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Availability and fractionation of trace elements in arid calcareous soils

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Abstract

Thirty seven soil samples were collected from seven agricultural regions in Saudi Arabia to investigate trace element availability and fractionation distribution. Di-ethylene tri-amine penta acetic acid extractable micronutrients ranged from 1.1 to 11.5 $\mu\text{g g}^{-1}$ for Fe, 0.2-3.7 $\mu\text{g g}^{-1}$ for Zn, 0.48-13.0 $\mu\text{g g}^{-1}$ for Mn, and 0.2-3.7 $\mu\text{g g}^{-1}$ for Cu. Based on published critical levels, Cu was sufficient for most crops in all soils. Four soil samples were low in Mn, 28 were low in Zn, and 31 were low in Fe. Fractionation of micronutrients (Fe, Cu, Zn, and Mn) in selected seven soil samples revealed that the exchangeable fractions were the smallest, with Zn and Cu below detection limits. Carbonate bound fractions showed the micronutrient concentrations in the order Mn>Fe>Cu>Zn. Oxide and hydroxide bound fraction was higher than the previous two fractions; the order of the metals was Fe>Mn>Zn>Cu. For the organic bound fractions, the order was Fe>Mn>Cu>Zn. The residual fraction was the largest. The order of residual micronutrients was Fe>Mn>Zn>Cu. Overall, and considering the total amount of the four micronutrients within each fraction, the five fractions followed the order: Residual>oxide bound>CO₃ bound>organic bound>exchangeable. Based on the data, it is recommended that Fe and Zn applications should be included in balanced fertilization programs. Mn and Cu are sufficiently available in the studied soils, and may not need to be supplied to crops

Key words: Arid, Calcareous, Exchangeable, Fractionation, Micronutrients

Introduction

Saudi Arabia is a vast country with approximately 2 million km² of arid land (Saudi Geological Survey, 2012). It represents about 5% of the arid zones of the world (Bashour et al., 1983). During the past three decades about 1.2 million hectares of desert soil have been converted into irrigated farming land, and are being intensively used for growing major field crops, fruit trees, and vegetables (Ministry of Agriculture, 2012). The agricultural soils of Saudi Arabia are in general coarse to medium textured, calcareous, low in organic matter, and moderately alkaline (Bashour et al., 1983; Ministry of Agriculture and Water, 1986;

Al Jaloud, 1988). Deficiency of Fe, Zn, Cu, and Mn is common in calcareous soils (Mortvedt et al., 1972; Tisdale et al., 1993). Al Jaloud et al. (1995) studied micronutrients fractions in selected Saudi soils and concluded that available Fe and Zn are low in most analyzed samples while Mn and Cu were present in adequate concentrations. Nevertheless, their study covered selected areas and a relatively small sample size. To our knowledge, there are no comprehensive trace elements availability and fractionation studies covering most agricultural areas of the country. Most of the previous studies looked at di-ethylene tri-amine penta acetic acid (DTPA)-extractable trace elements only, thus ignoring other potential pools of trace elements. In fact, many studies have reported significant correlations between the amounts of trace elements in chemical soil fractions and the amounts taken up in plant tissues (Canet et al., 1998; Qian et al., 1996; Zhang et al., 1998), suggesting the consideration of these fraction related pools in micronutrient research; correlations

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between trace-element soil fractions and trace element concentrations in crop tissue indicate that chemical fractions do relate to phyto-availability.

Several fractionation schemes for micronutrients availability and fractionation in agricultural soils have been reported in literature (McLaren and Crawford, 1973; Wagemann et al., 1977; Shuman, 1979; Shuman, 1985; Shober et al., 2007). Trace elements fractionations were also studied from environmental perspectives (Filgueiras et al., 2002; Ahdy and Youssef, 2011; Okbah et al., 2011). Tessier et al. (1979) developed a procedure for fractionation of micronutrients in calcareous soils, and many scientists adapted it to their specific research needs; this methodology is suitable for the current study because it has a separate step for the CO_3^{2-} bound fractions which are widely present in calcareous soils. It fractionates soil metals sequentially into five parts: exchangeable, carbonate bound, oxide (and hydroxide) bound, organic bound, and residual. Accurate determination of micronutrient fractions can help in predicting their potential bioavailability to crops under various environmental conditions; in arid environments and calcareous soils, the organic and carbonate fractions play a critical role in micronutrient biodegradation and mobilization (Chanem and Mikkelsen, 1987; Stone and Marsalek, 1996).

The objective of this study is therefore to assess the availability status and fractionation levels of Fe, Zn, Cu, and Mn in calcareous soils representing seven major agricultural regions of the arid environment in Saudi Arabia.

Materials and Methods

A total of thirty seven composite soil samples were collected from farmed lands, covering and representing each of the seven major agricultural areas. The cultivated crops are primarily wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), open field vegetables, and forages; the main forage is alfalfa (*Medicago sativa* L.); for these crops, the majority of mass and effective rooting system develops on the top 20 cm plowable soil layer. Annual irrigation water amounted to $7000 \text{ m}^3\text{ha}^{-1}$ for wheat and barley, $10000 \text{ m}^3\text{ha}^{-1}$ for vegetables, and $17000 \text{ m}^3\text{ha}^{-1}$ for forages. Salinity of irrigation water ranges from a high 3.3 to a low 0.9 dSm^{-1} in Qassim and Hail, respectively (Al Jaloud and Al Rabhi, 2013); Ca, Mg, Na, and Cl are high in Wadi Dawassir and Kharj, but low in Hail; micronutrient concentration in irrigation water was below the detection limits. Fertilizers programs and strategies were adapted to each region, given

the differences in soil physical and chemical properties, and environmental conditions. Crops grown on these soils received macro and micro nutrients as per regional recommendations (Al Safi Dairy Est., 2000; Errebhi and Al Jaloud, 2003). The collected samples were air dried, ground to pass through a 2 mm sieve, and stored for subsequent analyses. The $\text{CaCO}_3\%$, Electrical Conductivity (ECe), and pH were determined as outlined in USDA Salinity Laboratory Handbook 60 (Richards, 1954). The micronutrients were extracted by the DTPA technique, which was reported by Lindsay and Norwell (1978) to be an efficient procedure for simultaneous assessment of Fe, Zn, Cu, and Mn availability in calcareous soils. Extraction of micronutrients with DTPA solution is widely acceptable as it gave beneficial information about the availability of micronutrients in soils. The metal content (Fe, Zn, Cu, Mn) from DTPA-extraction was analyzed by Atomic Absorption Spectrophotometer, Perkin Elmer 503 (Perkinelmer, Inc. 940 Winter St. Waltham, MA 02451 USA, www.perkinelmer.com).

