Ecological Assessment of some Trace Elements Status in North Sinai

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ABSTRACT

The accumulation of trace elements in cropland soils poses a growing threat to sustainable agriculture development, and their dynamics throughout ecosystem components are among the most complicated issues to study and the most expensive to remediate. Hence, this paper proposes the forward mass balance modelling of any element as an approach to monitor and assess its status in cropland ecosystem, and to predict long-term results by computer simulations. Status of Fe, Mn, Zn, Cu, Ni, Mo and B in wheat and broad bean crops, irrigation water, fertilizers, and soil from North Sinai were investigated. The concentrations of the studied elements were within the permissible limits in most cases and beyond those limits in some cases. The seasonal input by irrigation and by fertilizers of each element was determined and the output by harvested crops and through leachate was estimated, all in units of g.ha^{-1} and g.kg^{-1}. Also, the baseline values of the studied elements in the study area were reported for future reference as well as the mathematical description of the proposed approach. The quantitative profiling indicated that the current land use has increased soil content of Mn, Zn, Ni, Mo and B. Irrigation water was identified as the cause of soil enrichment with B and Mo; manure was the main source of Ni and Zn; while both were the main sources of Mn. The equilibrium between the input and the output was found to be the status of Fe and Cu. Analysis of the results showed the need to an interactive multi-criteria risk assessment framework in which considers all ecosystem components and the local conditions.

Keywords: Mass balance, Monte Carlo simulation, Potentially hazard elements, Trace elements cycle

INTRODUCTION

Modern agriculture targeting intensive production has started what may be called agricultural pollution i.e. wastes, emissions, and discharges arising from farming activities; such risk increases in cases like crop production involving low-quality irrigation water and improper management, causing the degradation of the eco-system (Bruinsma, 2003). Of the pollutants arising from intensification pesticides and trace elements are the most complicated to study (Rickert, 1993) and the most expensive to remediate (Van Deuren *et al*., 2002). Generally, the problems associated with trace metal contamination have been well highlighted in the literature; including health hazard to human, and pollution to the natural resources (J?rup, 2003; Samia EL-Safy and El-Sayed, 2008; Moharem, 2016).

It is well known that the environmental fate of trace elements depends on the bioavailable content which usually has a wide variation. Trace elements in the environment may accumulate unnoticed to reach toxic levels, the soil environment is likely the most complex biological community. Soil contributes to a wide range of ecosystem services that are essential to the sustainable function of natural and managed ecosystems (Ragab *et al.* 2007, Filser *et al.* 2008).

Decisions on contaminated land management are based on various considerations, including plant toxicity and human health risks. Monitoring of soil quality and soil ecological assessment suffer from the absence of a commonly accepted framework that may act as a reference. From the technological perspective, the issues of wastewater treatment and remediation of trace elements contaminated soils can be solved (Terry and Banuelos 1999, Kurniawan *et al*. 2006, Pendergast and Hoek 2011). Applying such techniques efficiently so as to treat all the contaminated resources is currently not applicable and has many determinants. On the other hand, the impact of farm management system on both soil and crop product quality is a promising area for research. This area of work could provide applied recommendations on sustainable agricultural productivity, in addition to much scientific data that helps to deep understanding and modelling of different hazards processes in relation to impact on the ecosystem. Quantitative profiling of trace elements inputs to agricultural soils is necessary to determine the relative importance of different sources of every element (Nicholson *et al*. 2003, Mic? *et al*. 2006, Alloway 2013); whereas the quantitative investigation of trace elements outputs seems less common in the literature (e.g. Schnoor 1996). However, studies on both, trace elements inputs to soil and the environmental fate of these elements, are rare. The accumulation of such data within an accepted framework can lead to an accurate mathematical description of elements cycle.

The environmental hazard of trace elements pollution has many aspects. The main interests of the present study are human exposure, phytotoxicity, soil

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quality, and impact of leachate on groundwater quality. The possible source, pathway and sensitive recipient of each element will be considered; the essential measurements will be characterized, along with the related factors that affect trace elements transfer, seeking for parts that can be manipulated in order to minimize the risk and achieve the sustainability.

MATERIALS AND METHODS

Study area and field investigation

The research plan considered an investigation area in Sahl El Tina, between latitude 31°05´12″ to 30°50´20″ and longitude 32° 11´ 45″ to 32° 41´ 15″, the northwestern part of Sinai, Egypt (Fig. 1). The study area is irrigated with water through El Salam Canal. The area of land planned for agriculture is ≈20000 ha, of which ≈5000 ha are planted with the selected crops i.e. wheat (*Triticum aestivum*) and broad bean (*Vicia faba*). Surface (0-30 cm) and subsurface (30-60 cm) soil samples were collected from the selected sites. Regular samples of irrigation water and fertilizers were collected and stored. The "shoot mass" and "grain yields" of the two crops were determined by the end of the growing season. Plant samples were also collected and separated into straw/grains and straw/seeds, washed by tap water, then by distilled water, dried at 70 ˚C and grounded using stainless steel mill to fine powder before storing for chemical analysis. The air-dried soil samples were crushed, ground, and passed through a mesh sieve (2 mm) before storing for further analysis.

Fig. 1. Map showing the location of the study area

The configuration of the sampling locations was based on the conditioned Latin hypercube method (Minasny and McBratney 2006) using water quality and land use time as variables. Five subsections were identified. At each site, a number of samples were investigated. To predict the minimum number of soil samples required to estimate the average element concentration in the investigated environment, we employed the equation: $n = (ts/e)^2$ (Avery and Burkhart 1994) and the results of previous studies on the same area (Hafez *et al.* 2008, El-Sisi 2015) where; t is the t-statistic value selected for a given confidence level, s is the standard deviation, and e is the acceptable level of error or uncertainty. We assumed 100 degrees of freedom at 95% confidence level, the corresponding t value is 1.98, the standard deviation values of soil content of Mn and Zn were 0.82 and 0.48, respectively. For the sample mean to be within ± 0.5 mg/kg of the population mean, n values were found to be 11 and 4, respectively. Accordingly, each site was represented by 11 soil samples and a corresponding number of plant samples. Irrigation water and fertilizers samples were systematically collected at every application during the investigated season.

Laboratory work

Particle size distribution was performed using the pipette method for assessing soil texture for fractions less than 2 mm (Gee and Bauder, 1986). Values of pH and electrical conductivity (EC) were measured in 1:2.5 soil-water suspension and supernatant, respectively as described by Page *et al*. (1982). Soil organic matter (OM) was determined using the procedure of Walkely and Black as outlined by Page *et al*. (1982). These characterizations are presented in Table 1.

The Fe, Mn, Zn, Cu, Ni, Mo and B were extracted by 1 *M* NH_4HCO_3 in 0.005 *M* DTPA adjusted to a pH of 7.6 (Soltanpour, 1991), and the concentrations of elements were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) as described by Varma (1991). Total elements contents of the soil were digested with aqua-regia ($HCl:HNO_3$, 3:1) as described by Page *et al*. (1982), and measured using ICP-OES. Irrigation water examination was carried out as recommended in Standard Methods for The Examination of Water and Wastewater (APHA 2005). Plant samples were wet digested using H_2SO_4-H_2O_2 mixture according to Wolf (1982) and fertilizers samples were digested using HNO_3, HCl, and H_2O_2 as described in USEPA Method 3050B (2016). The acid digest was analyzed for Fe, Mn, Zn, Cu, Ni, Mo and B content using ICP-OES.

