

RATIONAL SEWAGE WATER UTILIZATION AND ITS IMPACT ON THE PROXIMATE AND NUTRITIONAL QUALITY OF CABBAGE (*BRASSICA OLERACEA* L.)

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Abstract. This study was conducted to evaluate the effect of different ratios of fresh and untreated sewage water irrigation on the proximate and nutritional quality of cabbage. The experiment consisted of four ratios of sewage to freshwater viz. 75%+25% (T1), 50%+50% (T2), 25%+75% (T3) and 0%+100% (T4), respectively, the control being 100% sewage water. The result for all irrigation matrices showed moisture% in a range between 86.82 and 89.89, crude protein% (1.64 to 2.88), crude fat% (0.31 to 2.28), crude fiber% (3.05 to 3.59), ash% (0.63 to 3.54), carbohydrate% (1.03 to 5.29) and energy Kcal/100 g (26.70 to 36.35), while the mineral composition for all irrigation matrices was found between (32.66 to 75.57) mg/100 g Ca, Vitamin C (10.67 to 32.21), Na (11.77 to 17.92), K (40.61 to 104.31), Zn (2.60 to 13.30), Cu (1.56 to 3.44), Fe (3.14 to 12.37), Mn (1.83 to 5.42), Mg (13.31 to 20.99) and Co (0.20 to 1.06). The result of the study suggested that the concentration of metal is within the Recommended Dietary Allowance (mg metal/day) of 100 g cabbage meal. The vegetable could be marketed as a protein supplement in deprived rural areas, and its high potassium content could be used to prevent hypertension and other cardiovascular diseases. The relatively high concentrations of zinc, iron, and manganese can prevent the problem of micronutrient deficiencies.

Keywords: *metals, untreated sewage, vegetable, healthy living, soil*

Introduction

Disposal and safe reusing of wastewater are significant issues that communities confront, especially in the case of expanding metropolises in developing nations. On the other, wastewater is a rich resource that can be utilized for agriculture purposes, but if untreated, it may exert health hazards. Hence, it is believed as a vital resource and a problem because a high amount of mineral nutrients and toxic metals may enter the ecosystem through direct irrigation without any treatment. Before its reuse for irrigation purposes in crop fields, a detailed study and analysis must be undertaken from the health perspective of the end consumer. In Pakistan, this problem in metropolitan cities, particularly cities like Karachi where no river system irrigation exists is a huge challenge to be addressed. Farmers often have no alternative; hence, they are dependent upon untreated municipal sewage water due to reason of unavailability of wastewater collection followed by treatment facilities (Friedel et al., 2000; Gori et al., 2019; Khan, 2020). Sewage's long-term use poses ecological dangers in the form of soil and groundwater pollution, when properly planned, executed, and managed, waste in agricultural areas has the potential to have a positive impact on the environment (Gupta et al., 2021). Both treated and untreated municipal sewage wastewater is used for

vegetable production at large without assessing its impact on the quality of these vegetables that constitute an integral component of the cropping pattern but the increasing pressure on food and cash crops has limited the area under vegetable chili, onion, garlic, lettuce, spinach, cauliflower, and cabbage, etc. to about 0.62 million hectares, which is 3.1% of the total cropped area (Bixio et al., 2006).

Cabbage (*Brassica oleracea* L.), is a leafy type of vegetable cultivated largely in Karachi and its periphery on municipal sewage water irrigation. It's a biennial seasonal vegetable, round-headed, and is exist in many colors but light green is common (Ren et al., 2013). It's a rich source of vitamin C, potassium, calcium, and fiber. Only 75 g of cabbage transfer 147 mg of potassium, 28.1 mg of vitamin C, and 36 mg of calcium. Assessment of proximate quality and quantitative determination of mineral nutrients, protein, fiber, fat, carbohydrate, moisture, and ash reflect to be transferred into the human body. Trace nutrients viz. Zn, Cu, Fe, Mn, and Ni are essential nutrients and are required in the plant life cycle. These nutrient elements play a crucial part in chlorophyll synthesis and carbohydrate production which boosts plant growth hormones and metabolic processes. Other functions include an increase in phosphorus and calcium transport, cellular division, and protein synthesis. They also facilitate the maturation of plants, bud formation, fruit thickness, elongation of coleoptiles, and the expansion of leaf disc (Mehes-Smith et al., 2013; Saini et al., 2021).

With the increasing scarcity of decreasing freshwater resources for the cultivation of crops, the utilization of sewage water as an alternative source is getting recognition in agriculture (Yu et al., 2022). The sewage water resource is rich in mineral nutrients required for plant growth but at the same time, the occurrence of some harmful bacteria, fungus, and heavy metals may exert a harmful impact on metal toxicity, phytotoxicity, and soil contamination and ultimately enter into the food chain (Eid et al., 2019; Mandal and Kaur, 2019). Due to the nature of shallow-rooted plants, cabbage may be grown with a 20 cm soil layer, known as A-horizon. Since, the upper soil regime is rich in metal contents, hence translocation in crop plants is likely enhanced (Sethy and Ghosh, 2013). Karachi is a large metropolitan city in Pakistan that lacks a river system for agriculture; hence, the majority of farmers are cultivating vegetables on municipal sewage water. Ultimately, the transportation of vegetables jeopardizes the health of consumers due to hyper-accumulation of metals and deteriorated quality (Panhwar et al., 2022). Cabbage extensively is cultivated in Karachi and is consumed as a salad or cooked, the proximate quality and metal accumulation from contaminated soil medium together with undiluted sewage water irrigation may be serious health hazards. The present study, therefore, was conducted to investigate the rational dilution of sewage wastewater and its utilization in cabbage cultivation to obtain safe produce.

Materials and Methods

Selection of site/ Study area

The experiment to investigate the rational application of sewage water and its impact on the nutritional and proximate quality of cabbage was conducted at the experimental field of Southern Zone Agricultural Research Center, University of Karachi (Latitude 24.9439039, longitude 67.1176509, Altitude 42.45m). A commonly grown cabbage cultivar (Asha) was selected for the study.