From each geographic region, one representative composite soil sample (the first row for the region, Table 1) was selected based on prior knowledge of these regions, the commonly dominating soil types and crops, and more importantly, on the surface area they represent for that region. Samples were used to determine soil texture by the hydrometer method (Foth et al., 1977), soil organic matter by the digestion procedure (Nelson and Sommers, 1996), and micronutrient fractionation (Tessier et al., 1979). The fractionation scheme of Tessier et al. (1979) was applied in this case because it involves a separate extraction step for the CO_3 bound fractions; therefore, it is suitable for calcareous soils. Fractionation provides the additional benefit of estimating the other forms in which Fe, Zn, Cu, and Mn are present in various soils components. Sequential chemical fractionation procedures segregate trace elements into soil fractions by subjecting the soil to a series of chemical reagents, each more destructive than the previous one (Zufiaurre et al., 1998; Tessier et al., 1979; Morabito, 1995). The following soil fractions are the most widely used and acceptable among the scientific community: (1) exchangeable ; (2) bound to carbonates; (3) bound oxides and hydroxides (reducible); (4) bound to organic matter and sulfides (oxidizable); and (5) residual: in the mineral lattice of silicates or nonreducible oxides or hydroxides (McLaren and Crawford, 1973; Sims and Kline, 1991; Morabito, 1995; Tessier et al.,

1979; Emmerich et al., 1982). The trace elements in the soil fractions are, ideally, indicative of their potential mobility and bioavailability, in a decreasing parallel to the order of the sequential extraction steps. The fractionation procedure was as follows:

Exchangeable

To 5 g soil sample, 40 mL of 1M magnesium chloride at pH 7.0 was added, and the content was shaken continuously for 1 hour at room temperature. After centrifugation, the supernatant solution was filtered and saved for analysis. The residue was washed with 20 mL water, and the washings were discarded.

Carbonate Bound

The residue from (1) was agitated continuously for 5 hours with 40 mL of 1M sodium acetate (pH 5.0). After agitation, the supernatant solution was filtered and stored for analysis. After extraction, the residue was washed with 20 mL of water, and the washings were discarded.

Iron-Manganese oxide bound

To the residue from (2), 100 mL of 0.04 M hydroxylamine hydrochloride was added in 25% (v/v) acetic acid (HOAc), and the extraction was carried out at $95\pm 2^\circ\text{C}$ in a water bath, with occasional agitation for 6 hours. After centrifuging, the residue was washed with the required amount of water (20 mL) and the washings were combined with the original extract after filtration to make up a total volume of 100 mL.

Organic Bound

The residue from (3) was first treated with 15 mL of 0.02 M nitric acid (HNO_3) and 25 mL of 30% hydrogen peroxide (pH 2.0) for 5 hours at $85\pm 2^\circ\text{C}$ in a water bath. A second 15 mL aliquot of 30% H_2O_2 was then added, and the contents were again heated to 85°C for 3 hours with intermittent agitation. After cooling, 25 mL of 3.2 M ammonium acetate (NH_4OAc) in 20% v/v HNO_3) was added and agitated continuously for 30 minutes. After centrifuging, the residue was washed with 20 mL of water and the washings were added to the extracted solution after filtration to make up a final volume of 100 mL.

Residual

For this study, 1 g of soil sample was taken from (4) and treated with 2 mL of 70% perchloric acid (HClO_4) and 10 mL of hydrogen fluoride (70% HF) in a platinum crucible. The contents were digested on a hot plate and when the residue became paste, a second addition of 1 mL of HClO_4

and 10 mL of HF was made. Again, the contents were digested to near dryness. Finally 1 mL of HClO_4 was added and evaporated again until the appearance of white fumes. The contents were then dissolved in 6N hydrochloric acid (HCl), filtered, and made up to 100 mL, then kept in clean plastic bottles for analytical work.

Metal content from fractionation was also analyzed by Atomic Absorption Spectrophotometry.

Results and Discussion

Soil samples

The regional sources of the soils samples and the analytical results are presented in Tables 1-3. The results show that soils have a wide range of CaCO_3 content, a narrow range of pH, different salinity levels, and various micronutrient concentrations.

DTPA-Extractable Micronutrients

Table 1 summarizes some important soil chemical properties of the thirty seven surface soil samples. DTPA-extractable Fe, Zn, Mn, and Cu concentrations are also given. Results of the chemical analyses show that the soil samples are slightly alkaline; pH ranges from 7.3 to 8.2 across all geographic regions, with no major difference among the regions, as the regional mean pH range varies from 7.6 to 7.9 (Table 1). Calcium carbonate data indicates that the soils are calcareous; CaCO_3 content ranges from a low of 3.3% to a high of 24.6%, with noticeable regional mean differences varying from 6.87% in Taif to 18.82% in Kharj. Salinity levels, measured by saturated paste extract Electrical Conductivity (ECe), indicate the presence of saline soils in all the regions, except Taif. Across regions, the EC ranges from 1.00 to 11.51 dS m^{-1} . This data agrees with previously reported findings for pH, calcium carbonate, and electrical conductivity in agricultural areas of Saudi Arabia (Al Safi Dairy Est., 2000; Errebhi and Al Jaloud, 2003; Sallam, 2002). The DTPA-extractable Fe, based on collected samples, ranges from 1.1-11.70 $\mu\text{g g}^{-1}$, but the ranges are narrowed to 2.84-5.65 $\mu\text{g g}^{-1}$ based on regional means (Table 1). DTPA-extractable Zn individual data ranges from 0.2 to 3.7 $\mu\text{g g}^{-1}$, but on regional average, the interval was 0.3-1.5 $\mu\text{g g}^{-1}$. Manganese individual data shows a wide range of (0.48-13.00 $\mu\text{g g}^{-1}$); however, for the averaged numbers across regions, the data narrowed significantly to (0.95-7.93 $\mu\text{g g}^{-1}$). DTPA-extractable Cu ranges from 0.22 to 2.80 $\mu\text{g g}^{-1}$ with no major change for the regional averaged data.

Table 1. Soil chemical properties and DTPA-extractable Fe, Zn, Mn, and Cu concentrations for thirty seven soil samples from seven different agricultural regions in Saudi Arabia.

