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Influence of Treated Wastewater Irrigation on Soil Nutritional-Chemical Attributes Using Soil Quality Index

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Abstract: Dwindling water resources have drawn global attention to the reuse of treated wastewater (TWW) for irrigation. However, the impact of continuous TWW applications on soil quality and the proper quantification and monitoring frameworks have not been well-understood. This study aims to provides an insight into the impact of flood irrigation of urban TWW on soil nutritional-chemical attributes and the potential application of multiple soil quality indices for a corn cropping system. To achieve that goal, we pursued the Total Data Set (TDS) and Minimum Data Set (MDS) approaches, as well as the Integrated Quality Index (IQI) and Nemoro Quality Index (NQI) models. A total of 17 soil nutritional-chemical indicators (0–50 cm depths) were determined for the soils irrigated with TWW (five sites) and well water (one site as control) in West Azerbaijan province in northwestern Iran. Results revealed a significant difference in the majority of soil nutritional-chemical attributes, IQI-TDS, NQI-TDS, IQI-MDS, NQI-MDS, and corn yield between the TWW-irrigated and well-irrigated soils. Irrigation with TWW resulted in a significant increase in the amount of organic matter and cation exchange capacity by 9–17% and 17–26%, respectively, macronutrients (N, P, K, Ca, and Mg) by 22–164%, and the majority of trace metals (Fe, Mn, Zn, and Cu) by 17–175%, suggesting an improvement in soil nutrients and an increase in productivity. Comparing to the soil in control sites, the TWW irrigation caused a notable increase in the values of IQI-TDS, NQI-TDS, IQI-MDS, and NQI-MDS models ranging 14.6–29.5%, 19.1–25.5%, 21.7–33.3%, and 18.4–23.7%, respectively. This implies that soil quality was ameliorated to a significant extent with TWW irrigation. These improvements resulted in a remarkable increase in corn yield ranging from 12.5% to 28.1%. The regression equations revealed that up to 78%, 47%, 72%, and 36% of the variance in the IQI-TDS, NQI-TDS, IQI-MDS, and NQI-MDS models, respectively, could be captured by corn yield. The results of the regression and correlation analyses showed that the IQI-MDS model was more accurate than the other models in assessing soil quality and predicting crop yield. These findings may be an effective and practical tool for policy making, implementation, and management of soil irrigated with TWW.

Keywords: wastewater irrigation; soil quality index; corn yield; well water; macronutrient; micronutrient

1. Introduction

Historically, limited water resources have presented significant challenges in sustainable food, feed, and fiber production across many arid and semi-arid regions of the world. Over the past few decades, water scarcity has been further exacerbated due to increasing population growth and the need for more agricultural production, climate change, and increased exploitation of groundwater by the agricultural, industrial, and service sectors.

The agricultural sector is the largest consumer of fresh water worldwide, accounting for the consumption of more than 70% of the freshwater resources in developed countries and 90% in developing countries [1]. This has made the reuse of unconventional water resources, e.g., salt water, brackish and grayish water, and municipal and industrial wastewater, inevitable for agricultural production. As of 2015, more than 8000 wastewater treatment plans have been registered worldwide, most being in Japan, the United States, Australia, and the European Union, respectively. Not all of the treated wastewater has been used for agriculture [2], according to Saliba et al., [3], more than 90% of wastewater used for cropland irrigation is untreated, especially in developing countries.

Sustainable use of wastewater in the agricultural sector requires proper utilization management and periodic monitoring of wastewater-irrigated soils to accurately address the trade-offs involved in wastewater irrigation [4,5]. Varying with the source of reuse water, benefits of can include increased soil macronutrients (N, P, and K) and micronutrients (Fe, Mn, Zn, and Cu) that can enhance soil fertility and crop productivity [6]. Previous studies [7] have shown that wastewater irrigation may supply 50–100% of the fertilizer requirements of certain crops (e.g., maize and wheat), which has profound implications for production economy. Nonetheless, the accumulation of heavy metals and organic pollutants have been documented as the most critical consequences of untreated wastewater irrigation, which may pose a threat to the health of the soil-water-plant system [6,8].

Soil quality is defined as the soil's readiness to support crop growth without soil degradation or environmental damage [9,10]. A quality soil is expected to function to sustain productivity, support human and animal health, and habitation (USDA, NRCS). Unsupervised use of wastewater can increase microbes, pathogens, and hazardous chemicals beyond the tolerable limits of agroecosystems, thereby reducing soil, water, and environmental quality [11–13]. Likewise, high concentrations of wastewater-generated salts may deplete soil organic matter and lead soil system toward an irreversible state of degradation. The pollutants may accumulate in soil or discharge into water bodies and threaten the food and environmental safety [14,15]. A well-known example is the Mezquital Valley in Mexico, where the application of untreated wastewater along with the lack of regular monitoring has turned the opportunity of an alternative water resource into a progressing challenge of soil and groundwater pollution [16]. With imminent future need for reusable water resources, practical soil quality surveillances and monitoring techniques should be identified and implemented to diminish the risk of soil, water, and environmental deterioration [17–20]. Advancement of soil quality assessment frameworks offer a potential for a practical monitoring of the status of soils exposed to wastewater irrigation. A wide range of soil quality assessment systems are available, among which the Soil Quality Index (SQI) has received considerable attention due to its simplicity, versatility, and quantitative flexibility [10]. Mostly input-oriented soil properties and functions in SQI are easily measurable, sensitive to environmental and managerial changes, and quantifiable. The SQI assessment has been wildly adopted around the world as a result of increasing importance of sustainable natural and agricultural ecosystems and food security [21].

Several studies around the world have examined the influence of wastewater irrigation on soil chemical quality using a single soil indicator or a suite of limited soil quality indicators (e.g., pH, soil electrical conductivity, organic matter, cation exchange capacity) [5,22,23]. Although each soil quality metric represents a static state of a certain soil property at a given time, integrating multiple metrics into a comprehensive and individual index and applying repeatedly over a time period will provide better insight into the overall state of soil agronomic processes and environmental sustainability. Moreover, comprehensive indices offer an opportunity to observe the interactions among multiple soil attributes [24]. However, there is a lack of information about the potential use of soil quality indices as an inspection tool for wastewater-irrigated soil quality and environmental health monitoring. Improved understanding of the chemical dynamics of TWW-treated soils and proper surveillance methodologies will aid producers and policy makers in efficient wastewater management for greater productivity while maintaining environmental health.

The objectives of this study were to: (1) investigate the effects of long-term TWW irrigation on soil chemical and nutrient dynamics, (2) assess the effectiveness of soil fertility quality indices, including integrated quality index (IQI) and Nemoro quality index (NQI) for monitoring the fertility and pollution of TWW-treated soils, (3) establish a minimum soil quality assessment data set based on the soil fertility indicators, and (4) clarify the relationship between scoring values of SQI and corn yield productivity.