Sowing method and irrigation cycle

Seed (20 g) was sown in a nursery bed (15 m²) where farmyard manure was added with residual soil followed by irrigations with fresh water. The main field was divided into sub-plot (3x3 m²) for each treatment and replicate. After 42 days of germination, seedlings were shifted to each subplot with a 20 cm planting distance. Raw sewage water was collected from the main discharge channel (Malir river), Sharafi goth, Karachi (Latitude: 24.863088, Longitude: 67.172576) with intervals of two weeks (Oct-Nov 2020), and dilutions were prepared in containers as per treatment scheme viz. (Control) C (100% SW), T1 (75%SW: 25%FW), T2 (50%SW: 50%FW), T3 (25%SW: 75%FW) and T4 (100%FW). Three replications of the randomized complete block design (RCBD) experiment were used. The treatments as irrigation sources were applied per recommended rate with agronomic intervals. Liquid NPK fertilizer (20:20:20) at 20 mL/plant with two split doses, first after 11 days and second after 35 days were applied.

Proximate analyses

At the maturation, samples from each trial plot were drawn followed by washing. Moisture contents on a fresh weight basis were determined, samples were then oven-dried at 105 °C, mashed, and preserved for further analytical analysis as under:

Proximate analysis of the sample was determined by the standard method of (AACC, 2000) viz. % moisture content on a fresh weight basis (method 44-15A), ash content (method 08-01), fiber content (method 32-10), and fat content (method 30-25) while crude protein % was performed with (method 2001.11) of (AOAC, 2002). Carbohydrate content (mg/100g) was calculated by the sum of all proximate parameters (%) subtracted by 100. Food energy was calculated through the Atwater Factor i.e. 4 kcal = 1 gram protein consumption; 4 kcal = 1 gram carbohydrate consumption; 9 kcal = 1 gram fat consumption, (kcal/g) = (Crude Protein* 4) + (Fat * 9) + (Carbohydrate * 4), where Crude Protein, fat and carbohydrate are in (%) values (Osborne and Voogt, 1978).

Nutritional mineral content analyses

Mineral contents (Zn, Cu, Fe, Mn, Mg, Co) in samples were analyzed through method No 9.10, (AOAC, 2000), and manufacturers' (Varian 220FS) operational manual settings. Analytical grade reagents and standards were used during the sample preparation and analysis performed in (ISO/IEC-17025) accredited laboratory, Food Quality & Safety Research Institute, PARC, Karachi.

Statistical analyses

By using Statistix 8.1 software, obtained data of all parameters were statistically analyzed to investigate the level of significance among treatments (two-way ANOVA). The post hoc test, least significance difference (LSD) was used for all treatments at a 5% level of significance (Analytical software, 2005).

Results and Discussion

Physicochemical characteristics of experimental soil, sewage, and freshwater

Soils are constituted of small particles, and the volume and distribution of these particles greatly affect the soil's characteristics. The textural class of the experimental field's soil was found to be sandy loam with 43.25 % of sand, 31.27% of silt, and 25.48% of clay (*Table 1*). Some of the physicochemical characteristics of soil and raw sewage are given in the following table.

Table 1. *Physicochemical characteristics of soil*

Sr. No.		Sand	Silt	Clay	Textural Class
01	Particle size (%)	43.25	31.27	25.48	Sandy loam

The trial field soil was found to be sandy loam (*Table 1*) with a pH of 8.1 ± 0.06 . The physicochemical properties of the control soil of the trial field, sewage, and water are given in *Table 2*. After the trial, a reduction in pH and an increase in EC were observed. Reduced pH was mainly because of neutralization and faster rate of nitrification, releasing free hydrogen ions in the soil and lowering soil pH (Hayes et al., 1990). At sites where wastewater is used for irrigation, an excessive buildup of total dissolved solids in the soil as a result of ongoing wastewater usage may increase soil conductivity. Additionally, Mohammad and Mazahreh (2003) found that soil watered with waste water had greater conductivity than soil irrigated with freshwater.

Table 2. *Physicochemical characteristics of experimental soil, sewage, and freshwater*

Sr. No	Properties	Soil ($\mu\text{g g}^{-1}$)		Water (mg/L)	
		Before Trial	After Trail	Sewage	Fresh
1	EC (dSm^{-1})	0.27±0.06	1.39±0.03	2.7±0.09	0.43±0.03
2	pH	8.1±0.01	7.7±0.03	7.9±0.02	7.2 ± 0.02
3	Organic matter (%)	16.51 ± 1.07	24.6±2.05	63.8±3.2	3.4±0.6
4	Total N (%)	1.61±2.5	2.33±1.3	31.12±2.03	3.5±1.91
5	Phosphorous (%)	0.74±0.09	11.86±1.5	15.1±0.12	0.08 ±0.03
6	Calcium (Ca)	935± 4.17	1192± 8.31	113.74± 1.3	102.11 ± 6.71
7	Sodium (Na)	3.63± 0.01	6.21± 0.12	8.66± 0.21	35.91 ± 7.02
8	Potassium (K)	143.04± 2.13	173.81± 3.44	11.39± 0.11	7.89 ± 4.89
9	Zinc (Zn)	41.32±0.31	176.4±3.22	291.32±6.41	1.52 ± 1.86
10	Copper (Cu)	8.71±0.09	22.37±0.61	38.73±2.32	1.34 ± 3.12
11	Iron (Fe)	85.10±1.72	183.47±1.71	317.54±9.84	0.37 ± 2.98
12	Manganese (Mn)	52.47±1.83	154.71±7.13	233.63±5.47	0.69 ± 3.01
13	Magnesium (Mg)	33.52±5.81	113.1±9.57	52.31±7.21	14.21 ± 1.51
14	Cobalt (Co)	3.21±0.03	9.34±0.12	23.17±1.83	1.31 ± 1.16

Proximate analyses

Moisture (%)

Data presented in *Fig. 1* revealed that the lowest moisture contents (86.82%) were recorded in cabbage leaves at C where trial plots were irrigated with 100% sewage water. The contents were found to increase with decreasing sewage water ratio and the highest increase (89.88%) was recorded at T3 sewage water diluted with 75% FW (freshwater) in the trial plot. The difference in moisture means was found statistically significant ($p < 0.05$).

