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Conducted and Investigate Arsenic (As), Cobalt (Co) Copper (Cu), Manganese (Mn), Lead (Pb), and Zinc (Zn) Contamination in Agricultural' Soils and Wheat Crops Projects at Three Regions in Libya

Youssef F. Lawgali, Andy A. Meharg and
Yousef M.T. Elgimati

Additional information is available at the end of the chapter

1. Introduction

Libya is one of the driest countries in the world [2]. The rainfall in the northern part of the country varies between 100–500 mm/year, while the southern region receives only 10 mm/year and some parts receive no precipitation at all [17]. Average evaporation rates are also high, ranging from 1.7 mm/day in the north to 6.9 mm/day in the south, much higher than the average annual rainfall. Irrigation water use has increased as part of the green revolution program to make a Libya self-sufficient in terms of food production, e.g. for wheat and barley. Agriculture in Libya developed remarkably during the last two decades, as can be seen from the large increase in the irrigated areas, which has doubled during the period 1975–2005 [11,15]. The cultivated area has also increased, from 282,250 ha in 1975 to 470,000 ha in 2000 [15]. Increased agricultural activities have resulted in higher demands for groundwater, irrigation water and applications of fertilizer and have also resulted in higher salinity (nitrate, chloride, Na, Ca, Mg, ammonia) and increases in some trace elements in soil [3]. The development in agriculture has occurred at great cost to the environment, and concern is now being expressed about the impact of agricultural chemicals. Whereas agricultural production increased from 1137 thousand tons in 1975 to 1779 thousand tons in 2000, the agrarian productivity per hectare decreased from 4 tons/hectare in 1975 to 3.5 tons/hectare in 1980 and 1990, and then showed a slight increase to 3.7 tons/hectare in 2000. Libya's annual import of fertilizer is about 2×10^8 metric tons, including fertilizer nutrients N, P205, and K20.1. [5,6-7]. [6] Observed that application of fertilizers to dry land not only increases plant shoot and stem

growth, but also increases evapotranspiration through development of a larger root system and greater extraction of stored water. [4.14] found that the amount of N and P fertilizer used in the Montanan North African soils ranged from 20–120 kg/ha and 0–30 kg/ha, respectively. However, under irrigated conditions, critical P levels are high (i.e. 12–15 mg/kg). The high pH affects the availability of many crop nutrients in the southern Libyan soil [13].

The objective of the present study was to establish levels of As and other trace elements in the grains and soils of the Libyan arable belt. Soil and wheat samples were collected from 3 Libyan agricultural regions, East (ESR), West (WSR) and South (SSR). Each region included several sampling districts (Fig.1).

2. Materials and methods

2.1. Sample preparation

Seventy-nine samples each of soils, shoots and wheat grains from arable land were collected for the study, representing major soil types and climatic regions of agronomic cultures in the Eastern, Western and Southern soil regions of Libya (ESR, WSR and SSR, respectively). Each region included several sampling districts (52, 10 and 17, respectively). Soil samples were taken from the root zone of each sample, and within the soil horizon (0–100 mm), using a spiral auger of 20–50 mm diameter. Three samples were taken around the plant to make composite soil samples and stored in airtight bags. The sampling was carried out between May 26th and June 30th in 2007. The sampling points are shown in Fig. 1.
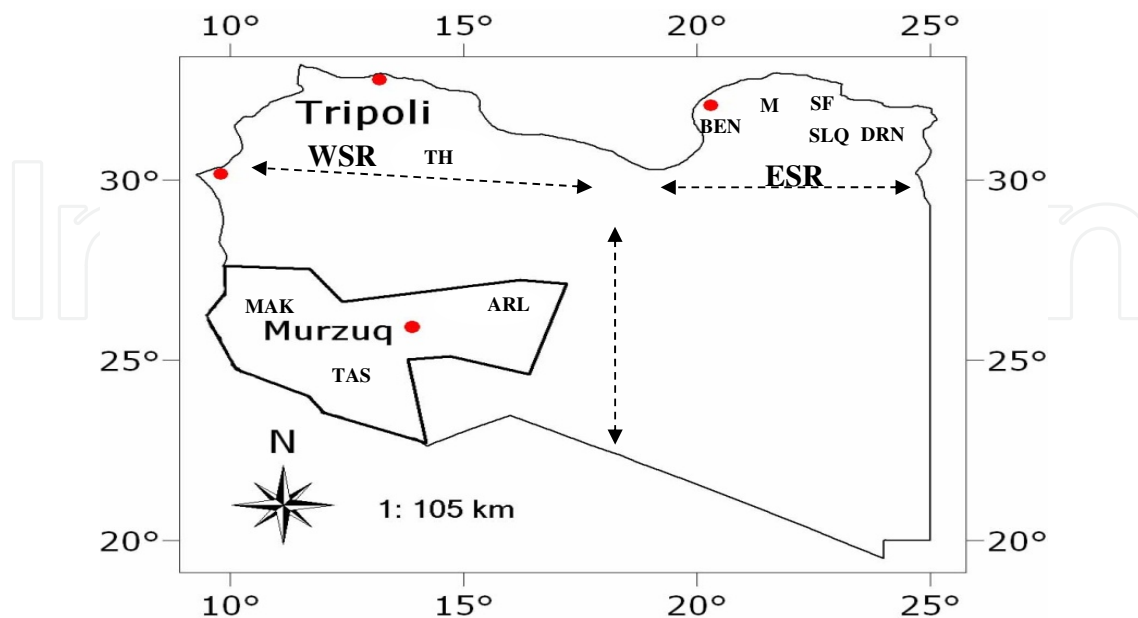
Figure 1. Soil survey sampling locations in Libya.

All samples were air-dried and homogenized by grinding and sieving through a 2 mm mesh. A soil sample of 0.2 g was placed in a digestion tube, 2 ml concentrated HNO_3 added and the sample pre-digested (i.e. left to stand overnight). 2 ml of H_2O_2 was added immediately before digestion on a digest block at 100 °C for 1 hour, 120 °Cfor 1 hour and then at 140 °C until samples were clear (*c*. 2 hours). Samples were then heated to 160 °C until the sample digest appeared clear or a pale soil color.

Quality control and assurance

Each batch of 40 samples digested included a blank, a spike and a soil reference material (NCS ZC 73007) (Table 1). The samples were allowed to cool, decanted into well-labelled 15 ml centrifuge tubes and made up to 10 ml with ultra pure decant deionised water (18.2 M) obtained from a Milli-Q system (Millipore) and analysed by ICP-MS. If the outcome of the SRM NCS ZC 73007 was above 25 % of the certified values, the analysis of the batch was rejected.

Soil sample analysis by ICP-MS

Cd, Pb, Cu, P, Zn, Co, Mn and As concentrations were measured in all soil sample digestions by An ICP-MS Agilent™ 7500c (Agilent Technologies, Tokyo, Japan) octopole reaction system (ORS)-ICP-MS with a Meinhard nebulizer was used to measure the elements Ti (m/z 49), Mn (m/z 55), Co (m/z 59), Cu (m/z 63), Zn (m/z 64, 66, 67, 68), As (m/z 75), Se (m/z 77, 78, 82) and In (m/z 115). Hydrogen (H) was employed as the reaction gas for the ORS, set at a flow rate of 1.8 ml/min. With this method, low detection thresholds can be obtained for elements such as metalloids that have high ionization energies (e.g. As).

Soil As extraction

Soil extraction to determine As fractionation was performed. Sample material was oven-dried at 90 °C for 48 hrs. Extracts were obtained by shaking 1 g of soil with 10 ml of 0.1 % HNO_3, as described by [10]. The soil was mixed with 10 ml of 0.1 % HNO_3 in 15 ml plastic centrifuge tubes shaken at a speed of 60 rpm for 24 hrs. After shaking, soil solids were separated from the solution by centrifugation at 2958 *g* for 15 min. The concentrations of As were determined as described above for the soil digestion. Quality controls (spikes and blanks) were run with each digest set of 40 samples. Concentrations were determined using five point calibrations.