2. Materials and Methods

2.1. Site Description and Field Work

The study was conducted in the Urmia plain ($45°15'$–$45°00'$ E, $37°45'$–$37°30'$ N) located in West Azerbaijan province in northwestern Iran (Figure 1). The site has a semi-arid Mediterranean climate with cold winters and hot summers. The average annual precipitation and temperature of the region are 330 mm and 13 °C, respectively, resulting in a Xeric soil moisture regime and a Mesic temperature regime. The soil of the study region has been developed on young alluvium deposits and is classified as Inceptions. The experimental cropping system at all sites consisted of continuously grown corn (*Zea mays* L., cultivar single-cross 704), growing from June to September (a period of about 120 days). Irrigation water was supplied from the outflow channel of the Urmia wastewater treatment plant. The wastewater at this treatment plant is generated from municipal, household, and local industrial units, refined through oxidation pools to deposit the suspended solid particles before using for irrigation as TWW. Conventional tillage and fertilization practices were standardized over TWW-irrigated and the control fields. During the course of the experiment (about 15 years) 100–150 kg ha^{-1} year^{-1} of urea fertilizer (CH_4N_2O) and 50–100 kg ha^{-1} year^{-1} of superphosphate fertilizer ($Ca(H_2PO_4)_2 \cdot H_2O$) were applied homogenously on both treatments. The entire amount of superphosphate fertilizer was preplant applied and soil incorporated before sowing seeds. The urea fertilizer was split applied, with the first application consisting of two-thirds of the total rate preplant soil incorporated, and the remainder top dressed at the tillering and stem elongation stage. During the five stages of corn irrigation, including germination, tillering and stem elongation, heading, flowering, and seed filling, a total of 5000 to 6000 m^3 ha^{-1} year^{-1}. TWW was applied through flood irrigation techniques following conventional irrigation practices. Corn and irrigation management dates were acquired from producers and the Department of Agricultural Services in the study region.

Within a total of 12 ha farm area, TWW and WW treatments were applied on identical land surface areas by farmers. The WW-irrigation was applied on a single 2 ha farm as control, while the TWW-irrigated area comprised five approximately 2-ha field sites located around the larger WW-irrigated area. The experiment area had similar land use, slope aspect and parent material so that the results could be compared. Accordingly, differences in soil quality indicators between the TWW-irrigated and control sites were assumed to be attributed to the irrigation treatment effects. After dividing the TWW and WW farm area to six 2-ha units (five units under TWW irrigation and one unit under WW irrigation), soil samples were collected in 2018–2019 growing seasons. The geographic center of each unit was the first soil sampling point, with subsequent composite samples collected on diagonal transects at 10–15 m intervals. The composite soil samples (a total of 30 samples) were mixtures of five sub-samples collected (depth of 0–50 cm) and each composite soil sample was analyzed in triplicate as described below (Section 2.2).
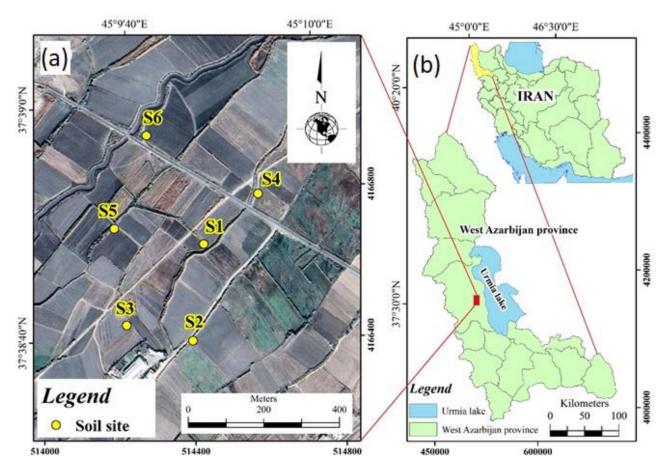
Figure 1. The close up of individual study sites (**a**) and location of the study region (**b**).

2.2. Laboratory Analysis

Soil samples were air-dried in the ambient laboratory conditions. Roots, stones, and other debris were removed from the soil, then passed through 2 mm sieves and stored until soil fertility indicators were determined. All soil samples were analyzed to determine soil fertility indicators using standard procedures (Table 1).

Table 1. Analytical laboratory methods used to identify soil variables.

Soil Variable	Protocol	Reference
pH	Saturated paste	Sparks et al. [25]
OM	Potassium dichromate oxidation	Sparks et al. [25]
CEC	sodium acetate extraction	Sparks et al. [25]
CCE	Acid neutralization	Nelson [26]
Total N	Kjeldahl approach	Bremner and Mulvaney [27]
Available P	Sodium bicarbonate	Olsen and Sommers [28]
Exchangeable Ca	Ammonium acetate extraction	Thomas [29]
Exchangeable Mg	Ammonium acetate extraction	Thomas [29]
Exchangeable K	Ammonium acetate extraction	Thomas [29]
Total Fe	Concentrated nitric acid	Soon and Abboud [30]
Total Mn	Concentrated nitric acid	Soon and Abboud [30]
Total Zn	Concentrated nitric acid	Soon and Abboud [30]
Total Cu	Concentrated nitric acid	Soon and Abboud [30]
Bioavailable Fe	Diethylene-triamine pentaacetic acid (DTPA) extraction	Lindsay and Novell's [31]
Bioavailable Mn	Diethylene-triamine pentaacetic acid (DTPA) extraction	Lindsay and Novell's [31]
Bioavailable Zn	Diethylene-triamine pentaacetic acid (DTPA) extraction	Lindsay and Novell's [31]
Bioavailable Cu	Diethylene-triamine pentaacetic acid (DTPA) extraction	Lindsay and Novell's [31]

OM, Organic matter; CEC, Cation exchangeable capacity; CCE, Calcium carbonate equivalent.

The chemical parameters of both treated wastewater and freshwater samples were measured by the methods described by Eaton et al. [32]. The concentration of metal was determined using a flame atomic absorption spectrophotometry (Shimadzu AA-6300) method.

2.3. Soil Quality Index (SQI)

To quantify the impact of TWW irrigation on soil quality, SQI was calculated using the Total Data Set (TDS) and Minimum Data Set (MDS) approaches. In the TDS approach, a total of 17 soil quality indicators including pH, organic matter (OM), CEC, total nitrogen (TN), C/N ratio, available P, exchangeable cations (Ca, Mg, and K), and total and bioavailable fraction of Fe, Mn, Zn, and Cu were measured. Principal component (PC) analysis was applied on TDS dataset to reduce multicollinearity among variables and to form the MDS dataset [33]. The PCs with eigenvalue ≥ 1 that explained at least 5% of the variance in the data were included [34–36]. For each PC, the indicators received the factor loading value within 10% of the highest weighing factor were retained for the MDS [9].