Region and Sample ID		pH	CaCO ₃ [%]	ECe [dS m ⁻¹]	Fe	Zn	Mn	Cu
					[μg g ⁻¹]			
Kharj	1	7.7	12.2	2.7	2.80	0.20	0.72	0.41
	2	7.5	23.0	5.4	4.00	3.70	4.82	0.52
	3	8.0	16.8	8.3	3.61	0.30	1.27	0.31
	4	7.9	19.9	6.2	2.95	0.52	2.31	0.28
	5	8.1	22.2	3.3	3.40	0.43	2.50	0.22
Mean		7.84	18.82	5.18	3.35	1.03	2.32	0.35
SD		±0.24	±4.41	±2.26	±0.49	±1.50	±1.58	±0.12
Delim	6	8.0	16.8	6.3	3.50	0.30	3.00	0.50
	7	7.8	6.9	2.8	3.66	0.52	3.30	0.24
	8	8.0	17.1	5.3	4.10	0.33	3.50	0.70
	9	7.5	24.6	8.5	6.70	1.41	6.00	0.40
	10	7.4	17.8	4.4	1.10	0.32	2.50	0.34
Mean		7.74	16.64	5.46	3.81	0.58	3.66	0.44
SD		±0.28	±6.32	±2.13	±1.99	±0.47	±1.36	±0.18
Qassim	11	7.6	4.6	6.0	3.00	0.24	4.20	0.38
	12	7.5	14.0	7.5	7.50	0.48	6.30	1.1
	13	7.9	9.7	1.7	3.30	0.50	6.30	0.56
	14	7.9	3.8	1.7	3.30	0.48	1.90	0.22
	15	8.0	12.3	3.5	2.92	0.43	2.2	0.30
Mean		7.78	8.88	4.08	4.00	0.43	4.18	0.51
SD		±0.22	±4.55	±2.60	±1.96	±0.11	±2.13	±0.35
Hail	16	7.8	8.9	1.7	3.00	0.26	3.4	0.26
	17	8.1	12.7	5.2	4.10	0.48	2.98	0.32
	18	7.9	18.3	3.3	2.73	0.33	4.10	0.54
	19	7.8	17.3	2.8	3.42	0.41	2.20	0.44
	20	7.8	17.5	2.9	3.30	0.38	2.18	0.38
Mean		7.9	14.94	3.18	3.30	0.37	2.97	0.40
SD		±0.13	±4.03	±1.28	±0.52	±0.08	±0.82	±0.11
Jouf	21	7.8	15.5	3.8	3.20	0.37	2.82	0.37
	22	7.7	14.3	5.5	4.53	0.29	3.44	0.28
	23	7.7	7.8	2.2	5.22	1.20	5.22	0.79
	24	7.6	8.2	4.1	3.21	0.80	3.85	0.41
	25	7.9	5.7	3.6	2.30	0.66	3.40	0.32
Mean		7.7	10.3	3.84	3.69	0.66	3.75	0.43
SD		±0.11	±4.33	±1.18	±1.17	±0.36	±0.90	±0.21
Wadi Dawasir	26	8.2	10.1	4.2	3.84	0.28	1.55	0.28
	27	7.8	13.8	7.40	3.00	0.32	0.50	1.44
	28	8.1	9.9	8.21	2.90	0.31	0.48	0.42
	29	7.3	8.2	11.51	1.10	0.32	0.60	0.30
	30	7.9	12.4	3.62	3.35	0.27	1.62	0.29
Mean		7.9	10.88	6.99	2.84	0.30	0.95	0.55
SD		±0.35	±2.21	±3.21	±1.04	±0.02	±0.58	±0.50
Taif	31	8.1	7.4	2.30	4.50	1.80	10.0	1.90
	32	7.7	11.5	3.30	3.50	0.86	7.80	1.14
	33	7.8	3.3	3.70	11.7	2.00	8.00	2.80
	34	7.7	4.5	1.00	3.66	0.22	4.70	0.64
	35	7.5	12.5	1.20	3.30	0.44	7.60	1.48
	36	7.4	3.8	1.50	9.10	3.20	13.0	1.82
	37	7.3	5.1	5.80	3.80	1.96	4.40	0.74
Mean		7.6	6.87	2.69	5.65	1.50	7.93	1.5
SD		±0.27	±3.75	±1.72	±3.65	±1.05	±2.97	±0.75
Mean, pooled		7.8	12.17	4.39	3.91	0.74	3.91	0.64
SD, pooled		±0.24	±5.77	±2.41	±1.98	±0.81	±2.74	±0.57

Table 2. Chemical and Physical properties of the soil samples representing all the agricultural regions of Saudi Arabia.

Location	pH	ECe (dSm ⁻¹)	CaCO ₃	OC ^a	Sand (%)	Silt	Clay	Textural Class
Kharj	7.7	2.7	12.2	0.10	92	2	6	Sand
Delim	8.0	6.3	16.8	0.10	43	25	32	Clay Loam
Qassim	7.6	6.0	4.6	0.73	50	16	34	Sandy Clay Loam
Hail	7.8	1.7	8.9	0.11	81	8	11	Sandy Loam
Jouf	7.8	3.8	15.5	0.10	79	10	11	Sandy Loam
Wadi D	8.2	4.2	10.1	0.24	87	8	5	Sand
Taif	8.1	2.3	7.4	0.92	50	31	19	Loam

a OC: Organic Carbon

It is interesting to notice that the highest mean concentrations for Fe, Zn, Mn, and Cu are found in Taif region. A probable explanation would be the presence of relatively high organic matter in this region (see Table 2). The relationship between high organic matter and high levels of micronutrients is supported by previous studies from the same and similar regions (Bashour et al., 1983; Al Jaloud et al., 1995). On the other hand, most of the low mean concentrations for Fe, Zn, Mn, and Cu are found in Wadi Dawassir region, most likely due to high pH, high CaCO₃ content, and high salinity. Iron is low in 31 of the 37 soil samples, and Zn is low in 28 of 37, when related to the critical levels of Lindsay and Norwell (1978). None of the surface samples is low in Cu, and only 4 samples are low in Mn. Tisdale et al. (1993) reported that calcareous soils, soils low in organic matter, soils with pH higher than 7.0, leached sandy soils, and newly leveled soils are frequently low in Fe and Zn. Most of these conditions appear to exist in nearly all the soils of the present study, and could be the cause for the observed Fe and Zn deficiencies. These findings confirm earlier studies by Ramoliya et al. (2004) who reported that high salinity decreased Zn and Fe accumulation in plants, whereas Cu and Mn remained nearly unchanged.