Soil As extraction and analysis by hydride generation (HG)

The 0.1 % $NHNO_3$ water-soluble As fraction was determined by hydride generation (HG, Perkin-Elmer A. Analyst 300) [10]; in order to achieve this, the system must first be calibrated using a standard curve. As^V was reduced to As^{III} by a mixture of hydrochloric acid (HCL) (30 % v/w), potassium iodide (KI) (10 % w/v) and ascorbic acid (5 % w/v). The solution was pumped into a gas-liquid separator and reacted with sodium borohydride and sodium hydroxide ($NaBH_4$) (0.2 % w/v solution in 0.1 M NaOH) to from arsenic hydride generation [10]. Sample concentrations were calibrated using a standard curve of 0.5, 1, 5, 10, 15 and 20 μg/l As, in 10 % HCl 1 % KI and further diluted where necessary. All As concentrations were below the limit of detection (LOD).

Soil As and other element extraction and analysis by ICP-MS

Since the analysis by hydride generation of all Asconcentrations were below the LOD, As and other elements (Cd, Pb, Ni, Cu, P, Zn, Cu, Co and Mn) were analysed with ICP-MS.

The analytical procedures used ICP-MS to extract As and other elements extraction from the soil are identical to those outlined in section 3.2.4 (Soil As extraction), as are the aristar grade reagents used.

Minitab v. 15 was used for all statistical analyses.

3. Results

The certified reference material (CRM) as well as the LOD and spike recoveries for each of the trace elements analysed are presented in Table 1.

	Co	Zn	Cu	As	Cd	Pb	Mn
CRM (%) n=4	87 ±0.1	66 ±1.7	87 ±1.3	103 ±0.2	101 ± 0.01	90 ±1.2	88 ±5.1
Spike (%) n=4	97 ±0.7	96 ±7.4	112 ± 3.1	123 ±2.5	81 ±0.1	97 ±1.2	104 ± 5.4
LOD (mg/kg)	0.01	0.30	0.20	0.01	0.01	0.03	0.14

Table 1. Quality control measurements for analysis of Co, Zn, Cu, As, Cd, Pb and Mn concentration in Libyan agricultural soils. (CRM = NCS ZC 73007).

It should be noted that the concentration of Cd in all samples was below the LOD. The descriptive statistics for trace element concentrations in agricultural soil investigated in this study. They are provided for each region, with a summary of the As levels and other trace element concentrations in soils sampled from ESR, WSR and SSR. A one-way analysis of variance (ANOVA) showed that the differences in As levels between location means are highly significant (P<0.001,). ESR recorded the highest mean As the level in Libyan soil (8.10 ± 0.48 mg/kg), followed by WSR (1.97± 0.41mg/kg) and SSR (1.70 ± 0.58 mg/kg), i.e. As mean concentrations in ESR are nearly 4.8 and 4.1 times higher than in SSR and WSR, respectively. Conversely, the average As levels from the three regions were below 10 mg/g dry weight (dwt). The concentration of As in the agricultural soil, therefore, ranged from 0.01–18.94 mg/kg in ESR, 1.19–2.48 mg/kg in WSR and 0.73–2.92 mg/kg in SSR.The underlying rock structure in ESR is composed of Lower Palaeozoic rocks. The clay agricultural soils of ESR recorded the highest mean As the level in Libyan soil (8.10 mg/kg); this may have some relation to the parent material.
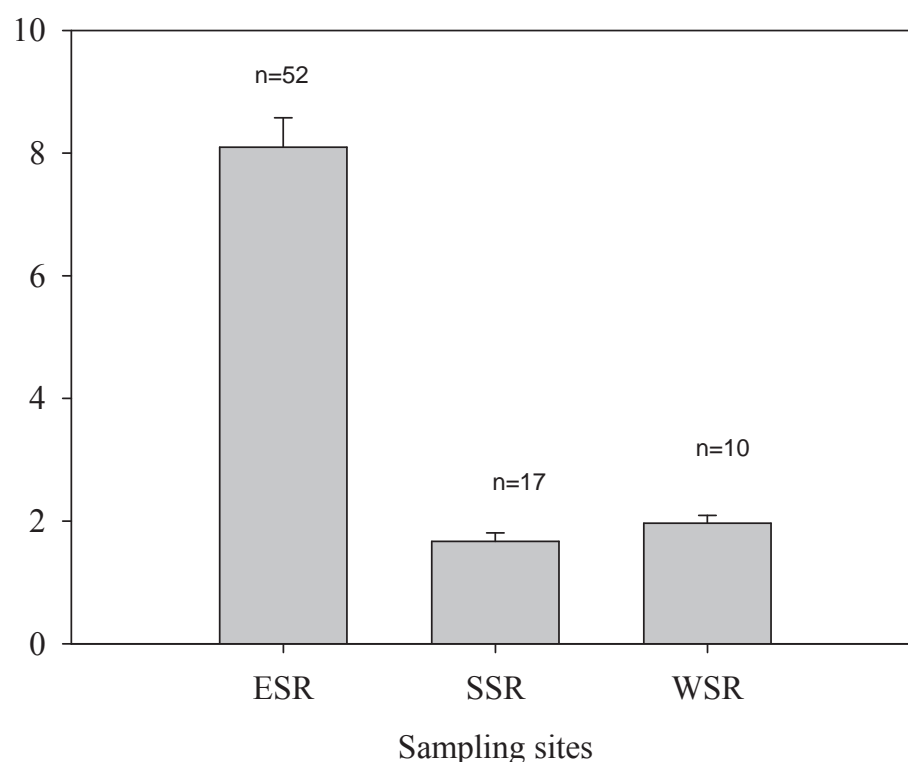
Figure 2. Mean As concentrations in agricultural soils from Libya (Error bars represent ± std. error).

The descriptive statistics for trace element concentrations in the Libyan agricultural soil investigated in this study are shown in Appendix.1, together with a summary of the levels of As and other trace elements.

3.1. Southern soil regions (SSR)

In SSR, the sites used for sampling were ARL, JAF and TAS (sites are shown in Fig.1). The mean As levels in sites in SSR decreased from TAS > JAF >ARL. In general, As levels were low in SSR, ranging from 1–2.9 mg/g, 0.7–1.8 mg/g and 1.1–1.7 mg/g for the TAS, JAF and ARL sites, respectively.

3.2. Eastern soil regions (ESR)

The sampling sites in ESR were BEN, DRN, HEN, MR, SF and SLQ (sites are shown in Fig.1). The mean As levels in these sites decreased from SF > DRN > BAY > MAR > HEN > BEN >SLQ. In general, As levels in ESR were high, ranging from 0.01 to 18.9 mg/kg.

Western soil regions (WSR)

Samples in WSR were taken from two sites, THR and SIRT (Fig.1). WSR recorded the second highest mean total As level compared with ESR and SSR (2 ± 0.1 mg/kg vs.8.1± 0.50 and 1.7± 0.14, respectively). The mean As levels in sites in WSR decreased from THR > SIRT (range 2–2.5 mg/g and 1.2–2.1mg/g for THR and SIRT, respectively).

Results of analysis of variance (ANOVA)

A one-way analysis of variance (ANOVA) was performed on each of the three regions studied. For SSR, the ANOVA showed that that the mean As levels between sites were not significantly different (SSR: $P=0.398$), but were for ESR and WSR ($P<0.0016$, $P<0.015$, respectively).

Multivariate analysis results

Principal component analysis (PCA)

PCA was applied in each region to assist in identifying sources of elements. 3-D plots of the PCA loadings are presented in Fig.3, where the relationships among the six trace elements are readily seen. As expected, four factors were obtained, accounting for 97.4, 98.0 and 99.4 % of the total variance in ESR, SSR and WSR, respectively. In ESR, Factor 1 is dominated by Co, Cu, Pb and Mn, while in SSR it was dominated by Co, Zn, As and Pb and in WSR by Co, Zn, As and Mn (accounting for 67.4, 69.9 and 90.7 % of the total variance, respectively). In each area, the loadings of certain minerals were lower than the others, which may, therefore, imply a quasi-independent behaviour within the group. These elements were Cu and Mn (0.42 and 0.4, respectively) for ESR, Co and Zn (0.5 and 0.4, respectively) in SSR and Zn and As (0.4 and 0.4, respectively) in WSR.