Within each PC, variables with greater coefficient values were selected and involved in MDS dataset [34]. When multiple indicators were found in a PC, Pearson's correlation analysis was used to determine redundant indicators [9]. The selected MDS indicators were transformed into dimensionless scores ranging between 0 and 1 using a scoring function method. Three types of standard scoring functions (SSF) were defined as: "more is better", "less is better", and "optimum is the best" based on the overall contribution of each variable to soil scoring functions:

The SSF equations are calculated by Equation (1) (more is better) and Equation (2) (less is better) [37].

$$SL_m = \frac{Xi - Mi}{Ma - Mi} \tag{1}$$

$$SL_l = \frac{Ma - Xi}{Ma - Mi} \tag{2}$$

where SL_m is a "more is better" function, SL_l is a "less is better" function, Xi is the indicator value, Mi is the minimum value of the soil indicator, and Ma is the maximum value of the soil indicator.

After calculating scores, Integrated Quality Index (IQI) [38] and Nemoro Quality Index (NQI) [39,40] were calculated for both TDS and MDS datasets using Equations (3) and (5), respectively:

$$IQI = \sum_{i=1}^{n} W_i \times S_i \tag{3}$$

in which S_i is the attribute score (linear or nonlinear), n is the number of soil attributes in the TDS and MDS approaches, and W_i is the weighting value of soil attribute. For both TDS and MDS dataset, the weight of the indicators was estimated by their communality via a PCA method [9,39]. The equation used to estimate the weight is shown in Equation (4):

$$W_i = \frac{C_i}{\sum_i^n C_i} \tag{4}$$

where W_i is the weighting of soil variable, C_i is the communality value of soil variable ranged from 0 to 1, and n is the number of variables.

$$\text{NQI} = \sqrt{\frac{P^2ave + P^2min}{2}} \times \frac{n-1}{n} \tag{5}$$

in which P^2ave and P^2min are the average and minimum scores of the selected attributes in each sample site, respectively.

2.4. Data Analysis

Statistical analyses were performed in SPSS 19 software package (SPSS INC., Chicago, IL, USA). Using an independent t-test, the means of different soil variables and different SQI scenarios were separated and compared pairwise between the TWW-treated soil and the control soil at 95% confidence interval. To select the most appropriate soil indicators for evaluating SQI, the principal component analysis (PCA) method was used. The PCA is the most common the multivariate technique which simplifies the data, eliminates multi-collinearity, and ranks the variables in decreasing order of importance [40,41]. Multiple regression models were employed to establish the relationship between different SQI models and corn yield using MS Excel software packages.

3. Results

3.1. Wastewater Characteristics

The results of the chemical analysis for TWW and well water (WW)are reported in Table 2. Overall, the concentration of chemicals was significantly ($p < 0.05$) higher for TWW than those of the WW control treatment. The mean value of EC was 1.9 to 2.3 times higher than its maximum allowable range for the TWW [42], indicating the increased salt concentration and possible increase of osmotic pressure which may hinder the proper water utilization by plants. Likewise, N, P, and Ca concentrations were above their maximum tolerable limits [42,43]. The trace metals concentration of TWW, except for Zn, were similarly above their maximum admissible range [42,43] for the irrigation practices. This may be associated with the discharge of trace metals from industrial units in nearby urban and suburban areas (e.g., batteries, painting centers, metal plating, and automotive services).

Table 2. The chemical composition of the treated wastewater (TWW) and well water (WW; control) in comparison with the allowable level of international standards.

Characterize	TWW		WW		WHO [42–44], FAO [44], Acceptable Level
	Range	Mean	Range	Mean	
pH	7.00–7.57	7.24 a	7.6–7.8	7.7 a	7.6
EC (dS m^{-1})	1.32–1.60	1.33 a	0.2–0.3	0.24 b	0.7
TSS (mg L^{-1})	24–52	39.2 a	0.68–2.1	1.1 b	20
Nitrate (mg L^{-1})	15.2–23.5	18.1 a	6.0–11.5	7.2 b	10
NH$_4^+$ (mg L^{-1})	15–8–25.1	19.2 a	0.02–0.05	0.03 b	5
Phosphorus (mg L^{-1})	4.9–7.1	5.2 a	0.00–0.02	0.01 b	1–3
Ca^{+2} (mg L^{-1})	89.4–168.0	141.8 a	45.0–75.0	64.0 b	75
Mg^{+2} (mg L^{-1})	31.2–75.6	49.32 a	15.0–35.0	25.0 b	50
Na$^+$ (mg L^{-1})	89.7–165.6	156.4 a	22.0–43.0	36.0 b	200
K$^+$ (mg L^{-1})	21.8–37.4	28.5 a	3.5–7.2	5.3 b	-
Cl$^-$ (mg L^{-1})	468–904	511 a	151–211	174 b	-
HCO$_3^-$ (mg L^{-1})	284–412	320 a	77–121	104.5 b	-
SO$_4^{-2}$ (mg L^{-1})	12–28	18.5 a	3.9–6.9	5.8 b	-
Fe (mg L^{-1})	5.1–7.1	5.6 a	3.1–4.1	3.8 b	5
Mn (mg L^{-1})	0.81–1.2	1.04 a	0.21–0.38	0.35 b	1
Zn (mg L^{-1})	0.77–0.96	0.87 a	0.01–0.02	0.02 b	2
Cu (mg L^{-1})	0.52–0.73	0.59 a	0.010–0.014	0.01 b	0.2

TWW, Treated wastewater; WW, Well water; EC, Electrical conductivity; TSS, Total suspended solids. Different letters in each row show significant differences at $p < 0.05$ based on the *t*-test.

Another possible source is the chemicals that are applied in residential areas and urban utilities and discharged to the urban wastewater [45].

3.2. Impact of TWW Irrigation on Soil Fertility Indicators

TWW irrigation resulted in a slight increase in soil pH ranging from 4% to 6% compared to the WW control (Table 3), which may be viewed as a negative change in soil quality in such as arid and semi-arid environment [46]. This may have contributed to the high level of soluble salts and calcium carbonate equivalent (CCE) in TWW as represented by EC and CCE values of TWW in Table 2. In most TWW-treated sites, a significant increase ($p \leq 0.5$) was evident in the OM content ranging from 17% to 26% higher than WW irrigated soils, which is consistent with the results reported by Bedbabis et al. [21] and Aydin et al. [47]. The presence of degradable and compostable substances in the wastewater is possibly responsible for the increased OM, which promotes the microbial activities of the decomposition processes and thereby increases the humus in the TWW-irrigated soil [48,49]. The total N was significantly increased by TWW irrigation ranging from 22 to 90%, likely due to the biodegradation of recalcitrant carbon compounds in the wastewater [50]. The contribution of carbon compounds to total N has been reported in several previous studies [5,51]. The C/N ratio was in the range of 8 to 15 in both TWW-irrigated soils and the control soil, implying the N mineralization which has profound implications for OM cycling and nutrient release [52]. Generally, the decomposition process of organic matter and the release of N in soils are likely to happen when the C/N ratio is lower than 20:1 [53].

Table 3. Mean comparison for the fertility indices of the treated wastewater (TWW)-irrigated soils and adjacent well water (WW)-irrigated soil.

