CHANGES IN FRACTIONS OF SOME MICRONUTRIENTS AS AFFECTED BY CONTINUOUS CROPPING AND LONG-TERM APPLICATION OF MINERAL AND ORGANIC FERTILIZER.

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ABSTRACT

Soil samples were collected from on-going long-term experiment at Bahtim area, Kalubia Governorate, Egypt, to study the distribution of various forms of iron, manganese, zinc and copper. The optimum dose-based treatments selected for the study were N(15kg/ fed), N(15kg/fed)-P, N(15kg/ fed)-P-K,N(30kg/fed),N(30kg/fed)-P,N(30kg/fed)-P-K,N(60kg/fed), N(60kg/fed)-P, N(60kg/ fed)-P-K, organic (FYM), and control (no fertilizer or manure). Differnet fractions of Fe, Mn, Zn and Cu in the soil were sequentially extracted using different extractants. DTPA- extractable Fe, Mn, Zn and Cu in soil increased in all treatments compared to control as a result of continuous cropping and fertilizer application. The amount of Fe, Mn, Zn and Cu in different fractions revealed the following order: exchangeable < organically bound < manganese oxides < crystalline iron oxides < amorphous iron oxides< residual. DTPA-Fe showed significant correlations with all Fe fractions except manganese oxides-Fe. DTPA- Mn showed significant correlations with all Mn fractions except crystalline iron oxides- Mn. DTPA- Zn showed significant correlation with all fractions of Zn except both exchangeable and organic matter- Zn. As for, DTPA- Cu results showed a significant correlation only with organic matter- Cu.

Keywords: fractions of Fe, Mn, Zn and Cu, long-term experiment, sequential extraction.

INTRODUCTION

Intensive cropping with nutrient exhaustive high yielding varieties coupled with the use of high levels of nitrogen, phosphorus and potassium (NPK) fertilizers for enhancing food production have depleted micronutrient contents in soil. Increased removal of micronutrients caused by higher yields of cultivars without adding micronutrient fertilizer has already made micronutrients a yield limiting factor (Takkar, 1996). Finite native reserves of these nutrients in soil are shrinking and becoming exhausted at a much faster rate in the absence of their replenishment. The deficiency of micronutrients in soil varies with different cropping systems because some crops or their varieties remove from the system larger quantities of particularly labile fractions or decrease their availability to the plant through a number of mechanisms. A part of the removed nutrient is recycled back as biomass in the form of roots, stubbles, leaves and so forth. Differences in the nature of root exudates, root activity, and management practices for each crop could lead to diverse changes in the microbial population and the chemical as well as the biochemical reactions. All these factors exert a strong influence on the various labile fractions or chemical pools of micronutrient cations in soil, which are assumed to have attributes of concentration, size, turnover rate, and equilibrium with other pools (Viets, 1962).

Long-term experiments (LTEs) are vital tools to examine the sustainability of modern intensive cropping. These experiments provide

valuable information regarding the impact of continuous application of fertilizers in varying combinations of nutrients on soil health and crop productivity and can be used for precise monitoring of changes in soil fertility and trends in yield levels achieved. (Behera *et al.,* 2009a).

The distribution and availability of heavy metals in soils is important when assessing the environmental quality of an area, since increased concentrations in soil, water and plants pose a serious threat to human and animal health. The origin of heavy metals in the soil is mainly geochemical (originating from the parent substrate) and partly anthropogenic (various sources of pollution). The soil solution considerably contains small amounts of the microelements, thus heavy metals occur in soil in water-soluble, exchangeable forms, bound to specific sites of the organic and inorganic soil components and in the structure of primary and secondary minerals (Jelic *et al.*, 2011).

The current study through some light on the changes that might take place in distribution of some micronutrient elements due to cropping and long term fertilization treatments.

MATERIALS AND METHODS

The long-term experiment (LTE) is being carried out at Bahtim area, kalubia Govermorate, Egypt since 1912, the treatments comprising different nutrient management options imposed in a randomized block design with three replicates for each one. Three rotations of cropping system have been used, 1 year rotation (cotton yearly), 2 years rotation (1.cotton, 2. Wheat then corn.), 3 years rotation (1. Cotton, 2. wheat than corn, 3. Wheat then corn). For this investigation eleven treatments, as detailed below, have been chosen from the one year rotation:

1. N_{15} : 15 nitrogen unit/ fed.
2. N_{15}-P : 15 nitrogen unit/ fed. +19 unit P_2O_5/fed.
3. N_{15}-P-K:15nitrogen unit/ fed.+19 unit P_2O_5/fed.+ 48 unit K_2O/fed.
4. N_{30} : 30 nitrogen unit/ fed.
5. N_{30}-P : 30 nitrogen unit/ fed.+19 unit P_2O_5/fed.
6. N_{30}-P-K:30 nitrogen unit/ fed.+19 unit P_2O_5/fed.+ 48 unit K_2O/fed.
7. N_{60} : 60 nitrogen unit/ fed.
8. N_{60}-P : 60 nitrogen unit/ fed. +19 unit P_2O_5/fed.
9. N_{60}-P-K:60 nitrogen unit/ fed. +19 unit P_2O_5/fed.+ 48 unit K_2O/fed.
10. Organic (20 m^3/ fed. farmyard Manure).
11. Control (unfertilized and unmanured).

The treatments included N_{30} and N_{60} have taken place since 1986.

Urea (46%)was used as a nitrogen fertilizer.

Trip superphosphate(46% P_2O_5)was used.

Potassium sulphate (48% K_2O)was applied.

Soil samples were collected using a screw-type auger from 0 to 15 cm depth, the subsamples were collected from four randomly chosen points in each plot and mixed thoroughly to obtain a representative soil sample. The samples were air dried, ground in a wooden pestle and mortar, and passed through a 2 mm sieve. The soil samples were analyzed for different forms of

iron, manganese, copper and zinc following the fractionation scheme developed by Shuman (1985) (Table,1).

The extractions were conducted in 50 mL polypropylen centrifuge tubes. Between each successive extraction, the supernatant was obtained by centrifuging at 3000 rpm for 15 mim and filtering.The residue concentration of the metal was determined after digestion of the soil with sulfuric- perchloric- nitric acids (H_2SO_4- $HClO_4$-HNO_3) mixture. The concentrations of Fe, Mn, Zn and Cu in the supernatant were measured by an atomic absorption spectrophotometer.