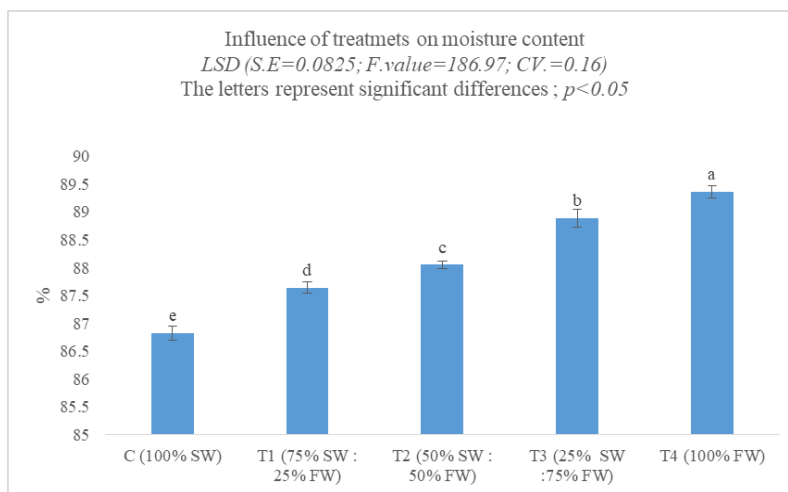


Figure 1. Influence of treatments on moisture content

The results are in agreement with Rehman et al. (2013) who reported moisture content of vegetables grown from sewage and fresh water in a range between 83.6-95.1% and 85.6-95.1%, respectively (*Fig. 1*). The present result for moisture was found to be marginally lower as compared to other studies of typical vegetables in the region. (Bux Baloch et al., 2015) estimated (%) the moisture in cauliflower as 90.62%, while (Roe et al., 2013) found moisture as 96% and 93.5% in lettuce and spinach respectively. Rumeza et al. (2006) concluded (%) moisture in their research and found 92.1%, 91.9%, and 91.0% in green cabbage, cauliflower, and lettuce respectively. The outcomes of the result are found to be nearly equal to 88.4% in green cabbage, and 88.2% in broccoli (Roe et al., 2013). The moisture difference may be due to irrigation with varying matrix proportions, sewage properties, and plant nutrient uptake. It is revealed from the literature that irrigation with fresh water leads to more moisture content in vegetables as compared to sewage water (Perveen et al., 2012; Yu et al., 2022). The observed value suggests that cabbage may have a short shelf life as bacteria that cause spoiling prefer foods with high moisture content, high moisture content is also reflective of low total solids in the cabbage.

Ash contents (%)

The ash content is an indication of mineral/inorganic parts of the subject of analysis. It is revealed in *Fig. 2* that ash (%) in cabbage leaves ranged between 0.63 and 3.35%. It was evident that the application of concentrated (100%) sewage irrigation water if

applied in cabbage fields enhanced ash contents which were reduced by each dilution of freshwater with sewage water viz. 75.35, 40.22, 30.59 and 17.84 % respectively at 25, 50, 75 and 100 %. Statistically, the influence of treatment on ash contents was found significantly different ($p < 0.05$).

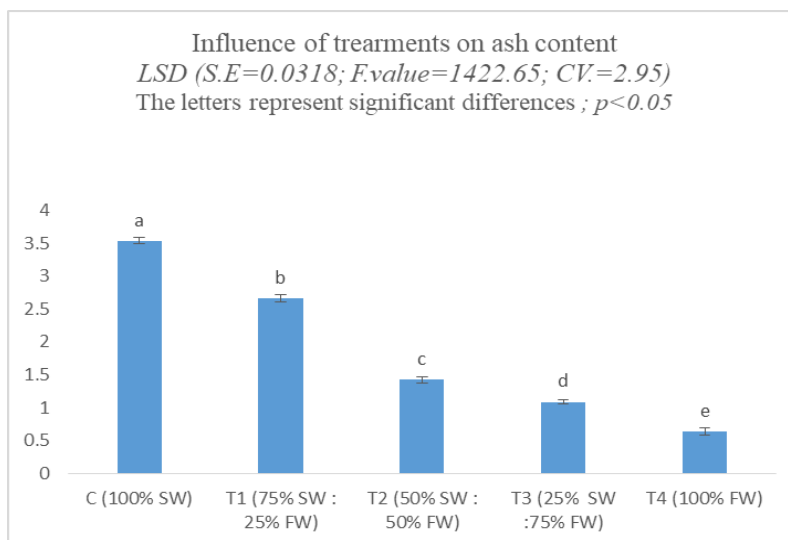


Figure 2. Influence of treatments on ash content

The value in this study (Fig. 2) is found higher in wastewater irrigated cauliflower 1.25% and also for freshwater irrigated cauliflower 1.65% than the reported value by Rehman et al. (2013). Total ash content in the present study was found higher in (%) compared to that of cauliflower 0.7, broccoli 0.6, carrot 0.6, and lettuce 0.4, but lower compared to 2.0 in spinach (Roe et al., 2013). Variations with reported literature may arise as a result of the experimental area's environmental conditions, different varieties, sewage, and freshwater composition. Micronutrients such as Fe, Mn, Zn, Cu, and Co are more soluble in acidic conditions and become more available to plants, sometimes at toxic levels. As the volume ratio of sewage (pH 6.0) increased from T4 (100% FW) to Control (100% SW), plant uptake of minerals also increased, leading to high ash content (Ron, 2013).

Fiber content (%)

Fiber contents of cabbage depicted in Fig. 3 disclosed that contents ranged between 3.04 and 3.59%. It was evident from the bars in the figure that in both the trial plots of C and T4 where concentrated (100%) SW and FW were applied, the contents were recorded 3.45% and 3.59% respectively. Reduction in contents was recorded at 50 and 75% dilution of fresh water with the sewage water. The effect of treatments on fiber content was found to be statistically non-significant ($p > 0.05$).