Hagen and Tucker (1982) reported that Mn deficiency may occur in aerated alkaline calcareous soils irrespective of texture or organic matter content. They found that Mn availability was affected by soil oxidation-reduction conditions. Similar results were reported by El Fouly (1983) on calcareous soils in Egypt. Generally, the presence of free CaCO₃, alkaline pH values, and the medium to coarse texture of the soil samples may account for Fe and Zn deficiencies in the soils (Table 2). These findings could not be supported by the present data; in fact, there is hardly any correlations

(Figure 1) between CaCO₃ and DTPA-Fe ($y = -0.064x + 4.698$ with $R^2 = 0.035$), and between CaCO₃ and DTPA-Zn ($y = -0.011x + 0.871$ with $R^2 = 0.006$). A steeper slope and higher R^2 are expected for this relationship (Figure 1 A and B). Further research and investigation is required for better understanding of this poor relationship. Deficiency of Fe and Zn is common in Saudi Arabia's calcareous soils (Al-Jaloud et al., 1995); Prasad et al., 1984). Similar findings were reported earlier for Fe and Zn deficiency in calcareous soils (Loizides, 1975; Jones and Kelso, 1977).

The present results indicate that the soils are adequate in DTPA-extractable Mn and Cu for crop cultivation, and are generally medium to high in the studied calcareous soils, in all the regions representing nearly the whole country of Saudi Arabia. Fuehring (1973) reported that Mn and Cu are much less susceptible to be deficient in calcareous soils than Fe and Zn. These findings are supported by our data; in fact the lack of correlation between CaCO₃ and DTPA-Mn ($y = -0.130x + 5.493$ $R^2 = 0.075$), and DTPA-Cu ($y = -0.033x + 1.045$ $R^2 = 0.110$) prove that CaCO₃ content has no effect on extractable Mn and Cu (Figure 1 C, D).

In order to test and validate the present results, we investigated micronutrient availability in a separate project. Two large scale wheat and potato field trials were conducted in Delim and Jouf regions to study crop response to foliar micronutrient applications (Unpublished data). The application of iron as Fe-EDDHA at a rate of 3 kg ha⁻¹ gave significant increase in yield for both crops. However, the addition of Zn in the form of Zn-EDTA at a rate of 2.5 kg ha⁻¹ increased the yields of both crops, but the increase was not significant. Application of Mn and Cu did not lead to any increase in yield.

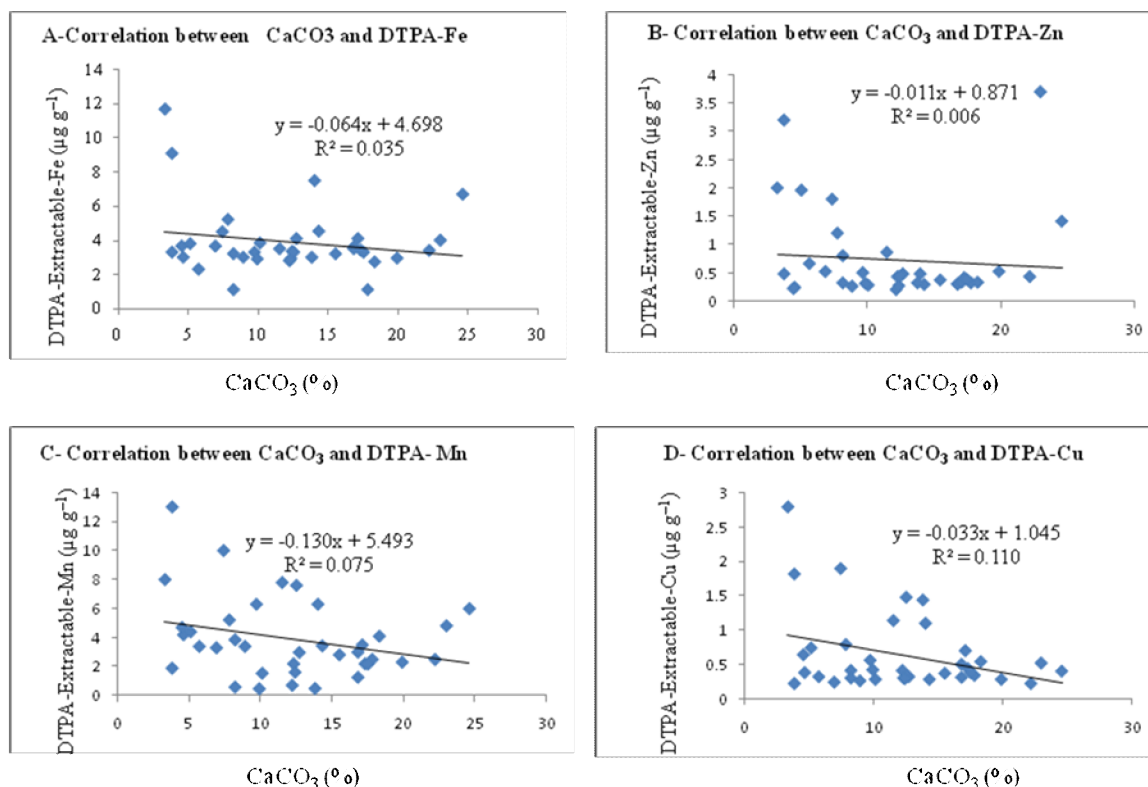


Figure 1. Correlation between CaCO_3 and DTPA-extractable iron, zinc, manganese and copper.

Fractionation of micronutrients

The concentrations of Fe, Zn, Mn, and Cu in the different fractions of the soils from all seven agricultural regions are given in Table 3.

Exchangeable fractions

The exchangeable fractions of micronutrients were by far the lowest among all fractions (Table 3). The exchangeable fractions of Zn and Cu in the seven soil samples were below the detection limits of the instrument. Out of the seven soil samples, 4 samples have exchangeable Fe at concentrations range $0.01\text{--}0.02 \mu\text{g g}^{-1}$, and 5 samples have Mn in exchangeable form at concentration range $0.20\text{--}3.91 \mu\text{g g}^{-1}$. Ahdy and Youssef (2011), studying the fractionation of heavy metals for environmental purposes, found similar results; in fact, they reported that Cu and Zn ranged from below the detection limit to $1.02 \mu\text{g g}^{-1}$. Data from Okbah et al. (2011) confirm these findings; Zn and Mn ranged from 0.29 to 1.13 and 0.8 to $2.0 \mu\text{g g}^{-1}$, respectively.