Table(1): Sequential extraction method for Fe, Mn, Zn and Cu in soil.

Step	Fraction	Solution ext.	Soil (g)	Solution (mL)	Conditions
1	Soluble and exchangeable	1 M Mg(NO$_3$)$_2$ (pH 7)	10	40	Shaking for 2 h
2	Organically bound occluded	0.7 M NaOCl (pH 8.5)	10	20	Boiling on water bath,for 30 min. stir occasionally
3	Mn oxides	0.1 M NH$_2$OH-HCl (pH 2)	1	20	Shaking 30 min
4	Amorphous iron oxides	0.2 M (NH$_4$)$_2$C$_2$O$_4$-H$_2$O 0.2 M H$_2$C$_2$O$_4$ (pH 3)	1	50	Shaking for 4 h in the dark
5	Crystalline iron oxides	Solution as for step 4 plus 0.1 M ascorbic acid	1	50	Boiling on water bath, for 30 min, stir occasionally

Soil analysis :
- Organic matter, soil pH, electrical conductivity and $CaCO_3$ content were determind according to Page *et al.,* (1982). Available nutrients were determined according to Cottenie et al., (1982).
- Available micronutrients; Fe, Mn, Zn and Cu were extracted by DTPA according to Lindasy and Norvell (1978) and determined using atomic absorption spectrophotometer.

statistical analysis :
- All obtained data were subjected to the statistical analysis of correlation and regression according to Snedecor and Cochran (1980).

RESULTS AND DISCUSSION

Major characteristics of the experimental soil.

Soil reaction (pH), electrical conductivity (EC), CaCO**₃** content, organic matter (OM), Fe, Mn, Zn and Cu extractable DTPA,available content of nitrogen, phosphorus and potassium are presented in Table (2).

The pH, EC, CaCO**₃** content and O.M of the soil varied from 7.91 to 8.22, 0.74 to 1.89 dS/m^{-1}, 4.86 to 7.20 % and 2.05 to 2.92%, respectively. These values not show any constant trend due to different treatments. Continuous cropping and fertilization resulted in a decrease in organic matter content by 0.87% from the organic treatment value to the (N_{30}) treatment. It is probably because of the need-based irrigations given with the existing good-quality irrigation water at the farm. No acid-forming fertilizers have been used during these years, and therefore no change in soil reaction occurred. Intensive cropping with even moderate supply of fertilizers might resulted in continuous return/ addition of greater amount of roots/stubbles to the soil, and this appears to be largely responsible for maintenance or imporvement of organic matter status. This view supported by some other workers also (Bellaki and Badanur, 1997).

Available DTPA - Fe content increased in all treatments compared to the control treatment level 5.18 mg/kg, as a result of continuous cropping and fertilization for many years. The magnitude of increase ranged from 0.09 to 5.33 mg/kg.

The available Fe content reminded higher than the critical level of Fe deficiency of 4.5 mg/kg in all the treatments even after continuous years of cropping. Available DTPA Mn in surface soil higher in case of the mineral and organic fertilizer treatments compared with the control treatment, however, it also remained higher than the critical level of Mn deficiency of 2.0 mg/kg. Continuous cropping and fertilizer use resulted in increases in available DTPA Zn in all the treatments as compared to control, as for Cu, there was no difference among the treatments with respect to DTPA extractable Cu in soil. It provides ample insight to the fact that different nutrient management options had no impact on Cu availabillity in this soil.

The DTPA-extractable Fe, Mn, Zn and Cu increased in all treatments as compared to control. This may be due to continuous addition of these nutrients as contaminants through fertilizers in spite of the continuous uptake by the crops over the years in addition to their no replenishment in the from of fertilizers. This finding is in agreement with the results obtaind by Li et al., (2007).

Inorganic P fertilizer may contain some micronutrients as impurities. The average concentrations of B, Cu, Fe, Mn, Mo and Zn in triple superphosphate were 174, 12.7, 12037, 376, 9.88 and 94.1 mg/kg, respectively. The results clearly indicate that relatively small additions of micronutrients were added over the long period of these experiments, thus explaining why treatment differences did not exist for total micronutrients in soil (Richards et al., 2011).

Changes in various fractions of micrnutrient in soil.
Iron

The amounts of soluble and exchangeable Fe in soil were in the range from 2.1 to 3.52 mg/kg soil, under different treatments (Table 3), showing no specific trend. The values of iron bound to organic matter were markedly increased by the different treatments as compared to the control treatments where the highest values existed with (N_{15}- P-K) and (N_{30} –P–K) treatments (6.03 mg/kg soil). Iron occluded by manganes oxides showed slight, increases due to the used treatments as compared to the control where the highest values existed with (N-P-K) treatments. Amorphous iron oxides fraction under various treatments did not follow any definite trend. The amount of Fe in the crystalline iron oxides fraction increased with increasing the rate of nitrogen fertilizer, the highest value was obtained due to (N_{60}-P-K) treatment (5926 mg/kg). The residual form of Fe contstitutes the dominant portion of Fe in all the soil treatments similar where obtained by Kuo et al., (1983).

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Manganese

Neither exchangeable Mn nor organically bound Mn showed any specific trend due to the different fertilization treatment (Table 4). Contents of exchangeable Mn varied from 1.09 to 2.95 mg/kg, whereas organically bound Mn value ranged from 2.86 to 5.45 mg/kg. The fraction of Mn occluded by manganese oxides also showed no definite trend where its highest amount was achieved due to the (N_{60}-p-k) treatment (16.3 mg/kg). Manganese predominantly existed in the amorphous iron oxides and crystalline iron oxides fractions due to all the fertilization treatments. Where its values ranged from 309 to 414 mg/kg, and 296 to 386 mg/kg, respectively. The residual form of Mn showed declining trend by decreasing nitrogen fertilizer rate from N_{60} to N_{15} treatments.

Zinc

Continuous cropping and fertilizer application for years resulted in fluctuating contents of exchangeable, organic matter bound and manganese oxides fractions of Zn in soil. Treatment and time affected these fractions which varied from 0.98 to 2.15, 3.06 to 4.84 and 45.15 to 99.0 mg/kg, respectively, (Table 5). Application of N fertilizer from 15 to 60 unit/fed increased all the fractions of Zn. The amounts of Zn in the different fractions revealed the following order: exchangeable < organically bound< manganese oxides < crystalline iron oxides < amorphous iron oxides < residual.