Characteristic	TWW-Irrigated Soil	WW-Irrigated Soil
	Site 1	
pH	7.93 a	7.5 a
OM (%)	2.62 a	2.2 b
CEC (cmolc kg^{-1})	24.30 a	17.7 b
CCE (g kg^{-1})	42.2 a	40.7 a
Total N (%)	0.14 a	0.09 b
C/N	11.7 a	14.18 b
Available P (mg kg^{-1})	20.63 a	15.2 b
Exchangeable Ca (cmolc kg^{-1})	15.25 a	12.42 b
Exchangeable Mg (cmolc kg^{-1})	4.85 a	3.55 b
Exchangeable K (cmolc kg^{-1})	1.52 a	1.05 b
	Site 2	
pH	7.8 a	7.5 a
OM (%)	2.83 a	2.2 a
CEC (cmolc kg^{-1})	25.45 a	17.7 b
CCE (g kg^{-1})	40.9 a	40.7 a
Total N (%)	0.17 a	0.09 b
C/N	8.94 a	14.18 b
Available P (mg kg^{-1})	23.52 a	15.2 b
Exchangeable Ca (cmolc kg^{-1})	15.26 a	12.42 b
Exchangeable Mg (cmolc kg^{-1})	7.45 a	3.55 b
Exchangeable K (cmolc kg^{-1})	2.75 a	1.05 b
	Site 3	
pH	7.84 a	7.5 a
OM (%)	2.77 a	2.2 b
CEC (cmolc kg^{-1})	23.82 a	17.7 b
CCE (g kg^{-1})	42.8 a	407 a
Total N (%)	0.11 a	0.09 b
C/N	14.6 a	14.18 a
Available P (mg kg^{-1})	22.30 a	15.2 b
Exchangeable Ca (cmolc kg^{-1})	18.65 a	12.42 b
Exchangeable Mg (cmolc kg^{-1})	5.93 a	3.55 b
Exchangeable K (cmolc kg^{-1})	1.65 a	1.05 b
	Site 4	

Table 3. *Cont.*

Characteristic	TWW-Irrigated Soil	WW-Irrigated Soil
pH	7.88 a	7.5 a
OM (%)	2.60 a	2.2 a
CEC (cmolc kg^{-1})	23.65 a	17.7 b
CCE (g kg^{-1})	43.1 a	40.7 a
Total N (%)	0.12 a	0.09 b
C/N	12.5 a	14.18 b
Available P (mg kg^{-1})	22.73 a	15.2 b
Exchangeable Ca (cmolc kg^{-1})	16.85 a	12.42 b
Exchangeable Mg (cmolc kg^{-1})	4.95 a	3.55 a
Exchangeable K (cmolc kg^{-1})	2.2 a	1.05 b
Site 5		
pH	7.9 a	7.5 a
OM (%)	2.67 a	2.2 b
CEC (cmolc kg^{-1})	23.7 a	17.7 b
CCE (g kg^{-1})	42.8 a	40.7 a
Total N (%)	0.13 a	0.09 b
C/N	11.91 a	14.18 b
Available P (mg kg^{-1})	18.90 a	15.2 b
Exchangeable Ca (cmolc kg^{-1})	14.15 a	12.42 a
Exchangeable Mg (cmolc kg^{-1})	4.15 a	3.55 a
Exchangeable K (cmolc kg^{-1})	2.02 a	1.05 b

Different letters in each row show significant differences at *p* < 0.05 based on the *t*-test.

Compared to the soil in the control site, there was a significant increase in soil available P ranging from 4 to 8.3 mg kg^{-1}, which can considerably reduce the need for phosphorus fertilizer. A similar result was found by the study of Thapliyal et al. [54] and Khawla et al. [22]. Soil CEC as an indicator of soil productivity, nutrient retention capacity, and the soil capacity to keep groundwater from cation pollution was another key soil attribute that was regulated by the TWW irrigation when compared to the control soil. Similar to the OM, CEC increased from 33 to 42% due to TWW irrigation. OM and clay fraction are the main factors responsible for greater soil CEC [50]. A significant accumulation of exchangeable Ca^{+2}, Mg^{+2}, and K$^+$ were found in TWW-irrigated versus control treatments, ranging from 14 to 50%, 37 to 101%, and 49 to 164%, respectively. Cation enrichment in the TWW-treated soil has also been reported by Bedbadis et al. [21] and Abegunrin et al. [48] in Tunisian (with a clay texture) and Nigerian (with a sandy loam texture) soils, respectively. Higher cations associated with TWW-treated soil may be direct result of a higher cation concentration compared to control treatment [45].

3.3. Effects of TWW Irrigation on Trace Metals Concentrations

The concentrations of available (extracted by DTPA) and total fractions of trace metals in the TWW-irrigated soils were higher than those in the WW-irrigated control soil (Table 4). The mean concentration of DTPA-extractable trace metals was in the order of Fe > Mn > Cu > Zn for both TWW-irrigated soils and control soil (Table 4). Except for DTPA-Fe, a significant increase occurred in all DTPA-extractable metals versus their counterparts in the control soils in the order of Cu (65–175%) > Zn > (36–73%) > Mn (25–31%) > Fe (17–22.5%) (Table 4). The results show that TWW-irrigated soils were richer in trace metals at all sites. The higher amount of metals in the TWW-irrigated soils might be directly related to the presence of these metals in the TWW or indirectly due to the higher solubility of the indigenous insoluble soil trace metals as a result of the interaction between the used wastewater and the subjected soils [22,45]. However, except for Cu whose concentration exceeded the acceptable limit [55], the remaining metals fell into the acceptable ranges. In most TWW-treated fields, DTPA-Cu was 1.3 to 1.4 times higher than its upper allowable range (2.5 mg kg^{-1}, Malakoti and Hamedani [55], indicating the possible risk of phytotoxicity. This accords well with the findings of Avci and Deveci [56] Kabata-Pendias [57].

Excessive accumulation of Cu in TWW-irrigated soils can be attributed to the a 3-fold above threshold [42–44] Cu concentration in TWW (Table 2).

Table 4. Means comparison for the trace metals of treated wastewater (TWW)-irrigated soils and adjacent well water (WW)-irrigated soil.