Dietary fiber is an essential component of *Brassica Oleaceae* var. *capitata* L. and other *Brassica* family vegetables. Cabbage is believed to contain 40% of soluble and 60% of insoluble fiber. Besides the insoluble fiber that acts only as a bulking agent of the stool preventing colon cancer, soluble fiber such as beta-glucan and glucomannan digest to form short-chain fatty acids, which lowers serum cholesterol levels thus decreasing the risk of coronary heart disease (Bourdon et al., 2001; Rodríguez et al.,

2006). Soluble fiber boosts the synthesis of hormones including cholecystokinin, GLP-1, and peptide YY, which gives the feeling of fullness (Bourdon et al., 2001). Persons who eat more soluble fiber have a diversity of gut bacteria and have better health results (Cani et al., 2009). The crude fiber content in all irrigation matrices of cabbage (Fig. 3) was found in a range between 3.05 and 3.59%, which is lower than the 4.7%-11% and 4.7%-10% in different vegetables irrigated through sewage and freshwater respectively (Rehman et al., 2013). Results are also lower than the 4% found in broccoli and 3.9% found in carrots (Roe et al., 2013). The difference within treatment is very less indicating the same metabolism of the plant to convert glucose into polysaccharides.

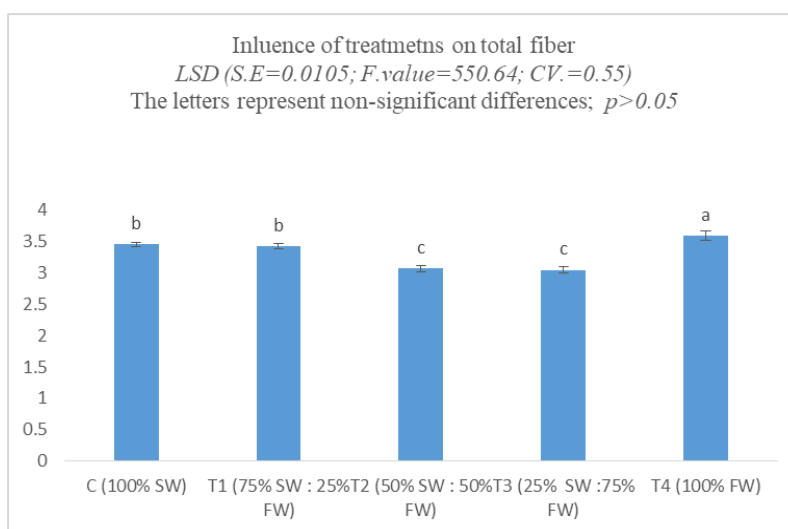


Figure 3. Influence of treatments on total fiber

Protein contents (%)

Data in Fig. 4 give out that protein contents reduced from 2.88% at C to 2.15%, 1.82%, 1.64%, and 1.87% at each of T1, T2, T3, and T4, respectively. This is evident from the depicted data that undiluted and 100% SW if applied as irrigated in trial plots, enhanced the protein content of cabbage. Dilution of SW with FW exerted a slight reduction in the contents. The effect of treatments on protein content was found to be statistically non-significant ($p > 0.05$).

Nitrogen is a building block of protein and it is inductive with the literature that sewage water contains more nitrogen as compared to freshwater. The results are comparable to 2.4% recorded for the same vegetable grown in freshwater (Roe et al., 2013). The results are found higher in cauliflower 26.2% for wastewater irrigation and 28.4% for freshwater irrigation studied by Rehman et al. (2013). According to literature research, Stress causes a decrease in soluble protein concentration in plants but an increase in soluble sugar content (Hsu and Kao, 2003; Guo et al., 2007).

Fat content (%)

Response of fat content in cabbage leaves upon treatments is shown in (Fig. 5) imparted that concentrated SW (100%) irrigation in trial plots, increased fat contents (2.28%) followed by 1.28% upon dilution with 75% FW (T3). At a dilution of

freshwater by 25, 50, and 100%, a higher reduction in contents on 50% and 75% was recorded. The effect of treatments on fat content was found to be statistically non-significant ($p>0.05$).