Copper

The forms of Cu in soil samples collected from the different treatments, are given in Table(6): The exchangeable Cu concentration varied from 0.92 to 2.08 mg/kg, while organically bound Cu varied from 1.28 to 2.62 mg/kg. The value of organically bound Cu was very low and was in agreement with finding of Pietrzak and Mc Phail (2004). Soil organic matter can affect the availability of element by chelating ions, making them more soluble and possibly more available for plant uptake. Additionally, O.M may act as a pH buffer. Soil pH affects metal solubility due to protonation and deprotonation of the hydration sphere. Shuman (1986) found that pH had the greatest effect on the exachangeable fraction of micronutrients, which was the perdominant plant available fraction. The forms of manganese oxides Cu, amorphous iron oxides Cu and crystalline iron oxides – Cu fluctuated without induce any definite pattern. A major portion of Cu content was found in the residual form.

Richards *et al.*,(2011) reported that the low of differences treatments due to such things as: (i) lateral movement of metals off the plots by wind or water or the combination of wind and water (i.e., the plots were not isolated) (ii) dilution of metals in the upper 0 to 15 cm by disking (i.e., in certain years the depth of disking may have exceeded 15 cm, (iii) leaching of metals, and (iv) plant uptake

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4-5

Correlation coefficients between different chemical fractions of some micronutrients and some soil characteristics.
Iron

Data presented in Table (7) show the correlation coefficients among the iron different fractions and some soil variables. Highly significant correlations were found between the exchangeable iron and available P, DTPA extractable Fe and Mn (r = 0.839**, 0.814** and 0.808**). Also, positive correlations were found between exchangeable iron and organic matter- Fe, amorphous iron oxides- Fe and crystalline iron oxides - Fe (r = 0.802**, 0.767* and 0.901**, respectively). The quantities of organic matter – Fe in the investigated soils showed positive correlation coefficients with available P, DTPA Fe, Mn and Zn (r = 0.788**, 0.663*, 0.898** and 0.649*, respectively). Similarly, significant relationships existed between organic matter- Fe and other Fe-fractions such as manganese oxides Fe, amorphous iron oxides and crystalline iron oxides (r = 0.602*, 0.816** and 0.806**, respectively). A perusal of the data indicates that manganese oxides- Fe was singificantly correlated with available P, DTPA Mn, Cu and crystalline iron oxides- Fe (r = 0.606*, 0.607*, 0.653* and 0.606*, respectively). However, the relationship between amorphous iron oxides –Fe, crystalline iron oxides-Fe fractions and the other soil charcteristics were similar, there exists positive correlation with available P, DTPA- Fe, Mn, Zn and both of them. These results are in agreement with those of Behera and singh(2010) who found that DTPA- extractable Fe in soil was effected directly by Fe associated with easily reducible manganese and Fe associated with organic matter and indirectly by the other fractions. This reveals the existence of dynamic equilibrium among various fractions of Fe in soil, and depletion of readily available Fe fraction is replenished from the other pools of soil Fe.

As for, residual- Fe fraction, data, show that this fraction had no significant correlation with any soil properties, except DTPA- Fe (r = 0.618*).

These results supported those of Behera and Singh (2010) who found that residual Fe constitutes a major protion of total Fe in soil. The Fe associated with easily reducible Mn and organic matter contributed directly to DTPA extractable Fe in soil. Residual Fe contributed directly to uptake Fe by plant.

Phosphorus showed significant correlations with most fractions of Fe. This may be attributed to the phosphorus fertilizer application which effect the availability of micronutrients by changing the pH when the fertilizer dissolves into solution or when phosphate and associated phosphate fertilizer cations react with soil solution content, for example, the dissolution of triple superphosphate (TSP) release H^+ into the soil solution and lowers soil pH (Shuman, 1988).

Manganese

As shown in Table,(8) a highly significant correlations were found between the exchangeable-Mn and available P, DTPA Fe, Mn, and Zn (r=0.798**, 0.764**, 0.954** and 0.642*, respectively). Moreover, similar trends were noticed with other fractions of Mn such as organically bound - Mn, manganese oxides-Mn, amorphous iron oxides-Mn and residual Mn (r= 0.907**, 0.772**, 0.754** and 0.867**, respectively).

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Also, the organic matter bound-Mn fraction followed the same trend mentioned before for exchangeable Mn fraction, with positive correlation with DTPA-Mn (r=0.906**). For the manganese oxides fraction positive and significant correlation coefficients were found between this fraction and each of available P, DTPA Mn and Cu (r=0.680*, 0.769** and 0.633*, respectively), also significant correlation coefficients were found with other fractions (amorphous iron oxide-Mn and residual-Mn, r=0.723* and 0.772**) respectively. The amounts of Mn extracted from the amorphous iron oxides fraction had significantly and highly positive correlations with available P, DTPA Fe, Mn, crystalline iron oxides-Mn and residual-Mn fractions. The content of manganese in the cystalline iron oxides had no significant correlation with any of the soil properties, except that mentioned before. The analysis of the correlation coefficients showed that the residual Mn content had positive correlation with DTPA-Mn (r=0.870**).

The availability of micronutrients to crops is controlled by many soil factors, such as pH, soil organic matter, temperature and moisture. Increased microbial activity can also result in a decrease in the oxidation – reduction potential of the soil, increasing Mn availability; consequently, manganese (II) forms only relatively weak bonds with organic ligands. The main ionic Mn species in a soil solution is $Mn^{2+,}$ and its concentrations decrease 100- fold per unit increase in soil pH (Milivojevic et al., 2011).

Zinc.

