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Effect of Marginal-Quality Irrigation on Accumulation of some Heavy Metals (Mn, Pb, and Zn) in *TypicTorripsamment* Soils and Food Crops

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Citation: Abuzaid, A.S.; Abdel-Salam, M.A.; Ahmad, A.F.; Fathy, H.A.; Fadl, M.E.; Scopa, A. Effect of Marginal-Quality Irrigation on Accumulation of some Heavy Metals (Mn, Pb, and Zn) in *TypicTorripsamment* Soils and Food Crops. *Sustainability* **2022**, *14*, 1067. https://doi.org/10.3390/su14031067

Academic Editors: Georgios Koubouris, José Alfonso Gómez, Luuk Fleskens and Giuseppe Montanaro

Received: 28 December 2021
Accepted: 12 January 2022
Published: 18 January 2022

Abstract: Lack of active sorption sites in sandy soils renders metals added by irrigation water more labile and increases their soil-to-plant transfer. Thus, this study investigated the long-term impacts of irrigation using sewage effluents and contaminated groundwater on metal accumulations in *TypicTorripsamment* soils, and edible parts of food crops. Nine sites in El-Gabal El-Asfar farm, south-eastern to the Nile Delta of Egypt, were selected. At each site, irrigation water, soil (0–30 cm), and the crop's edible part were sampled in triplicates and analyzed for Mn, Pb, and Zn. Results revealed significant ($p < 0.05$) differences in metal concentrations among water sources. Thus, constant irrigation caused significant spatial variations in total and available metal contents in soils. Total contents of Pb (in four sites) and Zn (in all sites) exceed the lithosphere range, while the available contents of the three metals exceeded the safe limits in all soils. The index of geo-accumulation indicated no Mn pollution but showed elevated pollution risks for Pb and Zn. The three metals showed high availability ratios, proving the effect of light soil texture. The multivariate statistical analysis indicated that Mn and Zn had similar geochemical behaviors in soils. Metal contents in all crop's edible parts surpassed the safe limits. The bioaccumulation factor (BAF) was less than 1.0 for Mn and Zn but higher than 1.0 for Pb. The highest BAFs occurred in cabbage leaves, indicating the phytoextraction potential of this species. Sufficient water treatment and proper remediation techniques are recommended to alleviate metal accumulation in food crops and their transfer via the food chain.

Keywords: marginal-quality water; irrigation; metals; food crops; sandy soils; soil pollution

1. Introduction

Marginal-quality water resources have increasingly become the predominant cost-effective and reliable alternative to conventional water in many countries in arid and semi-arid regions [1], including brackish groundwater, saline, and sodic drainage effluents, sewage, and other types of wastewater [2]. On the global scale, out of the total irrigated area of 310 million hectares (M ha), nearly 20 M ha (6.5%) are irrigated with treated and untreated wastewater [3], while 117 M ha (37.7%) are irrigated with brackish groundwater [2]. It is also estimated that at least 10% of the world's population consumes foods produced by irrigating with wastewater [4].

Compared with natural waters, marginal-quality waters contain a higher load of toxicants that may cause potential risks [1,5]. Metals are the most hazardous inorganic pollutants in soils, including essential (Fe, Mn, Zn, and Cu) and nonessential (Cd and Pb) elements for biological functions [6]. Once they enter soil ecosystems, their total contents persist for long periods, as they do not undergo any chemical or microbial degradation [7]. However, metal toxicity is closely related to the bioavailable fractions that can be easily taken up by living organisms and react with their metabolic machinery [8]. Metal availability in soils is dynamic and depends on various reactions like sorption, redox, complexation, and interaction with coexisting ions. These processes are governed by soil properties such as pH, organic matter, clay, $CaCO_3$, and oxides and hydroxides, which differ according to soil type [9,10].

Sandy soils are commonly distributed across the world and cover nearly 31% of the global land area [11], which includes soils with sand and loamy sand texture, and are mainly in Entisols. Most of them, under aridity conditions, occur in the *Torripsament* great group [12]. These soils are more vulnerable to pollution as metals are more labile due to the low sorption capacity [11]. A review for chemical pollution due to sewage irrigation in Egypt [13] reported lower metal retentions by *Torripsament* soils than *Torrifluvent* or *Calciorthid* soils. Lack of active sites increases the readily available free metal ions in soil solutions [14]. Under sewage irrigation in Nigerian sandy soils, Egwu and Agbenin [15] reported excessive Pb contents in leafy vegetables that were consistent with high free Pb^{2+} in soil solution. Metal ions may migrate to deep soils, causing large-scale groundwater pollution [16].

Since 1911, Egypt had an old experience in sewage irrigation in *TypicTorripsamment* soils in El-Gabal El-Asfar farm in the Eastern Desert [17]. The cultivation began on 200 ha that extended at 1260 ha in mid-1980 [18], and now 8400 ha are fully cultivated [19]. The area was irrigated with raw effluent until the operation of the treatment plant in the early 1990s. However, primary treated effluents were available only during the first 20 years, since the flow reached the plant and then reached double the capacity of the treatment works [19]. Continued sewage irrigation resulted in increasing the total and available metal contents in surface soils [20,21]. The percolation of these effluents extended also to shallow groundwater aquifers, causing groundwater contamination [22].

Initially, the El-Gabal El-Asfar farm was planned to be cultivated with forest trees. Therefore, previous studies focused mainly on metal accumulation in soils and groundwater. However, in recent years, forest trees have been replaced by food crops, which entail appropriate monitoring of potential metal accumulation in the food chain. The current work, therefore, aimed at investigating the effect of long-term irrigation using raw or partially treated sewage effluents and contaminated groundwater in this farm on the accumulation of Mn, Pb, and Zn in surface soils and edible parts of food crops grown there.

2. Materials and Methods

2.1. Study Area

The El-Gabal El-Asfar farm is located in Qalubiya Governorate about 25 km North-East of Cairo (Figure 1). The cultivation has been initiated since 1911 in the south and middle sections, and since 1960 in the north section [20]. The area is characterized by a hot arid summer and little rain in winter. The climate data (from 2000 to 2020) collected from the Belbaiss station (30°24′00″ N; 31°35′00″ E) indicate a mean annual temperature of 21.4 °C, where the highest (34.5 °C) occurs during July, while the lowest (7.6 °C) occurs during January. The total annual rainfall is 50 mm year^{-1} and the relative humidity ranges from 49.9 to 64.4%. The soils are classified as *TypicTorripsamments* with loamy sand being the predominant texture [23].