A leach test using an up-flow percolation column procedure was implemented in the laboratory to simulate the leaching behaviour of the element of interest. A 60 cm straight cylindrical column with an inner diameter of 5 cm, filled with 1500 g air-dried soil,

Table 1. Selected characteristics of the studied soil

Site No.	Land use time (year)	Soil depth (cm)	pH	EC (dS/m)	Particle size distribution (%)			Texture class	OM %
					Sand	Silt	Clay		
1	≈5	0-30	8.25	1.19	94.3	4.9	0.9	Sand	0.87
		30-60	8.15	2.23	92.4	5.1	2.5	Sand	0.53
2	≈5	0-30	8.23	1.05	88.9	3.3	7.8	Loamy sand	0.91
		30-60	8.41	2.18	95.0	3.6	1.5	Sand	0.36
3	≈10	0-30	8.12	2.66	36.1	39.4	24.5	Loamy	0.78
		30-60	8.34	1.65	62.9	19.9	17.2	Sandy loam	0.47
4	≈10	0-30	8.25	2.55	55.2	18.9	25.9	Sandy clay loam	0.75
		30-60	8.43	3.41	67.7	15.8	16.5	Sandy loam	0.69
5	≈10	0-30	8.65	3.60	57.6	16.1	26.3	Sandy clay loam	0.82
		30-60	8.59	5.32	72.4	5.7	21.9	Sandy clay loam	0.71

Table 2. The concentrations of elements in soil leachate (mg.L^{-1})

Soil No.	Fe	Mn	Zn	Cu	Ni	Mo	B
1	0.010	0.011	0.003	0.003	0.001	0.002	0.065
2	0.014	0.023	0.007	0.003	0.001	0.002	0.014
3	0.014	0.020	0.004	0.003	0.001	0.002	0.012
4	0.011	0.027	0.008	0.004	0.002	0.003	0.013
5	0.018	0.022	0.004	0.003	0.001	0.007	0.011
Mean	0.013	0.021	0.005	0.003	0.001	0.003	0.023

a 1 cm layer of silica sand was used at the bottom and at the top of the column. 0.001 *M* calcium chloride solution was used with a flow rate of 0.6 L.h^{-1}, entire solution volume was 5 L for each column to simulate field irrigation, five composite samples were used to represent the investigated sites. Each leachate was collected and chemically analyzed (Garrabrants *et al.* 2011) and the results shown in Table 2 were used in estimating leachate output.

Data analysis

Soil to plant element transfer factor (TF) was calculated as the ratio of element concentrations in plants and the corresponding concentrations in soil on dry weight basis. Daily intake of element (DI) was estimated according to the formula: $DI = C_{element} \times D_{food\ intake} / B_{average\ weight}$ where; $C_{element}$, $D_{food\ intake}$, and $B_{average\ weight}$ represent the element concentrations in plants (mg/kg), daily intake of food (kg) and average body weight (kg), respectively. Health risk indices (HRIs) for intake of elements through the consumption of food crops were calculated using the following equations: HRI = DI / RfD where; HRI is the human risk index through the consumption, DI is the daily intake of element (mg element/kg body weight/day) and RfD is the reference dose (WHO 2003).

Mass balance

The change in soil content of an element is the result of the net difference between input and output flows of that element. This can be mathematically expressed by the following equation: $G_t = (I_t - O_t)$ where; G is the change in total content of the soil, I is the integrated input and O is the overall output, all in (g.ha^{-1}) to a certain soil depth during a certain period of time (t).

Input: Such change contribution to the soil bioavailable pool is highly depending on soil chemistry phenomena, considering the dynamic of the element in the soil system, the equation is $D = (I - O)$ where D is the change in soil bioavailable content and *I* represents the modified input rates. The input rates are related to the form in which the element is added, and to soil chemistry phenomena which determine the fate of the added element, thus the equation represents *I* would be $I = f(I)$, any element concentration is the sum of sorbed amount to organic matter, clay, and primary minerals of the solid phase, and dissolved concentration in the soil solution; and since the distribution between solid and liquid phases in the soil is mainly controlled by surface adsorption–desorption reactions which are rapid and reversible so this function can be characterized by a thermodynamic equilibrium distribution such as Freundlich equation ($S = k_f \cdot C^b$) where; S is the sorbed concentration of the element in the solid phase. k_f is the distribution coefficient in L.kg^{-1} and b is dimensionless and typically ≤ 1 (Moolenaar 1997). For $b \approx 1$, the result is a linear sorption equation and as the adsorbed amount of the element in soil can be neglected if compared with the dissolved amount and assuming that all water content is soluble and mineral fertilizers content as well, the equations for their input rates - respectively- would be $I_w \approx$ Irrigation water application rate ($m^3.ha^{-1}$) . Element concentration in the applied irrigation water ($g.m^3$) and $I_f \approx$ Fertilizer application rate ($kg.ha^{-1}$) . Element concentration in the applied fertilizer ($g.kg^{-1}$). On the other hand, organic matter contribution to the soil bioavailable pool of an element is depending on its decomposition rate, therefore the equation for manure input rate could be $I_m \approx$ Manure application rate ($kg.ha^{-1}$) . Element concentration in the manure ($g.kg^{-1}$) . factor depends on decomposition rate. Janssen (1984) empirically determined a time-dependent factors for different organic materials, which were used in the calculations. Other sources (e.g. decompositions, rainfall, atmospheric depositions) of trace elements will be neglected in the calculations, because of its non-significance if compared with the agricultural usage during one growing season.

Output: The mass balance considers the amounts taken off the soil by the harvest and by leachate from the investigated layers, only plant parts which were harvested, the following equation was used to calculate output by plant: $O_h = C_p \, . \, Y$ where; C_p element concentration in plant part (g.kg), Y the yield of that plant part ($kg.ha^{-1}$) on dry weight basis. To estimate the output through leachate: $O_L = C_L. \, V_L$ where; C_L element concentration in leachate ($g.m^3$), V_L leachate volume (m^3). Leachate volume was estimated using the empirical formula described by Li and Gua (2011), $Q = (C_1A_1 + C_2A_2) \, . \, I \, . \, 10^{-3}$ where; Q Landfill leachate volume (m^3/d); A_1 Landfill operations area (m^2); A_2 Landfill cover area (m^2); C_1 Leaking landfill operation area coefficient (m^2); C_2 Coverage area landfill leaking coefficient; I The maximum annual or monthly precipitation at conversion value (mm/d).

In order to analyze the data, some default assumptions were chosen to be used after exploring the published literature regarding the required uncertainties. To estimate the potential hazard to human health through consumption of food crops grown in the area; we assumed that the intake of grains, bread, and other wheat-flour products vary from 2-4 servings/d to 8-10 servings/d, average of 4 was applied; intake of broad been seeds is 1-2 servings/d, only one serving per day was assumed; average body weight (bw) of adult is 70 kg; one serving weight is 50 g (WHO 2003). Also, Regarding the mass balance investigation of the studied elements, in the study area, during one season; the following hypothetical settings were assumed: (1) Pedological factors influence on the soil enrichment of the elements is very slight, thus, decomposition of soil mineral components considers insignificant input source in comparison with agricultural use input; also, rainfall (average of 80 mm/year) and other atmospheric depositions contribution to the soil pool of the studied elements is too little to be included as an input source (FAO 1998). (2) Leaching test results can be applied so as to estimate the leachate characteristics, a leaching coefficient of 0.2 was used (Li and Guo 2011, Garrabrants *et al.* 2001). (3) Manure contribution to soil bioavailable pool of the elements is correlated to its total content and decomposition rate, factors of (0.02-0.18) were considered (Janssen 1984). Based on field observations, erosion risk was also eliminated from the output pathways.

Computer simulation

The anticipation of long-term results was performed using Monte Carlo simulation, or probability simulation, which is a technique used to assess the impact of uncertainty in forecasting models (Mooney 1997), using random combinations of parameter values based on the results of the previous investigated variables. The parameter variables were described by normal probability on the basis of the Kolgomorov–Smirnoff test results. The simulation was produced in a Microsoft® Excel spreadsheet. In order to derive stable responses of the predicted values, the number of simulations was 10000. The model inputs are the range, average and standard deviation of the variables studied in the mass balance.

RESULTS AND DISCUSSION

Baseline of the investigation

The total and the DTPA-extractable contents of the investigated elements are shown in Tables 3 and 4.

The total content was found to be evenly distributed throughout soil surface and subsurface layers; whereas, the DTPA-extractable concentrations were found to be relatively higher, in cases of Fe, Mn and Cu, in the surface soil than their contents in the subsurface soil. Concentrations of Zn, Ni, Mo and B were evenly distributed among the surface and subsurface soil layers. Comparison between the soil content of the studied elements in different locations, taking into account the agricultural land use time, may indicate enrichment of the soil with the studied elements at some locations.