Based on the obtained results of correlation coefficients given in Table (9) exchangeable Zn showed highly significant and positively correlated with available P, DTPA Fe, Mn (r=0.856**, 0.687** and 0.879**, respectively). Also, similar trend exists with the other fractions of Mn such as organic matter Zn, Manganese oxide Zn, amorphous iron oxides Zn and crystalline iron oxides Zn (r=0.861**, 0.822**, 0.711** and 0.631**, respectively). A similar result was presented with organically bound Zn, positively correlated with the soil content of available P, Fe and Mn. Also, the amounts of Zn extracted from the organic fraction had significantly high positive correlations with the other fractions of Zn such as manganese oxides Zn, amorphous iron oxides Zn and crystalline iron oxides Zn (r=0.911**, 0.835** and 0.746**, respectively). The manganese oxides-Zn, showed somewhat similar results with soil characteristics. Positive correlation occurred between this fraction and available P, DTPA Fe, Mn and Zn. Manganese oxides Zn positive and significantly correlated with amorphous iron oxides Zn and crystalline iron oxides Zn (r=0.836** and 0.759**) respectively. The content of residual Zn showed positive correlation with organic matter content and DTPA Zn (r=0.781** and 0.706**) respectively. In this study, pH showed less pronounced negative correlation with all fractions of Zn.

Copper.

Data in Table (10) show that there was positive and significant correlations between exchangeable Zn and each of the organic matter – Cu, manganese oxides – Cu, amorphous iron oxides – Cu and crystalline iron oxides Cu (r= 0.895**, 0.910**, 0.922** and 0.815**, respectively).

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The amount of copper extracted from the organic matter, manganese oxides, amorphous iron oxides and crystalline iron oxides were positively correlated with available P and DTPA Mn. A perusal of the data indicates that organic matter- Cu significantly correlated with manganese oxides – Cu, amorphous iron oxides –Cu and Crystalline iron oxides Cu (r= 0.923[**], 0.863[**] and 0.882[**], respectively).

These results are in agreement with those reported by Randhawa and Singh (1996), who reported that amount of Cu in all the fractions, were significantly correlated with each other, except the organically bound Cu fraction and the residual and DTPA extractable Cu.

The copper associated with the residual fraction was negatively correlated with all parameters of soil except the copper fractions forms.

Since the various fractions are in a state of dynamic equilibrium in soil, the results that Cu associated with easily reducible Mn, Cu associated with carbonate and Cu associated with Fe and Al oxides fractions contribute to availability indirectly through some other fractions. These results corroborate the fact that Cu in soil solution, exchangeable, specifically , sorbed and organically bound fractions were potentially available for plant uptake. However, Cu in the hydroxide – occluded fractions is retatively unavailable for plant uptake (Behera *et al.*, 2009 b).

Stepwise regression analysis.

Backward stepwise multiple regression analysis was performed to further separate the effects of soil properties on micronutrient fraction. This analysis was only performed for the elements that significantly changed for each treatment. Data presented in Table (11) reveal that available phosphorus was found to explain most of the variability of exchangeable-Fe fraction while the inclusion of available Fe and Cu did not greatly improve the regression model. In the organic matter- Fe regression model, available Mn explained 90% of the variation.. However, with the exclusion of total CaCO3 from the model, 94% of the variability was explained.

Table (11): Stepwise regression equations between Fe fractions and some characteristics of the investigated soil samples.

Response	Step No.	Constant	Predictors	R-Sq	R (5%)
Soluble and exchangeable -Fe	1	1.17	0.278 P	70.36	0.84
	2	0.63	0.181 P + 0.163 Fe	84.58	0.92
	3	1.73	1.68 P + 0.246 Fe – 0.50 Cu	98.27	0.99
Bound to organic matte-Fe	1	1.64	0.68 Mn	80.63	0.90
	2	-0.08	0.63 Mn + 0.33 CaCO$_3$	87.23	0.94
Occluded by manganese oxides-Fe	1	0.52	4.9 Cu	42.69	0.65
	2	-1.86	4.0 Cu + 1.02 P	63.34	0.80
	3	9.93	4.2 Cu + 1.16 P – 5.6 O.M	80.33	0.90
	4	17.28	1.1 Cu + 1.5 P – 6.8 O.M +1.07 N	90.10	0.95
	5	19.86	1.6 P – 7.0 O.M + 0.129 N	89.41	0.95
Amorphous iron oxides- Fe	1	1575	315 Fe	82.11	0.91
	2	1232	207 Fe + 203 Mn	90.83	0.95
	3	419	199 Fe + 173 Mn + 436 O.M	94.60	0.97
Crystalline iron oxides-Fe	1	1386	449 Fe	92.15	0.96
	2	1027	335 Fe + 212 Mn	97.41	0.99
Residual-Fe	1	2084	335 Fe	38.18	0.62
	2	2909	409 Fe -992 EC	65.33	0.81

Amorphous iron oxides- Fe, was affected by DTPA – extractable Fe, but the inclusion of available Mn and organic matter content did not improve the regression model. The stepwise regression for crystalline iron oxides – Fe showed that the DTPA- extractable Fe and Mn explained 99% of the variability. This agrees with the simple correlation procedure. The best model for residual- Fe included DTPA- extractable Fe and EC with positive correlation for the former and negative correlation for the latter.

Data presented in Table (12) show that, exchangeable- Mn fraction, displayed the highest relationship with DTPA- extractable Mn . The inclusion of soil pH did not improve the model. This agrees with the simple correlation results, where a significant relationship existed between exchange – able- Mn fraction and DTPA- extractable Mn (r=0.954**). For organic matter- Mn, 91% of the variability is ascribed to DTPA- extractable Mn. This agrees with the simple correlation analysis. Similarly, the manganese oxides – Mn fraction was best explained by the inclusion of the variables of DTPA- extractable Mn and Cu into the regression model. .The best model for amorphous iron oxides- Mn included pH, DTPA- extractable P, Mn, Zn and Fe with positive correlations for pH , P, Mn, Fe and a negative correlation for Zn.. Results revealed that the model for crystalline iron oxides- Mn included available P, Cu, and organic matter content with a negative correlation with organic matter and positive correlations with the others. As for, residual- Mn, the best term regression model included available Mn, P and organic matter.The contribution factors on residual –Mn fraction are 87%, 5% and 5% For Mn , P and orgasmic matter respectively .