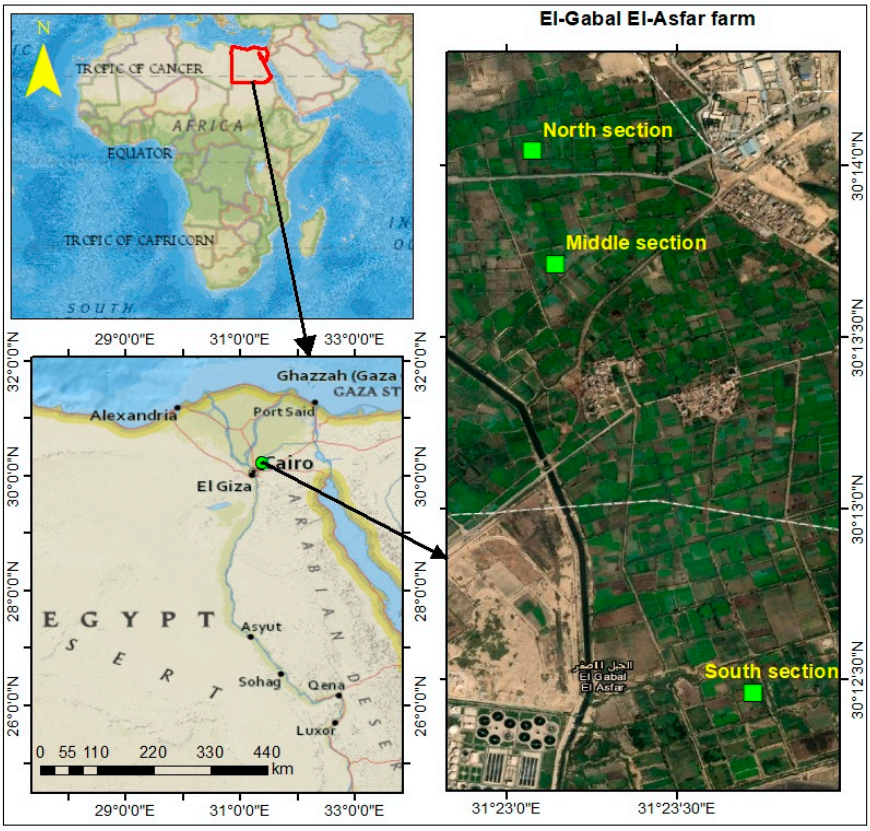

Figure 1. Location map of the studied area.

2.2. Sampling

Nine sites irrigated with different water sources were selected in the south, middle, and north sections inside the farm (three sites in each section). At each site, irrigation water, surface soil, and the edible part of the growing plant were sampled in triplicates (n = 27) (Table 1). Water samples were collected in 0.5 L polypropylene vials previously washed with 50% HNO_3 and double deionized water and acidified with 5 mL HNO_3. They were then transported in iceboxes to the laboratory and kept in the refrigerator at 4 °C until analysis. Surface soil samples (0–30 cm) were collected from fields adjacent to irrigation water sources also in triplicates using a stainless-steel auger, packed in polyethylene bags, and kept for laboratory analyses. The crop's edible parts (wheat grains, broad bean seed, and cabbage leaves) were sampled from the same sites where the soils were taken and kept in paper bags until analyses.

Table 1. Locations of irrigation water, soil, and plant samples collected from the studied area.

Section	Site	Code	Irrigation Water	Plant Species
South	Plot 5	1	Treated domestic wastewater	Broad bean (*Viciafaba*)
	Plot 8	2	Raw domestic wastewater	Wheat (*Triticumaestivum* L.)
	Plot 2	3	Raw domestic wastewater	Cabbage (*Brassica oleracea*)
Middle	Plot 5	4	Raw domestic wastewater	Wheat (*Triticumaestivum* L.)
	Plot 2	5	Treated domestic wastewater	Wheat (*Triticumaestivum* L.)
	Plot 8	6	Well water	Broad bean (*Viciafaba*)
North	Plot 5	7	Raw domestic wastewater	Cabbage (*Brassica oleracea*)
	Plot 2	8	Raw industrial wastewater	Wheat (*Triticumaestivum* L.)
	Plot 8	9	Well water	Broad bean (*Viciafaba*)

2.3. Laboratory Analyses

Water samples were digested according to APHA [24] using concentrated HNO_3-$HClO_4$-HF acids. Soil samples were air-dried and passed through a 2-mm mesh. Soil pH, electrical conductivity (EC), organic matter (OM), $CaCO_3$, and particle size distribution were analyzed according to Estefan et al. [25]. Total soil contents of Mn, Pb, and Zn were extracted using concentrated HNO_3-HF-HCl microwave-assisted digestion (MLS-1200 Mega. Milestone Inc., California, CT, USA) [26], while available contents were extracted using diethylenetriaminepentaacetic acid (DTPA) at pH = 7.3 [27]. The crop's edible parts were washed using tap water then deionized water, and oven-dried at 70 °C for 48 h. Thereafter, 0.5 g of the dried samples were digested using a mixture of concentrated HNO_3, H_2SO_4, and $HClO_4$ in a 10:1:4 ratio [25]. The concentrations of Mn, Pb, and Zn were measured using atomic absorption spectrometry (AAS) (AAnova 350 Analytic Jena GmbH, Thuringia, Germany).

2.4. Quality Control

All measurements were done in triplicates using chemicals of analytical grade. The analysis was carried in triplicates for each metal, and reference materials according to ISO/IEC 17025. A test of recovery for PTMs was performed at seven different concentration levels (1000, 500, 100, 50, 25, 12.5, and 6.25 $\mu g\ L^{-1}$). The average relative standard deviation resulted in lower than 5%.

2.5. Metal Accumulation in Soils and Crop's Edible Parts

The index of geo-accumulation (I_{geo}) and availability ratio (AR) have been used increasingly to describe metal accumulation behavior in soils. In addition, the bioaccumulation factor (BAF) was used for quantifying metal accumulations in the crop's edible parts.