Carbonate-bound fractions

The carbonate bound fraction ranges from $2.2\text{--}16.1 \mu\text{g g}^{-1}$ for Fe, $0.5\text{--}1.4 \mu\text{g g}^{-1}$ for Zn, $12.1\text{--}52.30 \mu\text{g g}^{-1}$ for Mn, and $0.8\text{--}2.8 \mu\text{g g}^{-1}$ for Cu. Shober et al. (2007), studying Zn and Cu and heavy metals,

reported similar concentration for Cu, but higher levels for Zn; this is possibly due to the lower pH and CaCO_3 values of Pennsylvania soils in the USA. Averaged over the seven geographic regions (see Table 3), the order of the metals in the CO_3 bound fraction is $\text{Mn } (30.89 \mu\text{g g}^{-1}) > \text{Fe } (6.86 \mu\text{g g}^{-1}) > \text{Cu } (1.61 \mu\text{g g}^{-1}) > \text{Zn } (1.01 \mu\text{g g}^{-1})$. Figure 2 shows that there is a very poor correlation between CaCO_3 and CO_3 -bound Mn ($R^2 = 0.047$). On the other hand, the carbonate contents of the soils are strongly related to the CO_3 bound fractions of Fe ($R^2 = 0.861$), Zn ($R^2 = 0.685$) and Cu ($R^2 = 0.527$). This indicates that CaCO_3 content of the studied desert soils has a strong effect on the CO_3 -bound Fe, Zn, and Cu micronutrient fractions. These results agree with the findings of Mustafa et al. (1988) who reported that a strong relationship existed between carbonate-bound Zn contents of soil and the CaCO_3 content of soil.

Fe-Mn oxide bound fractions

The oxide bound fraction is by far the second largest among all fractions, after the residual fraction, especially for Fe and Mn. The Fe-Mn oxide bound fractions varies from $190\text{--}898 \mu\text{g g}^{-1}$ with a mean of $573.14 \mu\text{g g}^{-1}$ for Fe; $1.9\text{--}8.5 \mu\text{g g}^{-1}$ with a mean of $5.43 \mu\text{g g}^{-1}$ for Zn, $22.0\text{--}238.9 \mu\text{g g}^{-1}$

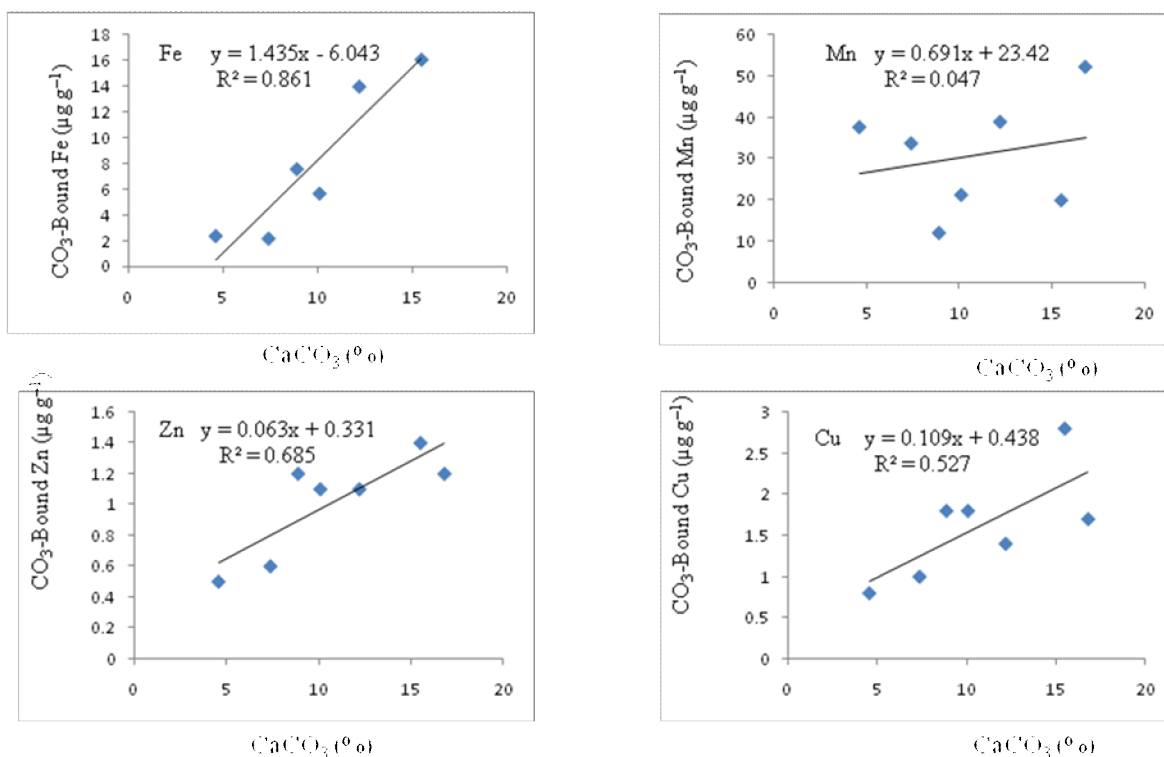
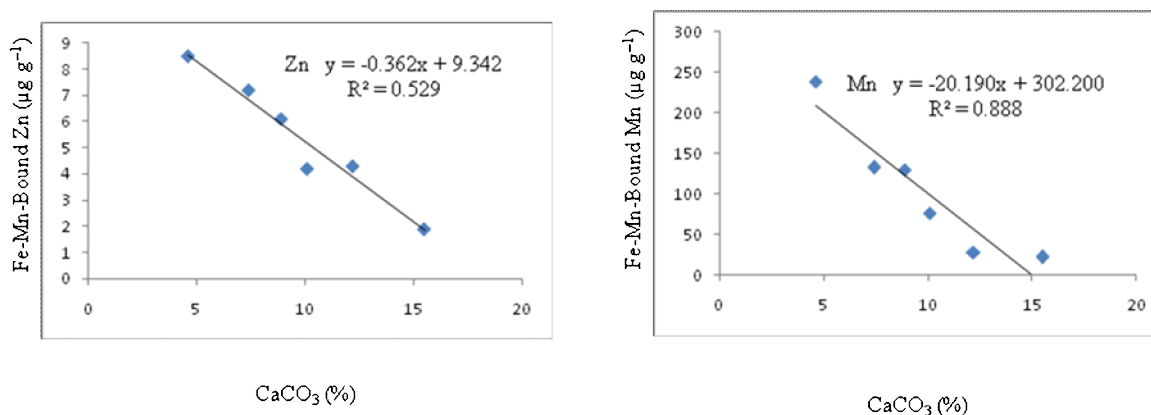
with a mean of $109.30 \mu\text{g g}^{-1}$ for Mn, and 2.1-5.1 $\mu\text{g g}^{-1}$ with a mean of $3.50 \mu\text{g g}^{-1}$ for Cu. Only Zn data agrees with earlier reports by Shober et al. (2007). These high concentrations are due to the fact that micronutrients are preferentially adsorbed on Fe oxide surfaces in soils (Parizanganeh et al., 2007). Similar results were found by Ahdy and Youssef (2011). Alidoust et al. (2012) reported that concentrations of Mn and Zn in the metal-organic complex in the rhizosphere zone decreased with proximity to the root, indicating that the Fe-Mn oxide fraction is an important source of these 2 trace elements for the plants. The coarse-textured