Concentrations of Fe, Mn, Zn, Mo and B in irrigation water ranged between 0.11-0.26, 0.01-0.71, 0.01-0.06, 0.003-0.018, and 0.05-0.17, respectively (Table 5). In 2006 the World Health Organization has published guidelines for the safe use of wastewater; the threshold levels of the studied elements for crop production are shown by the end of the table, these values are for water used on a continues basis at one site, with good irrigation practices i.e. 5000-1000 m^3.ha^{-1} per year. The concentrations of the investigated

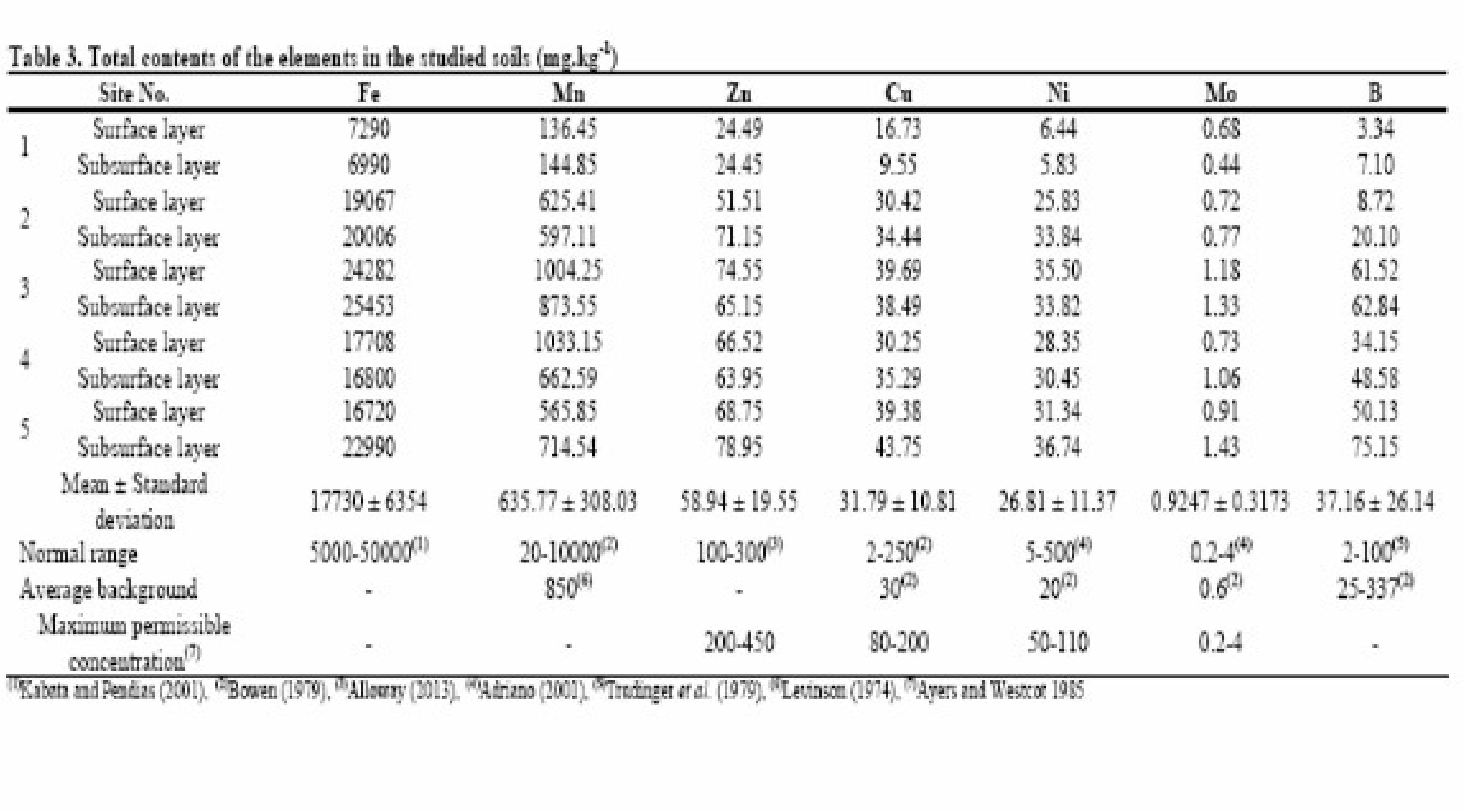
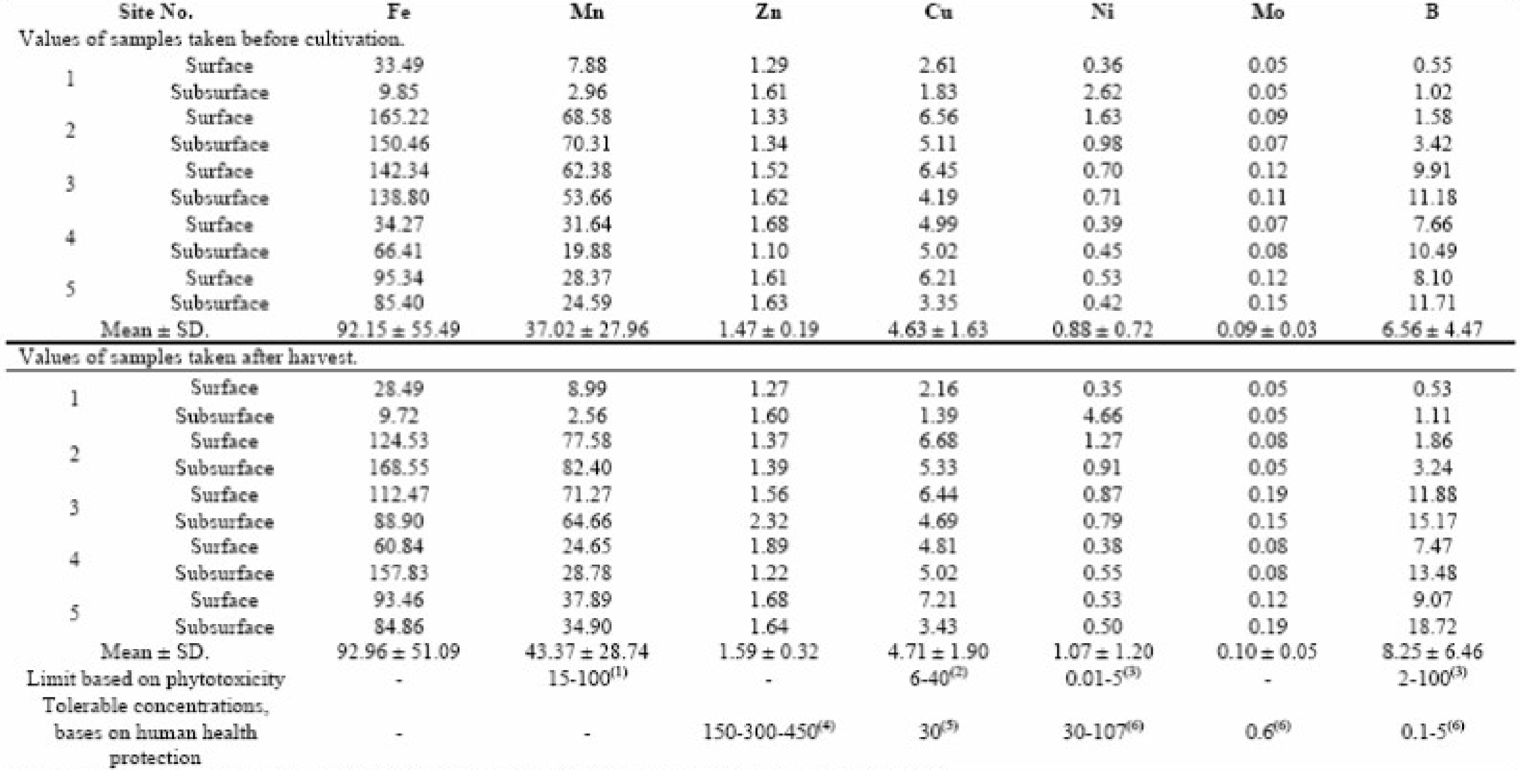


Table 3. Total contents of the elements in the studied soils (mg.kg^{-1})

Site No.		Fe	Mn	Zn	Cu	Ni	Mo	B
1	Surface layer	7290	136.45	24.49	16.73	6.44	0.68	3.34
	Subsurface layer	6990	144.85	24.45	9.55	5.83	0.44	7.10
2	Surface layer	19067	625.41	51.51	30.42	25.83	0.72	8.72
	Subsurface layer	20006	597.11	71.15	34.44	33.84	0.77	20.10
3	Surface layer	24282	1004.25	74.55	39.69	35.50	1.18	61.52
	Subsurface layer	25453	873.55	65.15	38.49	33.82	1.33	62.84
4	Surface layer	17708	1033.15	66.52	30.25	28.35	0.73	34.15
	Subsurface layer	16800	662.59	63.95	35.29	30.45	1.06	48.58
5	Surface layer	16720	565.85	68.75	39.38	31.34	0.91	50.13
	Subsurface layer	22990	714.54	78.95	43.75	36.74	1.43	75.15
Mean ± Standard deviation		17730 ± 6354	635.77 ± 308.03	58.94 ± 19.55	31.79 ± 10.81	26.81 ± 11.37	0.9247 ± 0.3173	37.16 ± 26.14
Normal range		5000-50000(1)	20-10000(2)	100-300(3)	2-250(2)	5-500(4)	0.2-4(4)	2-100(5)
Average background		-	850(6)	-	30(2)	20(2)	0.6(2)	25-337(2)
Maximum permissible concentration(7)		-	-	200-450	80-200	50-110	0.2-4	-