The I_{geo} measures soil pollution considering the total metal content in the soil (C_S) and the metal background value (C_B). It was calculated according to Kowalska et al. [28] as follows:

$$I_{geo} = \log_2\left[\frac{C_S}{1.5 \times C_B}\right]$$

The factor 1.5 normalizes metal variations due to natural processes. Metal contents in the sand stones were used as C_B. They were 500, 10, and 30 mg kg^{-1} for Mn, Pb, and Zn, respectively [6]. The I_{geo} indicates seven classes: Class 0 (unpolluted), $I_{geo} \leq 0$; class 1 (unpolluted to moderately polluted), $0 < I_{geo} \leq 1$; class 2 (moderately polluted), $1 < I_{geo} \leq 2$; class 3 (moderately to strongly polluted), $2 < I_{geo} \leq 3$; class 4 (strongly polluted), $3 < I_{geo} \leq 4$; class 5 (strongly to extremely polluted), $4 < I_{geo} \leq 5$; class 6 (extremely polluted), $I_{geo} > 5$.

The AR is an indicator of metal availability and mobility in soils. It quantifies the percentage of the available fraction to the total metal content in the soil as follows [29]:

$$AR = \left(\frac{\text{DTPA} - \text{extractable content}}{\text{Total content}}\right) \times 100$$

The BAF measures soil-to-plant metal transfer and the magnitude of metal accumulation in the edible parts. It was calculated according to Sahay et al. [30] as follows:

$$BAF = \frac{\text{Metal concentration in the plant edible part } (\text{mg kg}^{-1})}{\text{Total metal concentration in soil } (\text{mg kg}^{-1})}$$

2.6. Data Analyses

All statistical analyses were performed using SPSS 19.0 software (SPSS Inc., Chicago, IL, USA). One-way ANOVA followed by Tukey's significance difference (HSD) test at 5% probability level ($p < 0.05$) were calculated to compare metal means among the sites. Pearson's correlation coefficients were calculated to test the relationships between metals in irrigation waters and soils, and between metals and soil properties. The stepwise multiple linear regression (SMLR) was performed to relate metal ARs with soil properties. The principal component analysis (PCA) with Varimax rotation was applied on standardized soil data. Only factors with eigenvalues > 1 and that explained at least 5% of the variations in the data set were considered. The Hierarchical Cluster Analysis (HCA) using Ward's method of linkage and the squared Euclidean distance as a similarity measure was performed in order to detect different geochemical associations.

3. Results

3.1. Metal Concentrations in Irrigation Water

Results in Table 2 show that the mean Mn concentrations in all water samples surpassed the maximum allowable limit (MAL) 0.2 mg L^{-1} as set by FAO 29 guidelines [31] and the Egyptian code of practice [32]. On the other hand, mean concentrations of Pb and Zn were below the MAL of 5 mg L^{-1}. There were significant differences ($p < 0.05$) in metal concentrations among the sites and the highest concentrations were in site 8, while the lowest concentrations of Mn, Pb, and Zn were in sites 1, 9, and 2, respectively. Metal concentrations in irrigation waters followed the order of Mn > Zn > Pb.

Table 2. Mean metal concentrations in the investigated irrigation waters and soils.

	Irrigation Water, mg L^{-1}			Irrigated Soils, mg kg^{-1}					
				Total Content			DTPA-Extractable Content		
Site	Mn	Pb	Zn	Mn	Pb	Zn	Mn	Pb	Zn
1	0.24 ^{f}	0.005 ^{e}	0.18 ^{ab}	410.13 ^{c}	3.11 ^{f}	170.21 ^{c}	77.84 ^{c}	1.43 ^{b}	68.31 ^{c}
2	0.28 ^{e}	0.020 ^{d}	0.13 ^{b}	277.56 ^{f}	4.15 ^{f}	99.64 ^{g}	49.46 ^{g}	2.17 ^{ab}	21.05 ^{g}
3	0.25 ^{f}	0.024 ^{c}	0.19 ^{ab}	226.91 ^{g}	38.12 ^{c}	89.73 ^{h}	57.16 ^{f}	4.47 ^{a}	45.55 ^{e}
4	0.30 ^{de}	0.032 ^{b}	0.16 ^{b}	386.45 ^{e}	20.91 ^{d}	158.92 ^{d}	59.24 ^{f}	4.78 ^{a}	40.52 ^{f}
5	0.39 ^{ab}	0.004 ^{e}	0.18 ^{ab}	394.53 ^{d}	8.07 ^{e}	138.53 ^{e}	70.32 ^{d}	2.62 ^{ab}	60.09 ^{d}
6	0.31 ^{cd}	0.004 ^{e}	0.17 ^{b}	408.43 ^{c}	2.72 ^{f}	189.57 ^{b}	91.47 ^{a}	0.91 ^{b}	81.23 ^{a}
7	0.33 ^{c}	0.034 ^{b}	0.14 ^{b}	427.63 ^{b}	42.87 ^{b}	190.82 ^{b}	64.57 ^{e}	3.41 ^{ab}	45.52 ^{e}
8	0.41 ^{a}	0.043 ^{a}	0.28 ^{a}	452.72 ^{a}	50.43 ^{a}	198.41 ^{a}	84.29 ^{b}	3.01 ^{ab}	77.51 ^{b}
9	0.37 ^{b}	0.003 ^{e}	0.18 ^{ab}	388.44 ^{e}	2.91 ^{f}	130.45 ^{f}	77.21 ^{c}	1.25 ^{b}	67.21 ^{c}
NC	-	-	-	100–500	5–10	15–30	-	-	-
MAL	0.2 [1]	5.0 [1]	5.0 [1]	4000 [2]	200 [2]	300 [2]	5.0 [3]	2.0 [3]	1.25 [3]

Means with different letters indicate significant difference at 0.05 probability level; NC, natural content in the sandstones [6]; MAL, maximum allowable limit; [1] according to FAO 29 guidelines [31] and Egyptian standers [32]; [2] according to Edelstein and Ben-Hur [33]; [3] according to Gatta et al. [1].