Factor 2 is dominated by Zn and As in ESR, by Mn in SSR and by Cu and Pb in WSR (accounting for 23.1, 15.3 and 6.0 % of the total variance, respectively). Factor 3 is dominated in ESR by As and Pb, by Zn As and Cu Pb in SSR and by Zn and As in WSR (accounting for 4.1, 7.7 and 1.4 % of the total variance, respectively). Zn is negatively correlated with Cu in SSR, and with As in WSR. In each region, certain elements (As and Zn in ESR, Mn in SSR and Cu in WSR) were separated from the others by a large distance in the 3-D PCA loading plot, suggesting that these elements are poorly correlated and may have different sources (Fig.3). Factor 4 is dominated by Cu, As and Mn (accounting for 2.7 % of the total variance; Mn is negatively correlated with Cu and As) in ESR, Zn, As and Pb (accounting for 5.4 % of the total variance; Zn and Mn are negatively correlated with As and Pb) in SSR and Pb and Mn (accounting for 1.3 % of the total variance; Mn is negatively correlated with Pb) in WSR.

Pearson's correlation matrix for the trace element concentrations in agricultural soils from Libya.

The correlations between trace element concentrations in agricultural soils showed a high, positive, linear relationship (Table 2). To determine whether geochemical associations exist between the different trace elements analysed in this study, the datasets for agricultural soils from each region and soils from ESR, WSR and SSR were subjected to simple correlation analysis. A scatter plot for the trace element correlations that were found to be significant ($P<0.05$) in some of the soils studied are presented in Fig.4. The correlation analysis was also performed on the composite data sets of all agricultural soils for this study. The Pearson correlation coefficients and P-values for Co, Zn, Cu, As, and Pb were significant and all the analyses are shown in Table 2.

Manganese

A summary of trace element Pearson correlation coefficients of soils from different regions of Libya are shown in Table 2, Fig.4 and Appendices 3.11, 3.12 and 3.13.Mn concentration showed
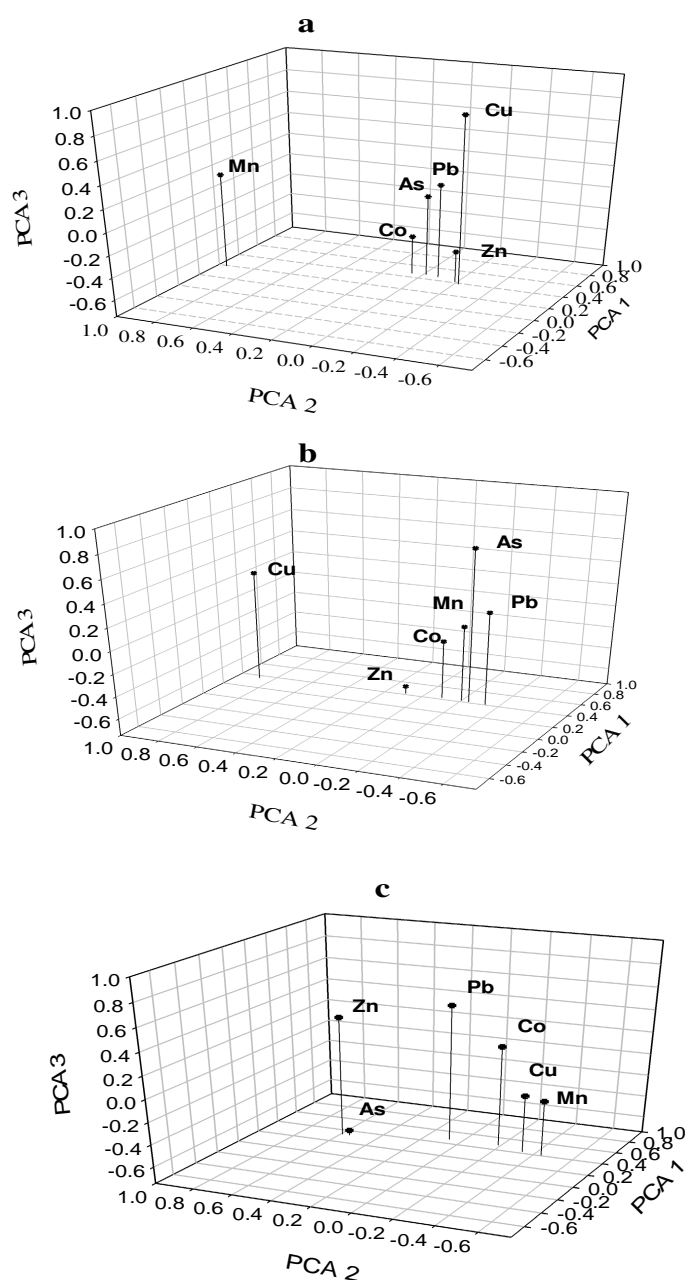
Figure 3. PCA loading plots for the three rotated components for a) SSR, b)WSR and c) ESR.

a significant correlation with Co, Zn, Cu and Pb in WSR and ESR. However, Mn is not correlated with As and Pb in ESR or SSR, respectively, or with the other metals (Co, Zn and Cu) in SSR, reflecting different sources for Mn and the other elements. Moreover, Mn is not correlated with As and not significant in ESR and SSR, which may suggest a common origin (Table 2 and Fig.4).

Lead

The Pb concentration showed a significant correlation with Co, Zn, Cu and As concentrations in all three of the agricultural soil regions (Fig.5a, b & c and Table 2).

Arsenic

As is not correlated with Co and Cu in ESR; however, As concentration showed a significant correlation with Zn concentrations in all three of the soil regions. Trace element correlations with As were slightly varied across regions. As is also positively correlated with Co, Cu and Zn in SSR and WSR (Table 2 and Fig.6a, b & c).

Zinc

Zn concentration correlated well with Co and Cu in soils from WSR and SSR sites but not with those from ESR (Table 2). The Cu-Zn and Zn-Co correlations, however, remained significant ($P<0.01$) when the analysis was performed on the composite data sets (Figs 3.7 and 3.8, respectively). [6]Reported that in Libya, depending on the crop and soil, farmers use an average of 100 kg/hectare of phosphate fertilizer annually.

	ESR	WSR	SSR
Mn-Co	(+ C *)	(+ C *)	(+ 0 NS)
Mn-Zn	(+ C *)	(+ C *)	(+ 0 NS)
Mn-Cu	(+ C *)	(+ C *)	(+ 0 NS)
Mn-As	(+ 0 NS)	(+ C *)	(+ C NS)
Mn-Pb	(+ C *)	(+ C *)	(+ 0 NS)
Pb-Co	(+ C *)	(+ C *)	(+ C *)
Pb-Zn	(+ C *)	(+ C *)	(+ C *)
Pb-Cu	(+ C *)	(+ C *)	(+ C *)
Pb-As	(+ C *)	(+ C *)	(+ C *)
As-Co	(+ 0 *)	(+ C *)	(+ C *)
As-Zn	(+ C *)	(+ C *)	(+ C *)
As-Cu	(+ 0 *)	(+ C *)	(+ C *)
Cu-Co	(+ C *)	(+ C *)	(+ C *)
Cu-Zn	(+ 0 *)	(+ C *)	(+ C *)
Zn-Co	(+ 0 *)	(+ C *)	(+ C *)

+: positive correlation (significant at $P< 0.05$)

−: negative correlation (significant at $P< 0.05$)