soils have a lower amount of Fe, Zn, Mn and Cu in the Fe-Mn oxide bound fraction than the medium textured soils. It is not clear why there are strong negative correlations (Figure 3) between CaCO_3 and Fe-Mn bound Zn ($R^2 = 0.529$), and Mn ($R^2 = 0.888$). The mean concentrations computed over the seven regions indicate that the metals in the Fe-Mn oxide bound fraction follow this order: Fe ($573.1 \mu\text{g g}^{-1}$) > Mn ($109.3 \mu\text{g g}^{-1}$) > Zn ($5.4 \mu\text{g g}^{-1}$) > Cu ($3.5 \mu\text{g g}^{-1}$) (Table 3). It is possible that a part of the Fe and Mn extracted in this fraction is derived from the parent oxide minerals during extraction with Hydroxylamine hydrochloride (Jenne, 1968).

Table 3. Micronutrient concentration in the different fractions for the soils representing the seven geographic regions.

Element	Location	Exchangeable	CO_3 Bound	Fe-Mn Oxide bond ($\mu\text{g g}^{-1}$)	Organic Bound	Residual
Iron	Kharj	0.01	14.0	698	10.4	14105
	Delim	0.01	5.3	542	8.1	20004
	Qassim	0.02	2.4	585	17.3	24800
	Hail	ND	7.6	898	21.2	8425
	Jouf	ND	16.1	190	12.1	4504
	Wadi Dawassir	ND	5.7	510	9.2	4790
	Taif	0.02	2.2	589	55.5	48780
Mean		NA	7.61	573.14	19.11	17915
Percent of Total (%)			0.04	3.10	0.10	96.76
Zinc	Kharj	ND	1.1	4.3	0.01	56.1
	Delim	ND	1.2	5.8	0.01	96.4
	Qassim	ND	0.5	8.5	0.90	92.6
	Hail	ND	1.2	6.1	0.61	71.6
	Jaof	ND	1.4	1.9	0.01	52.3
	Wadi Dawassir	ND	1.1	4.2	0.5	63.0
	Taif	ND	0.6	7.2	1.3	108.0
Mean		NA	1.01	5.43	0.48	77.14
Percent of Total (%)			1.20	6.46	0.57	91.77
Manganese	Kharj	ND	39.0	27.7	3.2	164.2
	Delim	0.2	52.3	137.3	10.1	227.9
	Qassim	3.91	37.7	238.9	36.2	367.4
	Hail	0.3	12.1	130.4	13.2	215.3
	Jouf	ND	20.0	22.0	3.0	155.7
	Wadi Dawassir	0.64	21.3	76.1	6.7	232.1
	Taif	1.32	33.8	132.7	25.3	698.4
Mean		NA	30.89	109.30	13.96	294.43
Percent of Total (%)			6.88	24.37	3.11	65.64
Copper	Kharj	ND	1.4	2.1	0.01	9.5
	Delim	ND	1.7	5.1	0.01	29.5
	Qassim	ND	0.8	2.4	0.9	40.3
	Hail	ND	1.8	5.1	0.4	26.5
	Jouf	ND	2.8	3.0	0.01	24.6
	Wadi D	ND	1.8	4.3	0.30	20.3
	Taif	ND	1.0	2.5	2.40	58.6
Mean		NA	1.61	3.50	0.58	29.9
Percent of Total (%)			4.54	9.83	1.62	84.01

ND: Not Detected, less than the detection limits of the method of analysis.

Figure 2. Correlation between CaCO_3 and CaCO_3 bound iron, zinc, manganese and copper.Figure 3. Correlation between CaCO_3 and Fe-Mn zinc and manganese.

Organic-bound fractions

The organic bound fractions range is $8.1\text{--}55.5 \mu\text{g g}^{-1}$ with an average of $19.11 \mu\text{g g}^{-1}$ for Fe, $0.01\text{--}1.3 \mu\text{g g}^{-1}$ with an average of $0.48 \mu\text{g g}^{-1}$ for Zn, $3.0\text{--}36.2 \mu\text{g g}^{-1}$ with an average of $13.96 \mu\text{g g}^{-1}$ for Mn, and $0.01\text{--}2.4 \mu\text{g g}^{-1}$ with an average of $0.58 \mu\text{g g}^{-1}$ for Cu. The concentrations of metals present in the seven soil samples in organic bound form represent a low proportion of total metal concentrations. The higher percentage of organic carbon is found in soil samples collected from Taif, Qassim, and Hail regions (0.73–1.05%). The same samples contain higher concentrations of all four metals in the organic fraction. This indicates that

organic bound micronutrients fraction is positively related to organic carbon in soil samples, as found earlier by Chanem and Mikkelsen (1987). A similar result was reported by Mandal and Mandal (1986). Shober et al. (2007) came to the same conclusion, and when soils were amended with additional organic matter, the organic-bound Cu and Zn concentrations increased significantly. Alidoust et al. (2012) found that the concentrations of organically bound Fe and Mn in soils decreased with the proximity to roots, suggesting that organic fraction is the main source for plant uptake. Averaged over the seven geographic regions (see Table 3), the order of metals in the organic bound

fraction is Fe ($19.11 \mu\text{g g}^{-1}$) > Mn ($13.96 \mu\text{g g}^{-1}$) > Cu ($0.58 \mu\text{g g}^{-1}$) > Zn ($0.48 \mu\text{g g}^{-1}$).

Residual fractions

The residual fraction of micronutrients is by far the largest among all fractions. In general, soils with high clay content contained higher amounts of residual micronutrients. Earlier research reported similar findings (Shober et al., 2007; Ahdy and Youssef, 2011; Okbah et al., 2011). The order of residual micronutrients, on average across regions, is in the following sequence: Fe ($17915 \mu\text{g g}^{-1}$) > Mn ($294 \mu\text{g g}^{-1}$) > Zn ($77 \mu\text{g g}^{-1}$) > Cu ($30 \mu\text{g g}^{-1}$). The residual fractions in soil samples collected from Taif region is the highest among all samples. This could be due to the fact that the soil samples in Taif region were derived from a metamorphic origin, while the other soil samples in the study were derived from sedimentary rocks. Residual (non-available) Fe and Zn fractions, on average, constitute 97% and 92% of total soil fractions, respectively. While residual fraction of Mn and Cu constitute lower proportions of total soil fractions, and the means are 66% and 84% for Mn and Cu, respectively. Due to non-availability of the residual fraction to crops, little research and limited publications have dealt with this proportion of soil trace elements. Furthermore, total trace-element concentrations determined by strong acid digestions (residual), have been proven to be a poor indicator of trace-element levels in crop tissue (Qian et al., 1996; Sims and Kline, 1991). The results of the fractionation analysis of the seven soil samples collected from arid calcareous soils in Saudi Arabia indicate that concentrations of micronutrients in the different fractions are: Residual > Fe-Mn oxide bound > CO_3 bound > organic bound > exchangeable (negligible).

