

RECLAMATION OF HIGH RESIDUAL SODIUM CARBONATE WATER WITH COMMERCIAL SULPHURIC ACID FOR SUSTAINABLE CROPPING AND SOIL CONSERVATION

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ABSTRACT. A study was carried out in field experimental area of directorate of land reclamation Punjab, Lahore, to investigate the effect of experimentally quantified commercial sulphuric acid (76%) on residual sodium carbonate (RSC) of water, soil quality and crop yield. The findings were clear indications of effectiveness of acid injection approach to treat water. The sulphuric acid application reduced the RSC value of 6.1 to nil by making (T₂) slight change in EC of water. This treated water not only improved the soil quality by decreasing its calcareousness from 20 to 17.2 making soil soft while the same increased to 23 in control (T₁), where not acid amendment was done. Similarly, SAR of soil was also restricted from an increase by acid treated water rather than the control set of experiment. To make RSC nil, 5.19 liters of sulphuric acids were injected in water for 3 acre inch irrigation. An increase

of 16.65% in grain yield of wheat crop was observed upon harvesting in T₂, in comparison with control. Ascorbic acid and total phenolic contents (TPC) were also high in T₂, followed by T₃ and T₁. All the changes in soil parameters and crop yield were found statistically significant.

Keywords: RSC; ground water; sulphuric acid; wheat crop; sustainability.

INTRODUCTION

In Pakistan, an important use of underground water is in field of agriculture. Due to climbing increase in population and urbanization the stress on ground water is severely damaging the water quality for its use in agriculture (Khattak *et al.*, 2012). Moreover, due to deficiency of

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surface water for irrigation in canal system of Punjab, Pakistan, is met by using underground water. It was reported that 70% tube wells in Indus basin are pumping unfit ground water (Kahlowan *et al.*, 2005). It has been observed through many scientific investigations that the ground water quality is not fit for crop production. Three major water quality parameters, electrical conductivity (EC), sodium absorption ratio (SAR) and RSC decides that water is fit or unfit for irrigation. A study in 20 different villages of Lahore indicated that 76.6% water samples were found unfit for irrigation. More precisely, 73.3% ground water samples were unfit regarding residual sodium carbonate (RSC) (Ali *et al.*, 2009). Another study revealed that the ground water quality of many districts in Punjab, like Gujranwala, Sialkot, Gujrat, Sheikhpura, Kasur, Rawalpindi, is unfit (Qureshi *et al.*, 2010). Another study reported that 82% ground water samples were unfit for irrigation having high RSC than permissible limits along Hudiera drain in Lahore (Khattak *et al.*, 2012). The situation is becoming worst day by day and for efficient agriculture sustainability is required in resources. Crop production may be enhanced by making efficient use of available resources. Unfit ground water having high RSC can be converted into fit water by decreasing its RSC. Water having high RSC means it contains heavy carbonate and bicarbonate contents ($RSC = HCO_3^- + CO_3^{2-} - Ca^{2+} + Mg^{2+}$), as compared to calcium and

magnesium ions. Due to high RSC, pH of water also increases, which results in precipitation of calcium and magnesium to increase the sodium contents in soil solution. Carbonate and bicarbonate ions can be converted into carbon dioxide on treatment with acidic substances hence reducing the RSC value for water (Nishanthiny *et al.*, 2010). Gypsum is frequently used to treat RSC component, but gypsum just adjust the ratio of calcium ions to reduce RSC. But the issue is to reduce the ionic species not only to deal theoretically, but to solve the issue scientifically. Further, gypsum dissolution is very slow and not a quick method to treat RSC. Sulphurous acid generators have used to treat RSC of water in Pakistan, but the method was not cost effective, especially for farmers having small land holdings (Ghafoor *et al.*, 1997). However, sulphuric acid is another option to treat high RSC of water to render it fit for irrigation (Griffin and Silvertooth, 1999). An objection comes to the issue that adding acid may enhance the EC of water, but this EC will not be harmful because sulphate ions are being added, which in turn useful and may increase the gypsum contents in soil. So, change in EC is not the problem as more benefit is being achieved by reducing the RSC. It was further reported that native calcium sulphate does not provide enough calcium to replace sodium ions from soil to manage saline sodic soils (Qadir *et al.*, 2001; Zia *et al.*, 2006). Current study was designed to treat RSC of ground water

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with sulphuric acid and to monitor the effects of reclaimed water on soil properties and on yield of wheat crop *Triticum aestivum* L. Wheat crop was selected because of its economic importance in agriculture based economy of Pakistan (Raza *et al.*, 2014). An important feature of study was to establish the effect of water quality on ascorbic acid contents of wheat leave as no earlier reports were available on this aspect in context of Pakistan and this was also novelty of current research.