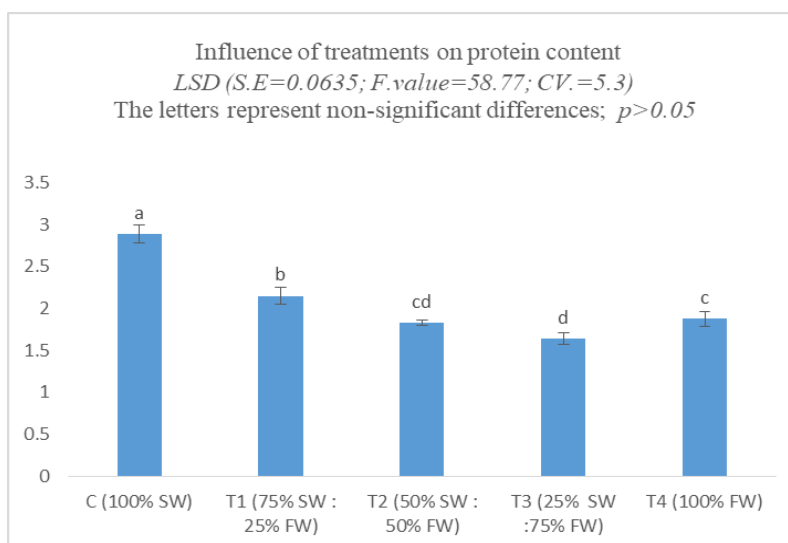


Figure 4. Influence of treatments on protein content

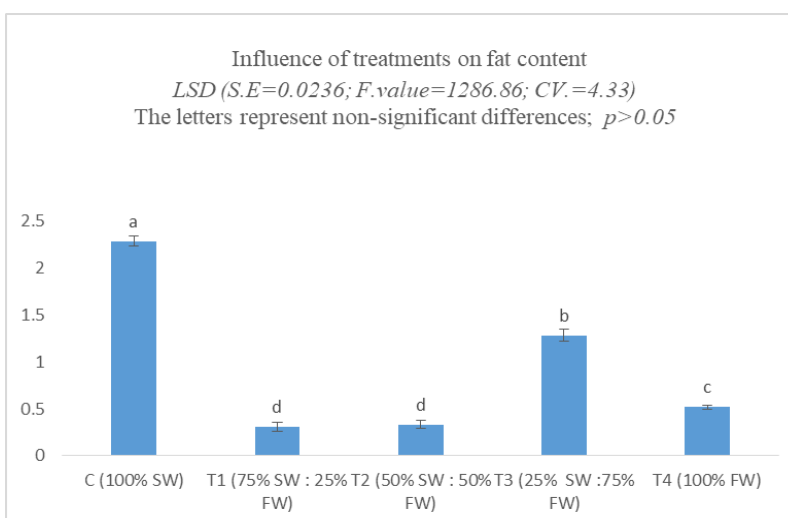


Figure 5. Influence of treatments on fat content

Dietary fats and oils are the primary sources of energy; however, a high-fat diet has been linked to obesity as well as some cardiovascular diseases such as atherosclerosis, cancer, and aging (Tayyeb, 2017). Lipids have a glycerol backbone, with two fatty acid tails and a phosphate group (PO_4). The variation of results is an indication of poor phosphorous availability and mobility. The result is found lower for T4 (100% FW) as compared with 21.8-37.5% in vegetables irrigated through sewage (Rehman et al., 2013).

Carbohydrates (mg/100 g)

In Fig. 6, carbohydrate contents within cabbage leaves showed an increasing trend upon each dilution of freshwater with concentrated (100%) sewage water. The contents ranged between 1.03 at C (100% SW) and 5.29 at T2 (SW and FW with 50:50%). With a slight decrease at 75% freshwater dilution, the contents were found higher at all treatments upon C. The trend revealed that freshwater addition enhances (-CHO) and other constituents, leading to enhanced metabolism within plants that result in higher production of carbohydrates. The impact of treatment on carbohydrate contents was found significantly different ($p < 0.05$).

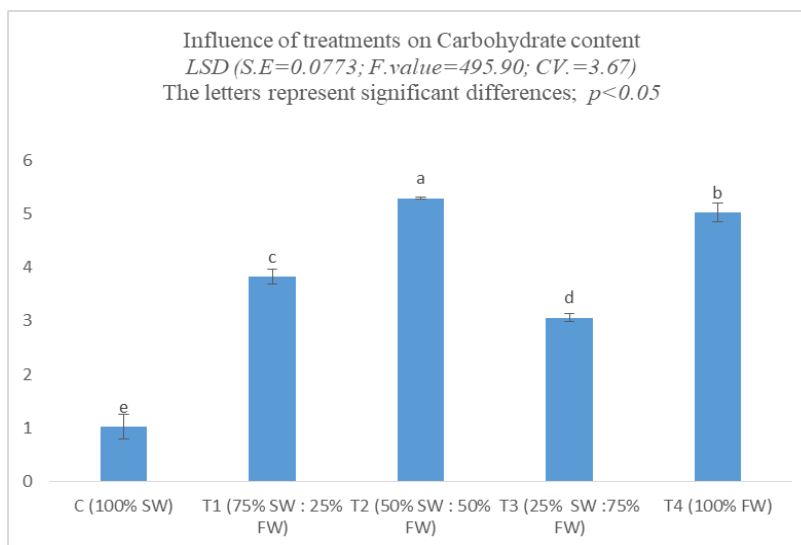
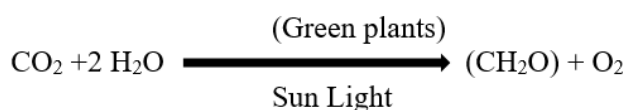


Figure 6. Influence of treatments on the carbohydrate content

The least carbohydrate was found in the control (100% SW). It is said that in the presence of toxic metal concentrations, vascular plants have been observed to produce lower chlorophyll concentrations, which are responsible for carbohydrate formation (Monni et al., 2001; Pätsikkä et al., 2002).



The variation in carbohydrate content is due to the different content levels of Cu, Fe, Mn, and Mg content which is mainly responsible for photosynthesis, oxygen transport, dissociation of water molecules into H^+ and OH^- , and sunlight absorption respectively (Weier et al., 1970). Light Reaction (Oxidation of water) and Dark Reaction (Calvin Cycle) work together to produce simple carbohydrates i.e. glucose molecules (Johnson, 2016).

Energy level (Kcal/100 g)

Response of treatments on energy levels in cabbage leaves is given in Fig. 7. Results showed that energy levels ranged between 26.69 and 36.16 Kcal/100 g at T1 (75% SW:

25% FW) and C (100% SW), respectively. The impact of treatments on energy was found to be non-significant ($p>0.05$).

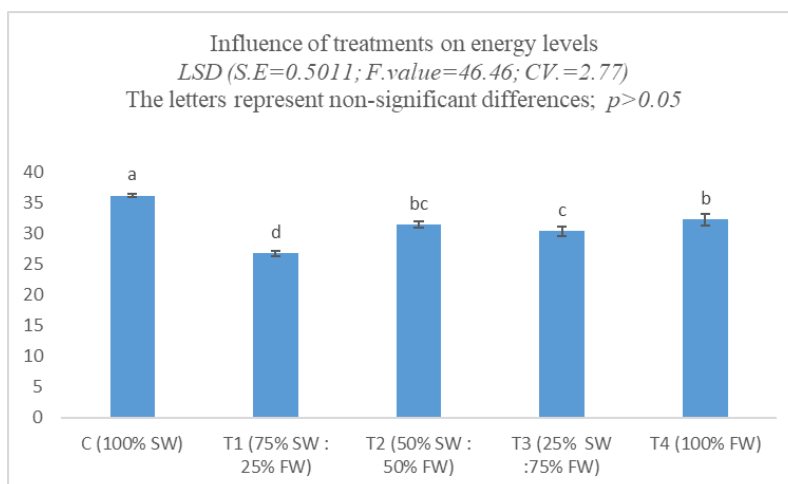


Figure 7. Influence of treatments on energy levels

The energy results show that, oddly, C (100% SW) irrigated cabbage produces more energy (36.35 Kcal/100 g) than the T4 (100% FW) 33.19 Kcal/100 g. As a result, their customers often believe it is a fallacy that sewage water irrigated vegetables will affect their health. The results obtained by using the Atwater factor are found to be very lower than 248.8-307.1 Kcal/100 g in some Nigerian native vegetables (Isong et al., 1999). Energy pattern for all irrigation matrices were found to be, Control > T4 > T2 > T3 > T1.