Appreciable amounts of trace elements are associated with the various fractions of the soils representing the different agricultural regions. These pools constitute important potential reserves of micronutrients; environmental and rhizosphere conditions will determine their mobilization capacity and bioavailability (Karimian and Ahangar, 1998; Ghasemi-Fasaei et al., 2009; Alidoust et al., 2012; Kasemaei and Fekri, 2012).

Combined carbonate-bound and organic-bound fractions of Fe, Zn, Cu, and Mn represent 3%, 6%, 15%, and 31% of total soil trace elements, respectively (Table 3). This important finding is a clear indication that Fe and Zn sources are negligible, whereas Cu and Mn are potentially available to crops in appreciable amounts in soils of the studied regions. These results also explain the

absence of Cu and Mn deficiency in all agricultural regions of Saudi Arabia; moreover, they elucidate why Fe and Zn deficiencies are common in crops grown on these soils; such deficiencies are easily corrected by application of Fe and Zn to these crops (Al Jaloud et al., 1995).

Conclusion

Mean soil pH ranged from 7.6 to 7.9, and CaCO_3 data (3.3-24.6%) indicate that the soils are mostly calcareous. Soil ECe data ($1.0\text{-}11.5 \text{ dS m}^{-1}$) indicate the presence of saline soils in all regions except Taif. Micronutrients DTPA-extractable ranges were $2.8\text{-}5.6 \mu\text{g g}^{-1}$ for Fe, $0.3\text{-}1.5 \mu\text{g g}^{-1}$ for Zn, $0.9\text{-}7.9 \mu\text{g g}^{-1}$ for Mn, and for $0.4\text{-}1.5 \mu\text{g g}^{-1}$ for Cu. High mean concentrations for Fe, Zn, Mn, and Cu are linked to the presence of high organic matter; low mean concentrations for Fe, Zn, Mn, and Cu are associated with high pH and CaCO_3 %. Iron and Zn were low in most soils. Few soils were low in Cu and Mn. Thus, it is recommended that Fe and Zn be included in crop fertilization programs. Fractionation of micronutrients reveals that, when averaged across all regions, the order of the metals content in the CO_3 bound fraction was Mn>Fe>Cu>Zn; the oxide-bound fraction followed the order Fe>Mn>Zn>Cu; the organic bound fraction led to the sequence Fe>Mn>Cu>Zn; and the residual fraction was Fe>Mn>Zn>Cu. The fractionation study showed that the residual fraction was the highest, followed by the remaining fractions in this order: oxide bound> CO_3 bound>organic bound>exchangeable.

References

- Ahdy, H. H. and D. H. Youssef. 2001. Fractionation analysis of some heavy metals in sediments of the north-western part of the Red Sea, Egypt. *Chem. Ecol.* 27(5):427-443.
- Al Jaloud, A. A. 1988. Water use efficiency for crop production in Saudi sandy soils using synthetic polymers. Ph. D. dissertation, Gent State University, Gent, Belgium.
- Al Jaloud, A. A., and M. A. Al Rabhi. 2013. Mineral concentration of irrigation water in Saudi Arabia and effect on In-Situ estimation of soluble salts, and practical recommendations. In Press. *Proceedings of the International Conference on Agricultural Technologies in Arid Lands*. 19-21 March 2013. Riyadh, Saudi Arabia.
- Al Jaloud, A. A., M. M. Rafi, and I. I. Bashour. 1995. Fractionation of micronutrients in

- selected soils from Saudi Arabia. Arab Gulf J. Sci. Res. 13(1):93-107.
- Al Safi Dairy Est. 2000. Soil and water analysis data, and crop yields. In: Annual Report. Central Region. Kharj, Kingdom of Saudi Arabia.
- Alidoust, D., S. Suzuki, S. Matsumura and M. Yoshida. 2012. Chemical speciation of heavy metals in the fractionated rhizosphere soils of sunflower cultivated on a humic Andosol. Commun. Soil Sci. Plant Anal. 43(17):2314-2322.
- Bashour, I. I., A. S. Al-Mashhady, J. D. Prasad, T. Miller and M. Mazroa. 1983. Morphology and composition of some soils under cultivation in Saudi Arabia. Geoderma 29:327-340.
- Canet, R., F. Pomares, F. Tarazona and M. Estela. 1998. Sequential fractionation and plant availability of heavy metals as affected by sewage sludge applications to soil. Commun. Soil Sci. Plant Anal. 29(5-6):697-716.
- Chanem, S. A. and D. S. Mikkelsen. 1987. Effect of organic matter on changes in soil zinc fractions found in wetland soils. Commun. Soil Sci. Plant Anal. 18:1217-1234.
- El-Fouly, M. M. 1983. Micronutrients in arid and semi-arid areas: levels in soils and plants and the need for fertilizers with reference to Egypt. In: proceedings of the 17th colloquium of the International Potash Institute, Rabat and Marrakech. Morocco, Publisher Bern. Switzerland. pp. 163-173.
- Emmerich, W. E., L. J. Lund, A. L. Page and A. C. Chang. 1982. Solid-phase forms of heavy metals in sewage sludge-treated soils. J. Env. Qual. 11(2):178-181
- Errebhi, M. A. and A. A. Al Jaloud. 2003. Water and soil databases. In: Database for Soil, Water, and Tissue Analyses for Saudi Arabia. Sabic Technical Report. Riyadh, Kingdom of Saudi Arabia.
- Filgueiras, A. V., I. Lavila and C. Bendicho. 2002. Chemical sequential extraction for metal partitioning in environmental soil samples. J. Environ. Monit. 4:862-857.
- Foth, H. D., L. V. Withee, H. S. Jacobs and S. I. Them. 1977. Laboratory manual for introductory soil science. Wm. C. Brown Publishers, Dubuque, Iowa.
- Fuehring, H. D. 1973. Response of crops grown on calcareous soils to fertilization, FAO Soils Bull. 21:53-71.
- Ghasemi-Fasaei, R., M. Maftoum, V. Olama, B. Molazem and M. Tavajjoh. 2009. Manganese release characteristics of highly calcareous soils. Commun. Soil Sci. Plant Anal. 40(7-8):1171-1182.
- Hagen, J. and B. Tucker. 1982. Fertilization of dry land and irrigated soils. Advanced series in Agricultural Science. 12, Springer Verlag. Berlin-Heidelberg-New York.
- Jenne, E. A. 1968. Controls of Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and waters. The significant role of hydrous Mn and Fe oxides. In Trace Inorganics in Water. Adv. Chem. Ser. 73:337-387.
- Jones, S. W. and I. Keslo. 1977. The micronutrient status of soils in Al-Hasa and at the Agricultural Research Center, Hufuf, Univ. College of North Wales, Bangor, U.K., Ministry of Agriculture and Water, Riyadh, Saudi Arabia Joint Publication No.101:3-7.
- Karimiam, N., and A. G. Ahangar. 1998. Manganese retention by selected calcareous soils as related to soil properties. Commun. Soil Sci. Plant Anal. 29(9-10):1061-1070.
- Kasemaei, L. S., and M. Fekri. 2012. Effect of organic matter on the release behavior and extractability of copper and cadmium in soil. Commun. Soil Sci. Plant Anal. 43(17):2209-2217.
- Lindsay, W. L. and W. A. Norwell. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42:421-428.
- Loizides, P. 1975. The sandy soils of the Kingdom of Saudi Arabia, FAO Soils Bull. 25:225-227.
- Mandal, L. N. and B. Mandal. 1986. Zinc fractions in soils in relation to zinc nutrition of lowland rice. Soil Sci. 142:141-148.
- McLaren, R. G. and D. V. Crawford, 1973. Studies on soil copper. The fractionation of copper in soils. J. Soil Sci. 24:172-181.
- Ministry of Agriculture. 2011. Estimated total crop areas by region in the Kingdom of Saudi Arabia. Agriculture statistical year books, 1986-2012. Riyadh, Saudi Arabia.