3.2. Metal Concentrations in the Irrigated Soils

Mean total Mn contents (Table 2) in all soils were within the normal range (NR) of 100–500 mg kg^{-1} [6] and below the MAL for agricultural soils of 4 g kg^{-1} [33]. The Pb contents in sites 3, 4, 7, and 8 exceeded the NR of 5–10 mg kg^{-1}; however, they were below the MAL of 200 mg kg^{-1}. The Zn contents in all soils were above the NR of 15–30 mg kg^{-1} but below the MAL of 300 mg kg^{-1}. Metal contents displayed significant ($p < 0.05$) spatial variations, and the highest contents were in site 8. The total metal content followed the order of Mn > Zn >Pb. Regarding the DTPA-extractable contents, mean values of Mn and Zn in all soils exceeded the MAL of 5.0 and 1.25 mg kg^{-1}, respectively [1]. Except for sites 1 and 9, Pb contents in all sites surpassed the MAL of 2.0 mg kg^{-1}. The available metal contents showed significant ($p < 0.05$) spatial variations and followed the order of Mn > Zn > Pb.

Results reported in Table 3 show that the total Mn and Pb in soils showed highly significant ($p < 0.01$) positive correlations with their concentrations in irrigation waters. The DTPA-extractable Pb and Zn in soils showed highly significant positive correlations with their corresponding contents in irrigation water, while both DTPA-extractable Mn and total Zn in irrigated soils showed no significant correlations with irrigation waters.

Table 3. Pearson's correlation coefficient (r) and probability (p) value between metal concentrations in irrigation water and irrigated soils.

Irrigation Water	Soil Content	r	*p*-Value
Mn	Total	0.517	**
	Available	0.178	ns
Pb	Total	0.849	**
	Available	0.656	**
Zn	Total	0.284	ns
	Available	0.522	**

ns, not significant; ** significant at $p < 0.01$.

3.3. Metal Geo-Accumulation and Availability Ratio

Figure 2 shows that values of I_{geo} for Mn were less than zero in all sites. The I_{geo} values for Pb were below 0 in 5 sites (1, 2, 5, 6, and 9), below 1 in site 4 (unpolluted to moderately polluted), and below 2 in sites 3, 7, and 8 (moderately polluted). The I_{geo} values for Zn were below 1 in site 3 (unpolluted to moderately polluted class), below 2 in sites 1, 2, 5, and 9 (moderately polluted class), and below 3 in sites 6, 7, and 8 (moderately to highly polluted class). The I_{geo} values indicate metal accumulation in the order of Zn > Pb > Mn.

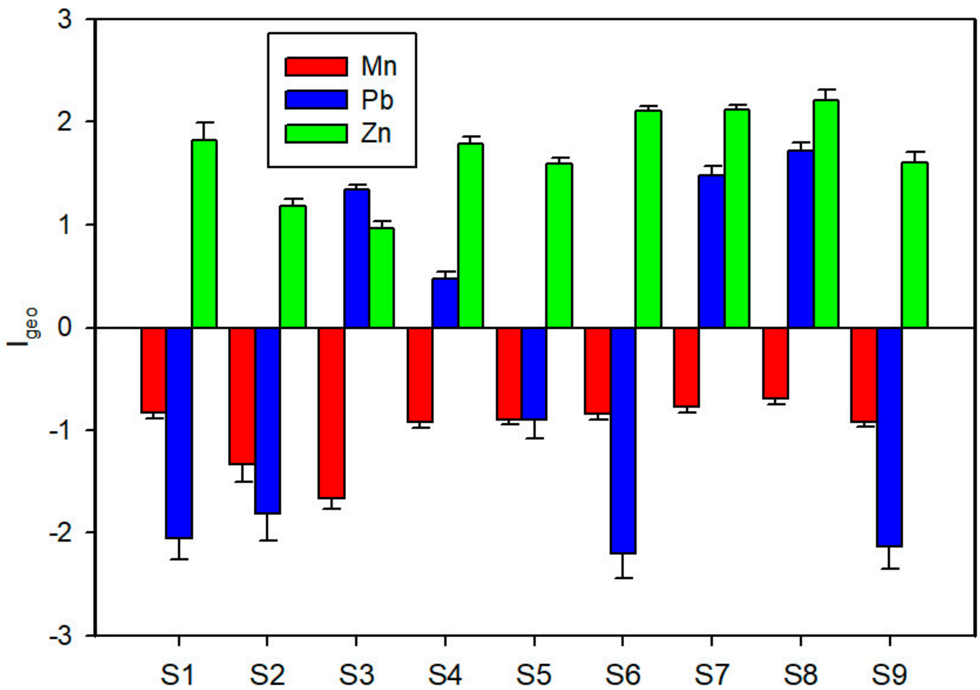

Figure 2. Metal geo-accumulation indices (I_{geo}) in the studied sites (S).

As shown in Figure 3, the three metals displayed different ARs in soils. The metal ARs occurred in the order of Zn > Pb > Mn.

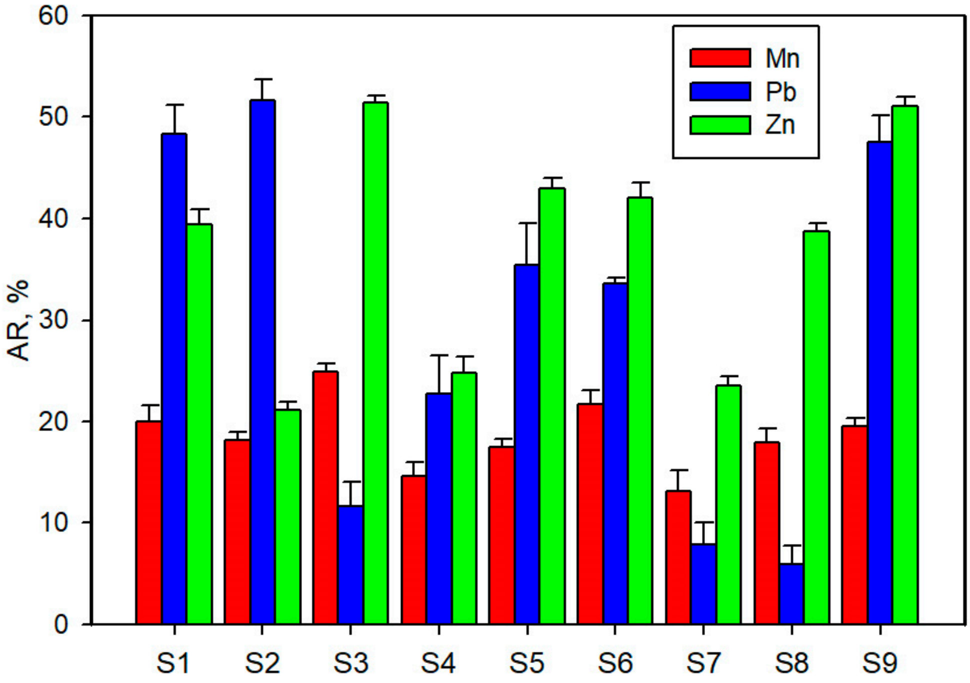

Figure 3. Metal availability ratio (AR) in the studied sites (S).