Food energy and its co-relation with proximate analyses

The correlation matrix demonstrated the relationships between the proximate values of moisture, crude protein, crude fat, crude fiber, carbohydrate, and food energy for cabbage (Table 3). Fat and proteins are the main sources of energy. A significant positive correlation between energy and fat ($r=0.73$) as well as protein ($r=0.57$) was developed at 0.01 and 0.05 levels. Highly strong negative relationship were established between carbohydrate and protein ($r=-0.74$), fat ($r=-0.93$) and ash ($r=-0.75$). This indicates that cabbage with high carbohydrates will tend to have less protein, fat and inorganic minerals. A highly significant negative correlation was established between moisture and crude protein ($r=-0.85$), ash ($r=-0.77$), and crude fiber ($r=-0.55$) at 0.01 and 0.05 levels.

Nutritional mineral analyses of *Brassica oleracea* L.

Calcium (mg/100 g)

The data in Table 4 showed higher accumulation of Ca^{++} in cabbage leaves upon C (100% SW) followed by T1 (75% SW), T2 (50% SW), T3 (25% SW) and T4 (0% SW). Increasing FW with SW before irrigation in the field exerted a negative impact and the contents were reduced at each dilution. Further, statistical analysis of data revealed that differences in calcium content of cabbage leaves were found non-significant ($p>0.05$).

Table 3. Pearson's correlation coefficients among proximate composition values in Cabbage

	Moisture (%)	Crude protein (%)	Crude fat (%)	Crude fiber (%)	Ash (%)	Carbohydrate (%)	Energy (Kcal/100g)
Moisture (%)	1.00	-0.85**	-0.23	-0.55*	-0.77**	0.31	-0.38
Crude protein (%)		1.00	0.67**	0.49	0.88**	-0.74**	0.57*
Crude fat (%)			1.00	0.07	0.56*	-0.93**	0.73**
Crude fiber (%)				1.00	0.25	-0.13	0.17
Ash (%)					1.00	-0.75**	0.23
Carbohydrate (%)						1.00	-0.46
Energy (Kcal/100g)							1.00

* and **, Correlation is significant at the 0.05 and 0.01 levels (2-tailed), respectively

Magnesium (mg/100 g)

Results given in *Table 4* imparted that (100% SW) application for irrigation purposes in fields increases Mg contents of cabbage leaves whereas if applied after dilution with FW the contents are found reduced. The higher accumulation was recorded (20.99 mg/100 g) at C (100% SW) followed by 17.26, 14.11, 13.75, and 13.31 mg/100 g at T1, T2, T3, and T4, respectively. The statistical analysis of means showed that the difference in accumulated Mg content at each treatment was significant ($p < 0.05$).

Sodium (mg/100 g)

In *Table 4*, the Na^+ accumulation trend in cabbage is depicted. The data revealed that the contents ranged between 11.77 and 17.92 mg/100 g. It is evident from data that increasing FW dilution in each treatment with concentrated (100%) SW before application in cabbage fields, enhances the content in cabbage leaves whereas a slight decrease was observed at T4 (100% FW). Analysis of variance in means among treatments, the Na^+ contents were found significant ($p < 0.05$).

Potassium (mg/100 g)

Table 4 showed that a slight increase in K^+ accumulation in cabbage leaves at T1 and T2 upon C was recorded but at T3 and T4 the magnitude of contents was higher. The contents ranged between 40.61 and 104.31 mg/100 g. The statistical analysis of means exerted a significant impact ($p < 0.05$) on the translocation of K^+ from the soil labile pool.

Table 4. Variation in mineral content of irrigation matrices in cabbage mg/100g

Parameters	Control (100% SW)	T1 (75% SW+25% FW)	T2 (50% SW+50% FW)	T3 (25% SW+75% FW)	T4 (0%SW+ 100% FW)	*DRI/AI (mg/day)	DIM (mg/person/day)	*UL
Ca	75.57 ± 0.75d	65.58 ± 1.20c	63.54 ± 2.01c	51.63 ± 0.94b	32.66 ± 0.84a	1000(1000)	0.118(0.1142)	2500
Mg	20.99 ± 0.02e	17.26 ± 0.07d	14.11 ± 0.09c	13.75 ± 0.05b	13.31 ± 0.17a	420(320)	0.033(0.031)	350
Na	11.77 ± 0.58a	12.77 ± 0.34b	16.19 ± 0.19d	17.92 ± 0.11e	13.73 ± 0.38c	1500(1500)	0.028(0.027)	ND
K	45.61 ± 1.25b	49.42 ± 1.16c	40.61 ± 1.40a	97.48 ± 0.82d	104.31 ± 2.07e	3400(2600)	0.164(0.158)	ND
Vitamin C	10.67 ± 0.60a	12.92 ± 0.28b	21.70 ± 0.65c	26.06 ± 0.47d	32.21 ± 0.51e	90(75)	0.05(0.04)	2000
Zn	13.30 ± 0.90e	10.54 ± 0.46d	5.94 ± 0.86c	4.46 ± 0.63b	2.60 ± 0.73a	11(8)	0.021(0.02)	40
Cu	3.44 ± 0.06e	2.95 ± 0.08d	2.15 ± 0.05b	2.37 ± 0.10c	1.56 ± 0.09a	0.9(0.9)	0.0054(0.0052)	10000
Fe	12.37 ± 0.08e	8.33 ± 0.05d	4.23 ± 0.08c	3.57 ± 0.06b	3.14 ± 0.06a	8(18)	0.019(0.018)	45
Mn	5.42 ± 0.05d	4.51 ± 0.03c	2.43 ± 0.08b	2.38 ± 0.07b	1.83 ± 0.04a	2.3(1.8)	0.0085(0.0082)	11
Co	1.06 ± 0.06d	0.72 ± 0.05c	0.44 ± 0.05b	0.21 ± 0.02a	0.20 ± 0.05a	-	0.0017(0.0016)	-