Characteristic	TWW-Irrigated Soil	WW-Irrigated Soil
Site 1		
DTPA-Fe (mg kg^{-1})	8.5 a	7.1 a
DTPA-Mn (mg kg^{-1})	6.5 a	5.2 b
DTPA-Zn (mg kg^{-1})	1.89 a	1.4 b
DTPA-Cu (mg kg^{-1})	2.49 a	1.84 b
Total-Fe (g kg^{-1})	23.6 a	21.0 a
Total-Mn (mg kg^{-1})	512 a	373 b
Total-Zn (mg kg^{-1})	41.7 a	20.3 b
Total-Cu (mg kg^{-1})	56.3 a	39.9 b
Site 2		
DTPT-Fe (mg kg^{-1})	8.7 a	7.1 b
DTPA-Mn (mg kg^{-1})	6.8 a	5.2 b
DTPA-Zn (mg kg^{-1})	2.42 a	1.4 b
DTPA-Cu (mg kg^{-1})	3.14 a	1.84 b
Total-Fe (g kg^{-1})	23.8 a	21.0 a
Total-Mn (mg kg^{-1})	522 a	373 b
Total-Zn (mg kg^{-1})	51.95 a	20.3 b
Total-Cu (mg kg^{-1})	55.4 a	39.9 b
Site 3		
DTPT-Fe (mg kg^{-1})	8.1 a	7.1 b
DTPA-Mn (mg kg^{-1})	6.6 a	5.2 b
DTPA-Zn (mg kg^{-1})	2.35 a	1.4 b
DTPA-Cu (mg kg^{-1})	2.78 a	1.84 b
Total-Fe (g kg^{-1})	22.30 a	21.0 a
Total-Mn (mg kg^{-1})	510 a	373 b
Total-Zn (mg kg^{-1})	42.8 a	20.3 b
Total-Cu (mg kg^{-1})	55.03 a	39.9 b
Site 4		
DTPT-Fe (mg kg^{-1})	8.8 a	7.1 b
DTPA-Mn (mg kg^{-1})	6.7 a	5.2 b
DTPA-Zn (mg kg^{-1})	2.5 a	1.4 b
DTPA-Cu (mg kg^{-1})	3.47 a	1.84 b
Total-Fe (g kg-1)	23.7 a	21.0 a
Total-Mn (mg kg^{-1})	517 a	373 b
Total-Zn (mg kg^{-1})	44.7 a	20.3 b
Total-Cu (mg kg^{-1})	57.2 a	39.9 b
Site 5		
DTPT-Fe (mg kg^{-1})	8.3 a	7.1 a
DTPA-Mn (mg kg^{-1})	6.5 a	5.2 b
DTPA-Zn (mg kg^{-1})	2.49 a	1.4 b
DTPA-Cu (mg kg^{-1})	3.48 a	1.84 b
Total-Fe (g kg^{-1})	23.6 a	21.0 a
Total-Mn (mg kg^{-1})	513 a	373 b
Total-Zn (mg kg^{-1})	41.1 a	20.3 b
Total-Cu (mg kg^{-1})	60.1 a	39.9 b

Different letters in each row show significant differences at $p < 0.05$ based on the t-test.

Similar to the DTPA-extractable form, the concentration of total forms of trace metals showed an ascending order of Fe > Mn > Cu > Zn in the TWW-irrigated soils and control soil (Table 4). Except for Fe, TWW irrigation significantly increased the total form of metals versus their counterparts in the control soils in the order of Zn (102–156%) > Cu > (38–51%)

Mn (37–40%) > Fe (12–13%). Nevertheless, the total forms of all metals were within the desirable limits [57]. Moreover, significant correlations ($p < 0.05$, e.g., r = 0.54 for Fe, r = 0.51 for Mn, r = 0.49 for Zn, and r = 0.56 for Cu) between DTPA and total fractions of all trace metals, suggests that they likely have been initiated from the same TWW source [58,59].

3.4. Influence of TWW Irrigation on Soil Quality Indices (SQI)

3.4.1. TDS Method

In TDS approach, seventeen soil chemical quality indicators including pH, OM, CEC, total N, C/N ratio, available P, exchangeable cations (Ca, Mg, and K), and total and bioavailable fraction of Fe, Mn, Zn, and Cu were measured and evaluated in conjunction with soil productivity. Among all indicators, available P and total Mn, respectively had the highest and lowest weighting coefficients, thus having the most and least influences on the final SQI-TDS scoring results (Table 5). The IQI-TDS model proposed in the study can be calculated using the following equation. The indicators are ordered by their weighting coefficients as follows:

$$
\begin{aligned}
IQI-TDS = {} & 0.069\ P + 0.067 OM + 0.066\ K + 0.065 total\ N + 0.063 total\ Zn + 0.062 DTPA\ Fe + \\
& 0.062 DTPA\ Zn + 0.061\ CEC + 0.06 total\ Cu + 0.57 total\ Fe + 0.057 DTPA\ Cu + \\
& 0.056 exchangeable\ Ca + 0.055 exchangeable\ Mg + 0.052\ \tfrac{C}{N} + 0.049\ pH + 0.049 DTPA\ Mn \\
& + 0.045\ total\ Mn
\end{aligned}
\tag{6}
$$

Table 5. The communality and weight values of each soil variable for both TDS and MDS approaches.

Soil Attribute	TDS Methods		MDS Methods	
	Communality	Weight	Communality	Weight
pH	0.691	0.049		
OM (%)	0.952	0.067	0.891	0.165
CEC (cmol kg^{-1})	0.869	0.061		
Total N (%)	0.919	0.065	0.922	0.172
C/N	0.742	0.052		
Available P (mg kg^{-1})	0.985	0.069	0.988	0.184
Exchangeable Ca (cmol$_c$ kg^{-1})	0.805	0.056		
Exchangeable Mg (cmol$_c$ kg^{-1})	0.788	0.055		
Exchangeable K (cmol$_c$ kg^{-1})	0.929	0.066	0.948	0.177
DTPT-Fe (mg kg^{-1})	0.844	0.062	0.771	0.144
DTPA-Mn (mg kg^{-1})	0.698	0.049		
DTPA-Zn (mg kg^{-1})	0.878	0.062		
DTPA-Cu (mg kg^{-1})	0.810	0.057		
Total-Fe (g kg^{-1})	0.812	0.057		
Total-Mn (mg kg^{-1})	0.644	0.045		
Total-Zn (mg kg^{-1})	0.919	0.063	0.876	0.163
Total-Cu (mg kg^{-1})	0.898	0.063		

Based on the IQI-NQI and IQI-TDS models, the nutritional/chemical quality of the study soil was categorized into five grades, ranging from I to V (Table 6). The assigned range illustrates the descending chemical-nutritional soil quality trend as represented by SQI. In TWW-irrigated soils, the mean IQI and NQI values based on the TDS (IQI-TDS and NQI-TDS) ranged from 0.7 (site 5) to 0.79 (site 2) and 0.56 (site 5) to 0.59 (site 4), respectively. This corresponds to III to II quality grades for both IQI and NQI models (Figure 2; Table 6). This is a typical range of soil nutritional/chemical quality grade in semi-arid climates as reported by several previous studies [35,36,60–62]. Soils with grade II quality either as IQI or NQI has generally been reported with suitable nutritional condition for appropriate plant growth while grade III has been characterized with some nutritional limitations [37,62].

Table 6. Categorization of soil quality grades using different methods.