- Ministry of Agriculture and Water. 1986. Soil Atlas of the kingdom of Saudi Arabia. Riyadh, Saudi Arabia.
- Morabito, R. 1995. Extraction techniques in speciation analysis of environmental samples. *Fresenius J. Anal. Chem.* 351(4-5):378-385.
- Mortvedt, J. J., P. M. Giordano and W. L. Lindsay. 1972. Climatic and soil conditions promoting micronutrient deficiency in plants. In: *Proceedings of 'Micronutrients in agriculture.* Publisher Soil Sci. Soc. Am., Inc. Madison, Wisconsin, USA.
- Mustafa, M. A., A. I. Ayed and O. A. Mahgoub. 1988. Zinc sorption by some Saudi calcareous soils. *Arab Gulf J. Sci. Res.* 6B(1):9-20.
- Nelson, D. W. and L. E. Sommers. 1996. Total carbon, organic carbon, and organic matter. In: A. L. Page et al. (Eds.) pp.9:961-1010. *Methods of Soil Analysis, Part 2, 2nd Ed., Agronomy, Am. Soc. Agron., Inc. Madison, WI.*
- Okbah, M. A., S. M. Nasr and S. M. Kasem. 2011. Fractionation of trace metals (Mn, Zn, Cu, Pb) in Red Sea sediments, Gulf of Adan, Yemen. *Chem. Eco.* 27(1):81-90.
- Parizanganeh, A., V.C. Lakhan and H. Jalalian. 2007. A geochemical and statistical approach for assessing heavy metal pollution in sediments from southern Caspian coast. *Internat. J. Env. Sci. Technol.* 4:351-358.
- Prasad, J. D., I. I. Bashour and A. Al-Shanghitti. 1984. Availability of micronutrient in selected Saudi soils. *Arab Gulf J. Sci. Res.* 2:259-266.
- Qian, J., Z. J. Wang, X. Q. Shan, Q. Tu, B. Wen and B. Chen. 1996. Evaluation of plant availability of soil trace metals by chemical fractionation and multiple regression analysis. *Env. Pollut.* 91(3):309-315.
- Ramolia, P. J., H. M. Patel and A. N. Pandey. 2004. Effect of salinization of soil on growth and macro- and micro-nutrient accumulation in seedlings of *Acacia catechu* (Mimosaceae). *Ann. Appl. Biol.* 144:321-332.
- Richards, L. A. (Editor). 1954. Diagnosis and improvement of saline and alkali soils. USDA Agricultural Handbook No. 60 US Govt. Printing Office, Washington, D.C.
- Sallam, A. S. 2002. Evaluation of some soils in Najd Plateau, central region, Saudi Arabia. *J. Saudi Soc. Agric. Sci.* (1):21-40.
- Saudi Geological Survey (SGS). 2012. The Kingdom of Saudi Arabia, Realities and Statistics. 1st Ed. Riyadh, Saudi Arabia.
- Shober, A. L., R. C. Stehouwer and K. E. MacNeal. 2007. Chemical fractionation of trace elements in biosolid-amended soils and correlation with trace elements in crop tissue. *Commun. Soil Sci. Plant Anal.* 38(7-8):1029-1046.
- Shuman, L. M. 1979. Zinc, manganese, and copper in soil fractions. *Soil Sci.* 127:10-17.
- Shuman, L. M. 1985. Fractionation method for soil microelements. *Soil Sci.* 140:11-22.
- Sims, J. T. and J. S. Kline. 1991. Chemical fractionation and plant uptake of heavy metals in soils amended with co-composted sewage sludge. *J. Env. Qual.* 20(2):387-395.
- Stone, M. and J. Marsalek. 1996. Trace metal composition and speciation in street sediment: Sault Ste. Canada. *Water Air Soil Pollut.* 87:149-169.
- Tessier, A., P. G. C. Campbell and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51:844-851.
- Tisdale, L. S., L. N. Nelson, D. J. Beaton and L. H. Havlin. 1993. Soil fertility and fertilizer 5th ed. Prentice Hall, New Jersey 07458, U.S.A.
- Wagemann, R., G. J. Brunskill and B. W. Graham. 1977. Composition and reactivity of some river sediments from the Mackenzie Valley, N.W.T., Canada. *Env. Geol.* 1:349-358.
- Zhang, T. H., X. Q. Shan and F. L. Li. 1998. Comparison of two sequential extraction procedures for speciation analysis of metals in soils and plant availability. *Commun. Soil Sci. Plant Anal.* 29(7-8):1023-1034.