The regression equations (Table 4) show that the most significant soil variables affecting Mn AR were, positively, pH and EC, and, negatively, clay, silt, and $CaCO_3$. Likely, with the exception of clay, these variables were the most effective drivers for Zn AR. On the other hand, Pb AR showed different associations since the most significant soil variables were, positively, OM and clay, and negatively, sand content.

Table 4. Stepwise multiple linear regression between soil properties and metal availability ratio.

Metal	Regression Model	*p*	R^2
Mn	$-70.44 + 11.37pH - 0.51Silt - 0.67Clay + 7.24EC - 0.12\ CaCO_3$	<0.001	0.86
Pb	$425.90 + 5.66OM + 9.61Clay - 7.30Sand$	<0.001	0.82
Zn	$-233.44 + 37.66EC + 30.47pH - 1.02CaCO_3 - 1.07Silt$	<0.001	0.66

R^2 is the coefficient of determination.

3.4. Multivariate Statistical Analysis

Pearson's correlation matrix (Table 5) indicates no significant metal correlations with pH or sand, while all metals showed correlated negatively with OM, except available Pb. Total Pb and available Zn and Mn correlated positively with EC, while total Mn and Zn were correlated positively with $CaCO_3$. Total Mn correlated positively with silt content, while total and available contents of Mn and Zn correlated positively with clay. In particular, total metals showed highly significant positive correlations with their available fractions. Total Mn correlated positively with total and available Zn but negatively with available Pb. Total Zn correlated positively with available Mn. Available Mn correlated positively with available Zn but negatively with available Pb. There was a negative correlation between the available contents of Pb and Zn.

Table 5. Correlation matrix between metal contents and soil properties.

	pH	EC	OM	$CaCO_3$	Sand	Silt	Clay	T–Mn	T–Pb	T–Zn	A–Mn	A–Pb
pH	1.000											
EC	0.061	1.000										
OM	−0.197	−0.443 *	1.000									
$CaCO_3$	0.255	0.631 **	−0.326	1.000								
Sand	−0.449 *	0.069	0.537 **	−0.124	1.000							
Silt	0.502 **	0.109	−0.557 **	0.121	−0.731 **	1.000						
Clay	0.281	0.275	−0.536 **	0.431 *	0.073	0.338	1.000					
T–Mn	−0.055	0.249	−0.742 **	0.482 *	−0.202	0.458 *	0.685 **	1.000				
T–Pb	−0.049	0.502 **	−0.506 **	0.190	−0.234	0.263	−0.117	0.071	1.000			
T–Zn	−0.059	0.272	−0.693 **	0.457 *	−0.223	0.345	0.491 **	0.912 **	0.254	1.000		
A–Mn	0.313	0.459 *	−0.608 **	0.326	−0.087	0.272	0.529 **	0.704 **	−0.107	0.694 **	1.000	
A–Pb	−0.309	0.167	0.323	−0.105	0.261	−0.197	−0.225	−0.430 *	0.510 **	−0.322	−0.692 **	1.000
A–Zn	0.307	0.567 **	−0.632 **	0.268	−0.088	0.246	0.472 *	0.642 **	−0.034	0.616 **	0.976 **	−0.649 **

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

The PCA (Table 6) shows that the four PCs explained 84.48% of the total variance. These components accounted for 29.91, 19.08, 18.92, and 16.57 % of the total variance, respectively. The PC1 was dominated by total and available Mn and Zn with high positive loadings and OM with high negative loading. Soil pH and silt (high positive loading) and sand (high negative loading) dominated PC2, while EC and $CaCO_3$ dominated PC3. The PC4 contained total and available Pb with high positive loadings.

Table 6. Principal component analysis of the studied variables.

Parameter	**PC1**	**PC2**	**PC3**	**PC4**
Eigenvalue	5.553	2.169	1.919	1.342
Variance, %	29.907	19.083	18.919	16.573
Cumulative, %	29.907	48.990	67.909	84.482
Indicator	Eigenvectors			
pH	−0.227	**0.697**	0.396	−0.429
EC	0.217	−0.052	**0.861**	0.340
OM	**−0.742**	−0.473	−0.277	−0.162
$CaCO_3$	0.196	0.074	**0.803**	0.015
Sand	−0.139	**−0.927**	0.097	−0.123
Silt	0.315	**0.830**	0.029	0.020
Clay	0.554	0.051	0.375	−0.235
Total Mn	**0.963**	0.112	0.518	−0.084
Total Pb	0.133	0.346	0.231	**0.862**
Total Zn	**0.920**	0.097	0.580	0.055
DTPA-Mn	**0.667**	0.101	0.102	−0.458
DTPA-Pb	−0.404	−0.226	0.007	**0.799**
DTPA-Zn	**0.613**	0.102	0.139	−0.396

Bold-face numbers indicates highly loaded variables (>0.6).

The HCA (Figure 4) indicates the predominance of two main groups. The first group was subdivided into four subgroups: (1) available Mn and available Zn; (2) total Mn and total Zn-clay; (3) EC and $CaCO_3$, and (4) pH-silt. The second one included two subgroups: OM and sand occurred in one subgroup and total and available Pb in the other one.