MATERIAL AND METHODS

A field experiment was conducted in Field Experimental Area of Directorate of Land Reclamation, Canal Bank Moghalpura Lahore. The experiment was arranged in a Randomized Complete Block Design (RCBD) consisting of three treatments of acid (T_1 = control (no acid addition), T_2 = fully treated per 3 acre inch irrigation and T_3 = half treated as per requirements / 3 acre inch irrigation), applied by mixing with water. The treatments were replicated thrice. Sulphuric acid was applied to neutralize RSC of unfit tube well water, according to discharge in water channel. It was experimentally determined through titration that how much sulphuric acid (76% pure) was required to completely neutralize RSC value of 5.6(2013), 5.8(2014) and 6.1(2015) for 3 acre inch irrigation or 305640 liters of water. Wheat crop (Faisalabad, 2008) was sown as test crop. Phosphorus (as diammonium phosphate) and nitrogen fertilizers (as urea) at the rates of 200 and 350 kg ha⁻¹, respectively, were added to the all plots. In each plot (40.5 m²), there were twenty

seeding lines with 9 m length. Plots were thinned to final plant density of about 19 plants m⁻² at seedling stage. Weeds were controlled mechanically as needed. Grain yields were taken at maturity by harvesting the 1.0 m² area of the two inner rows of each plot at the end of April. Grain yield was adjusted to a 10.0% moisture basis. Pre and post harvesting soil sampling was done to investigate the effect of treatments on soil quality in terms of reclamation. All data were analyzed by the GLM procedure using the Statistix v. 8.1 (Analytical Software, 2005). Means were compared using LSD Test at 5% probability level. Complete water and soil analysis were also performed with respect to treatments. Soil sampling was done up to 10 inches, so that the root zone area may also be studied for wheat crop. Sodium adsorption ratio (SAR) and residual sodium carbonate (RSC) were calculated by following formula:

$$SAR = \frac{Na^+}{(Ca^{2+} + Mg^{2+})^{1/2}}$$

$$RSC = (HCO_3^- + CO_3^{2-} - Ca^{2+} + Mg^{2+})$$

(Richards, 1954).

Both SAR and RSC were used to determine the sodicity of water and soil. However, SAR is more specific to soil quality and RSC is attributed to water quality and directly represents the quantitative aspects of sodicity (Nishanthiny *et al.*, 2010).

Acid quantification

Acid requirement was calculated through acid base titrations in laboratory using phenolphthalein as indicator. Amount of acid required to completely neutralize the RSC of 10 ml of ground water was extended to 3 acre inch water quantity by unity method.

Electrical conductivity (EC) was determined by conductivity meter HANNA EC-215 (Portugal) and hydrogen ion concentration (pH) was determined by Jenway 3510, UK. Sodium and potassium were determined on flame photometer, Jenway PFP-7 UK. Weighing balance of Sartorius, Germany was utilized. All the chemicals procured for the purpose were of analytical grade and mainly of Sigma and Merck.

Determination of ascorbic acid contents

Ascorbic acid contents were determined by little modification in method developed by Raghu *et al.* (2007). Fresh chopped wheat leaves were milled by using pestle and mortar in 10g/L of oxalic acid solution. After filtration volume of filtrate was made up to 100 ml and coupled with 2,4 Dinitrophenylhydrazine to form osazone giving red color. Color intensity was matched with standard ascorbic acid solutions of 0-25 mg/ml concentrations.

Determination of total phenolic contents

Gallic acid was taken as internal standard to determine total phenolic contents (TPC). Plant extracts were mixed with 45 ml of distilled water. Then, 1 ml of Folin-Ciocalteu reagent was added and stayed for three minutes, followed by addition of 3 ml of 2% Na₂CO₃. The resultant mixture was allowed to shake for 2 h. Absorbance of mixture was taken at 760 nm at UV-1700 Shimadzu, Japan spectrophotometer. TPC were expressed as µg of gallic acid equivalent/gram of dry mass (Slinkard and Singleton, 1977). Cost analysis was done on basis of prevailing market prices of acid and wheat grain in Pakistan.

RESULTS AND DISCUSSION

Ground water quality

The analysis results of tube well water indicated that water was completely unfit regarding RSC and EC (*Table 1*). RSC of water started to increase from 5.6 meqL⁻¹ to 6.1 meqL⁻¹ during period 2013-2015.

Table 1 - Ground water quality deterioration from 2013 – 2015

Year of experiment	Ph	EC	RSC (meqL ⁻¹)	SAR
2013	7.95c	1.6b	5.6bc	4.7c
2014	8.33b	1.7ab	5.8b	5.3b
2015	8.45a	1.8a	6.1a	5.8a

Water having RSC >2.5 meqL⁻¹ is said to be unfit for irrigation purpose, due to high contents of bicarbonates or carbonates or both. Water with high RSC is considered very harmful for crops, as it deposits sodium carbonate in soil, which in excess may develop

black color on soil surface. EC of water is considered an important water quality parameters, as it reflects the total dissolved solids (TDS). EC also varied from 1.6 dScm⁻¹ to 1.8 dScm⁻¹ for the same time duration. EC greater than 1.5 dScm⁻¹ is also considered

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harmful for soil and crop (Alobaidy *et al.*, 2010), as high value reflects the contribution of ionic species formed from dissolution of salts, especially sodium salts.