Results of the stepwise regression analysis are summarized in Table (13). The best model For exchangeable – Zn included DTPA –extractable Mn and organic matter content explained 98% of the variability. For organic matter – Zn Fraction the best model included only available Mn. In the manganese oxides-Zn fraction the best term regression models included available Mn ,K ,P and total CaCO3. The Contribution factors on manganese oxides – Zn are 89% For Mn, 5% For K , 2% for CaCO3 and 2% For P. The stepwise regression For amorphous iron oxides – Zn showed that the inclusion of DTPA –extractable Mn , Zn ,Fe ,and EC explained 98% of the variability. The best model for crystalline iron oxides –Zn included only DTPA –extractable Fe. As for, residual –Zn Fraction, best model included organic matter and EC. These variables explained 90% of the variability.

Once again, data presented in Table (14) reveal that the best model for exchangeable – Cu Fraction included available Mn, organic matter content and EC. The contribution factors on exchangeable –Cu are 87% . 8% and 2% for available Mn, organic matter and EC, respectively . In the fraction of organic matter –Cu regression model,   reveal that available P, Cu ,Mn ,and organic matter explained 97% of the variation ,while the inclusion of total CaCO3 did not greatly improve the regression model. In the manganese oxides – Cu fraction ,the best model included available Mn, Cu, organic matter content and total CaCO3. The contribution factors on manganese oxides –Cu are 82%, 7%, 5% and 5% for available Mn, Cu, organic matter and total CaCO3, respectively .

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The stepwise regression for amorphous iron oxides – Cu showed that the best model included available Mn ,Fe , and organic matter. The mood for crystalline iron oxides – Cu included only DTPA –extractable Fe explained 71% of the Variability. As For, residual – Cu the best term regression models included DTPA- extractable Fe and organic matter content with positive correlation for Fe and negative correlation for organic matter.

CONCLUSION

It can be concluded that concentration of DTPA – extractable Fe, Mn, Zn and Cu increased in all treatments as a result of continous cropping and fertilizer application. The distribution of different fraction of micronutrient under different treatments was inconsistent. Micronutrient additions through impurities in inorganic fertilizer were small relative to total soil micronutrient concentrations. On the other hand, long-term application of organic amendments increased the soil total micronutrient contents and DTPA – extractable micronutrients.

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التغيـر فـي صـور بعـض العناصـر الصـغرى وتأثرهـا بالزراعـة المسـتمرة والاضـافات المستديمة من الاسمدة المعدنية والعضوية.

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تم جمع بعض العينات من أراضي التجربة المستديمة المقامـة في منطقـة بهتيم – محافظـة القليوبيـة – مصـر. وذلك لدراسة توزيع الصور المختلفة لكل من الحديد، المنجنيز، الزنك والنحاس –وقد تم اختيار إحدى عشر معاملـة من المعـاملات المقامة ي

١- ١٥ كجم نيتروجين للفدان N_{15} .

٢- ١٥ كجم نيتروجين للفدان + ١٩ كجم فوسفور للفدان($P - N_{15}$)

٣- ١٥ كجم نيتروجين للفدان + ١٩ كجم فوسفور للفدان + ٤٨ كجم بوتاسيوم للفدان ($N_{15} - P - K$).

٤- ٣٠ كجم نيتروجين للفدان (N_{30}).

٥- ٣٠ كجم نيتروجين للفدان + ١٩ وحدة فوسفور للفدان ($N_{30} - P$)

٦- ٣٠ كجم نيتروجين للفدان + ١٩ كجم فوسفور للفدان + ٤٨ كجم بوتاسيوم للفدان ($N_{30} - P - K$)

٧- ٦٠ كجم نتروجين للفدان، (N_{60})

٨- ٦٠ كجم نتروجين للفدان + ١٩ كجم فوسفور للفدان ($N_{60} - P$)

٩- ٦٠ كجم نتروجين للفدان + ١٩ كجم فوسفور للفدان + ٤٨ كجم بوتاسيوم للفدان($N_{60} - P - K$)

١٠- السماد البلدي ٢٠م٣ /فدان

١١- معاملة الكنترول (بدون إضافات معدنية أو عضوية)

تـم استخلاص الصـور المختلفـة للعناصـر الصـغرى بواسطة استخلاص متتـابع بمـواد كيميائيـة مختلفـة. العناصـر الصغرى المستخلصة بواسطة DTPA أظهرت ارتفاع في جميع المعـاملات مقارنـة بمعاملـة المقارنـة وذلك نتيجـة الزراعـة المتتالية والاضافات التسميدية المستديمة.

وقد اتخذت صور العناصر الصغرى الترتيب التالي:

الصورة المتبادلـة > الصـورة المرتبطـة بـالمواد العضـوية > الصـورة المرتبطـة بأكاسيد المنجنيز > الصـورة المرتبطـة بأكاسيد الحديد المتبلورة > الصورة المرتبطـة بأكاسيد الحديد الغير متبلورة> المتبقي.

أظهر الحديد المستخلص بواسطة DTPA إرتباطا معنويا مع كل صورة من صور الحديد المختلفـة مـا عدا تلك المرتبطة بأكاسيد المنجنيز ، بينما أرتبط المنجنيز المستخلص بواسطة DTPA معنويا مع مختلف صور المنجنيز مـا عدا المنجنيز المرتبط بأكاسيد الحديد المتبلورة، أمـا الزنك المستخلص بواسطة DTPA فقد أظهر إرتباط معنوى مـع صـور الزنك المختلفة ما عدا كلا من الصورة المتبادلـة والصورة العضوية ،،واخيرا أظهر النحاس المستخلص بواسطة DTPA إرتباطا معنويا مع النحاس المرتبط بالمادة العضوية فقط.