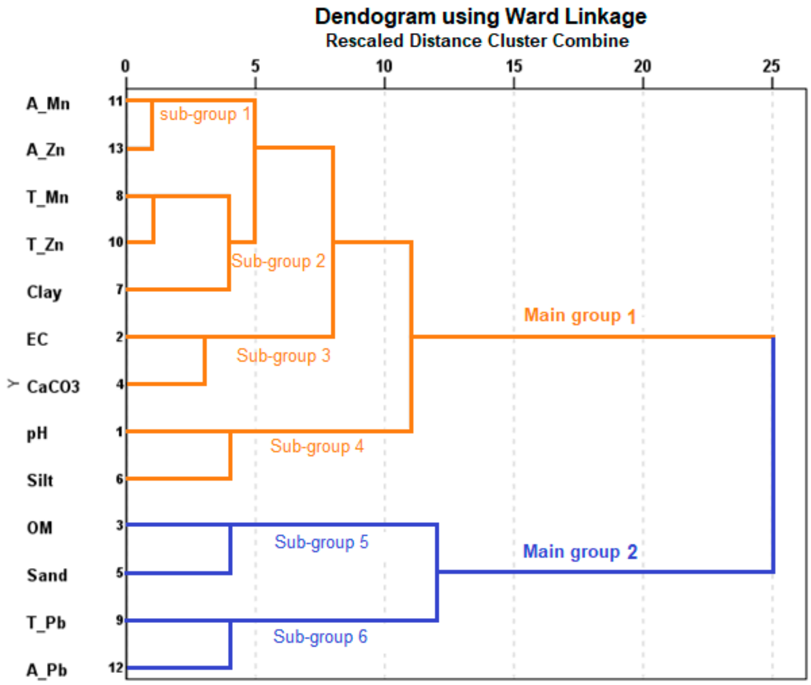

Figure 4. Dendrogram for the variable clusters in soils (T, total; A, available).

3.5. Metals in the Crop's Edible Parts

Figure 5 shows that Mn contents exceeded the MAL for food crop of 133.0 mg kg^{-1} [34]. According to Kabata-Pendias [6], the MAL of Pb is 0.6, 2.0, and 2.4 mg kg^{-1} for wheat grains, legume seeds, and cabbage leaves, respectively. Thus, Pb contents in the crop's edible parts exceeded the safe limits. Zn contents crossed the MAL of 27 mg kg^{-1} for wheat grain, 38 mg kg^{-1} for broad bean seeds, and 31 mg kg^{-1} for cabbage leaves [6].

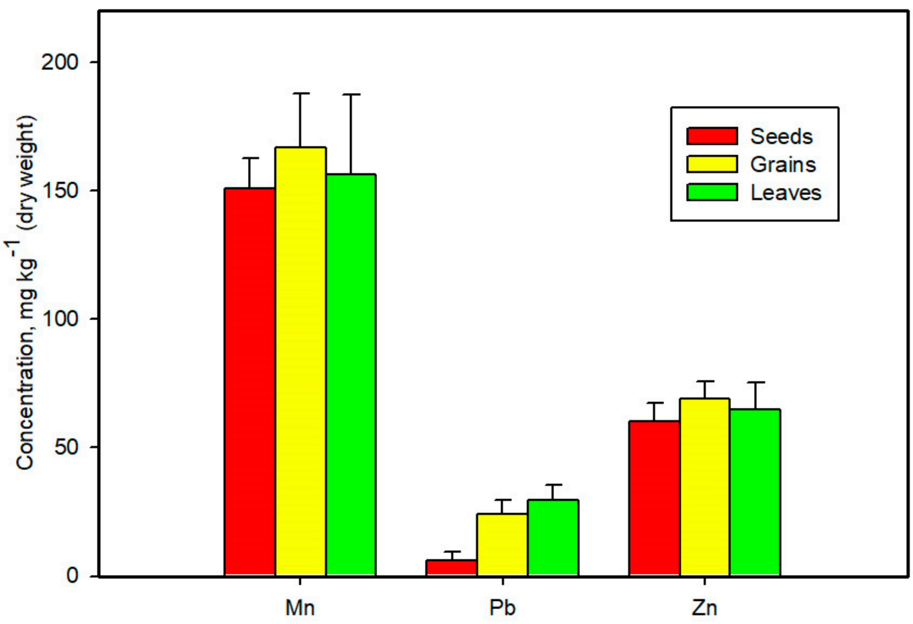

Figure 5. Metals concentrations in the crop's edible parts.

Metal contents in the crop's edible parts followed the order of Mn > Zn > Pb. The calculated BAF (Figure 6) shows values lesser than unity for Mn and Zn, but is higher than unity for Pb in all crop's edible parts. The metal BAF followed the order of Pb > Zn > Mn.

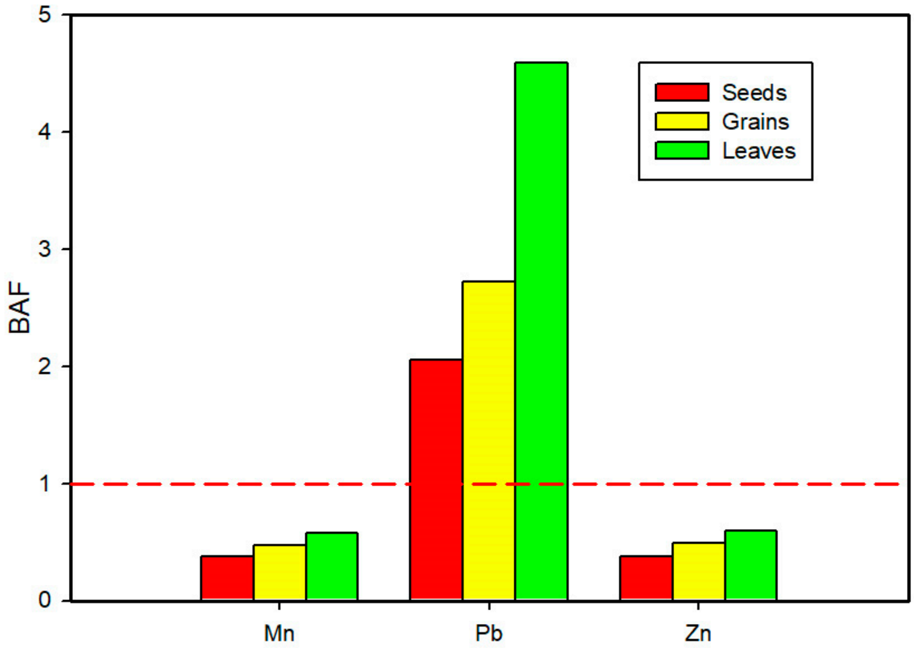

Figure 6. Metal bioaccumulation factor (BAF) in the crop's edible parts.