SQI Scenario	Soil Quality Grade				
	I (Very High)	II (High)	III (Moderate)	IV (Low)	V (Very Low)
IQI-TDS	>0.80	0.73–0.80	0.66–0.73	0.59–0.66	<0.59
NQI-TDS	>0.62	0.57–0.62	0.52–0.57	0.47–0.52	<0.47
IQI-MDS	>0.82	0.76–0.82	0.68–0.76	0.60–0.68	<0.60
NQI-MDS	>0.58	0.49–0.58	0.43–0.49	0.37–0.43	<0.37

Figure 2. The comparison of soil quality grades between the TWW-irrigated soils (S1–S5) and the control soil (S6). Symbols I, ..., IV indicate the categorization of soil quality grades (I, very high grade; II, high grade; III, moderate grade; IV, low grade).

Compared to the control soil, the IQI-TDS and NQI-TDS values were higher in the TWW-irrigated soils by 14.6% to 29.5% for the IQI-TDS model and 19.1% to 25.5% for the NQI-TDS model (Figure 3). This is associated with an upsurged soil quality grade from IV to III in most soil sites treated by TWW irrigation (Figure 2), indicating a positive effect of TWW irrigation on soil quality indices calculated by nutritional/chemical indicators. Our results corroborate the findings of previous studies conducted by Chen et al. [63] and Lyu and Chen [64], who found that SQI and soil health conditions were improved by TWW irrigation. Among different soil sites under TWW irrigation, the highest increases in IQI-TDS and NQI-TDS values were related to sites 2 and 4 where the highest increases were observed in the values of P, OM, and K versus the control. These indicators are consistent with the strongest indicators affecting the TDS approach with respect to the weight of each indicator (Table 5), thereby resulting in a greater increase in IQI-TDS and NQI-TDS in sites 2 and 4 than in the other sites. Phosphorus, OM, and K are the most important factors for soil productivity indices which have widely been considered for soil quality assessment [37,63,65,66].
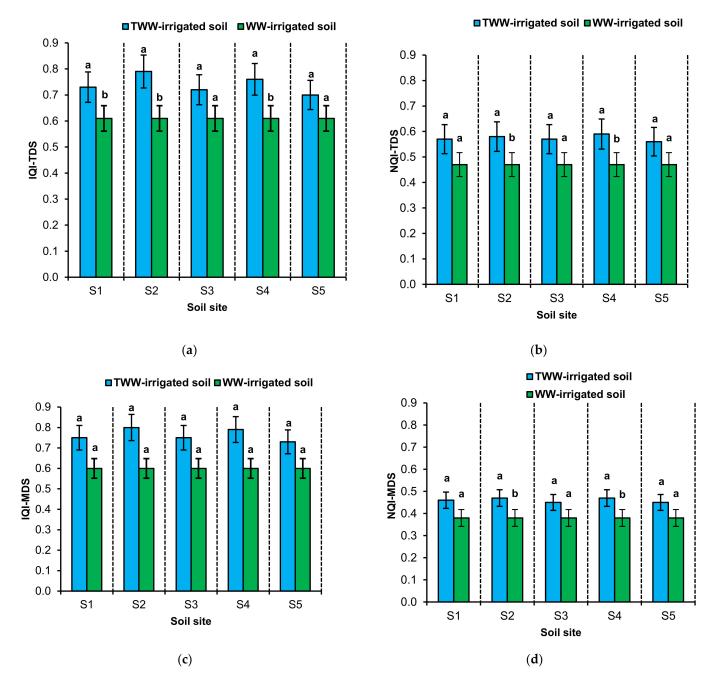
Figure 3. The comparison of the mean values of different SQI models in well water (WW)-irrigated soil and treated wastewater (TWW)-irrigated soils at individual sites: IQI-TDS (**a**), NQI-TDS (**b**), IQI-MDS (**c**), and NQI-MDS (**d**). Different letters indicate significant differences at $p < 0.05$ based on the t-test. The bars represent the standard deviation (SD) of means.

3.4.2. MDS Method

The indicators of the MDS dataset were specified using PCA analysis, which is an effective and common approach to reduce the multidimensionality of dataset in agricultural and biological studies [33,36,41]. As illustrated in Table 7, first and second principal components (PCs) with eigenvalues of >1 ranging from 5.96 to 6.35, explained 83.83% of the total variance in dataset. The first PC captured 46.59% of variability, comprising OM, CEC, available P, DTPA-extractable Fe and DTPA-extractable Zn, and total Zn. Under this PC, only a significant correlation ($p < 0.01$) was observed between OM and CEC and between DTPA-Fe and DTPA-Zn (Table 8), so OM, available P, DTPA-Fe, and total Zn were retained in the MDS dataset. PC2 explained 37.24% of the total variance with greater weighting factor for total N (a load of 0.83) and exchangeable cations of Ca, Mg, and K

in the order of K> Ca> Mg. Exchangeable Ca, Mg, and K were significantly correlated with each other ($p < 0.01$), but not well correlated with total N (Table 8). Thus, total N and exchangeable K were selected to be involved in MDS dataset. Organic matter, available P, DTPA-Fe, total Zn, total N, and exchangeable K were selected to form the final MDS dataset. Thus, the number of soil quality indicators was reduced from 17 in the TDS to 6 most critical indicators in the MDS. This means that a reduction of over 60% occurred in the initial dataset to maintain only nutritionally significant and independent indices in MDS dataset. Given the weight of each indicator, the IQI-MDS model can be calculated using the following equation.

$$IQI - MDS = 0.184 available\ P + 0.177 exchangeable\ K + 0.172 total\ N + 0.163 total\ Zn + 0.157 OM + 0.144 DTPA\ Fe \tag{7}$$

Table 7. Results of principal component analysis (PCA) for soil quality variables.

PCs	PC1	PC2
Eigenvalue	6.35	5.96
Variance (%)	46.59	37.24
Cumulative variance (%)	46.59	83.83
Eigenvectors		
pH	0.60	0.55
OM	**_0.85_**	0.09
CEC	0.76	0.53
Total N	0.21	**_0.83_**
C/N	0.63	0.23
Available P	**_0.87_**	0.41
Exchangeable Ca	0.34	0.79
Exchangeable Mg	0.28	0.80
Exchangeable K	0.44	**_0.85_**
DTPT-Fe	**_0.78_**	0.49
DTPA-Mn	0.56	0.57
DTPA-Zn	0.70	0.63
DTPA-Cu	0.67	0.59
Total-Fe	0.61	0.60
Total-Mn	0.59	0.52
Total-Zn	**_0.76_**	0.67
Total-Cu	0.64	0.57

Bold-underlined soil variables were involved in the MDS.