(1)Kabata and Pendias (2001), (2)Bowen (1979), (3)Alloway (2013), (4)Adriano (2001), (5)Trudinger *et al.* (1979), (6)Levinson (1974), (7)Ayers and Westcot 1985

Table 4. The amounts of available elements in the studied soils (mg.kg^{-1})



Site No.		Fe	Mn	Zn	Cu	Ni	Mo	B
Values of samples taken before cultivation.								
1	Surface	33.49	7.88	1.29	2.61	0.36	0.05	0.55
	Subsurface	9.85	2.96	1.61	1.83	2.62	0.05	1.02
2	Surface	165.22	68.58	1.33	6.56	1.63	0.09	1.58
	Subsurface	150.46	70.31	1.34	5.11	0.98	0.07	3.42
3	Surface	142.34	62.38	1.52	6.45	0.70	0.12	9.91
	Subsurface	138.80	53.66	1.62	4.19	0.71	0.11	11.18
4	Surface	34.27	31.64	1.68	4.99	0.39	0.07	7.66
	Subsurface	66.41	19.88	1.10	5.02	0.45	0.08	10.49
5	Surface	95.34	28.37	1.61	6.21	0.53	0.12	8.10
	Subsurface	85.40	24.59	1.63	3.35	0.42	0.15	11.71
Mean ± SD.		92.15 ± 55.49	37.02 ± 27.96	1.47 ± 0.19	4.63 ± 1.63	0.88 ± 0.72	0.09 ± 0.03	6.56 ± 4.47
Values of samples taken after harvest.								
1	Surface	28.49	8.99	1.27	2.16	0.35	0.05	0.53
	Subsurface	9.72	2.56	1.60	1.39	4.66	0.05	1.11
2	Surface	124.53	77.58	1.37	6.68	1.27	0.08	1.86
	Subsurface	168.55	82.40	1.39	5.33	0.91	0.05	3.24
3	Surface	112.47	71.27	1.56	6.44	0.87	0.19	11.88
	Subsurface	88.90	64.66	2.32	4.69	0.79	0.15	15.17
4	Surface	60.84	24.65	1.89	4.81	0.38	0.08	7.47
	Subsurface	157.83	28.78	1.22	5.02	0.55	0.08	13.48
5	Surface	93.46	37.89	1.68	7.21	0.53	0.12	9.07
	Subsurface	84.86	34.90	1.64	3.43	0.50	0.19	18.72
Mean ± SD.		92.96 ± 51.09	43.37 ± 28.74	1.59 ± 0.32	4.71 ± 1.90	1.07 ± 1.20	0.10 ± 0.05	8.25 ± 6.46
Limit based on phytotoxicity		-	15-100(1)	-	6-40(2)	0.01-5(3)	-	2-100(3)
Tolerable concentrations, bases on human health protection		-	-	150-300-450(4)	30(5)	30-107(6)	0.6(6)	0.1-5(6)

(1)Freeman and Hutchinson 1981, (2)Follett *et al.* 1981, (3)Adriano 2001, (4)do Monte 2007, (5) Ayers and Westcot 1985, (6)WHO 2006

Table 5. Irrigation water content of the studied elements (mg.L^{-1})

Site No.	Fe	Mn	Zn	Cu	Ni	Mo	B
1	0.02	0.02	0.02	<0.002	<0.0005	0.003	0.15
2	0.02	0.01	0.02	<0.002	<0.0005	0.003	0.06
3	0.01	0.01	0.06	<0.002	<0.0005	0.004	0.05
4	0.26	0.71	0.01	<0.002	<0.0005	0.003	0.17
5	0.11	0.44	0.02	<0.002	<0.0005	0.018	0.12
Recommended maximum concentration(1)	0.1-5	0.2-1.5	2	0.2	0.2	0.01	0.7-3

(1)WHO 2006

elements are still below the permissible levels except for Mn and Mo in sites No. 4 and 5. Accordingly, long-term use of such water might cause ecological risk when using for irrigation (Mohamed 2013).

Concentration of the elements in the mineral fertilizers and manure were all within the permissible limits (Table 6); yet, the excessive use of organic fertilizer under such arid climatic conditions, may lead to soil enrichment of potentially toxic trace elements (Moharem 2016).

Concentration of the studied elements in the different parts of the investigated plants and their yield are shown in Table 7.

Table 6. Concentration of the studied elements in the applied fertilizers (mg.kg^{-1})

Fertilizer	Fe	Mn	Zn	Cu	Ni	Mo	B	Application rate kg.ha^{-1}	
								Wheat	Broad bean
Superphosphate	6852	125.18	112.05	15.04	22.08	4.11	0.002	240	240
Potassium sulphate	650	21.50	7.65	0.91	0.01	0.12	0.001		120
Ammonium sulphate	904	33.46	4.89	0.85	3.05	0.34	0.001		240
Ammonium nitrate	840	29.52	8.12	2.10	2.01	0.41	0.001	480	
Manure	2040	302.25	204.17	93.10	14.80	4.42	39.80	15000	15000
Permissible concentration(1)	-	-	200-600	80-200	50-110	4-20	100		

(1)Brinton (2001)

Table 7. Plant contents of the studied elements (mg.kg^{-1} D.W)

Harvest	Site No.	Fe	Mn	Zn	Cu	Ni	Mo	B	Yield kg.ha^{-1}
Wheat grain	1	303	44	19	6	1.6	2.0	1.6	4410
	2	299	58	25	8	1.1	1.0	1.5	4301
	3	395	82	15	10	1.4	5.1	1.8	3593
	4	1053	99	21	8	3.1	1.0	4.6	4012
	5	282	60	26	8	1.0	1.0	2.3	4197
Wheat straw	1	655	38	15	5	1.7	1.6	2.4	4820
	2	875	84	117	9	5.5	2.6	13.2	4579
	3	570	79	62	9	2.3	1.8	20.9	3615
	4	984	213	15	6	2.2	3.0	65.1	4217
	5	555	44	76	6	3.2	1.6	2.5	4579
Broad bean seed	1	738	23	45	20	3.4	10.4	9.8	1495
	2	512	21	53	16	3.7	13.5	0.4	1484
	3	1260	33	68	22	3.9	7.3	0.7	1391
	4	1639	33	71	24	4.0	15.5	10.9	1418
	5	922	24	68	18	2.9	6.5	0.7	1181
Broad bean straw	1	863	40	23	17	2.8	2.1	3.0	1555
	2	509	19	17	11	2.0	2.5	6.4	1499
	3	707	44	22	33	2.5	8.6	16.2	1402
	4	1507	66	27	19	4.8	1.0	17.4	1446
	5	695	37	31	13	2.3	2.5	3.5	1196

Table 8 revealed that TF of Fe was notably high at sites 1 and 4 where the soil available content was relatively low; the linear relationship can be observed by excluding the values from those sites. The influence of irrigation water on Fe uptake was clear at site 4, such correlation is also confirmed statistically (Table 9), where the correlation coefficient (*r*) values ranged between 0.74 and 0.88 for the relation between water concentration and plant content of Fe. TF of Mn shows similar observation, where Mn soil to plant TF was highest at site 1 where the soil DTPA extractable Mn was low, whilst the significant relation was observed between water concentration and straw content of Mn. TF of Zn suggests that plant species is in dominant position as its (TF) values and (r) values showed no significant relation, that also was the case for Cu, Ni, Mo and B. However, such results in addition to the large range of transfer factors reported in the literature (Cui *et al.* 2004) show that the concentration of an element in soil is not the only factor influencing its transfer, plant physiology and irrigation water quality must be considered.

The data in Tables 7 and 10 show that elements concentration in edible plant parts and the corresponding reference daily dose were within the safe limits. The values of Health risk index refer to potential accumulation to hazard levels for Fe, Mn and Mo. Taking into account other exposure sources (e.g. water, other foods) adds Zinc and Nickel to this potential risk through consumption of such food, especially on long-term cases such as local farmers and their families. Iron is an essential element for most life on Earth, increased exposure to iron poses a risk only in some cases of heredity. Zinc, Copper and Nickel are among the current list of Priority Pollutants, according to USEPA. Nickel is carcinogenic, Manganese toxicity has been reported through dietary overexposure and is evidenced primarily in the central nervous system (WHO 2003).