4. Discussion

4.1. Metal Concentrations in Irrigation Water

The El-Gabal El-Asfar sewage effluents are rich in Mn, which has been reported by Abdel-Shafy and Abdel-Sabour [35]. High Mn in the groundwater affirms contamination due to sewage irrigation. Abo el Abas [22] reported that the mean Mn concentration in groundwater from this farm was 0.26 mg L^{-1}. Low concentrations of Pb and Zn reflect minor contamination, which agrees with the results of previous studies. The highest Pb concentrations were 0.02 mg L^{-1} in the sewage effluents [20], and 0.09 mg L^{-1} in the groundwater [36], while the highest Zn concentrations were 0.38 mg L^{-1} in the sewage effluents [35], and 0.26 mg L^{-1} in the groundwater [36]. Metal water contents were affected by the source and degree of treatment, which explains variations among water sources. Usually, industrial wastewaters, especially raw effluents, contain a higher concentration of metals than municipal or groundwater [1].

4.2. Metal Concentrations in the Irrigated Soils

The total metal contents indicated a safe limit of Mn in soils that is in harmony with the results obtained by Abdel El Lateef et al. [36] who reported a maximum total Mn content of 1.41.0 mg kg^{-1} in surface soils of El-Gabal El-Asfar farm. Normally, Mn is a major crustal element and occurs in various rocks and minerals [6]. The total Pb content in four sites would result in potential risks, which is consistent with the results obtained by Elbana et al. [20] who reported a total Pb range of 7.0–273.0 mg kg^{-1} in surface soils of El-Gabal El-Asfar farm. Compared with Mn and Pb, total Zn content would pose potentially higher risks. This result is similar to that reported by Abdel El Lateef et al. [36] who reported a range of 69.7 to 166.0 mg kg^{-1} for total Zn in surface soils of El-Gabal El-Asfar farm.

Irrigation with different water sources caused spatial variations in the total metal contents. The highest metal contents in site 8 went hand-by-hand with the concentrations in the raw industrial effluents. Previous case studies reported higher metal contents in soils irrigated with industrial effluents than in those irrigated with sewage effluents [37] or groundwater [38]. Total metal content in soils was similar to that in waters, indicating the effect of irrigation on soil metal content [1]. This effect was depicted by correlation results that proved substantial contributions of irrigation to the total contents of Mn and Pb in soils. However, irrigation had a secondary role in the build-up of total Zn in soils, while the major source might be agrochemicals like fertilizers and pesticides [13].

The available metal contents pointed to increased risks for Mn and Zn (in all sites), and Pb (in seven sites). These findings are in line with those reported by Abdel-Shafy and Abdel-Sabour [35] who reported that the DTPA-extractable contents of Mn, Pb, and Zn in El-Gabal El-Asfar farm were 35.61, 11.74, and 43.78 mg kg^{-1}, respectively. The increased metal availability could be partially explained by the light soil texture. This interpretation could be confirmed by lower metal partitioning in the available fraction reported for other soil types under sewage irrigation. In the Nile Delta *TypicTorriorthent* soils, mean DTPA-extractable contents were 1.98 mg kg^{-1} for Pb [39] and 1.01 mg kg^{-1} for Zn [40].

Variations in soil properties and plant species might result in significant variations of the available metal contents [10]. Total and available metal contents showed dissimilar contents among the sites; however, they showed a uniform order. This means that the metal availability in soils depended on the total content [7]. Irrigation waters also regulated metal availability (especially Pb and Zn), which was indicated by correlation results. However, Mn availability was strongly associated with other factors with the lesser contribution of irrigation waters [10].

4.3. Metal Geo-Accumulation and Availability Ratio

Results of I_{geo} indicate that the soils were not polluted with Mn. Usually, soil pollution with Mn results from intensive industrial activities, especially heavy industries [41]. On the other hand, I_{geo} values for Pb and Zn point to elevated risks for Pb (in four sites) and Zn (in all sites). This demonstrates also that anthropic activities played significant roles in the accumulations of Pb and Zn in the soils. Out of the three metals, Zn had the highest I_{geo} values, which affirms that Zn was derived from point- and non-point sources

The three metals did not have the same availability in soils, probably due to variations in soil properties [9]. The SMLR affirms this explanation as soil pH, EC, $CaCO_3$, and silt explained 66% of the total variation of Zn AR, and these factors with the clay explained 86% of the total variation of Mn AR. The soil pH falls within the range of 7.12–7.85 that might increase the soluble species of $MnOH^+$ [42] and $ZnOH^+$ [43]. These species might be tightly retained by soil minerals [44] that had negative associations with ARs for Mn and Zn. Complexation with salt-derived anions and competition with salt-derived cations might increase ARs for Mn and Zn [45]. The Pb AR depended on OM, clay, and sand that explained 82% of the total variation. Soluble Pb-organic complexes commonly formed in alkaline soils [44] might dominate in soils and be preserved with increasing clay fractions but leached with increasing sand fractions.

Results of ARs prove that application of marginal-quality water to light-textured soils would result in increased metal toxicity. This hypothesis is supported by high Pb AR regardless of being a highly immobile element. In addition, lower ARs reported for metals in other Egyptian soils under constant sewage irrigation promote this conclusion. For instance, in *TypicHaplosalid* and *VerticTorrifluvent* soils in the Northern Nile Delta, Aitta et al. [46] reported that AR for Mn did not exceed 1%. Moreover, Abuzaid et al. [40] reported that ARs for Pb and Zn in *TypicTorriorthent* soils of the South-Eastern Nile Delta did not exceed 10 and 2%, respectively.

4.4. Multivariate Statistical Analysis

Soil pH and sand content had fairly narrow ranges, and thus they showed slight effects on metal contents. Unlikely, EC, OM, $CaCO_3$, silt, and clay effectively governed metal contents. Salt-derived anions and cations could preserve metals and increase their availability [45]. The metals were chiefly bound to soil minerals, which has been indicated by El-Demerdashe et al. [47] who reported greater partitioning of Mn, Pb, and Zn in the sulfide and carbonate fractions in El-Gabal El-Asfar soils. The $CaCO_3$ was involved in the retentions of Mn and Zn with a lesser extent to Pb. Hu et al. [48] reported that Zn and Pb in sewage-irrigated soils in China were mostly concentrated in the carbonate-bound fractions.