Table (2): Some chemical characteristics of the investigated soil samples.

treatments	EC dS/m paste ext.	pH (1:2.5)	SP	O.M %	CaCO3 %	Soluble ions(meq/L)								Available nutrient (mg/kg soil)						
						Ca^{++}	Mg^{++}	Na^+	K^+	CO_3^-	HCO_3^-	Cl^-	SO_4^-	N	P	K	Fe	Mn	Zn	Cu
N_{15} (N)	0.74	8.22	62.0	2.15	4.86	5.0	1.3	0.67	0.24	0.0	1.8	2.0	3.41	15.68	4.30	335.0	5.56	4.42	3.67	2.80
N_{15}-P (N-P)	1.36	8.03	63.5	2.25	6.48	8.3	2.8	1.42	0.48	0.0	4.0	4.5	4.50	13.54	6.10	355.0	5.74	4.22	4.11	2.82
N_{15}-P-K (N-P-K)	1.38	7.91	60.5	2.27	6.84	8.8	3.0	0.86	0.36	0.0	4.5	5.3	3.22	15.68	6.80	485.0	6.79	6.64	3.62	2.93
N_{30} (N)	0.92	8.04	60.0	2.05	6.48	5.8	1.0	1.93	0.16	0.0	2.0	2.8	4.09	40.77	2.80	215.0	5.27	4.00	3.29	2.80
N_{30}-P (N-P)	0.74	8.12	58.5	2.17	6.12	4.0	1.3	1.54	0.21	0.0	2.0	3.0	2.05	35.68	3.70	215.0	5.71	4.32	3.18	3.39
N_{30}-P-K (N-P-K)	1.78	8.01	59.5	2.12	6.48	9.5	3.3	3.86	0.46	0.0	4.5	6.5	6.12	37.63	7.40	225.0	6.50	6.27	4.48	3.18
N_{60} (N)	1.59	7.99	58.0	2.30	5.40	8.3	3.0	3.52	0.31	0.0	4.5	6.5	4.13	51.36	3.50	225.0	5.66	4.48	4.05	3.25
N_{60}-P (N-P)	1.81	7.94	60.0	2.62	6.12	10.3	3.8	3.67	0.31	0.0	4.8	8.0	5.28	50.95	5.30	230.0	5.97	5.37	4.27	3.86
N_{60}-P-K(N-P-K)	1.74	7.98	60.0	2.42	5.40	10.0	3.5	3.26	0.29	0.0	5.0	6.8	5.25	53.31	7.00	285.0	10.51	6.48	4.99	3.88
Organic	1.12	7.89	60.0	2.92	7.20	6.5	1.8	1.62	0.31	0.0	2.0	3.5	4.73	31.36	5.10	375.0	7.00	5.98	5.94	2.58
Control	1.89	7.93	62.5	2.32	6.12	9.5	5.0	3.28	0.31	0.0	5.0	7.8	5.29	11.04	4.40	355.0	5.18	3.62	2.86	2.80

Table (3): Effect of the different fertilization treatments on distribution of Fe (mg/kg soil) fractionation of the investigated soils.

Treatments	Soluble and exchangeable	Organically bound occluded	*Occluded by manganese oxides*	*Amorphous iron oxides*	*Crystalline iron oxides*	*Residual*
N_{15} (N)	2.33	4.14	13.02	3143.0	3682.0	3890.0
N_{15}-P (N-P)	2.75	5.08	16.08	3265.0	3886.0	3210.0
N_{15}-P-K (N-P-K)	3.08	6.03	18.52	3836.0	4712.0	4030.0
N_{30} (N)	2.10	4.23	15.72	3149.0	3700.0	3990.0
N_{30}-P (N-P)	2.15	5.23	16.68	3288.0	3900.0	5210.0
N_{30}-P-K (N-P-K)	3.07	6.03	20.50	3761.0	4734.0	4230.0
N_{60} (N)	2.17	4.23	15.02	3128.0	3776.0	4140.0
N_{60}-P (N-P)	2.09	5.23	17.40	3945.0	3987.0	3240.0
N_{60}-P-K(N-P-K)	3.52	6.00	20.56	4715.0	5926.0	5350.0
Organic	3.06	6.00	11.42	4010.0	4628.0	5120.0
Control	2.26	4.00	10.46	3085.0	3664.0	3210.0

Table (4): Effect of the different: fertilization treatments on distribution of Mn(mg/kg soil) fractionation of the investigated soils.

Treatments	Soluble and exchangeable	Organically bound occluded	Occluded by manganese oxides	Amorphous iron oxides	Crystalline iron oxides	Residual
N_{15} (N)	1.87	3.07	12.00	378.0	308.0	261.0
N_{15}-P (N-P)	1.66	4.11	14.36	359.5	345.5	234.0
N_{15}-P-K (N-P-K)	2.65	5.35	15.90	397.5	325.5	371.0
N_{30} (N)	1.46	3.32	12.46	327.0	304.0	302.0
N_{30}-P (N-P)	1.75	4.39	15.11	368.5	313.0	287.0
N_{30}-P-K (N-P-K)	2.92	5.45	16.00	392.5	355.0	359.0
N_{60} (N)	1.64	3.32	14.00	324.0	304.0	290.0
N_{60}-P (N-P)	1.88	4.30	15.28	356.5	315.0	299.0
N_{60}-P-K(N-P-K)	2.95	5.38	16.30	414.0	386.5	354.0
Organic	2.40	4.82	13.70	320.0	230.5	326.0
Control	1.09	2.86	11.00	309.5	296.0	172.0

Table (5): Effect of the different fertilization treatments on distribution of Zn (mg/kg soil) fractionation of the investigated soils.

Treatments	Soluble and exchangeable	Organically bound occluded	Occluded by manganese oxides	Amorphous iron oxides	Crystalline iron oxides	Residual
N_{15} (N)	1.14	3.11	7.42	68.00	22.75	115.0
N_{15}-P (N-P)	1.13	3.95	9.00	69.55	31.95	99.6
N_{15}-P-K (N-P-K)	2.06	4.53	10.96	84.70	30.80	112.0
N_{30} (N)	1.03	3.18	7.98	67.40	25.05	113.0
N_{30}-P (N-P)	1.19	4.07	9.64	70.55	28.45	117.0
N_{30}-P-K (N-P-K)	2.15	4.71	12.84	85.40	33.75	110.7
N_{60} (N)	1.02	3.11	9.22	64.00	31.50	109.0
N_{60}-P (N-P)	1.52	4.19	10.42	75.80	26.20	117.0
N_{60}-P-K(N-P-K)	2.12	4.84	11.48	99.00	43.05	115.0
Organic	1.17	4.16	10.93	94.00	33.30	178.0
Control	0.98	3.06	7.04	45.15	21.35	105.8

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Table (6): Effect of the different fertilization treatments on distribution of Cu (mg/kg) fractionation of the investigated soils.