Different letters within a row are statistically different from each other (P<0.05). *(The National Academy of Sciences 2005); DRI=Dietary Reference Intakes for male and female (parenthesis values) age 31-50; DIM=Daily Intake of Metal; AI= Adequate intake (written in bold); ND not determinable owing to a lack of specific toxicological effect

Vitamin C (mg/100 g)

Data presented in *Table 4*, disclosed that contents of vitamin C in cabbage leaves increased at all treatments T1, T2, T3, and T4 upon C. The Trend was evident that if plants are irrigated after dilution of concentrated SW with FW at 25%, 50%, 75% even 100% respectively, cabbage leaves may be found enriched with vitamin C contents. Statistical analysis showed a significant ($p < 0.05$) difference in treatments upon ascorbic acid.

Ascorbic acid is an antioxidant and plays a critical function in preventing physiological stress (Guo et al., 2005). The concentration of Vitamin C was found highest in C (100% SW), it is documented that ascorbate not only takes part in the proper functioning of chlorophyll but also has a key role in the direct scavenging of ROS and the removal of H_2O_2 through the water-water cycle (Asada, 1999; Awad et al., 2015), keeping the plant healthy in stress condition. The lowest concentration of vitamin C at T4 (100% FW) is inductive in a less stressful environment.

Zinc (mg/100 g)

Response of treatments on Zn uptake within cabbage leaves is depicted in *Table 4*. The data bars of treatments showed that higher contents (13.30 mg Zn/100 of leaves) were found at C (100% SW application) followed by 10.54, 5.93, 4.46, and 2.61 mg/100 g at 75%, 50%, 25% and 100% addition of FW, respectively. The statistical analysis showed that the difference in means was significant ($p < 0.05$). The root zone mechanism is also responsible for their varying concentrations of accumulation due to plant leaf deposition and retention efficiency (Zhuang et al., 2009; Hongjian et al., 2020).

Copper (mg/100 g)

Copper (Cu^{++}) contents ranged between 1.56 and 3.44 mg/100 g cabbage leaves (*Table 4*). The contents were found to decrease from 2.95, 2.36, 2.15, and 1.56 at T1, T2, T3, and T4 upon C with increasing FW dilution with SW ratios. The impact of treatment on copper contents was found significantly different ($p < 0.05$). The trend depicted in the figure revealed that concentrated sewage discharge contained higher Cu^{++} contents (*Table 2*) and uptake efficiency of cabbage root, resultant accumulation in leaves as well enhanced.

Iron (mg/100 g)

Results presented in *Table 4* revealed that irrespective of differential contents, Fe^{++} accumulation in cabbage leaves ranged between 3.13 and 12.36 mg/100 g. Considerable decrease in contents was found with increasing FW dilution ratio viz. 25, 50, 75, and 100% at T1, T2 T3, and T4, respectively. Statistically, the difference was found significant ($p < 0.05$).

Manganese (mg/100 g)

Results in *Table 4* show that higher Mn accumulation in cabbage leaves was recorded at C (100% SW). Each dilution of concentrated (100%) SW when applied in trial plots, the decrease in contents was observed in the order of 4.51, 2.43, 2.38, and 1.83 mg Mn^{++} /100 g of cabbage leaves at T1, T2, T3, and T4, respectively. The means of all treatments were found non-significant ($p > 0.05$).

Cobalt (mg/100 g)

Data regarding the accumulation of Co contents in cabbage leaves is given in *Table 4*. Co contents (0.19 mg/100 g) was recorded at T4 (100% FW) followed by T3 (0.21 mg/100 g), T2 (0.43 mg/100 g) and T1 (0.72 mg/100 g) upon C (100% SW). From the trend of decreasing contents, it was evident that each dilution ratio of FW with SW applied in the trial field resulted in a decrease in Co contents within cabbage leaves. Statistically, the effect of irrigation on Co content was found non-significant ($p > 0.05$). The lowest Co metal concentration in cabbage could be attributable to their concentration in soil, charge, size, attraction for other molecules, synergism, and antagonism (Zhuang et al., 2009).

Metal accumulation and their mobility

The present study results are in coherence with Farooq et al. (2008) where the addition of sewage into freshwater tends to accumulate more metals in soil and growing vegetables. The concentration of bidentate metals was found usually be higher in soil because metals having higher oxidation states are more likely to bond with soil such as Zn, Cu, and Mn (Loeppert, 2008; Sahay et al., 2019). The acidic sewage solubilizes micronutrient Fe, Mn, Zn, Cu, and Co more effectively which hereby move to plant, sometimes at toxic levels. The ability of soil to form iron complexes with aluminosilicate lattice is also the reason for increasing the iron concentration in soil (Moralejo and Acebal, 2014). Besides this, soil enzyme activity and soil ecological environment also take an important part in plant growth and its functioning. Because Fe and Cu have an antagonistic relationship (Feldman et al., 2008), an increased Fe level in the soil has resulted in less Cu accumulation. The same relationship is established in cabbage where a low concentration of cobalt has been observed.