Table 8. Pearson correlation coefficients between Cd concentration of different wheat parts and with selected soil properties.

	pH	CEC	OM	TN	A-P	E-Ca	E-Mg	E-K	T-Fe	T-Mn	T-Zn	T-Cu	D-Fe	D-Mn	D-Zn	A-Cu
pH	1.00															
CEC	0.21	1.00														
OM	0.31	042	1.00													
TN	0.17	0.37	0.45	1.00												
A-P	0.25	0.19	0.33	0.27	1.00											
E-Ca	−0.12	0.28	0.11	−0.11	−0.1	1.00										
E-Mg	−0.14	0.22	0.13	−0.14	−0.13	0.69 **	1.00									
E-K	0.11	0.19	0.17	−0.2	0.15	0.77 **	0.75 **	1.00								
T-Fe	−0.18	0.07	0.38	0.04	−0.02	−0.08	−0.05	0.09	1.00							
T-Mn	−0.15	0.04	0.33	0.07	−0.02	−0.1	−0.11	0.01	0.43	1.00						
T-Zn	−0.13	0.02	0.36	0.1	−0.04	−0.14	0.13	−0.07	0.58 *	0.39	1.00					
T-Cu	−0.1	−0.08	0.44	0.22	0.12	−0.06	−0.08	0.11	0.38	0.31	0.42	1.00				
D-Fe	−0.14	0.04	0.41	0.24	−0.11	−0.11	−0.13	−0.1	0.54 *	0.31	0.29	0.22	1.00			
D-Mn	−0.15	0.06	0.39	0.2	−0.12	−0.09	0.04	0.06	0.35	0.51 *	0.23	0.19	0.22	1.00		
D-Zn	−0.1	0.01	0.28	0.16	−0.08	−0.1	−0.07	−0.03	0.3	0.15	0.49 *	0.21	0.31	0.2	1.00	
D-Cu	0.07	0.09	0.52 *	0.26	0.06	−0.08	−0.1	0.01	0.18	0.12	0.23	0.56 *	0.14	0.11	0.21	1.00

* and ** indicate significant level at 0.05 and 0.01, respectively. TN, Total N; A-P, Available P; E-Ca, Exchangeable Ca; E-Mg; Exchangeable Mg; E-K; Exchangeable K; T-Fe, Total Fe; T-Mn, Total Mn; T-Zn, Total Zn; T-Cu, Total Cu; D-Fe, DTPA-Fe; D-Mn, DTPA-Mn; D-Zn, DTPA-Zn; D-Cu, DTPA-Cu.

Among all the selected indicators in the MDS, available P had the highest contribution (18.5%) to IQI-MDS, followed by exchangeable K (17.8%), total N (17.3%), total Zn (16.3%), OM (15.7%), and DTPA-Fe (14.4%), almost a similar order to those occurred for the TDS dataset. Soil OM and macronutrients (N, P, and K) are the fundamental soil quality indicators due to their central role not only in soil nutritional affluence, but also in a greater soil physical strength and biological vitality [25,36,42,65,67]. Given the inclusion of trace metals (e.g., Fe and Zn) in the MDS dataset, the metals may highlight a wider viewpoint of soil nutrition for soil operators and scientists, who usually focus on microelements such as N, P and K when applying fertilizer [67]. Fe and Zn are two important metals driving many physiological functions of crops (e.g., the synthesis of chlorophyll, membrane integrity, reproduction, etc.) and are necessary and crucial nutrients for corn growth and its quantitative and qualitative grain yield [68]. Additionally, useful information regarding the soil functions such as micronutrient availability and crop productivity can be obtained by measuring trace metals [37,68]. In this study, the corn yield had a weak significant correlation with total Fe (r = 0.22, $p < 0.05$) and DTPA-Zn (r = 0.28, $p < 0.05$). Although the available Fe and Zn values of the TWW-irrigated soils were acceptable (Fe = 8–10 mg kg^{-1}, Zn = 2–3 mg kg^{-1}), auxiliary practices may still be necessary for maintaining the optimal range of available soil trace metals, such as Fe and Zn, in order to improve corn yield.

The mean values of the IQI-MDS and NQI-MDS models were in the range of 0.73 (site 5) to 0.80 (site 2) and 0.45 (site 5) to 0.47 (sites 2 and 4) in the TWW-irrigated soils, respectively, which is almost similar to the trend observed for the TDS dataset (Table 6). Regarding both IQI-MDS and NQI-MDS models, in the majority of TWW-irrigated soil sites, grade III was developed while grade IV was observed in the control soil, reflecting one grade of improvement in soil quality by TWW irrigation (Figure 2; Table 6). As with the TDS dataset, TWW irrigation resulted in a significant increase in the values of the IQI-MDS and NQI-MDS models ranging from 21.7 to 33.3% and 18.4 to 23.7%, respectively. This suggests that soil quality improvement dataset increased by TWW irrigation. Evidence for this trend is a significant increase in corn yield in the TWW-irrigated soils compared to the control soil as described in the next section. Given the fact that the influencing factors (i.e., climate, topography, parent material, soil type, soil use, and conventional cultivation methods) on soil quality were similar between the TWW-irrigated and control soils, it was assumed that any differences between their soil quality could be attributed to the effects of TWW irrigation. Other studies have also shown the beneficial and improving impacts of wastewater irrigation on soil quality [6,41,56].

3.5. Relationship between SQI and Corn Yield

As shown in Figure 4, TWW irrigation significantly raised corn yield in almost all soil sites (Figure 4), ranking in the order of S2 (28.1%) > S4 (26.6%) > S1 (20.3%) > S3 (18.8%) > S5 (12.5%). Different soil sites responded to TWW irrigation differently likely as a result of antecedent differences in physicochemical soil attributes [46]. However, TWW-irrigated sites with varying magnitudes, consistently exhibited nutritionally richer soil than in control site. The significant contribution of TWW irrigation to corn yield can be associated with the higher nutrient enrichment in TWW soils, which directly affects crop performance and yield outcome. This implication is supported by statistically significant correlation ($p < 0.05$) between the concentration of soil nutrients and corn grain, e.g., r = 0.42 for OM, r = 041 for total N, r = 0.38 for available P, r = 0.34 for exchangeable K, r = 0.31 for DTPA-Fe, and r = 0.29 for DTPA-Zn. According to the literature, soil fertility indicators are the important attributes and critical functions affecting crop growth and yields as well as SQI, which are usually correlated with crop yields [68,69]. Our results are in accordance with the those of Khawla et al. [22], Disciglio et al. [70], and Urbano et al. [71] who reported the beneficial effects of TWW irrigation (mainly nutrient contents of the wastewater) on increasing tomato and lettuce yields and corn biomass.
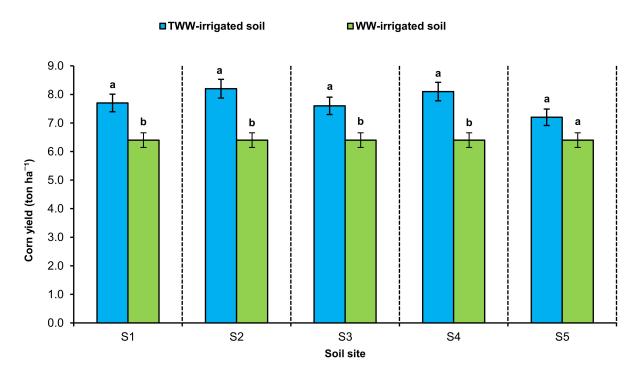
Figure 4. The comparison of the mean values of corn yield in well water (WW)-irrigated soil and treated wastewater (TWW)-irrigated soils in different soil sites. Different letters indicate significant differences at $p < 0.05$ based on the t-test. The bars represent the standard deviation (SD) of means.