Treatments	Soluble and exchangeable	Organically bound occluded	Occluded by manganese oxides	Amorphous iron oxides	Crystalline iron oxides	Residual
N_{15} (N)	0.97	1.44	6.20	19.10	8.30	39.00
N_{15}-P (N-P)	1.11	1.82	7.25	18.10	8.90	36.40
N_{15}-P-K (N-P-K)	2.00	2.38	9.24	24.70	9.85	31.90
N_{30} (N)	0.94	1.72	7.26	19.30	9.80	38.80
N_{30}-P (N-P)	1.18	2.05	8.24	22.85	9.10	33.90
N_{30}-P-K (N-P-K)	2.08	2.57	9.26	27.55	10.50	33.30
N_{60} (N)	0.95	1.62	7.26	18.15	8.50	33.20
N_{60}-P (N-P)	1.40	2.12	8.34	19.50	9.15	32.40
N_{60}-P-K(N-P-K)	2.06	2.62	9.38	28.80	11.35	32.10
Organic	1.10	1.20	7.36	19.65	8.45	31.60
Control	0.92	1.28	6.00	17.45	7.30	30.40

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Table (7): Correlation coefficients (r)among the different fractionations of Fe and some soil characteristics.

Soil characteristics	Fe fractionation					
	Soluble and exchangeable	Organically bound occluded	Occluded by manganese oxides	Amorphous iron oxides	Crystalline iron oxides	Residual
EC	0.273	0.195	0.263	0.376	0.340	-0.317
pH	-0.357	-0.424	-0.011	-0.458	-0.366	0.048
O.M	0.267	0.395	-0.286	0.533	0.300	0.209
CaCO3	0.249	0.495	-0.017	0.141	0.091	0.012
Available N	-0.014	0.193	0.473	0.443	0.341	0.421
P	0.839**	0.788**	0.606*	0.696*	0.745*	0.074
K	0.450	0.243	-0.253	0.128	0.179	-0.141
DTPA Fe	0.814**	0.663*	0.531	0.906**	0.906**	0.618*
Mn	0.808**	0.898**	0.607*	0.861**	0.855**	0.452
Zn	0.664*	0.649*	0.141	0.706*	0.624*	0.462
Cu	0.063	0.281	0.653*	0.547	0.425	0.214
Soluble and exchangeable Fe						
Organic matter Fe	0.802**					
Manganese oxides Fe	0.448	0.602*				
Amorphous iron oxides Fe	0.767*	0.816**	0.550			
Crystalline iron oxides Fe	0.901**	0.806**	0.606*	0.925**		
Residual Fe	0.459	0.512	0.247	0.504	0.608*	

*and ** indicate significance at the 0.05 and 0.01 probability levels, respectively

Table (8): Correlation coefficients (r) among the different fractionation of Mn and some soil characteristics.

Soil characteristics	Mn fractionation					
	Soluble and exchangeable	Organically bound occluded	Occluded by manganese oxides	Amorphous iron oxides	Crystalline iron oxides	Residual
EC	0.194	0.277	0.265	0.040	0.364	0.007
pH	-0.217	-0.374	-0.234	0.238	0.192	-0.218
O.M	0.205	0.262	0.111	-0.256	-0.501	0.125
CaCO3	0.154	0.423	0.180	-0.216	-0.276	0.238
Available N	0.271	0.249	0.464	0.089	0.197	0.486
P	0.798**	0.806**	0.680*	0.708*	0.560	0.491
K	0.177	0.173	-0.080	0.114	-0.177	-0.008
DTPA Fe	0.764*	0.684*	0.600	0.611*	0.479	0.586
Mn	0.954**	0.906**	0.769*	0.664*	0.264	0.870**
Zn	0.642*	0.572	0.419	0.139	-0.122	0.516
Cu	0.311	0.359	0.633*	0.476	0.582	0.324
Soluble and exchangeable Mn						
Organic matter Mn	0.907**					
Manganese oxides Mn	0.772**	0.890**				
Amorphous iron oxide Mn	0.754*	0.685*	0.723*			
Crystalline iron oxides Mn	0.394	0.377	0.553	0.761*		
Residual Mn	0.867**	0.814**	0.772**	0.601*	0.244	

*and ** indicate significance at the 0.05 and 0.01 probability levels, respectively

Table (9): Correlation coefficients (r) among the different fractionation of Zn and some soil characteristics.

Soil characteristics	Zn fractionation					
	Soluble and exchangeable	Organically bound occluded	Occluded by manganese oxides	Amorphous iron oxides	Crystalline iron oxides	Residual
EC	0.418	0.290	0.350	0.024	0.283	-0.256
pH	-0.264	-0.346	-0.402	-0.252	-0.296	-0.326
O.M	-0.010	0.269	0.300	0.419	0.262	0.781**
CaCO3	0.107	0.360	0.358	0.250	0.074	0.436
Available N	0.233	0.257	0.442	0.390	0.463	0.107
P	0.856**	0.836**	0.743*	0.634*	0.629*	-0.040
K	0.144	0.127	-0.040	0.126	0.003	0.188
DTPA Fe	0.687*	0.704*	0.610*	0.790*	0.863**	0.204
Mn	0.879**	0.859**	0.890**	0.894**	0.705*	0.344
Zn	0.326	0.539	0.648*	0.795*	0.693*	0.706*
Cu	0.477	0.468	0.431	0.307	0.420	-0.265
Soluble and exchangeable Zn						
Organic matter Zn	0.861**					
Manganese oxides Zn	0.822**	0.911**				
Amorphous iron oxide Zn	0.711*	0.835**	0.836**			
Crystalline iron oxides Zn	0.631*	0.746*	0.759*	0.807**		
Residual Zn	-0.093	0.178	0.274	0.495	0.185	

- ***and ** indicate significance at the 0.05 and 0.01 probability levels, respectivel**

Table (10): Correlation coefficients (r) among the different fractionation of Cu and some soil characteristics.