Statistically viewing, changes in parameters mentioned in *Table 1* were different from each other. So, trend of increase in values was a considerable entity regarding water quality degradation and phenomenon became worst with the passage of time. RSC being the major criterion (Salman and Elnazer, 2015) for fitness, if irrigation water was found to had increasing

trend and exhibited very high value than the permissible limits.

Acid quantification

Acid amendment in water is rapid method to reduce RSC of water to or below 2.5 meqL^{-1} , as per requirement (Mehboob *et al.*, 2011). As the water quality was continuously on change, so the amount of acid required to neutralize the RSC was also variable in respective years. The performance based quantification of acid is given in *Table 2*.

Table 2 - Quantification of sulphuric acid for complete neutralization of RSC

Year of experiment	RSC of water	Sulphuric acid quantity in liters for 3 acre inch irrigation
2013	5.6bc	4.70c
2014	5.8b	4.88b
2015	6.1a	5.19a

The quantification of acid to completely neutralize the RSC was purely titration based as there seems no linear relationship between the RSC and quantity of acid. It was ultimate fact that an increase in RSC demanded more acid to get neutralized. The increase in acid requirement with respect to RSC was also statistically significant indicating the true reference marking.

Soil characteristics

The loamy clay textured soil was also observed to undergo deterioration with the passage of time upon irrigation with poor quality water having high EC and RSC. Both

parameters increased the salt contents of soil as indicated by statistically significant climbing values of EC, SAR, ESP and calcareousness for the control plots in *Table 3*.

SAR is the change in soil physical structure as sodium ions replace the calcium and magnesium ions in soil and resultantly soil becomes hard. An increase in ESP and SAR signified the augmented deposition of sodium ions in soil, associated with reduction in soil fertility. Decrease in soil fertility means decrease in crop yield (Minhas, 2010), hence affecting the economy of country.

Table 3 - Deteriorating soil quality of field experimental area sodic water for sustainable rice yields (Paddy and Water Environment, 4: 153-162)

Year of experiment	pH	EC (dScm ⁻¹)	SAR	Exchangeable sodium percentage (ESP)	Calcareousness as CaCO ₃
2013	8.22c	0.82c	4.7c	5.36c	20c
2014	8.45b	0.87b	5.3b	6.17b	21b
2015	8.59a	0.95a	5.8a	6.81a	23a

Effect of acidification of water on soil properties

Soil properties were monitored by measuring the various quality parameters throughout the experimental years. Detail analysis comparison for three consecutive years (*Table 4*) clearly demonstrated the beneficial impact on soil quality parameters. Due to poor quality ground water use, soil pH was increased from 8.22(2013) to 8.59(2015) in control treatment. High

pH value of water associates with ability to dissolved lime, hence increasing the carbonate contents (Ayers and Westcot, 1985). That was not the case where acid amendments were applied. As T₂, where full dose of acid was added as per requirement, soil pH decreased up to 7.26 and up to 7.83 for T₃ in 2015. Similar were the findings for SAR under T₂ and T₃ sets where SAR increased in control (Halliwell *et al.*, 2001).

Table 4 - Impact of acid treated water on soil quality from 2013-2015

Year of experiment	pH			EC			SAR			Calcareousness as CaCO ₃		
	T ₁	T ₂	T ₃	T ₁	T ₂	T ₃	T ₁	T ₂	T ₃	T ₁	T ₂	T ₃
2013	8.22	8.0	8.15	0.82	0.95	0.87	4.7	4.6	4.6	20	19.8	19.8
2014	8.45	7.54	8.0	0.87	1.10	1.00	5.3	4.4	4.5	21	18.6	18.9
2015	8.59	7.26	7.83	0.95	1.25	1.11	5.8	4.3	4.4	23	17.2	18.2

However, the EC of soil was increased against the treatments T₂ and T₃, but this increment was within permissible limits. Moreover, sulphates ions added in soil decreased the soil calcareousness, which improved the soil porosity and

aeration. So, the acid treated water reclaimed the soil too. At the end year 2015 the calcareousness value for control soil was 23 higher than findings in T₂ and T₃, respectively. The increase in calcareousness of soil in control protocol was due to

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continuous addition of carbonates present in untreated water.