Simulation results

Main addition sources and depletion ways of the studied elements through the investigated crop production processes are shown in Table 11, and presented in Figures 2, 3, 4, 5, 6, 7, and 8. During the investigated growing season. The predicted soil enrichment rates of the studied elements are summarized in terms of Statistics (Table 12).

Table 8. Soil to plant transfer factors (TF) of the studied elements

Plant part	Site No.	Fe	Mn	Zn	Cu	Ni	Mo	B
Wheat grain	1	14.0	8.0	13.3	2.9	1.1	38.1	2.0
	2	1.9	0.8	18.8	1.3	0.8	12.8	0.6
	3	2.8	1.4	9.8	1.9	1.9	44.7	0.2
	4	20.9	3.8	14.9	1.5	7.3	13.2	0.5
	5	3.1	2.3	15.9	1.7	2.1	7.6	0.2
Wheat straw	1	30.2	7.0	10.1	2.3	1.1	29.5	3.0
	2	5.5	1.2	87.6	1.5	4.2	33.3	5.3
	3	4.1	1.4	39.4	1.6	3.3	15.9	2.0
	4	19.6	8.3	10.7	1.2	5.1	39.5	7.2
	5	6.2	1.7	47.0	1.3	6.7	11.7	0.3
Broad bean seed	1	34.1	4.3	31.3	8.8	2.3	198.1	12.5
	2	3.2	0.3	39.9	2.7	2.8	173.1	0.2
	3	9.0	0.6	43.1	4.2	5.5	64.6	0.1
	4	32.6	1.3	51.2	4.8	9.6	204.0	1.2
	5	10.2	0.9	41.8	3.8	6.1	49.2	0.1
Broad bean straw	1	39.8	7.3	15.6	7.8	1.9	40.0	3.8
	2	3.2	0.3	12.4	1.8	1.5	32.1	2.6
	3	5.0	0.8	13.8	6.2	3.6	76.1	1.5
	4	29.9	2.6	19.0	3.7	11.5	13.2	1.9
	5	7.7	1.4	18.8	2.8	4.8	18.9	0.4
Range		1.8-39.8	0.3-8.3	9.8-87.6	1.2-8. 8	0.8-11.5	7.6-204.0	0.1-12.5

Table 9. Statistical correlation between element contents in plants and its content in both, irrigation water and soil

The investigated relation	Statistical parameter	Fe	Mn	Zn	Cu	Ni	Mo	B
Wheat grain content and water content	r	0.879	0.620	-0.664	-	-	-0.267	0.665
	r^2	0.772	0.385	0.440	-	-	0.071	0.443
Total output by grain yield and total input by water	r	0.891	0.737	-0.729	-	-	-0.290	0.719
	r^2	0.793	0.543	0.531	-	-	0.084	0.518
Wheat grain content and soil DTPA extractable	r	-0.355	0.213	-0.173	0.640	-0.374	0.243	0.471
	r^2	0.126	0.045	0.030	0.410	0.140	0.059	0.222
Wheat straw content and water content	r	0.553	0.704	0.154	-	-	-0.468	0.397
	r^2	0.306	0.495	0.024	-	-	0.219	0.158
Total output by wheat straw yield and total input by water	r	0.450	0.719	0.028	-	-	-0.410	0.423
	r^2	0.202	0.516	0.001	-	-	0.168	0.179
Wheat straw content and soil DTPA extractable	r	-0.074	0.039	-0.029	0.783	0.237	-0.332	0.397
	r^2	0.005	0.002	0.001	0.614	0.056	0.110	0.157
Bean seed content and water content	r	0.747	0.413	0.261	-	-	-0.629	0.873
	r^2	0.559	0.171	0.068	-	-	0.396	0.762
Total output by seed yield and total input by water	r	0.711	0.246	0.241	-	-	-0.704	0.865
	r^2	0.506	0.060	0.058	-	-	0.496	0.749
Bean seed content and soil DTPA extractable	r	-0.269	0.003	0.421	-0.051	-0.039	-0.698	-0.263
	r^2	0.072	0.000	0.177	0.003	0.002	0.487	0.069
Bean straw content and water content	r	0.869	0.721	-0.143	-	-	-0.087	-0.039
	r^2	0.755	0.520	0.021	-	-	0.008	0.001
Total output by bean straw yield and total input by water	r	0.869	0.721	-0.143	-	-	-0.087	-0.039
	r^2	0.755	0.520	0.021	-	-	0.008	0.001
Bean straw content and soil DTPA extractable	r	-0.645	-0.477	0.633	0.048	-0.462	0.458	0.602
	r^2	0.416	0.228	0.401	0.002	0.214	0.210	0.362

r: correlation coefficient, r^2 : coefficient of determination.

Table 10. The selected criteria to estimate the health risk of consuming edible parts of the investigated crops

Value description		Fe	Mn	Zn	Cu	B	Ni	Mo
Wheat grain content (mg.kg^{-1})	range	282-1053	43.5-99	15.4-25.75	6.35-9.85	1.5-4.6	1-3.05	1-5.05
	mean	466	68.6	21.25	7.85	2.36	1.61	2.01
Broad bean seed content (mg.kg^{-1})	range	512-1639	20.5-33.1	45.3-71.2	15.9-23.9	0.4-10.9	2.9-4	6.5-15.5
	mean	1014	26.8	61.02	19.96	4.5	3.58	10.64
Limit in food(1) (mg.kg^{-1})		425	91	99.4	73.3	-	67	-
Wheat product's daily intake (mg/kg bw)	range	0.8-3.0	0.12-0.28	0.04-0.07	0.02-0.03	0.004-0.013	0.003-0.009	0.003-0.014
	average	1.3	0.196	0.061	0.022	0.007	0.005	0.006
Broad bean daily intake (mg/kg bw)	range	0.37-1.17	0.015-0.024	0.03-0.05	0.011-0.017	0.0003-0.0078	0.002-0.003	0.005-0.011
	average	0.7	0.02	0.04	0.014	0.003	0.003	0.008
Reference dose(1) (mg/kg bw/day)		0.7	0.14	0.3	0.5	0.2	0.02	0.005
Health risk index	Wheat	2.86	1.76	0.23	0.05	0.05	0.31	1.84
	Broad bean	1.03	0.14	0.15	0.03	0.02	0.13	1.52

Joint FAO/WHO Expert Committee on Food Additives 2001

Table 11. Major input sources and output pathways in the studied season (g.ha^{-1})

Value description		Fe	Mn	Zn	Cu	Ni	Mo	B
Irrigation water, input	Range	99-1798	88-4943	74-418	-	-	18-126	336-1183
	Average	590	1661	182	7	1.75	43	749
Based on an application rate of 7000 m^3.ha^{-1}, and the data in Table 5, where 0.5 x detection limit was used to calculate averages of Cu and Ni.								
Fertilizer, input	Mineral	1994	42	30	4	6	1	0
	Manure	3045	1620	487	143	17	5	47
Wheat, output	Range	3480-8378	375-1297	146-644	53-72	13-30	11-25	18-292
	Average	5074	668	336	62	20	17	96
Broad bean, output	Range	1522-4504	59-141	103-139	37-77	6-13	11-24	5-41
	Average	2627	96	117	54	9	20	20
Leachate, output	Range	13-25	15-38	4-11	3-6	1-3	2-10	15-91
	Average	19	29	7	4.4	1.4	4	32

Table 12. Statistical parameters of the simulation results (g.ha^{-1} per season)

Parameter	Fe	Mn	Zn	Cu	Ni	Mo	B
Minimum	-4782	-2605	-152	20	26	-100	42
Maximum	6771	8029	859	155	60	150	1369
Mean	556	2623	356	88	41	28	676
Std Dev	1489	1317	129	18	4	33	170

