Remediation of Heavy Metals in Soil Treated with Industrial Sludge Using Rock Phosphate

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THE PRESENT study was conducted to test the ability of rock phosphate, applied as a single amendment, to remediate heavy metals such as Fe, Mn, Zn, Cu, Co, Pb, Ni and Cd phytotoxicity in industrial sludge-polluted soils. A factorial field experiment was carried out using a virgin sandy soil at the Experimental Station of the Egyptian Atomic Energy Authority, Egypt. Industrial sludge and rock phosphate were added at the rates of 0, 20, 40 and 80 ton/fed and 0, 100, 200 and 400 kg/fed, respectively. Sorghum (Sorghum vulgare) was used as an indicator plant and after 70-day growth period, sorghum shoots and roots were taken, oven-dried at 70 °C and dry matter yield was recorded. Samples of sorghum shoots and roots were dry-ashed for determining of tested heavy metals content.

The obtained results show that industrial sludge (IS) application significantly increased the dry matter (DM) yield of both sorghum shoots and roots and these increases were more obvious with the application of rock phosphate (RP) as compared with the control. Heavy metals content in sorghum plants increased with increasing IS application while the application of RP at any rate reduces the heavy metals content in plant in most cases. Increasing the rate of applied IS irregularly increased the content of Ni in sorghum organs. Application of RP, soundly and significantly reduced Co content in sorghum shoots and roots. The obtained results clearly show that plants grew best in the presence of rock phosphate and did not accumulate tested heavy metals to the same extent as sludge alone-treated soil.

Keywords: Remediation, Sorghum, Industrial sludge, Rock phosphate, Heavy metals.

Sewage sludge is valuable source of nitrogen, phosphorus and organic matter, however, industrial sludge may contain concentrations of heavy metals that can limit their acceptability for use on agricultural land. Land disposal of municipal sewage sludge and effluents has been recently attracting the public eye because of the disposal problems associated with increasing amounts of these wastes produced by urban and industrial activities. Land disposal is often more economical than other treatment alternatives (Andriano, 1986). One of the major environmental problems associated with land use of sewage sludge is the addition of potentially toxic heavy metals to soils and can cause potential problems such as phytotoxicity or elevated metals transfer to food chains.

In developing countries like Egypt, little attention is focused on pretreatment of urban or industrial wastewater sludge. Mostly the sludge is directly mixed with agricultural soils as supplement fertilizer. In absence of any pretreatment of sewage sludge to remove any excess of toxic elements from sludge, it is feared that their presence accelerates uncontrolled absorption of metals by various parts of plants and fruits during growth creating a potential health hazard.

Government regulations are becoming more stringent with regard to the addition of such materials to soils used for the production of food crops. Therefore, success or failure of sludge utilization in agriculture depends not only on sludge properties and loading rate but also on chemical and mineralogical characteristics of soils to which sludge is applied. Sewage sludge utilization on agriculture land must be regulated to minimize the heavy metals contamination of soils. Guidelines have been adopted in many countries, but with widely differing recommendations. These guidelines are based on one or more of the following:

Heavy metals concentration in applied sludge and loading rate to agriculture land may not exceed defined limits,

These heavy metals are less likely to cause problems if added in several small increments rather than in large increments,

Heavy metal concentrations in soil may not exceed defined limits and Fertilizer value (nitrogen and phosphorus).

The concentration of heavy metals in sewage sludge is largely dependent on the types and amounts of urban and industrial discharges into the sewage treatment systems and to the amount added in the convenience and treatment system.

Remediation of excessive soil metals *in situ* is receiving new attention because the alternative, soil removal and placement, is very expensive, requires disposal of the removed soil and may achieve no better environmental remediation than *in situ* treatments (Kukier & Chaney, 2000). Removal of heavy metals accumulated in soils is necessary to reduce their risk and several problems related to the presence of high levels of such metals in soils.

Thus, the objective of this study was to evaluate the effectiveness of rock phosphate to reduce the plant availability of tested heavy metals for sorghum plants grown on a sandy soil treated with different rates of industrial sludge.

Material and Methods

A virgin sandy soil at the Experimental Station of the Egyptian Atomic Energy Authority, Egypt, was used to establish a field experiment. Different characteristics of the used soil were determined according to the standard methods outlined in Page et al. (1982) being shown in Table I. Dredged industrial sludge was collected from Mostorod Industrial Wastewater Collector Drain, North of Cairo, Egypt, air-dried, ground to pass through a 2 mm sieve and prepared for analysis. Sludge analyses and rock phosphate were listed in Table 2.