NS: not significant at $P< 0.05$
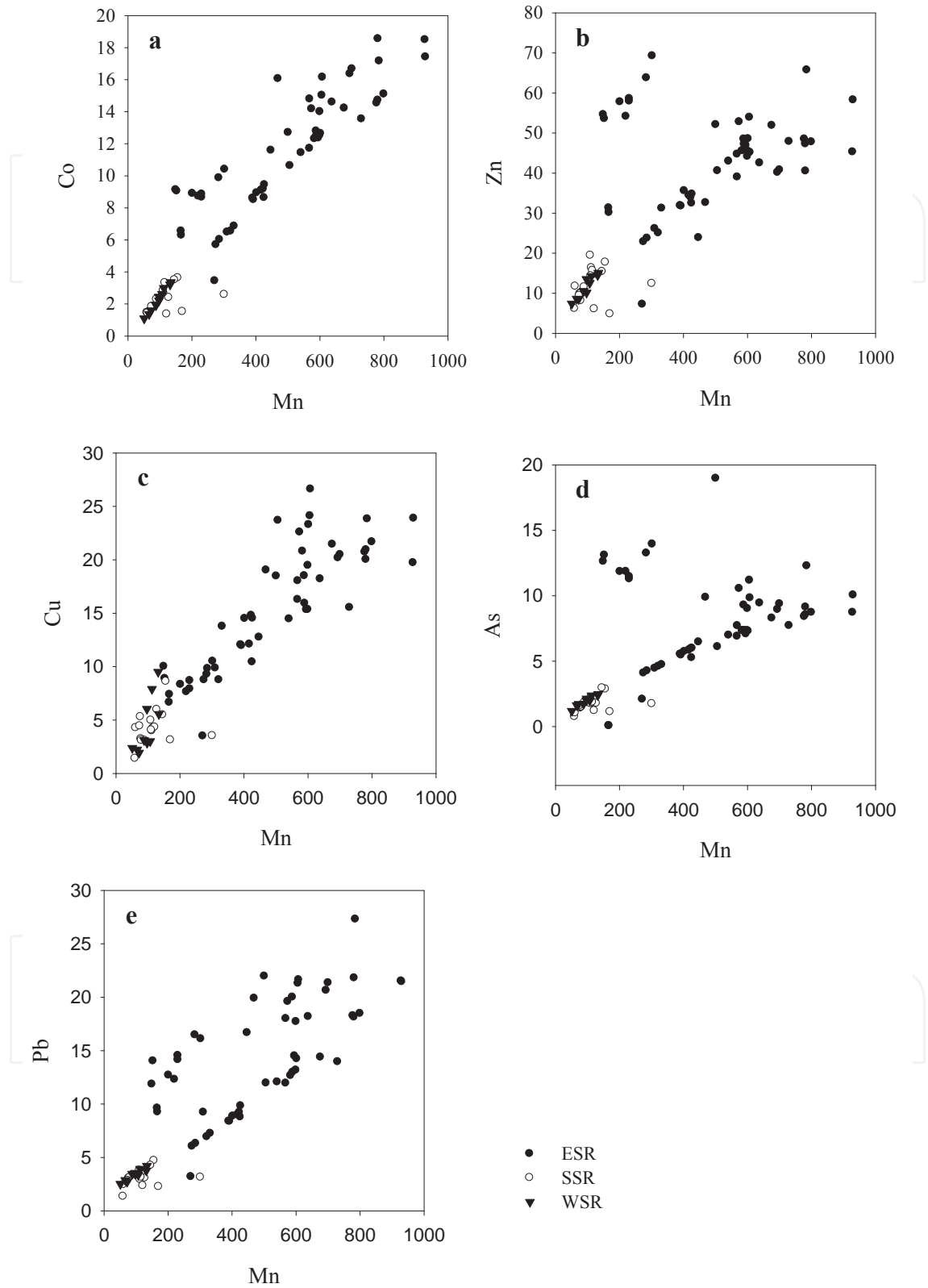
*:significant at $P< 0.05$

0: no correlation

C: correlation ($r> 0.50$)

Table 2. Summary of trace element correlation in soils from different regions of Libyan soils (see for correlation coefficients and P-values).

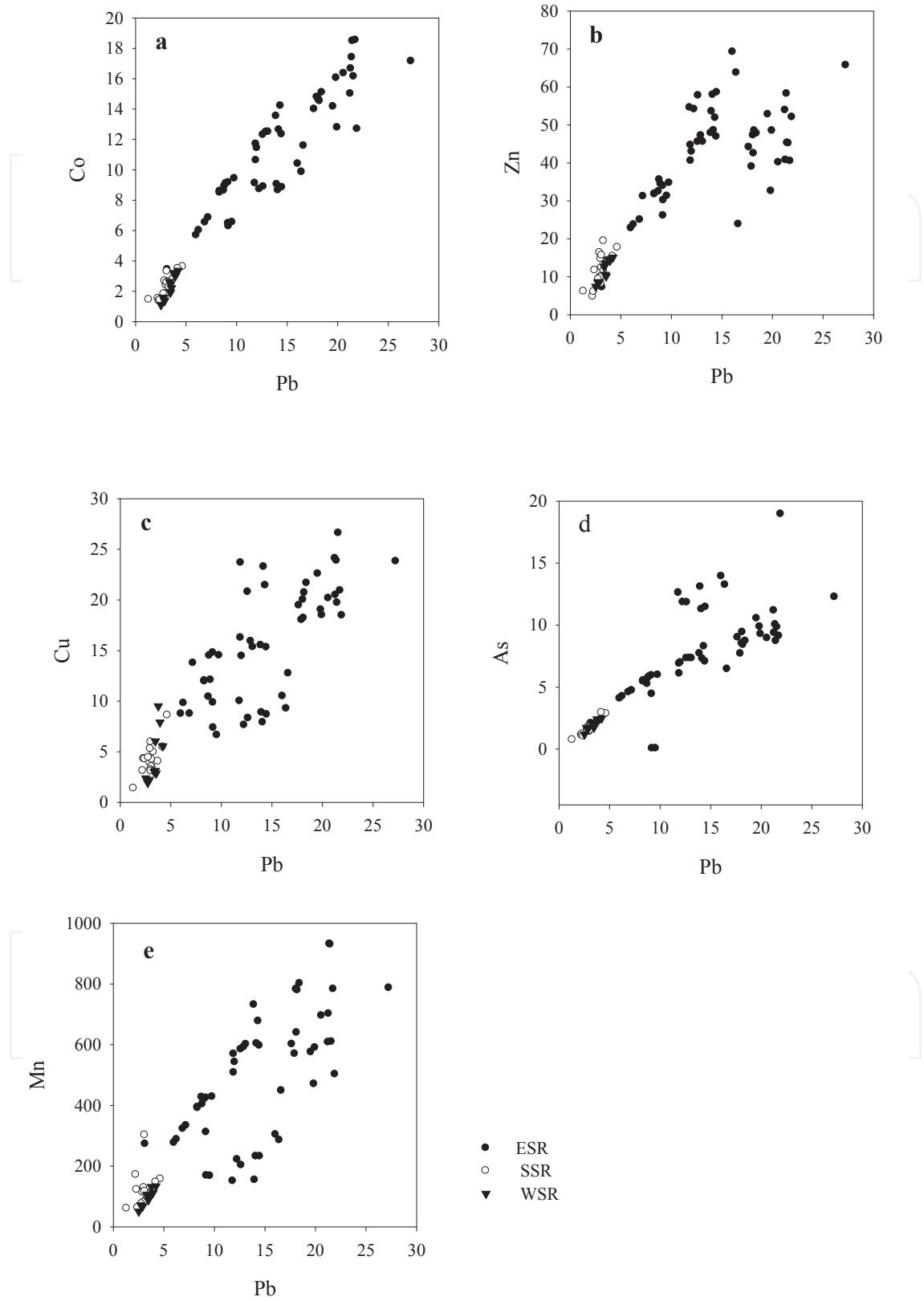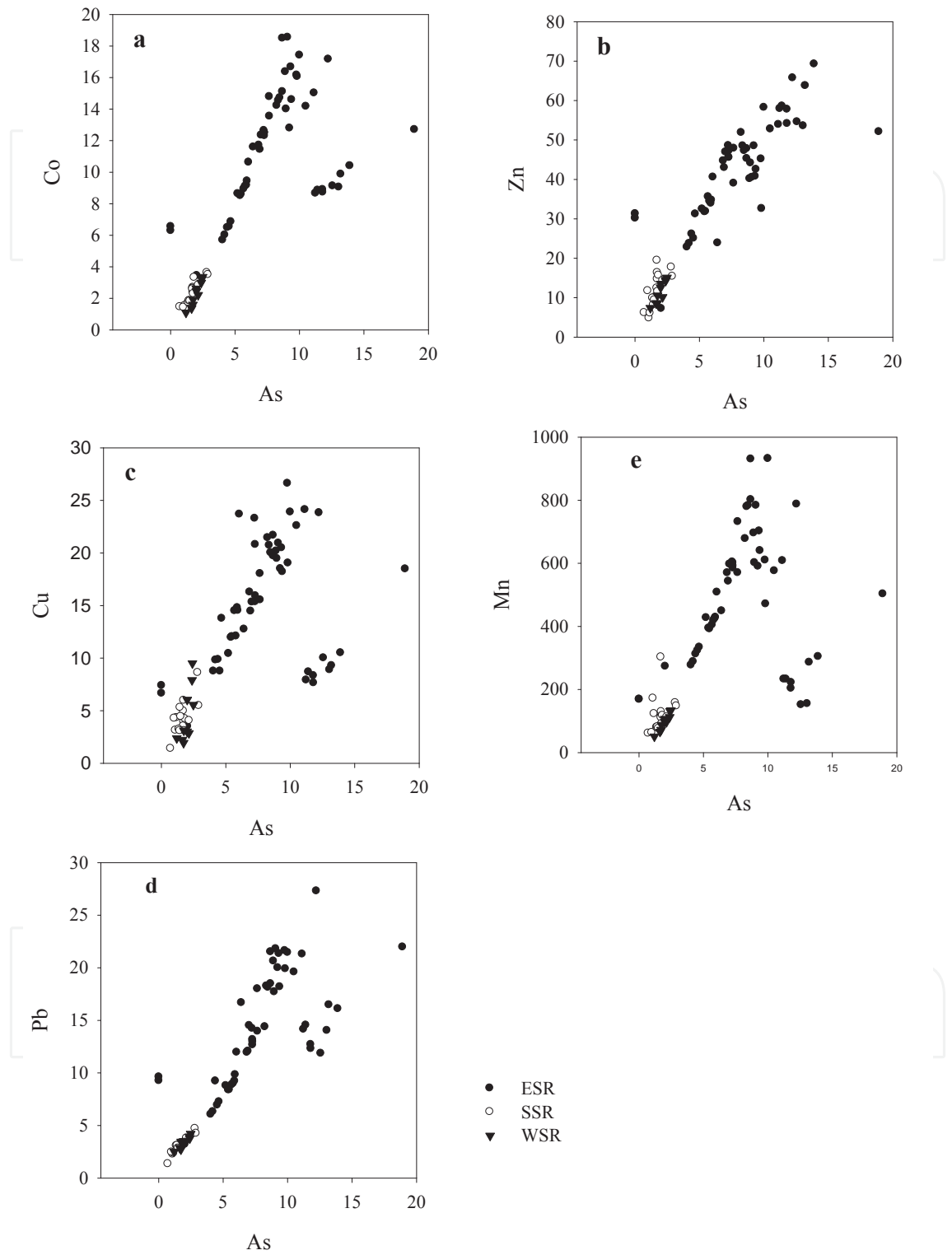**Figure 4.** Mn correlations against other trace elements in agricultural soils from ESR, SSR and WSR sites.