Metal absorption by the plant is largely determined by the chemical form and concentration of the metal (Bordin et al., 1992). Ionic reactions/availability of nutrients to plants are mainly affected by electrostatic interactions in the solutions phase. Due to the polarity of water, both anions and cations in soil solution surround the water molecules and form solvation spheres which stabilizes their charges (Li et al., 2021) thereby decreasing their (cations/anions) mobility to the plant system (He et al., 2015). The overall concentration for all metals in T4 (100% FW) was found low when compared with C (100% SW) (*Table 4*). According to Verma and Dubey (2001), under metal toxicity, a larger quantity of produced soluble sugar may provide an adaptation mechanism for maintaining a favorable osmotic potential. The current and prior investigations (Rehman et al., 2018; Khan et al., 2019; Sabeen et al., 2019; Ugulu et al., 2019; Mir et al., 2020; Ullah et al., 2022) showed that food crops cultivated in polluted soil, irrigated with sewage/waste may pose a health risk to the locals.

Correlation of nutritional mineral contents

The correlation matrix in *Table 5* depicted mineral interactions in cabbage. Results revealed that Ca had a very significant positive correlation with Zn ($r = 0.88$) and Fe ($r = 0.80$) at 0.01 level. The strongest significant positive correlation was developed between Fe and magnesium ($r = 0.99$) while the strongest significant negative correlation was found between vitamin C and Zn ($r = -0.97$). A non-significant, weakest positive correlation was established between sodium and potassium ($r = 0.38$) and a

non-significant weakest negative correlation was developed between sodium and calcium ($r = -0.32$).

Table 5. Pearson's correlation coefficients among metals in cabbage

	Ca	Vit-C	Na	K	Zn	Cu	Fe	Mn	Mg	Co
Ca	1.00	-0.94**	-0.32	-0.89**	0.88**	0.89**	0.80**	0.82**	0.79**	0.85**
Vit-C		1.00	0.57*	0.83**	-0.97**	-0.95**	-0.91**	-0.95**	-0.90**	-0.93**
Na			1.00	0.38	-0.66**	-0.49	-0.75**	-0.71**	-0.74**	-0.73**
K				1.00	-0.74**	-0.65**	-0.64*	-0.66**	-0.62*	-0.75**
Zn					1.00	0.95**	0.97**	0.98**	0.96**	0.98**
Co						1.00	0.92**	0.96**	0.92**	0.90**
Fe							1.00	0.98**	0.99**	0.98**
Mn								1.00	0.97**	0.96**
Mg									1.00	0.97**
Co										1.00

* and **, Correlation is significant at the 0.05 and 0.01 levels (2-tailed), respectively

Conclusion

Vegetables are a very common food in southern Asia and people consume them on daily basis. The result of the study suggested that the concentration of metals is within the Recommended Dietary Allowance (mg metal/day/100 g meal). But care should be taken with meal size/portion per day because a bigger portion meal can lead to metal toxicity. *Brassica oleracea* var. *capitata* L. is a good energy food source and, as such, may be beneficial in a weight-loss program.

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APPENDIX

Table 1A. Effect of different treatment of chemical properties of cabbage

Treatment	Moisture (%)	Protein (%)	Fat (%)	Fiber (%)	Ash (%)	Carbohydrate (%)	Energy Kcal/100g	Calcium (mg/100g)
T-1	86.82E	2.88 A	2.28 A	3.45 B	3.53 A	1.03 E	36.16 A	75.57 A
T-2	87.64 D	2.15 B	0.31 D	3.42 B	2.66 B	3.82 C	26.69 D	65.58 B
T-3	88.05 C	1.82 CD	0.33 D	3.07 C	1.42 C	5.29 A	31.45 BC	63.53 B
T-4	88.35 B	1.64 D	1.28 B	3.04 C	1.08 D	3.06 D	30.32 C	51.63 C
T-5	89.88 A	1.87 C	0.51 C	3.59 A	0.63 E	5.02 B	32.25 B	32.66 D
Statistical analysis								
SE	0.0825	0.0635	0.0236	0.0105	0.0318	0.0773	0.5011	0.7819
SS	15.2666	2.84777	8.57807	0.72317	17.2330	35.5431	140.002	3237.91
F	186.97	58.77	1282.86	550.64	1422.65	495.90	46.46	441.36
CV	0.16	5.30	4.33	0.55	2.95	3.67	2.77	2.34
Means	significantly different	significantly not different	significantly not different	significantly not different	significantly different	significantly different	significantly not different	significantly not different

Table 1B. Effect of different treatment of chemical properties of cabbage

Trtmt	Vitamin (mg/100g)	Sodium (mg/100g)	Potassium (mg/100g)	Zinc (mg/100g)	Copper (mg/100g)	Iron (mg/100g)	Manganese (mg/100g)	Magnesium (mg/100g)	Cobalt (mg/100g)
T-1	10.67 E	11.77 E	45.61 D	13.30 A	3.44 A	12.36 A	5.42 A	20.99 A	1.06 A
T-2	12.92 D	12.77 D	49.42 C	10.54 B	2.95 B	8.33 B	4.51 B	17.26 B	0.72 B
T-3	21.70 C	16.19 B	40.61 E	5.94 C	2.15 D	4.23 C	2.43 C	14.11 C	0.43 C
T-4	26.06 B	17.92 A	97.48 B	4.45 D	2.36 C	3.57 D	2.38 C	13.75 D	0.21 D
T-5	32.21 A	13.73 C	104.31 A	2.60 E	1.56 E	3.13 E	1.83 D	13.31 E	0.19 D
Statistical analysis									
SE	0.3286	0.2098	0.8473	0.1153	0.0487	0.0310	0.0198	0.0586	0.0135
SS	969.760	76.8190	11349.1	235.589	6.29438	187.981	29.1776	126.826	1.63020
F	748.49	145.42	1317.27	1476.79	221.48	16278.4	6181.74	3082.11	740.90
CV (%)	2.75	2.51	2.17	2.71	3.38	0.85	1.04	0.64	4.47
Means	significantly different	significantly different	significantly different	significantly different	significantly different	significantly different	significantly not different	significantly different	significantly not different

ELECTRONIC APPENDIX

This manuscript has an electronic appendix.