The study was a randomized complete block design (factorial) with three replicates. The area of each plot was 1 m². The factors under study were: industrial sludge (4 treatments 0, 20, 40 and 80 ton/fed) to get different heavy metal-polluted soils and additives (4 treatments 0, 100, 200 and 400 kg rock phosphate/fed). Prior to fertilization and seedling, sludge and different additives (rock phosphate) at the aforementioned rates were added to the soil, thoroughly mixed in each plot to a depth of approximately 30 cm, watered to saturation and drained to flush the soil pore volume. The moistened soil was left for 2 weeks to allow chemical equilibrium to occur and then was re-mixed prior to seed planting.

TABLE 1. Some physical and chemical characteristics of the tested soil.

Pa	Textural		
Sand	Silt	Clay	class
90.5	6.3	3.2	Sandy

	b - chemical												
CEC	EC*	pH**	CaCO3	Organic									
Mole Kg-1	dSm ⁻¹		%	matter %	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K [⁺]	CO ₃	HCO ₃	Cl	SO ₄	
9.3	0.5	8.2	1.0	1.7	1.8	0.8	3.1	0.4	-	2.1	2.0	2.0	

^{*} in saturation extract.

TABLE 2. Elemental content of the used industrial sludge and rock phosphate.

	Total elements											
Elements	N	P	К	Fe	Fe Mn Zn Co Co Cr Ni Cd Pb							
	(%) (mg/kg)											
Industrial sludge	2.10	0.74	0.25	1375	5865	2989	489	485	298	665	36.5	2125
Rock phosphate				7.5	31.5	105	21.5	3.5	26	38.8	2.3	163

^{**} in 1:2.5 soil water suspension.

Sorghum (Sorghum volgare) was used as an indicator plant. Nitrogen fertilizer as urea (46.5% N) was applied at a rate of 50 kg/fed at three equal doses during growth stage (germination, vegetation and before the flowering stage). For each plot, about 100 grains of sorghum were planted and laterthinned to 80 plants per plot. Moisture content of the soil was maintained at about field capacity, through the entire growth period. At day-70, sorghum shoots and roots samples were taken. The roots were washed with tap water to remove any adhering soil particles and then shoots and roots were rinsed 3 times with distilled water. Plant samples were oven dried at 70 °C to a constant weight, finely ground in a stainless steel mill and samples of the powdered material (1.0 g each) were dry-ashed in a muffle furnace at 450 °C for 16 hr. Ashed plant samples were digested with 2 ml of concentrated HNO₃ on a hot plate and then refluxed for 2 hr with 10 ml of 3 M HCL.

Digested samples were filtered and diluted to 25 ml. The described digestion procedure is a modification of AOAC method No. 895 (Issac, 1990). Samples were analyzed for Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb and Cd using Atomic Absorption Spectrometry (AAS) with background correction.

Surface soil samples were collected at the end of the experiment. Total and DTPA-available Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb and Cd were determined according to standard methods of Page *et al.*, (1982) using Atomic Absorption Spectrometer (AAS).

Statistical analysis

Biological data for experiments was statistically analyzed, using statistical software program (PC-Mstat) according to Power (1985). ANOVA (Two ways) and Least Significant Deference (L.S.D) were determined according to Gomez & Gomez (1984).

Results and Discussion

Total and available heavy metals in soil as affected by sludge and Rock phosphate treatments

Total Fe, Mn, Zn, Cu, Co, Cr, Ni, Cd and Pb in tested soil as affected by sludge and rock phosphate application are shown in Table 3. As shown in Table 3 increasing sludge rate of application up to 80 ton//fed has significantly increased total heavy metal content in soil by several order of magnitude. The application of sludge to agricultural lands has caused many people to express concern about the safety of this practice. They are concerned that the metals may either accumulate in soils to levels that cause phyto-toxic conditions or accumulate in plants at levels that adversely affect the health of the consumers. Aitken et al. (1997) indicted that (after using industrial sludge for 4 years) the high rate of applications increased the soil content of Zn, Cr, Ni, Cu and Pb especially in depth of 10-15 cm. A high heavy metal content of sludge is the most important hindrance to their use in agriculture. Although Purves (1977) reported that in practice the concern with using sludge commonly is only their phyto-toxicity due

to excesses of Zn, Cu, and Ni, their content of Cd in particular, as well as of Pb and Hg, should be of concern as serious health risks.