Figure 5. Pb correlations against other trace elements in agricultural soils from ESR, SSR and WSR sites.

Figure 6. As correlations against other trace elements in agricultural soils from ESR, SSR and WSR sites.
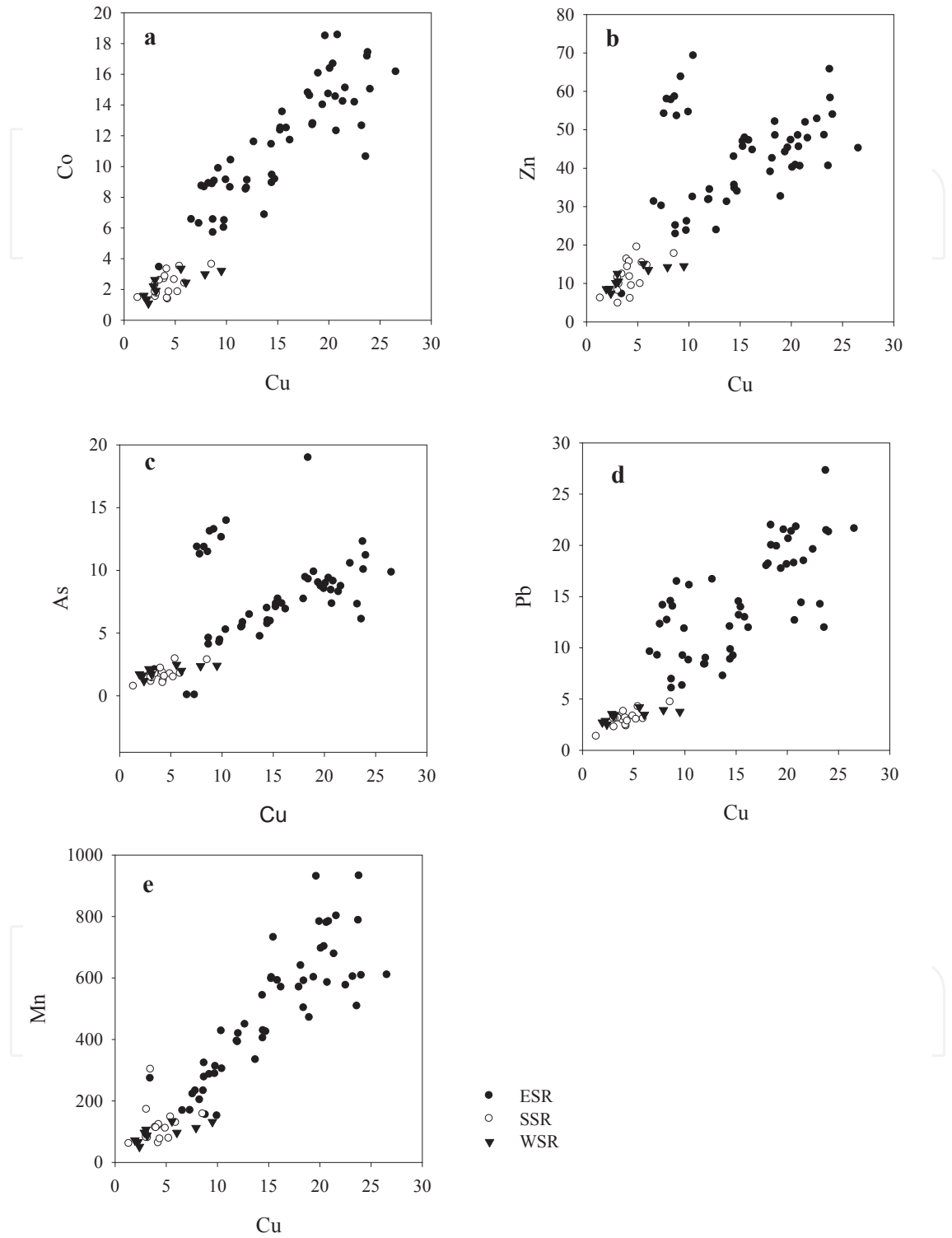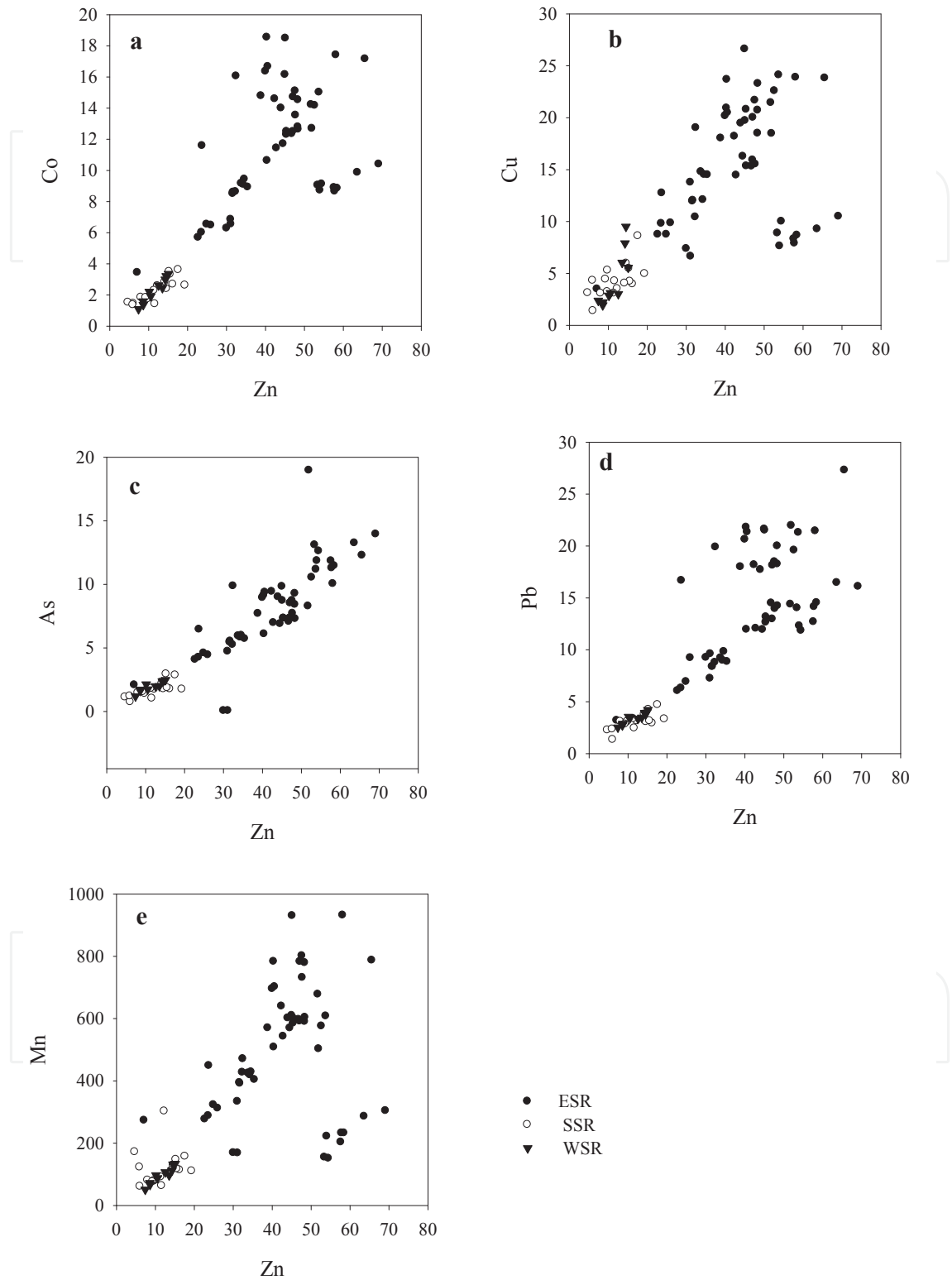
Figure 7. Cu correlations against other trace elements in agricultural soils from ESR, SSR and WSR sites.