The clay minerals could adsorb Mn and Zn forming outer-sphere complexes that protect them from leaching to be readily available for plant uptake. Moreover, the Mn oxides might occur in the silt-sized aggregates [49]. The strong relations between total metals and their available fractions reflect the poor sorption ability of the soils that renders metals mostly readily available. This is because active sorption sites (clay minerals, Fe-Mn oxides, and humic substances) can strongly retain metals and restrict their mobility [14]. This may also point to a similar origin for total and available fractions [50]. Metal associations indicate the similar geochemical behaviors of Mn and Zn that greatly differed from that of Pb [51].

Results of the PCA affirm the conclusions depicted by correlation results. The PCA confirmed the similar geochemistry of Mn and Zn. Moreover, the PCA showed that Mn and Zn were completely related to soil inorganic components [52]. The soil-specific factors played substantial roles in controlling metal behaviors in soils. The predominance of Pb (total and available) solely in the same PC affirms the unique behavior of Pb in the studied soils [53]. Results of the HCA agreed well with those of correlation and PCA. The first and second sub-groups confirm the similar behaviors of Mn and Zn that were regulated by the clay content. The third and fourth sub-groups included variable shaving further contributions to Mn and Zn. This is indicated by the linkages of these two sub-groups with the first and second ones. The second main group contained OM and sand that controlled Pb transformations.

4.5. Metals in the Crop's Edible Parts

The metal contents in the crop's edible parts indicate that Mn was the predominant metal, followed by Zn and Pb. This goes normally with the elemental requirements as Mn and Zn are vital micronutrients for plant metabolism. However, excessive metal contents point to potential health risks. Application of marginal-quality waters caused a metal build-up in the soils, and thus accumulated in plant tissues. Wastewater irrigation in Egypt caused accumulations of Pb and Zn higher than the safe limits in broad bean seeds [54], wheat grains [55], and cabbage leaves [56]. However, lower Mn contents than in the current work were found, where the reported concentrations in the same studies were 26.0, 36.83, and 106.67 mg kg^{-1}, respectively. This might be a result of higher Mn contents in the investigated soils.

The crop's edible parts showed varied BAFs due to different soil metal contents and plant species [57]. The plants could uptake Mn and Zn but they were less efficient in accumulating them in the edible parts [30]. This indicates a set of barriers along plant bodies and limited translocation in both xylem and phloem [58]. Lower BAFs for Mn and Zn than unity were reported in wheat grains [55] and cabbage leaves [59] grown on sewage-irrigated soils. However, these species were able to uptake, translocate, and accumulate Pb in edible parts [30]. Higher Pb BAF than unity occurred in broad bean seeds [54], wheat grains [59], and cabbage leaves [56] grown on wastewater-irrigated soils.

The highest BAFs in cabbage leaves indicate the phytoextraction potential of cabbage plants. Brassica species have been proved a success for remediation of even high concentrations of metals, such as Pb and Zn [57,60]. Feleafel and Mirdad [61] reported that edible portions of lettuce and cabbage were the higher Pb accumulator compared with other vegetables grown on Egyptian polluted soils. The highest Pb BAF in all crops could explain that Pb uptake is a non-selective phenomenon and occurs through several mechanisms. Moreover, Pb^{2+} competes strongly with Mn^{2+} and Zn^{2+} in polluted soils [62].

5. Conclusions

This work investigated the long-term impacts of irrigation using raw or partially treated sewage effluents and contaminated groundwater on the accumulations of Mn, Pb, and Zn in *TypicTorripssament* soils and the crop's edible parts in El-Gabal El-Asfar. Irrigation with different water sources resulted in significant variations in soil metal concentrations (total and available). The highest metal contents occurred in soil irrigated with raw industrial effluents. The total metal content would pose increased risks for Pb (in four sites) and

Zn (in all sites), while the available contents showed elevated risks for the three metals. Soil properties played significant roles in controlling metal ARs. The I_{geo} values indicated no Mn pollution but showed elevated pollution risks for Pb and Zn. The ARs support the hypothesis that marginal-quality water irrigation in light-textured soils would increase metal severity. Both Mn and Zn had similar geochemical behaviors, while Pb shows different associations in soils. Metal concentrations in the crop's edible parts indicate potential health risks. The growing plant species could uptake, translocate, and accumulate Pb considerably in their edible parts. The highest metal BAFs in cabbage leaves demonstrate the phytoextraction potential of the *Brassica* species. Constructing small-scale wetland systems, biological filtration and using effective filters through irrigation can upgrade the marginal-quality water. Furthermore, in situ field remediation techniques through the application of metal stabilizer substances (such as humic substances) are recommended to mitigate metal accumulation in the crop's edible parts, and thus their possible transfer in the food chain. Otherwise, changing the crop pattern considering nonfood crops (bioenergy oil, bio-diesel fuel, and cellulose production crops) is an alternative promising strategy.

Author Contributions: Conceptualization: A.S.A. and M.E.F.; methodology: A.S.A., M.A.A.-S., A.F.A., H.A.F. and M.E.F.; software: M.A.A.-S., A.F.A. and M.E.F.; validation: M.A.A.-S., A.F.A., M.E.F. and H.A.F.; formal analysis: M.A.A.-S. and A.F.A.; investigation: M.A.A.-S., A.F.A. and H.A.F.; data curation: A.S.A, M.A.A.-S., A.F.A., H.A.F. and M.E.F.; writing—original draft preparation: A.S.A., M.A.A.-S., A.F.A., H.A.F., M.E.F. and A.S.; writing—review and editing: A.S.A., M.A.A.-S., A.F.A., H.A.F., M.E.F. and A.S.; visualization: A.S.A., M.A.A.-S., A.F.A., H.A.F., M.E.F. and A.S.; supervision: A.S.A., M.E.F. and A.S.; project administration: M.E.F.; funding acquisition: A.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The manuscript presented a scientific participation between the scientific institutions in two countries (Egypt and Italy). The authors are grateful to the scientific institutions of two countries for their support in carrying out the work. The authors would like to express their deep appreciation to Mohamed A.E. AbdelRahman, National Authority for Remote Sensing and Space Sciences (NARSS), for his valuable help in this work.

Conflicts of Interest: The authors would like to hereby certify that no conflict of interest in the data collection, analyses, and the interpretation in the writing of the manuscript, and in the decision to publish the results. Authors would like also to declare that the funding of the study has been supported by the authors' institutions.

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