TABLE 3. Total heavy metals content in soil as affected by sludge and Rock phosphate application.

Sludge Rate ton /fed	Rock phosphate		Total heavy metal content (mg/kg)									
	kg / fed	Fe	Mn	Zn	Cu	Co	Cr	Ni	Cd	Pb		
Control	0	7900	431	205	18.9	22.5	12.2	32.8	2.30	138		
	100	8020	409	227	20.1	20.0	13.6	34.8	2.80	132		
	200	8210	385	241	21.7	18.5	16.3	37.0	3.40	119		
	300	8420	330	248	24.3	14.9	18.8	41.9	4.00	-110		
М	ean	8138	389	230	21.3	19.0	15.2	36.6	3.1	125		
20	0	22140	737	258	29.2	32.9	20.4	47.9	5.20	235		
	100	23170	705	285	31.1	31.4	21.7	48.2	5.70	125		
	200	24140	673	305	35.6	29.0	23.5	52.7	6.50	219		
	300	26030	579	339	36.2	27.6	25.7	56.8	7.00	211		
М	еап	23870	674	297	33.0	30.2	22.8	51.4	6.10	198		
40	0	27380	811	358	32.6	37.9	26.8	55.8	7.90	243		
	100	28060	782	373	34.1	36.0	28.8	57.6	8.50	234		
	200	25330	747	393	37.7	33.1	31.3	60.5	9.10	227		
	300	30350	711	421	40.6	29.9	34.1	62.8	9.50	217		
М	ean	27780	763	386	36.3	34.2	30.3	59.2	8.75	230		
80	0	32830	883	480	37.6	41.2	37.4	62.8	10.4	262		
	100	35440	815	502	38.2	38.2	39.9	64.5	11.0	248		
	200	34710	779	529	42.7	35.3	34.4	67.8	11.7	236		
	300	36450	724	552	44.8	32.2	46.9	71.0	12.1	226		
М	ean	34858	800	516	40.8	36.7	39.7	66.5	11.3	243		

Zinc increased from 205 to 552 mg/kg due to industrial sludge application. As it could be seen, total-Zn in amended soil exceeds the permissible levels (250 mg/kg Zn according to Kabata - Pendias & Pendias (1984) by several orders of magnitude. Total-Cu, in tested contaminated soils was within the permissible

levels (rank from 18.9 to 44.6 mg Cu/kg) while Cu levels in soils which considered being toxic is in the range of 60-125 mg/kg according to Kabata - Pendias & Pendias (1984).

Total Co levels ranged from 14.9 to 41.2 mg/kg and the application of RP tend to decrease total Co levels. Rashad *et al.* (1995) found that the normal level of Co in the alluvial soils of Nile Delta ranged between 3.7 and 5.5 mg/kg with an average of 4.7 mg/kg. Concerning contaminated Egyptian alluvial soils little work was done on cobalt. El-Leithi (1986) studied the effect of industrial activities on the soils of Nile Delta. He found that total content of Co in these soils ranged between 11.2 and 36.1 mg/kg with an average of 23.7 mg/kg. El-Gamal (1980) found that total Co ranged from 30.36 to 41.40 mg/kg with an average of about 36.5 mg/kg in El-Gabal El-Asfar soil irrigated with industrial sludge for several years. Total Cr in tested contaminated soils was also within the permissible levels according to Alloway (1990), Cr-toxic levels ranged between 75 to 100 mg/kg. Twenty one surface (0 – 30 cm) soil samples were collected from different locations in Egypt representing non-moderately and highly polluted soils (Abdel-Sabour & Zohny, 2003). The results indicated that Cr content in non-polluted soil samples ranged between 17.57 to 25.0 mg/kg.

Chromium content in moderately polluted soils ranged between 34.65 to 41.45 mg/kg. The highest Cr levels ranged from 71.97 to 87.03 mg/kg were observed in soil samples collected from, either highly polluted agricultural soils due to prolonged irrigation with industrial wastewater or surface soil samples from industrial sites. Abdel-Sabour et al. (1998) reported that total Cr content in different Egyptian soils which varied between 11.6 up to 179 mg/kg depending on soil types and land usage (e.g., agricultural practices, exposed to industrial activity or solid or liquid waste disposal).