Figure 8. Zn correlations against other trace elements in agricultural soils from ESR, SSR and WSR sites.

Overview of total shoot, soil and grain As for ESR, SSR and WSR

A one-way analysis of variance (ANOVA) was performed on each of the three regions studied. The ANOVA showed that that the mean As levels for grain between sites were not significantly different (P=0.662), but that those for soil and shoot were (soil: P<0.001; shoot: P<0.002). Fig.9 shows a comparison of the distribution of As concentrations in the shoot, soil and grain from ESR, WSR and SSR.
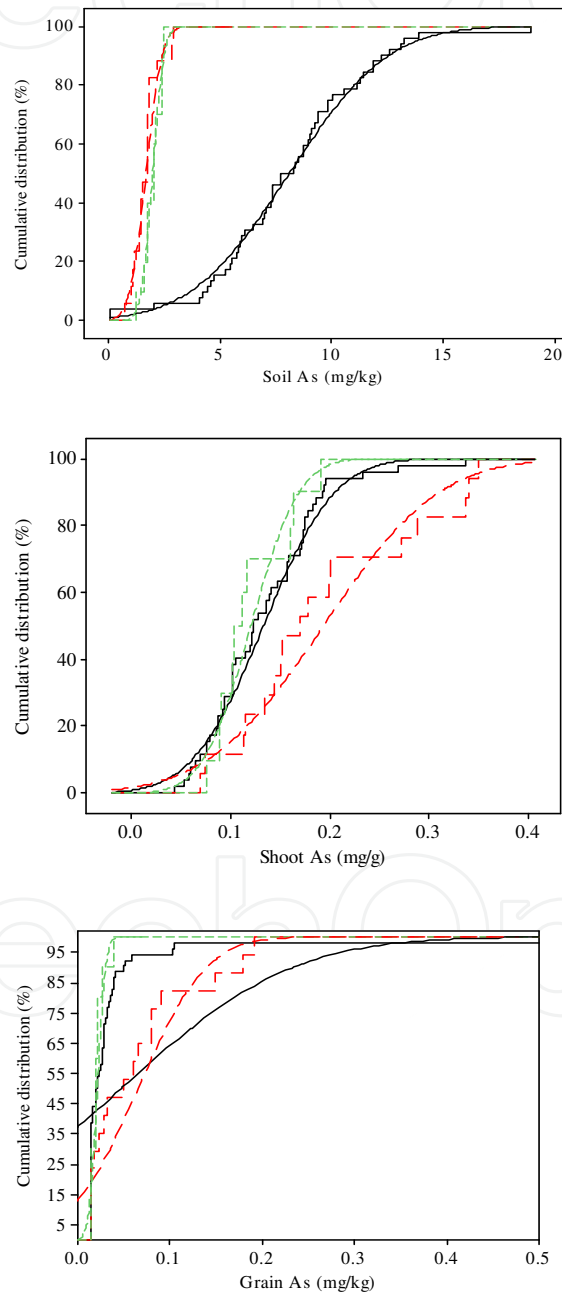
Figure 9. Cumulative ranked distribution of As concentrations in Libyan agricultural soil, shoot and grain from ESR (solid), WSR (dash) and SSR (square dot).

The mean shoot As content for SSR (range 0.07–0.35 mg/kg; mean: 0.19 ± 0.02 mg/kg) was higher than for ESR (range 0.04–0.34 mg/kg; mean: 0.13 ± < 0.01 mg/kg) and WSR (range 0.01–0.19 mg/kg; mean: 0.12 ± < 0.01mg/kg). At the 50th percentile, shoot As content for SSR (0.17 mg/kg) was more than 1.5 times that recorded for ESR (0.12 mg/kg) and WSR (0.11 mg/kg; Fig.9).

ESR recorded the highest mean As level in Libyan soil (8.10 ± 0.48 mg/kg, range 0.01–18.94 mg/kg), followed by WSR (1.97± 0.41 mg/kg, range 1.19–2.48 mg/kg) and SSR (1.70 ± 0.58 mg/kg, range 0.73–2.92 mg/kg), i.e. mean As concentrations in ESR are nearly 4.8 and 4.1 times higher than in SSR and WSR, respectively.

The mean grain As content for SSR (range 0.02–0.2 mg/kg; mean: 0.07±0.01 mg/kg) was also significantly higher (P< 0.01) than for ESR (range 0.02–1.1 mg/kg; mean: 0.05 ± 0.02 mg/kg) and WSR (range 0.02–0.04 mg/kg; mean: 0.02 ± < 0.01mg/kg). At the 50th percentile, grain As content for SSR (0.05 mg/kg) was over twice that recorded for ESR (0.02 mg/kg) and WSR (0.02 mg/kg; Fig.9).