Soil characteristics	Cu fractionation					
	Soluble and exchangeable	Organically bound occluded	Occluded by manganese oxides	Amorphous iron oxides	Crystalline iron oxides	Residual
EC	0.424	0.330	0.286	0.211	0.148	-0.671*
pH	-0.289	-0.069	-0.292	-0.073	-0.053	0.780**
O.M	-0.013	-0.259	0.031	-0.123	-0.177	-0.568
CaCO3	0.149	0.014	0.241	0.025	0.042	-0.307
Available N	0.227	0.391	0.465	0.324	0.513	-0.133
P	0.863**	0.671*	0.678*	0.695*	0.565	-0.398
K	0.147	0.162	-0.071	-0.040	-0.206	-0.237
DTPA Fe	0.692*	0.563	0.636*	0.749*	0.709*	-0.360
Mn	0.871**	0.642*	0.819**	0.773**	0.674*	-0.443
Zn	0.319	0.091	0.337	0.289	0.311	-0.278
Cu	0.475	0.670*	0.598	0.486	0.531	-0.298
Soluble and exchangeable Cu						
Organic matter Cu	0.895**					
Manganese oxides Cu	0.910**	0.923**				
Amorphous iron oxide Cu	0.922**	0.863**	0.873**			
Crystalline iron oxides Cu	0.815**	0.882**	0.867**	0.867**		
Residual Cu	-0.382	0.169	-0.346	-0.267	0.018	

*and ** indicate significance at the 0.05 and 0.01 probability levels, respectively

Table (12): Stepwise regression equations between Mn fractions and some characteristics of the investigated soil samples.

Response	Step No.	Constant	Predictors	R-Sq	R (5%)
Soluble and exchangeable -Mn	1	-0.68	0.533 Mn	91.11	0.97
	2	-13.71	0.595 Mn + 1.59 pH	96.18	0.98
Bound to organic matte-Mn	1	0.18	0.80 Mn	82.10	0.91
Occluded by manganese oxides-Mn	1	7.96	1.23 Mn	59.13	0.77
	2	3.74	1.01 Mn + 1.71 Cu	75.62	0.87
Amorphous iron oxides- Mn	1	276	16.1 P	50.11	0.71
	2	-1343	20.5 P + 199 pH	76.87	0.88
	3	-1661	12.2 P + 234 pH + 16.3 Mn	86.07	0.93
	4	-1518	11.1 P + 219 pH + 24.0 Mn − 13.7 Zn	92.60	0.96
	5	-1438	10.0 P + 209 pH+ 19.2 Mn − 16.8 Zn + 7.4 Fe	96.86	0.98
Crystalline iron oxides-Mn	1	1554	52 Cu	33.92	0.58
	2	343	56 Cu − 87 O.M	64.25	0.80
	3	337	44 Cu − 99 O.M + 13.7 P	90.52	0.95
Residual-Mn	1	60.38	46.4 Mn	75.77	0.87
	2	51.94	67.3 Mn − 19 P	85.32	0.92
	3	195	78.6 Mn − 23.3 P − 77 O.M	94.16	0.97

Table (13): Stepwise regression equations between Zn fractions and some characteristics of the investigated soil samples.

Response	Step No.	Constant	Predictors	R-Sq	R (5%)
Soluble and exchangeable -Zn	1	-0.50	0.377 Mn	77.24	0.88˙
	2	0.91	0.441 Mn − 0.75 O.M	90.77	0.95˙
	3	0.83	0.417 Mn − 0.81 O.M	95.45	0.98˙
Bound to organic matte-Zn	1	1.22	0.53 Mn	73.82	0.86˙
Occluded by manganese oxides-Zn	1	2.31	1.46 Mn	79.27	0.89˙
	2	3.52	1.61 Mn − 0.006 K	88.65	0.94˙
	3	0.65	1.54 Mn − 0.00078 K + 0.59 CaCO$_3$	92.91	0.96˙
	4	0.84	1.18 Mn − 0.0089 K + 0.62 CaCo$_3$ + 0.34 P	95.95	0.98˙
Amorphous iron oxides- Zn	1	12.26	12.3 Mn	79.95	0.89˙
	2	3.48	9.0 Mn + 6.3 Zn	87.68	0.94
	3	10.71	10.2 Mn + 6.1 Zn − 90 EC	93.69	0.97
	4	9.23	8.2 Mn + 5.1 Zn − 9.9 EC + 2.7 Fe	96.75	0.98
Crystalline iron oxides-Zn	1	7.59	3.5 Fe	74.42	0.86
Residual-Zn	1	-32.34	64 O.M	60.92	0.78
	2	-22.83	73 O.M − 22.3 EC	81.34	0.90˙

Table (14) :Stepwise regression equations between Cu fractions and some characteristics of the investigated soil samples.

Response	Step No.	Constant	Predictors	R-Sq	R (5%)
Soluble and exchangeable -Cu	1	-0.57	0.377 Mn	75.80	0.87
	2	0.85	0.441 Mn – 0.75 O.M	89.37	0.95
	3	0.77	0.416 Mn – 0.82 O.M + 0.26 EC	94.46	0.97
Bound to organic matte-Cu	1	0.78	0.217 P	45.08	0.67
	2	-0.87	0.173 P + 0.601 Cu	71.64	0.85
	3	0.82	0.192 P + 0.62 Cu – 0.794 O.M	87.30	0.93
	4	1.04	0.082 P + 0.55 Cu – 1.032 O.M + 0.217 Mn	94.42	0.97
	5	1.15	0.554 Cu – 1.11 O.M + 0.314 Mn	92.08	0.96
	6	-0.12	0.726 Cu – 1.251 O.M + 0.267 Mn + 0.214 $CaCO_3$	97.49	0.98
	7	-0.16	0.072 P + 0.718 Cu – 1.176 O.M + 0.185 Mn + 0.203 $CaCO_3$	99.27	0.99
Occluded by manganese oxides-Cu	1	3.32	0.882 Mn	67.02	0.82
	2	0.86	0.753 Mn + 1.0 Cu	79.45	0.89
	3	3.68	0.881 Mn + 0.97 Cu – 1.44 O.M	87.47	0.94
	4	-0.56	0.727 Mn + 1.53 Cu – 1.91 O.M + 0.71 $CaCO_3$	97.90	0.99
Amorphous iron oxides- Cu	1	7.17	2.80 Mn	59.80	0.77
	2	21.65	3.46 Mn – 7.7 O.M	79.82	0.89
	3	20.84	2.31 Mn – 8.1 O.M + 1.19 Fe	89.32	0.95
Crystalline iron oxides-Cu	1	5.82	0.53 Fe	50.27	0.71
Residual-Cu	2	9.85	0.64 Fe – 2.03 O.M	68.70	0.83
	1	-152.7	23.3 pH	60.87	0.78

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