Total Ni enhanced in treated soils from 32.8 to 71.0 mg/kg. Whereas the normal total content of Ni levels in the alluvial soils of the Nile Valley and Delta ranged between 21.0 and 44.0 mg/kg (average = 32.0 mg/kg) as reported by Rashad *et al.* (1995). However, very small amount of this total was found in available form, it ranged between 0.38 and 1.04 mg/kg (with an average=0.66 mg/kg). The impact of intensive industrial activities on soil characteristics and total Ni content was evaluated (Abdel-Sabour & Rabie, 2003). The amount of total Ni in uncultivated control soil (A) ranged between 40.8 and 43.8 mg/kg, while in cultivated control soil (B) ranged between 52.0-67.0 mg/kg. Rashad *et al.* (1995) reported that the amount of total Ni in nonpolluted alluvial soils of Nile Delta ranges between 21.0 and 44.0 mg/kg with an average of 32.0 mg/kg. While the contaminated soils showed higher values ranged from 98.0 and 177.0 mg/kg.

The application of sludge and/or RP enhanced total Cd levels in tested soils to a serious level up to 12.1 mg Cd/kg. Normal total-Cd in soils lies between 0.04-1.0 mg/kg, and toxic level of Cd ranged between 3-8 mg/kg (Kabata - Pendias & Pendias, 1984). Lund *et al.* (1981) reported that total Cd content in soils of non-polluted are usually 1.0 mg/kg. The information obtained from a survey of the

natural levels of Cd in a great number of samples representing the major cropproducing areas in Egypt indicates that total Cd contents in the sandy soils range widely from 2.6 to 15 mg/kg (Kandil, 1994; Sedky, 1995 and Mohamed, 1998).

Total lead ranged between 138 to 226 mg/kg due to IS and/or RP treatments. The situation of Pb in some Egyptian soils was elucidated by Yousry & El-Sherif (1977). They reported that Pb ranged between 58 and 282 mg/kg. Concerning contaminated alluvial soils of Egypt, El-Sabbagh (1991) and Ramadan (1995) found that industrial activities and irrigation with wastewater increased both total and available Pb in the surface layer of soils at Mostorod area. El-Sabbagh (1991) found that the total Pb content in the surface layer ranged between 17.0 and 48.0 mg/kg with an average of 29.0 mg/kg. While, Ramadan (1995) reported that the total content of Pb ranged between 84.4 and 101.1 mg/kg with an average of 92.8 mg/kg,

Rock phosphate is often used as a soil amendment to supply Ca and P. On the other hand, RP application resulted in a slight increase in tested heavy metals levels in soil in case of Fe, Zn, Cu, Cr, Ni, and Cd while Mn, Co and Pb levels decreased. Analysis of sludge and RP samples showed that sludge contains 1375, 5865, 2989, 489, 485, 298, 665, 36.5 and 2125 mg/kg of total Fe, Mn, Zn, Cu, Co, Cr, Ni, Cd and Pb, respectively. While RP contains 7.5, 31.5, 105, 21.5, 3.5, 26, 38.8, 2.3 and 163 mg/kg of total Fe, Mn, Zn, Cu, Co, Cr, Ni, Cd and Pb, respectively.

Knowledge of soil total content of heavy metals provides only limited information; as this can seldom be correlated with availability to plants and does not show how the metal is bound in the soil. DTPA extraction was assumed to simulate plant available fraction and used widely to evaluate bioavailable metals fractions. Similar trend for available tested heavy metals was observed due to both sludge and RP application. As shown in Table 4 DTPAextractable heavy metals increased due to sludge or RP addition. Available Fe ranged between 6.5 up to 18. 5 mg/kg. Concerning the contaminated soils, Yousry et al. (1982) found that the DTPA extractable Fe in Helwan soils which lie between the industrial area ranged between 0.7 and 20.0 mg/kg. In the soils of El-Saff area which are irrigated with industrial wastes, Rabie et al. (1996) reported an increase in DTPA extractable especially in their surface layer. El-Nasher (1985) found that available Fe increased 17 folds due to irrigation with sewage effluents. Hassan (1997) in his study on the soils of Mostorod area found that DTPA extractable Fe ranges from 6.0 to 29.0 mg/kg in the soils irrigated with industrial effluents compared to 2.5 mg/kg in the non-cultivated soils in the same area. It is of interest to mention that soils containing less than 4.5 mg/kg available Fe are considered as deficient soils, as reported by Lindsay & Norvell (1978).