The ranges of total grain, shoot and soil As concentrations over the three regions studied were relatively wide; however, the distribution was markedly skewed, with 65 % in ESR having grain, shoot and soil As concentrations of < 0.03, 0.17 and 9.9 μg, respectively, 21 % in SSR < 0.09, 0.28 and 1.8, respectively and 12 % in WSR < 0.02, 0.16 and 2.4, respectively (Fig.9).

As transfer from soil to shoot and grain

The range of As shoot/soil transfer factors (shoot/soil TFs) was considerable. Minimum and maximum shoot/soil TFs were 0.06 for ESR, 0.04–0.29 for SSR and 0.04 for WSR, while means and medians were 0.1 and 0.02, respectively, for ESR; 0.13 and 0.12 for SSR and 0.06 and 0.06 for WSR. In SSR, the median shoot/soil TF was nearly twice as high as that in ESR and WSR. In this study, transfer of As was an order of magnitude greater from shoot to grain, despite lower rates of soil to grain transfer. The differences in these transfer ratios may be due to differences in As speciation. [18],reported that, in general, higher shoot As levels were consistent with low grain/shoot transfer factors.

Estimation of bioavailable As concentrations by nitric acid extraction

Nitric acid extraction is a widely used method of estimating the bioavailable concentration of elements. The precision of the results in the present work was controlled by analysis of CRM, blank and spike samples. The correlation factors showed good precision, with the exception of two analytical bioavailable and total results (Table 3). A summary of the bioavailable As in soils sampled from ESR, WSR and SSR are shown in Table 3. A one-way analysis of variance (ANOVA) showed that the differences in As levels between location means are highly significant (P<0.001, Table 3). SSR recorded the highest mean levels of bioavailable soil As (0.05 ± 0.01 mg/kg) (Fig.10). In contrast, the highest total mean As level was recorded in ESR (8.10 ± 0.48 mg/kg;.Table 3 and Fig.11b). The mean bioavailable As concentrations in the three regions studied decreased from SSR > ESR > WSR (Table 3) and was in general low, ranging from 0.02–0.07 mg/g, 0.02–0.03 mg/g and 0.01–0.14 mg/g for SSR, ESR and WSR, respectively. Bioavailable concentrations of As are 1–5 % of the total concentrations. In this study, the highest median bioavailable / median total (B/T) As was recorded in SSR (Table 3, Fig.10 and 3.11b).

| Regions Elements	T	T	T	B	B	B		(B/T)*100
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	r[a]	B/T[b]
	Mean	Median	Range	Mean	Median	Range		%
As ESR	7.81	8.45	24.36	0.02	0.01	0.13	0.1	0.2
SSR	4.05	2.48	6.50	0.05	0.05	0.05	−0.4	**2.0**
WSR	4.42	3.96	7.16	0.02	0.02	0.02	−0.1	0.5
Co ESR	11.49	11.63	15.11	0.76	0.02	5.59	0.4	0.2
SSR	2.27	2.27	2.26	0.10	0.02	0.33	−0.4	**0.9**
WSR	2.28	2.33	2.26	0.02	0.02	0.01	0.9*	0.7
Cu ESR	15.39	15.32	23.12	0.29	0.06	2.30	0.3*	0.4
SSR	4.28	4.22	7.21	0.08	0.05	0.33	−0.1	**1.2**
WSR	4.46	3.07	7.57	0.04	0.05	0.05	0.6	1.5
Pb ESR	14.36	14.06	24.11	0.22	0.01	2.98	0.2	0.1
SSR	3.05	3.04	3.36	0.01	0.01	0.06	−0.2	**0.3**
WSR	3.39	3.46	1.69	0.00	0.01	0.01	−0.6	0.3
Mn ESR	492.30	504.60	780.60	58.50	8.50	300.50	0.5*	**1.7**
SSR	117.80	111.40	241.50	14.17	1.34	72.57	0.7*	1.2
WSR	95.66	96.89	82.96	1.15	0.98	2.50	−0.3	1.0
Ni ESR				0.72	0.10	4.32		
SSR				0.19	0.15	0.29		
WSR				0.09	0.10	0.03		
P ESR				7.66	1.95	105.61		
SSR				52.80	33.40	154.40		
WSR				8.92	9.96	12.27		

[a]**Correlation is significant at the 0.05 level

[b]B/T= Median bioavailable/ Median total %

Table 3. The descriptive statistics for total (T) and bioavailable (B) trace element concentrations in Libyan soils (mg/kg).

There was no correlation between the mean total and the bioavailable As concentrations in ESR and WSR. However, there was a negative correlation between the mean total and the bioavailable As in SSR. [16]. reported that appreciable As can move with leaching water, especially in coarse-textured soils. The mean and median bioavailable As concentration values for SSR were close to the those for WSR and ESR (Table 3). The correlation factors between the bioavailable and the total element concentrations were: 0.073, –0.419 and –0.097 (As); 0.371, –0.349 and 0.892 (Co); 0.318, –0.124 and 0.614 (Cu); 0.24, –0.161 and –0.545 (Pb); and 0.466, 0.659 and –0.309 (Mn) for ESR, SSR and WSR, respectively (Table 3, Fig.10). Adriano (1986) reported that As mobility and phytotoxicity is usually greater in sandy than in clayey soils. The SSR samples had high B/T bioavailable As, Co, Pb and Mn contents, compared to B/T total elements (Table 3 &Fig.10). In these samples, the levels of bioavailable elements were derived from P

