06
40	40-60	4.21	4.38	60	36.54	37.45
	60-80		3.43	80	36.54	40.88
	80-100	1.30	1.96	100	37.85	42.84
	0-20	20.05	20.70	20	20.05	20.70
60	20-40	7.65	7.05	40	27.70	27.75
	40-60	1.16	.	60	28.85	27.75

Whereas 20 tons per hectare of FIWGM and 300 and 360 cm of leaching water have been used, 24 and 29 tons of gypsum sodium equivalent have been removed, respectively. In a previous study conducted at this research site, the application of 20 and 40 tons per hectare of mined gypsum, along with 360 cm of gypsum leaching water, removed an exchangeable sodium equivalent of 38 and 56 tons of gypsum per hectare (Bahçeci 2008).

As can be seen in Figure 4, when 40 tons of FIWGM were applied per hectare, the quantity of sodium leachable removed from the soil profile is approximately 43 tons per hectare. However, as the doses of FIWGM increase, the amount of exchangeable sodium leached did not increase at the same rate. The effect of the treatment material at lower doses was higher and the effect of the treatment agent at high doses applied to the removal of interchangeable sodium was found to be lower.

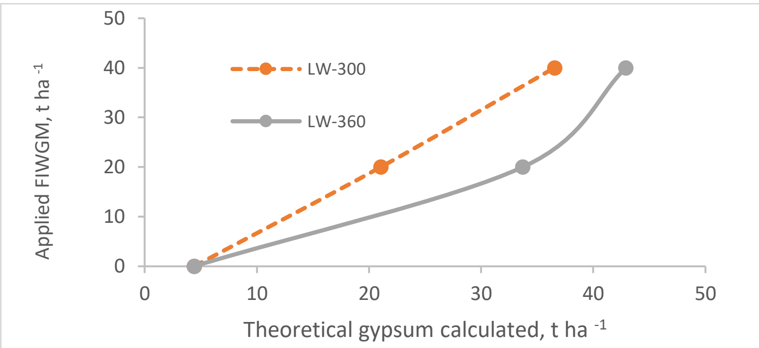

Figure 4- Gypsum calibration curves at two leaching waters levels for 100 cm soil profile

The amount of FIWGM required can be estimated to reclaim sodic-soil using these calibration curves in Figure 4. For example, if the required FIWGM was theoretically calculated at 20 tons per hectare, in this case 10 tons per hectare of FIWGM and 360 cm of leaching water used, the quantity of exchangeable sodium removed would be 20 tons per hectare of gypsum equivalent for 100 cm of soil depth.

The time required to infiltrate the applied water is estimated to be approximately 380 hours or 16 days using the cumulative infiltration curve in Figure 2. The time required for improvement is calculated by adding weighting intervals to the infiltration time.

3.4 Boron leaching

High boron concentrations were formed in the experimental area by the evaporation of shallow groundwater. Consequently, while the upper layer of the soil has a high boron excess in the research area, the boron concentration in the lower layers has been low.

To improve is very difficult boron soils. The amount of water required for boron leaching in soils with a high boron content by nature is approximately twice the amount required for salt leaching (USSL 1981; Hoffman 1986). Rehabilitation of boron soils is costly and time-consuming and labour-intensive. However, it is still a common view that more accurate and consistent results are obtained with on-site field trials.

In this research, along with leaching water applications, the boron content also decreased and, at the end of 360 cm of leaching water, the boron concentration decreased to 2 ppm in the upper soil and lower levels in the lower layers (Table 6, Figure 5).

As explained in the method, using the average data obtained, a regression analysis has been conducted to determine the relationship between the boron left after leaching and the ratio of the water depth applied to the soil depth based on the initial boron concentration in the soil.

Table 6- Average boron status (ppm) in test plots before and after leaching

Soil depth, cm	*Leaching water, cm*							
	0	*30*	*60*	*120*	*180*	*240*	*300*	*360*
0-20	13.30	9.17	10.23	5.72	3.87	2.27	3.03	2.08
20-40	3.74	3.45	5.90	4.82	3.62	1.32	1.41	1.88
40-60	2.73	0.97	2.78	2.04	1.83	1.52	1.80	0.50
60-80	1.19	0.18	2.30	1.04	1.38	0.10	1.61	0.15
80-100	1.89	0.56	0.90	0.81	1.26	0.20	1.15	0.10

A statistically significant logarithmic relationship between leaching water depth (D_{lw})/soil depth (D_s) and remaining boron/initial boron values (B/B_o) has been identified. As a result of the regression analysis, the equation obtained is as follows: $B/B_o = 0.622 - 0.168 \text{Ln}\, D_{lw}/D_s$, ($R^2 = 0.921^{**}$).

As can be seen, the resulting equation has a high correlation coefficient, which is statistically significant at $p = 0.01$.

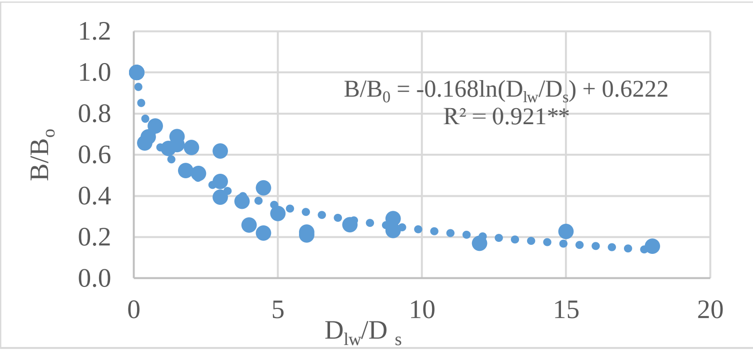

Figure 5- Boron leaching curve

4. Conclusions

The field experiments have demonstrated that an increase in FIWGM application rate up to 40 tons per hectare has resulted in significant increase in the removal of exchangeable sodium. Results also indicated that the application of 20 tons FIWGM per hectare, along with 300 and 360 cm water could remove the exchangeable sodium equivalent to 23.21 and 29.16 tons per hectare gypsum, respectively.

When 40 tons of FIWGM have been used per hectare, sodium equivalent to 42.89 tons of gypsum has been removed from the soil profile. Whereas, if 60 tons of FIWGM was applied to a hectare with 300 and 360 mm of leaching water, the amount of sodium leached has been only 28.85 and 27.75 tons of equivalent gypsum, respectively. This suggests that the quantity of water applied has not been sufficient to dissolve the FIWGM applied at high doses.

Since soil infiltration capacity has been very low, it is highly recommended to start with the application of 10 tons per hectare of FIWGM and to increase the amount of application needed to gradually remove salts and sodium exchangeable from the soil profile.

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