TABLE 4. Available he	eavy metais	content	in soil	88	affected	by	sludge	and	rock
phosphate a	pplication.								

Sludge Rate	Rock phosphate	DTPA-extractable heavy metal content (mg/kg)										
ton /fed	kg / fed	Fe	Mn	Zn	Cu	Co	Cr	Ni	Cd	Pb		
Control	0	6.50	5.76	7.35	0.98	0.67	0.83	0.63	0.38	3.60		
	100	6.85	6.14	7.89	1.07	0.78	0.95	0.77	0.45	3.99		
	200	7.10	6.41	8.28	1.17	0.85	1.12	0.87	0.53	4.26		
	300	7.53	6.72	8.93	1.33	0.97	1.32	0.91	0.63	4.35		
N	1ean	7.00	6.26	8.11	1.14	0.82	1.06	0.80	0.50	4.05		
20	0	7.53	6.87	11.8	1.85	1.52	2.12	1.81	1.07	6.4		
į	100	9.41	8.88	12.2	2.03	1.59	2.31	1.92	1.15	6.80		
ļ	200	9.67	9.16	12.8	2.31	1.65	2.46	2.07	1.28	7.09		
	300	10.06	9.58	13.8	2.44	1,71	2.74	2.34	1.40	7.52		
N	lean	9.17	8.62	12.7	2.16	1.62	2.41	2.04	1.23	6.95		
40	0	10.72	10.28	18.2	3.93	1.92	4.25	2.9	2.15	11.41		
}	100	13.60	13.36	19.2	4.21	2.67	4.66	3.51	2.26	12.25		
}	200	14.25	14.06	19.9	4.69	2.92	5.04	3.78	2.39	12.48		
	300	14.71	14.55	20.7	5.00	3.05	5.50	3.96	2.56	12.63		
M	lean	13.3	13.06	19.5	4.46	2,64	4.86	3.54	2.34	12.19		
80	0	15.24	15.11	22.8	6.38	3.21	6.56	4.18	3.78	13.21		
-	001	16.61	16.59	24.5	6.69	3.61	7.17	4.73	3.96	14.72		
1	200	17.72	17.78	24.8	7.38	3.93	7.68	5.19	4.18	15.94		
	300	18.51	18.62	25.7	7.92	4.16	8.30	5.51	4.33	16.81		
M	lean	17.02	17.03	24.5	7.09	3.73	7.45	4.90	4.04	15.81		

Available Mn increased from 5.8 up to 18.6 mg/kg due to sludge treatment. El-Leithi (1986) found that DTPA-extractable Mn ranged between 5.01 and 34.43 mg/kg with an average of 19.7 mg/kg in contaminated alluvial soils of Nile-Delta. Ramadan (1995) studied the effect of industrial activities on the soils of Mostorod area. He reported that the concentration of available Mn in the surface layer ranged between 7.40 and 16.98 mg/kg with an average of 12.19 mg/kg.

Available Zn ranged between 7.35 up to 25.7 mg/kg, while reported normal levels of available Zn ranged between 2.6 and 9.6 mg/kg with an average of 6.31 mg/kg (Rashad *et al.*, 1995) while Aboulroos *et al.* (1996) reported that this value ranged between 0.73 and 4.44 mg/kg with an average of 2.10 mg/kg.

Available Cu increased due to sludge and RP applications from 0.98 to 7.92 mg/kg. Rashad *et al.* (1995) found that normal available Cu levels ranged between 1.2 and 9.4 mg/kg with and average of 5.73 mg/kg.

On the contrary to total Co levels due to IS and/or RP treatments, available Co enhanced due to both treatments. Available Co increased from 0.67 up to 4.16

mg/kg. Rashad *et al.* (1995) indicated that available Co normal levels in Egyptian soils ranged from 0.04 to 0.11 mg/kg with an average of 0.07 mg/kg. Aboulroos *et al.* (1996) reported that the concentration of available Co in these soils ranged between 0.13 and 0.28 mg/kg with an average of 0.19 mg/kg.