fertilization) [12]. The low correlation value for total Cd is because the concentrations were lower than the ICP-MS detection limit. Weathering will increase bioavailability of trace elements in SSR. [1],found that at P:As ratios of 4:1 or greater, phytotoxicity on wheat was markedly reduced and deduced phytotoxicity to be a function of P concentration.
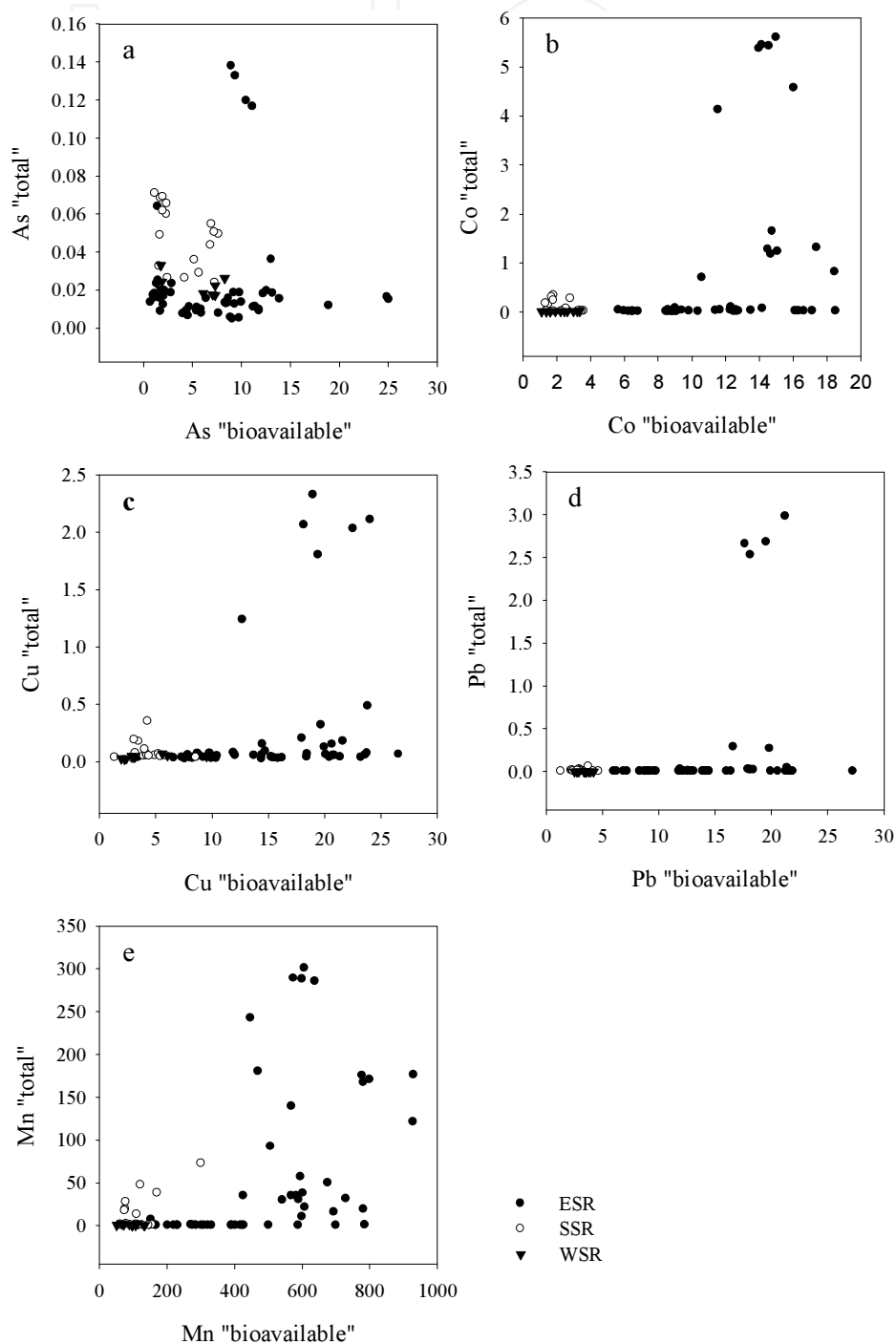
Figure 10. Scatter diagram of total vs. bioavailable trace element concentrations in agricultural soils from ESR, SSR and WSR.
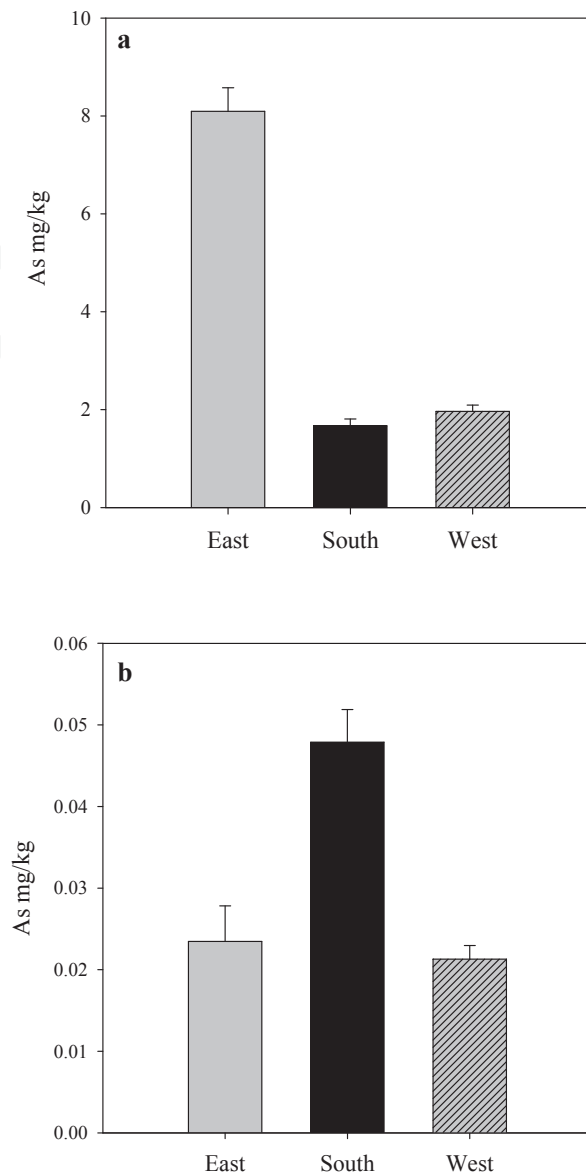
Figure 11. Comparison of (b) soil extractable of As with (a) total soil concentrations in Libya

4. Discussion

Total As mean concentrations in ESR are nearly 4.8 and 4.1 times higher than in SSR and WSR, respectively. Total As loads in ESR may be related to the soil parent material, which is comprised of subsequently covered Lower Palaeozoic rocks. This may be the reason why the clay agricultural soils of ESR have the highest background levels of As. This is in agreement with [8], who reported higher concentrations of trace elements in Eastern Libyan soil than in other areas. In the present study, the trace elements present in Eastern Libyan soil (Co, Zn, Cu,

As, Cd, Pb and Mn) were nearly five times higher than in WSR and SSR. Trace element concentrations in agricultural soils showed positive linear correlations (Table 2).

In this study, transfer of As was an order of magnitude greater from shoot to grain, despite lower rates of soil to grain transfer. In addition, this study considered samples of soil, shoot and wheat grains from arable land with a sampling design that allowed for the consideration of intra-field variations. The differences in these transfer ratios may be due to differences in As speciation. [18]reported that, in general, higher shoot As levels were consistent with low grain/shoot transfer factors. Although this similarity in trends for plants from varying geographical locations strongly suggests the involvement of plant physiological regulation, the actual mechanisms involved are still far from clear. However, the findings from the present study indicate that As transfer to grain isgoverned by multiple factors (Fig. 7.1). The bioavailability of trace elements in soils is influenced by a wide array of biophysical factors (Fig. 7.1), including pH, redox potential, organic matter content and soil texture. These factors were, however, not considered in the experimental/sampling design since the main thrust of the field studies was to establish the contribution of elevated soil As to grain As levels.

In this study, the highest median bioavailable / median total (B/T) As was recorded in SSR (Table 3, Fig.10 and 3.11b).[15]reported that appreciable amounts of As can move with leaching water, especially in coarse-textured soils. This is in agreement with the [9], which reported that As mobility and phytotoxicity is usually greater in sandy than in clayey soils. The SSR samples had high B/T bioavailable As, Co, Pb and Mn contents, compared to B/T total elements (Table 3 &Fig.10). In these samples, the levels of bioavailable elements derived from P fertilization (Hurd-Karrer 1939) and the high pH affects the availability of many crop nutrients in the southern Libyan soil [12]. Weathering will increase bioavailability of trace elements in SSR. [10]found that at P:As ratios of 4:1 or greater, phytotoxicity on wheat was markedly reduced and deduced phytotoxicity to be a function of P concentration.

The present study agrees with [16], who reported that the available soil moisture holding capacity for silty clay loams is three times higher than for loamy sands. Therefore, in the present study, total As mean concentrations in ESR are nearly 4.8 times higher than in SSR. Total As loads in Libyan agricultural soil may be related to the soil moisture holding capacity, with different types of soil having varying capacities and also different levels of As.

5. Future research

- To investigate the differential efficiency with which the main species of As found in Mediterranean conditions wheat are transferred to the grain, resulting either from remobilised shoot As, or coming direct from the soil.

- Effects of As on As uptake, speciation, and nutrient uptake by winter wheat (*Triticum aestivum* L.) under hydroponic conditions.

- Determination and comparison of total As concentrations and speciation in different parts of the wheat plant at various stages of growth and in different genotypes.

- Future research needs to focus on the balance of trace elements in an agro-ecosystem, elaboration of soil chemical and biochemical parameters that can be used to diagnose soil contamination with or deficiency in trace elements, and quantification of trace metal transport from an agro ecosystem to the environment.

- Investigate the relationship between mobility and leaching of As and soil profile depth.

- Set up baseline concentrations of As in Libya soil and wheat. This is of great importance since Libya, as a nation, consumes an enormous quantity of rice.

- The determination of the trace elements iron, zinc, phosphors, cobalt and cadmium in Libyan arable soils is essential for the management of fertilizers and pest side in that soils projects.

Acknowledgements

Author details

Youssef F. Lawgali[1*], Andy A. Meharg[2] and Yousef M.T. Elgimati[3]

*Address all correspondence to: yogaly6@yahoo.com

1 Department of plant production, University of Sirte, Libya

2 School of Biological,Queen's University Belfast, UK

3 Benghazi University, Libya

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