Impact on crop yield

Yield of wheat grain also revealed the positive signs of acid treatment. A high yield was obtained from T₂ plots with full dose of acids, as compared with T₃ and T₁ plots. The differences in yield were statistically significant emphasizing the effectiveness of acid amendment. The wheat grain yield data was the

average of three crops in 3 base years: 2013, 2014 and 2015.

It was found that 16.65% increase in grain yield was calculated in comparison to control set of crop (Fig. 1). The acid amendment increases soil properties and helps in growth of crops by increasing percolation and decreasing calcareousness (Kahlowan *et al.*, 2000) is verified in agro-climatic conditions of Lahore city.

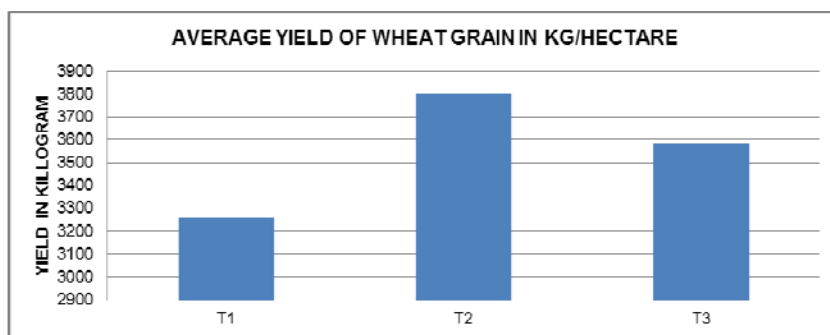


Figure 1 - Wheat grain yield on average basis for base year 2013-2015 with respect to treatments

This increment in produce was of high economic importance and may play a key role in agriculture based economy of Pakistan and may strengthen the backbone of country to mitigate the food security threats for growing population.

Ascorbic acid concentration

Ascorbic acid is an antioxidant and plays an important role to encounter reactive oxygen species removing the stress on plants, especially in leaves (Zhang *et al.*, 2015). The ascorbic acid contents of wheat leaves for control (T₁) were

0.93 ± 0.09 and for T₂, 1.53 ± 0.14 mg/g of fresh mass. For T₃, ascorbic acid content was 1.07 ± 0.19 in between T₁ and T₂. So, maximum concentration of ascorbic acid was found in T₂, where acid fully neutralized the RSC of water. It has been proved that the treated water or good quality water exhibited potentially positive impacts on the ascorbic acid contents in leaves of wheat. Ascorbic acid contents increased in treatment, where unfit irrigation water was completely reclaimed by using sulphuric acid, probably due to fact that ascorbic acid

developed resistance in wheat plants against oxidative stress, osmotic pressure and pathogens (Khan *et al.*, 2011).

Total phenolic contents (TPC)

Maximum TPC of 34.33 ± 2.00 mg/g dried extract were measured in leaves of wheat crop, where fully neutralized RSC water (T_2) was applied and minimum TPC of 14 ± 1.20 mg/g dried extract were found in control, where water applied was untreated having high RSC. Ascorbic acid and TPC analysis indicated that response of antioxidant in plants is highly specific to quality of water. Phenolic compounds are responsible for antioxidant activities of plants both *in vivo* and *in vitro* and represent the quality of crop or plant (Raza *et al.*, 2009).

Cost effectiveness

Whether the method of acid injection was cost effective or not gained a serious concern, as the farmer community majority with small land holding might be able or not to pay the cost of acid. To reduce high RSC like 6.1 to nil, 5.19 liters of commercial sulphuric acid were required, which costing Rs.51.90 Pak rupees or 2 US dollars per 3 acre inch irrigation. Wheat crop needed on average four irrigations consumed 207.6 Pak rupees or 8 US dollars per wheat crop. While the yield increment of 5.5 mond/acre or 543 kg/hectare valued 6875 Pak rupees or 67 US dollars. So, a huge difference in cost and income can be an impetus to

adapt the approach by farmers in Pakistan.

However, quantity of acid to be added purely based on analytical testing. A layman or farmer cannot calculate the amount of acid to treat RSC of water. So, the analysis of water is a mandatory step towards furtherance of technique and analysis facility is provided by Directorate of Land Reclamation Punjab, Lahore, at very low cost. After analysis, the scientists may advise the quantity of acid to be added if water comes out to be unfit regarding RSC. This method is only for those water samples, which are unfit only due to high RSC.

CONCLUSION

The reclamation of unfit ground water having high RSC can be utilized in a sustainable way by treating with specific amount of commercial sulphuric acid, which is very cheap. Not only the soil quality, but crop yield also increases by applying acid in running unfit water. However, the amount of acid required can only be found by performing analysis of water samples in laboratory. Safety measures must be taken during the injection of acid in water, as sulphuric acid is very corrosive. These findings may be exploited in farmer community through awareness campaigns. Moreover, the engineering companies may develop a safe technology to add right amount of acid for specific time period to achieve rational outcomes.

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