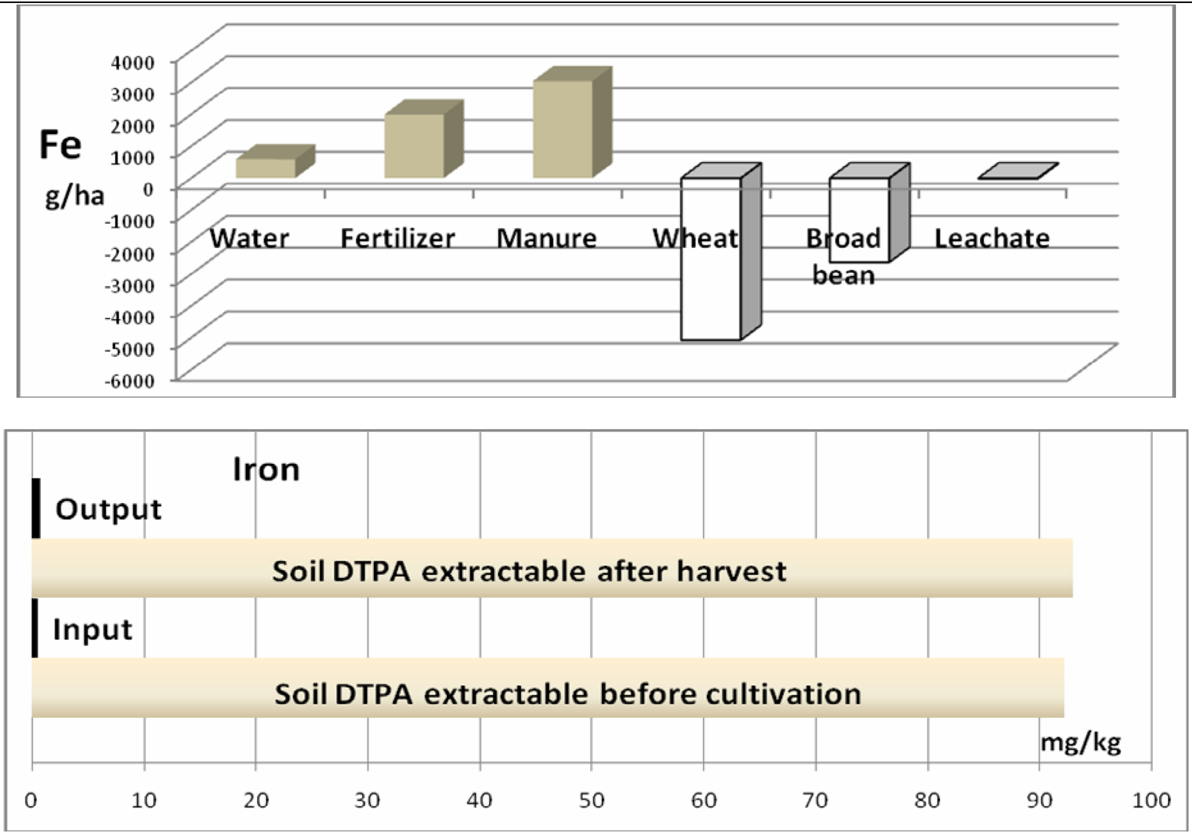


Fig. 2. Illustration of the mass balance of Iron

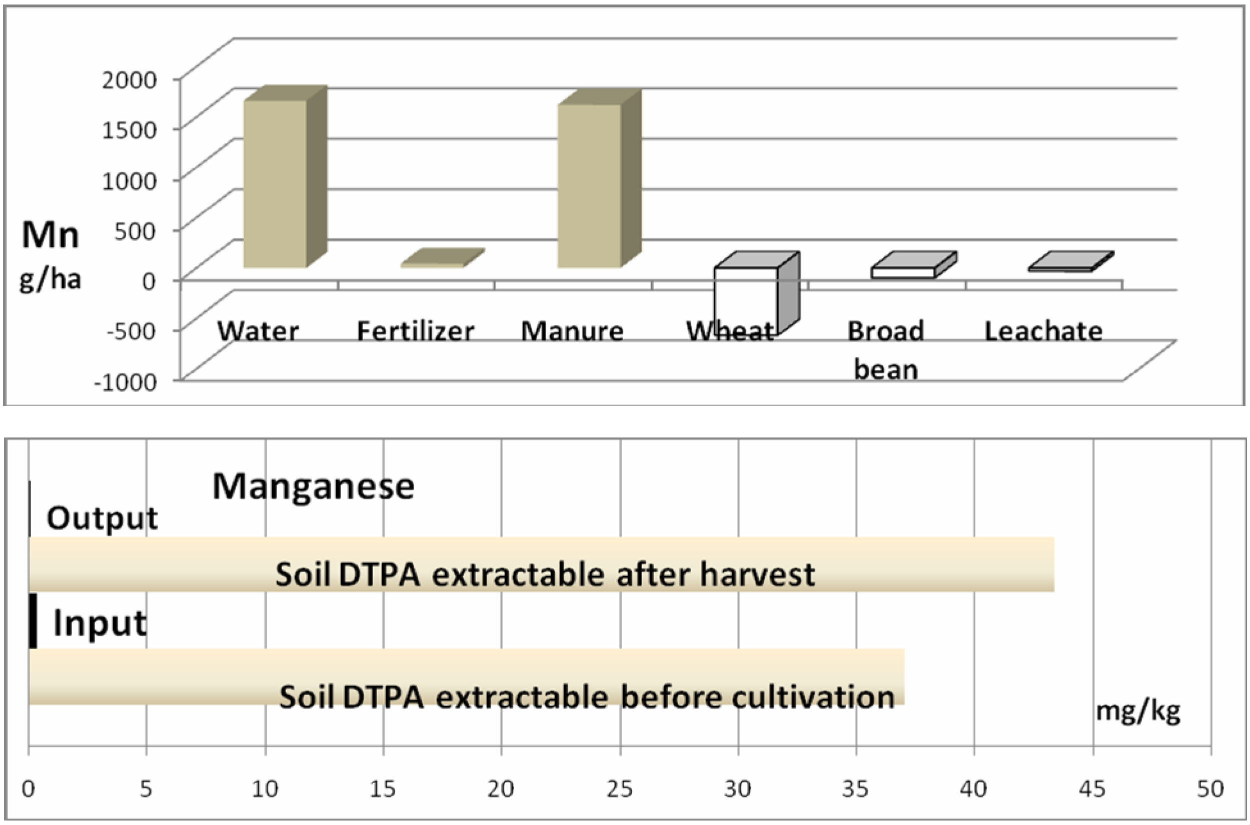


Fig. 3. Illustration of the mass balance of Manganese

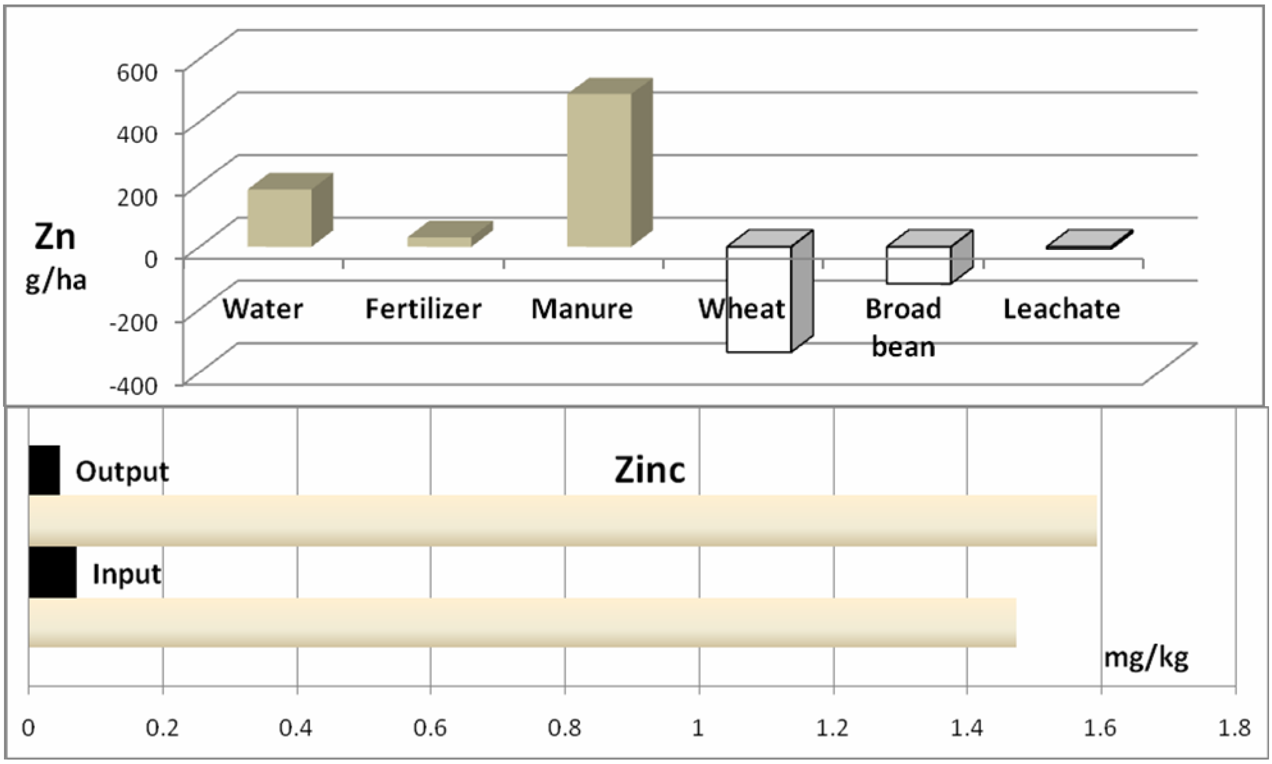


Fig. 4. Illustration of the mass balance of Zinc

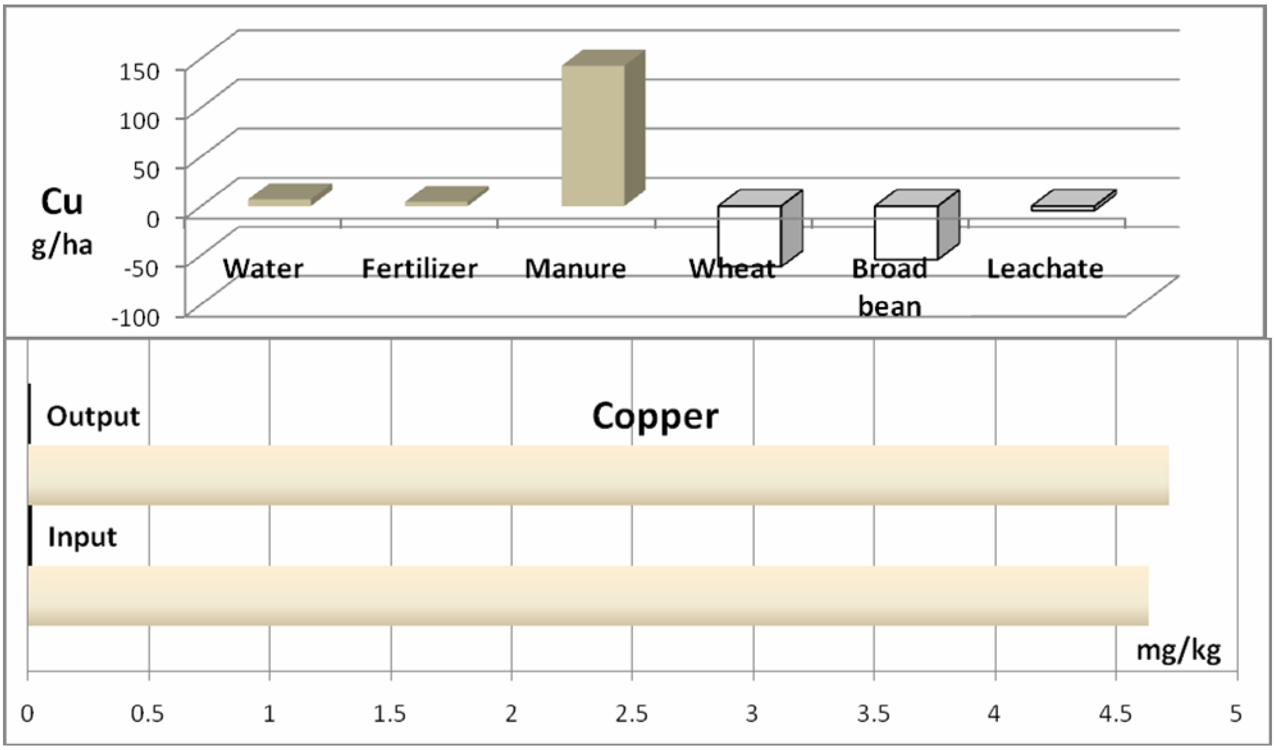


Fig. 5. Illustration of the mass balance of Copper

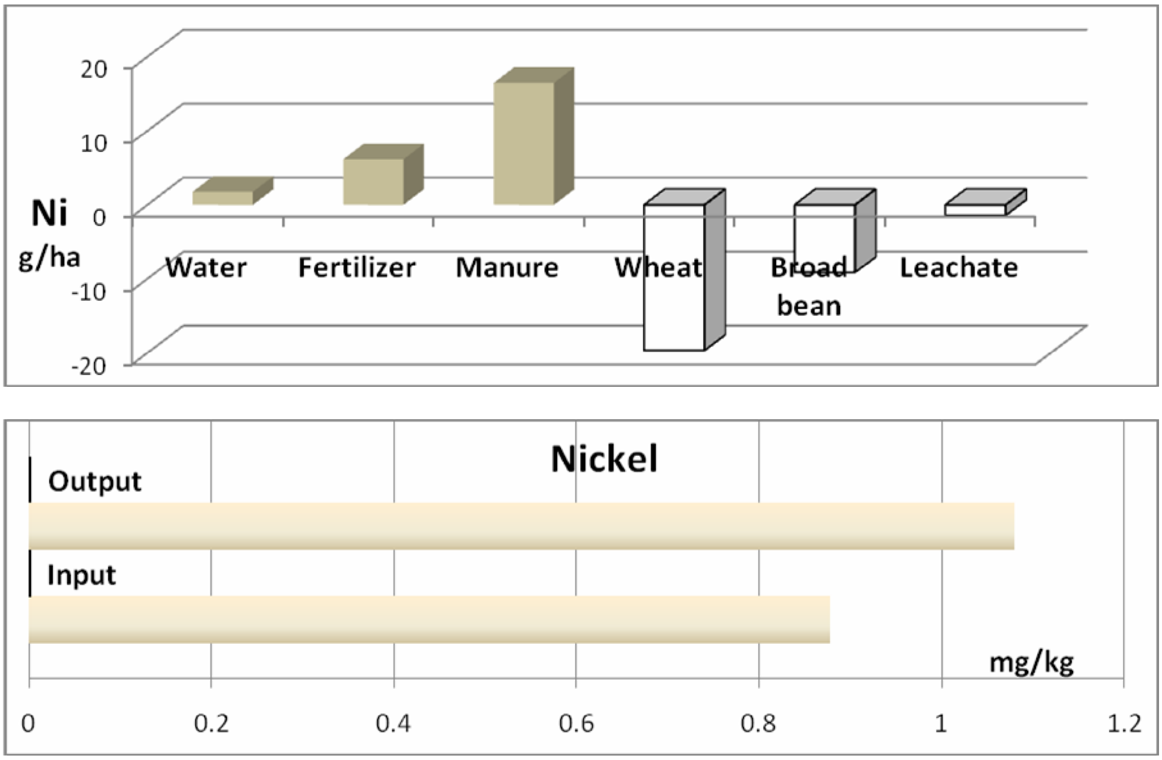


Fig. 6. Illustration of the mass balance of Nickel

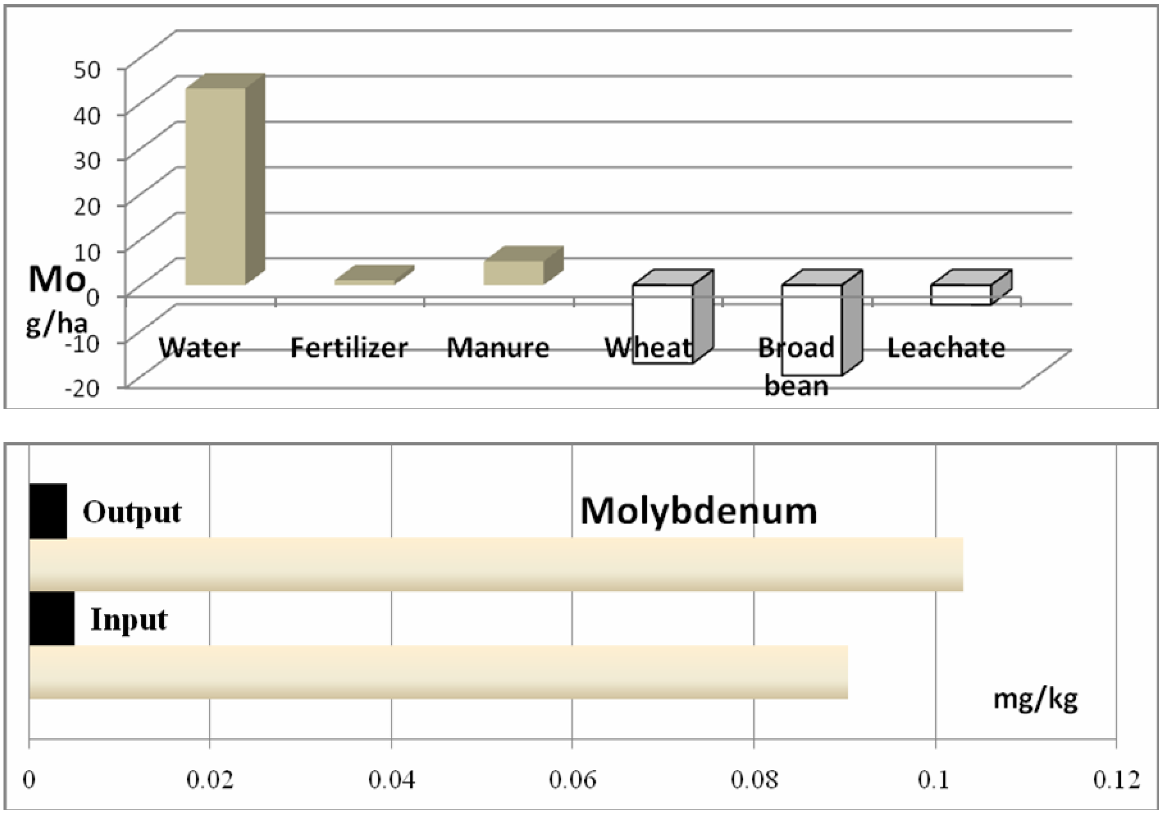


Fig. 7. Illustration of the mass balance of Molybdenum

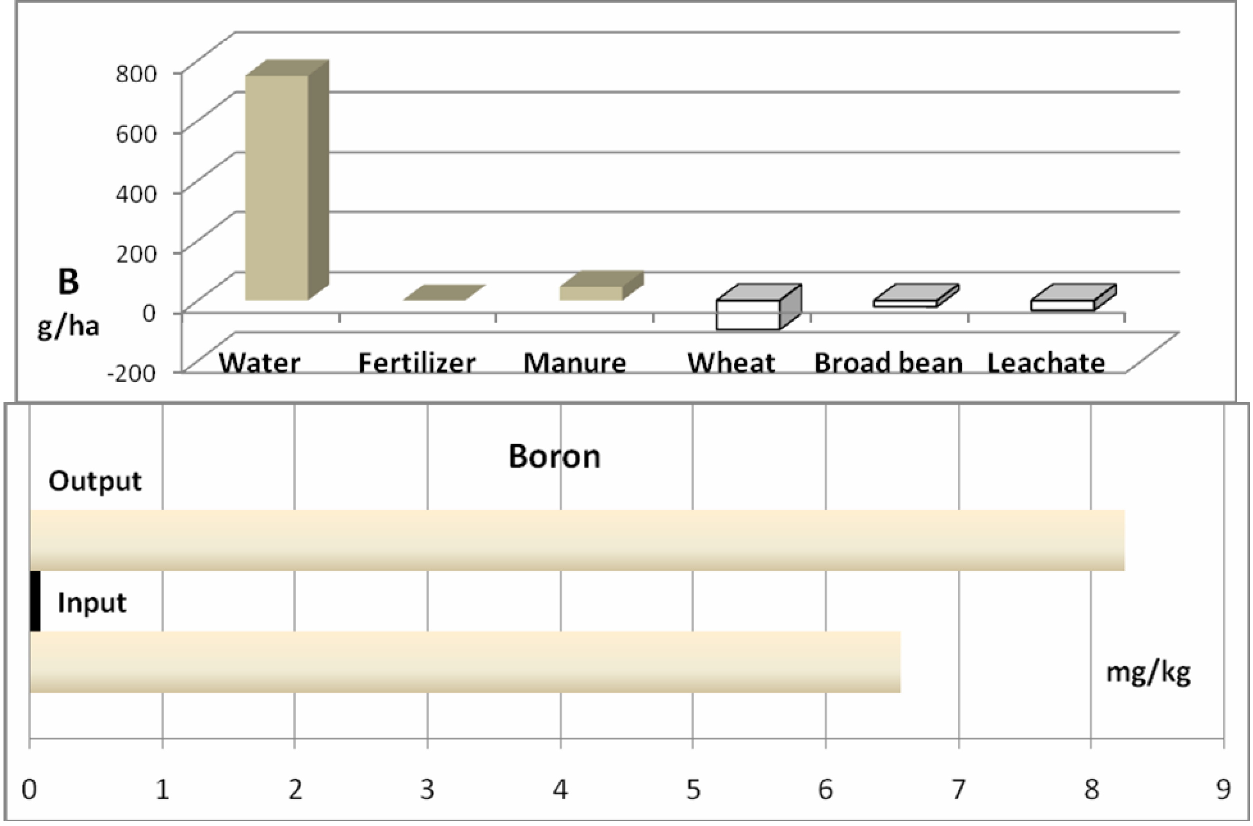


Fig. 8. Illustration of the mass balance of Boron

Iron

The simulations show an enrichment probability of 65%, the predicted 90th percentile was 2458.57 g.ha^{-1} per season (i.e. 90% of the results are less than 2458). Sensitivity analysis show that the prediction model for Fe status is significantly correlated to plant uptake followed by irrigation water content.

Manganese

The probability of Mn enrichment is 98%, 90th percentile value was 4322 g.ha^{-1}, with high sensitivity to irrigation water quality, followed by plant uptake then manure content of the element.

Zinc

The simulation of Zn input/output suggests a 100% enrichment probability. 90th percentile is 524 g.ha^{-1}, Zn prediction model was found to be most sensitive to plant uptake and water content evenly.

Copper