The linear regression analysis was carried out between SQI and corn yield to verify how well the SQI represented the corn yield. As shown in Figure 5, all SQI models (IQI-TDS, NQI-TDS, IQI-MDS, and NQI-MDS) revealed a significant relationship with the corn yield (with an R^2 in the range of 0.36–0.78), implying that TWW irrigation positively affected corn yield in parallel to the changes in SQI. Previous studies around the world have reported a comparable range of R^2 values (0.4–0.89) explaining yield outcomes with SQI models [37,41,71,72].

The regression equations between different SQI models and corn yield are given as follows:

$$Corn\ yield\ =\ 6.183(IQI-TDS)+3.019\ R^2\ =\ 0.783\ P < 0.01 \tag{8}$$

$$Corn\ yield\ =\ 12.501(NQI-TDS)+0.289\ R^2\ =\ 0.467\ P < 0.05 \tag{9}$$

$$Corn\ yield\ =\ 4.707(IQI-MDS)+4.111\ R^2\ =\ 0.719\ P < 0.01 \tag{10}$$

$$Corn\ yield\ =\ 8.037(NQI-MDS)+3.859\ R^2\ =\ 0.363\ P < 0.05 \tag{11}$$

These relationships show that IQI and NQI models with two dataset size and arrangement systems of TDS and MDS explained 36 to 78% of the variability in corn yield which indicates an overall positive influence of TWW irrigation on soil nutritional quality and corn crop growth and yield. The IQI method was, however, more accurate than the NQI method in predicting corn performance as indicated by the higher correlation coefficient. These differences may be due to the fact that the combination of scoring and weighting is applied for soil variables in the IQI method, whereas the NQI model is calculated only based on the average values and the minimum score of the variables [71,72].
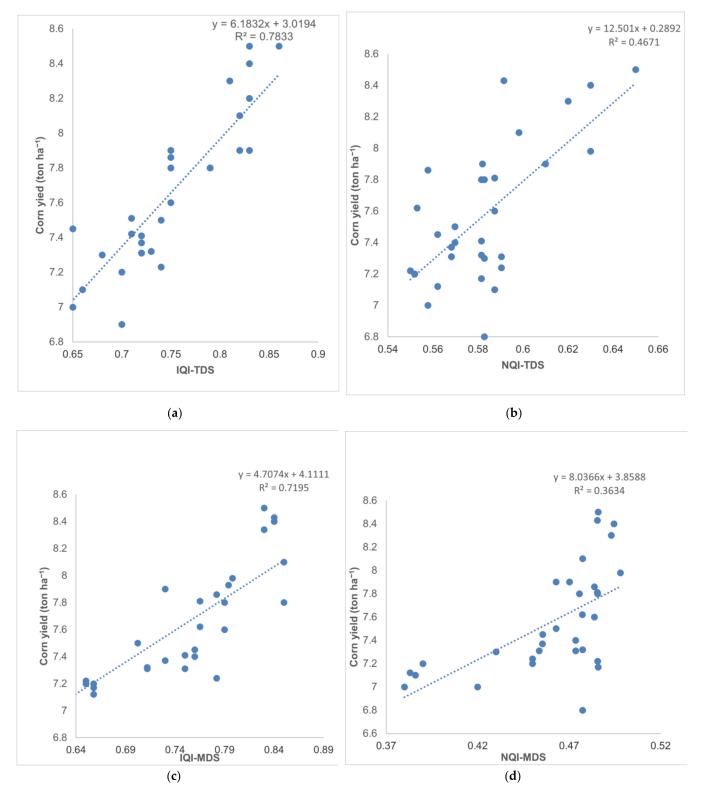
Figure 5. The linear regression analysis between different SQI models and corn yield: IQI-TDS (**a**), NQI-TDS (**b**), IQI-MDS (**c**), and NQI-MDS (**d**).

In short, the IQI-TDS model was more accurate than the other models in assessing soil quality and predicting corn yield because of its higher regression coefficient (Equation (7)). Comparing the different SQI models, it was observed that the consistency between TDS and MDS was higher in the IQI method than in the NQI method (Table 8), showing that IQI-MDS can provide adequate information for assessing soil quality in the region like the IQI-T

model. Therefore, we suggest that the IQI-MDS model is optimal for estimating soil quality and predicting crop yields in the examined region as suggested in previous studies [37,73]. Assessing soil quality by MDS model can lead to (1) the reduction of the number of indicators used in assessing SQI, (2) the time of laboratory analysis, and (3) the cost of determining effective variables [36,41]. There was a pronounced significant correlation between IQI-TDS and IQI-MDS ($p < 0.01$) (Table 9) and a less significant correlation between other models, e.g., IQI-TDS versus NQI-TDS ($p < 0.05$, r = 0.68), IQI-MDS versus NQI-TDS ($p < 0.05$, r = 0.59), and IQI-MDS versus NQI-MDS ($p < 0.05$, r = 0.64).

Table 9. Correlation matrix for eight SQIs.

	IQI-TDS	IQI-MDS	NQI-TDS	NQI-MDS
IQI-TDS	1.00	0.94 **	0.68 *	0.62 *
IQI-MDS	0.94 **	1.00	0.59 *	0.64 *
NQI-TDS	0.68 *	0.59 *	1.00	0.71 *
NQI-MDS	0.62 *	0.64 *	0.71 *	1.00

**. Correlation is significant at the 0.01 level. *. Correlation is significant at the 0.05 level.

4. Conclusions

The framework of the study involved an analysis of soil variables, indicator classification, scoring, weighting, and SQI calculation. Over ten years of TWW irrigation, a clear pattern of changes has been produced in the fertility indicators. Different SQI scenarios (IQI-TDS, IQI-MDS, NQI-TDS, and NQI-MDS) were calculated based on a total of 17 soil nutritional-chemical attributes and corn yield. TWW irrigation resulted in a significant accumulation of OM, CEC, nutrients (N, P, K, Ca, and Mg), and the majority of trace metals depending on soil site. This implies that TWW irrigation can not only be used to increase the availability of irrigation water given the water scarcity, but it can also improve soil nutrients level and increase productivity. Compared to the control soil, the values of IQI and NQI for the TWW-treated soil were higher by 14.6–29.5% and 19.1–25.5% for the TDS approach using 17 soil variables and by 21.7–33.3% and 18.4–23.7% for the MDS approach using six soil variables, respectively. These improvements were linked to at least one class of promotion in soil quality grade in all soil sites showing that soil quality was ameliorated to a remarkable extent by TWW irrigation. The results indicated that the IQI-MDS model was a more preferable index than the other models evaluated with respect to the correlation analyses among different SQI models and regression equations between corn yield and different SQI models. These findings may assist producers and policymakers with an effective and practical framework for monitoring of nutrients and contaminants in soils under wastewater irrigation.

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