Copper mass balance prediction model reveals a 100% enrichment probability. 90th percentile value was 110 g.ha^{-1}, sensitive to manure content then plant uptake.

Nickel

The simulation show a 100% probability of enrichment. 90th percentile is 47 g.ha^{-1}, prediction is first correlated to mineral fertilizers content of the element, then irrigation water content.

Molybdenum

80% enrichment probability was predicted, 70 g.ha^{-1} is the 90th percentile seasonal enrichment rate, sensitive to irrigation water quality.

Boron

Boron mass balance simulation shows a 100% probability of enrichment. The predicted 90th percentile was 892 g.ha^{-1}, most sensitive to water content followed by plant uptake.

CONCLUSION

The study of trace elements flux through ecosystem components is necessary for successful ecological evaluation. Complexity of the system and the influence of soil chemistry, irrigation water quality, and plant species, lead to the importance of the site specific assessment including mass balance. Risk can be reduced through a better linking between the transfer processes and the dominant factors.

Analysis of the results showed the need to an interactive multi-criteria risk assessment framework in which considers all ecosystem components and the local conditions. The Monte Carlo simulations allowed the effects of parameter uncertainty to be estimated. The accumulation of the proper data would help to accrue modeling of the trace elements cycle in the ecosystem.

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الملخص العربي

تقييم حيوي بيئي لحالة بعض العناصر الدقيقة في شمال سيناء

أسامة محمد عبد المطلب و شريف محمود إبراهيم و شيرين شحاتة مريد

استعمال مياه منخفضة الجودة لري المحاصيل وفي ظل سوء الإدارة، يمثل خطر يزحف ببطء مهددا استمرارية التنمية الزراعية. ويعتبر انتقال وتراكم العناصر الصغرى من أكثر الأمور تعقيدا في هذا الشأن، ولذا تقترح هذه الدراسة نهج مبسط لرصد و تقييم الأخطار البيئية المحتملة وأهم العوامل المؤثرة في نظام التربة المعقد. تم دراسة حالة سبعة عناصر (حديد، منجنيز، زنك، نحاس، نيكل، موليبدنم، بورون) في أراضي مزروعة بالقمح و الفول البلدي بمنطقة سهل الطينة – شمال سيناء، و تبع ذلك تقييم الأخطار المحتملة لكل عنصر باستخدام المقاييس المناسبة. وجدت تركيزات العناصر في الحدود الآمنة إلا في حالات قليلة. تم تقدير المضاف من كل عنصر بواسطة مياه الري و الأسمدة المستعملة خلال الموسم وكذلك المستنفذ بواسطة النبات والرشح و تم تقدير القيم المرجعية للعناصر في منطقة الدراسة. أظهرت النتائج أن تراكم عناصر المنجنيز والزنك والنيكل والموليبدنم والبورون في التربة كان نتيجة النشاط الزراعي، وكانت مياه الري المصدر الرئيسي لعنصري الموليبدنم والبورون والسماد العضوي مصدر النيكل والزنك. بينما ساهم كل من مياه الري السماد العضوي بنصيب متساو في تراكم المنجنيز. الحديد و النحاس وجد أنهم في حالة توازن بين المدخلات و المخرجات. تحليل الأخطار البيئية المحتملة أكد ضرورة التقييم المتكامل والحاجة إلى نظام رصد أرقام مرجعية مناسبة للمنطقة وظروفها.