Both DTPA-extractable Cr (ranged from 0.83 to 8.30 mg/kg) and Ni (ranged from 0.63 to 5.51 mg/kg) increased due to IS and/or RP application with similar trend as Zn, Cu, and Co. Cd ranged between 0.38 up to 4.33 mg/kg while Aboulroos *et al.* (1996) recorded 0.02-0.04 mg/kg (average 0.018 mg/kg) for available Cd in normal Egyptian soils. Regarding available Cd in the surface layer off contaminated soils, 0.57-0.79 mg/kg was reported with an average of 0.68 mg/kg (Ramadan, 1995). Concerning the levels of available-Cd in tested soils, data showed highest values than there reported for Egyptian soils. Rashed *et al.* (1995) reported that available Cd in normal alluvial ranged between 0.03 to 0.06 mg/kg however, in contaminated soils Rabie *et al.* (1996) reported that available-Cd in El-Saff contaminated soils was about 0.35 mg/kg. Our data indicate that sludge addition enhanced DTPA-Cd concentrations 0.50, 1.23, 2.34 and 4.06 mg/kg due to increase in sludge addition 0, 20, 40 and 80 ton/fed, respectively.

Higher levels of available Pb were obtained in this study compared to previously reported data. Rashad *et al.* (1995) found that the normal level of available Pb ranged from 1.4 to 2.5 mg/kg with an average of 1.9 mg/kg. Aboulroos *et al.* (1996) recorded 0.78-2.46 mg/kg with an average of 1.39 mg/kg for available Pb in these soils. While reported available Pb levels in contaminated soils was ranged between 4.37 and 10.63 mg/kg with an average of 7.5 mg/kg (Ramadan, 1995). Pb ranged from 3.6 up to 16.81 mg/kg due to sludge addition. RP can contain heavy metals, salts, and other possible contaminates and their use as soil amendments may be constrained by a lack of knowledge about their potential environmental effects.

It is worth mentioning that the rate of increase in available-Zn was the highest amongst the tested metals. While the opposite was true in case of Cd. Similar trend for available Cu, Cr and Cd was observed, however the rate of increase of available Cd was the highest (8.13 folds of control), followed by Cr (7.00 folds of control), then available Cu was increased by 6.22 fold of control due to sludge addition. The lowest rate if increase in available-Zn was noticed (only 3.02 folds of control). Rashed *et al.* (1995) indicated that available-Cu in alluvial soils of Nile Delta ranged between 1.2 and 9.4 mg/kg with an average of 5.73 mg/kg. Aboulroos *et al.*(1996) reported that normal levels of available-Cu ranged between 1.26 to 3.78 mg/kg.

Generally, organic waste application to agricultural land has added to the heavy metals pool in soils and has been the subject of many studies (Chang et al. 1984; Chaney, 1992 and Abdel-Sabour & Mohamed, 1994). Heavy metals originating from various organic waste sources accumulate in soil surface, and their fate depends on soil chemical and physical properties. Movement of heavy metals with water in soils requires that the metal be in the soluble phase or associated with

mobile particulate. Organic matter and hydrous oxides, as ionic sorption sites, strongly affect metal mobility in the soil profile.

Plant yield

Data obtained as indicated by the dry weight of plant shoots and roots (Fig. 1) show that plant growth was positively affected by the application rate of industrial sludge (IS), which could be attributed to the addition of plant nutrients within the sludge treatment. These results are in agreement with those obtained by Aboulroos et al. (1989); King & Hajjar (1990) and Mehana & Farag (1999). Data also shows that application of rock phosphate (RP) significantly increased yield of sorghum shoots and roots. Increasing the rate of applied RP increased slightly the yield of sorghum shoots and roots as shown in Fig. 1.

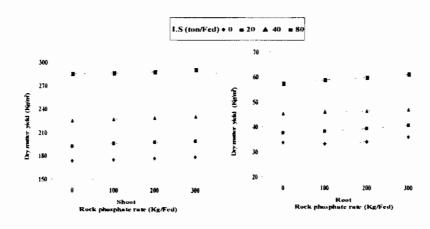


Fig. 1. Dry matter yield of sorghum plants (Kg/m²) as affected by industrial sludge and rock phosphate application.

Heavy metals in plant

Nutritive trace elements (Fe, Mn, Zn, and Cu) significant increase in sorghum due to IS application while synergetic effects were observed due to RP application Tables 5 and 6. The later behavior could be easily explained by P and Ca (due to RP application) interactions with other trace elements.

Results obtained in Table 5 show that application of IS increased Co content in sorghum shoots and roots with increasing the application rate of IS. In this concern, the rate the rate of increase in Co content was 47.8, 119.2 and 179.1 % when Is was applied 20, 40 and 80 ton/Fed respectively. The comparable increases in Co content in sorghum roots were 46.7, 68.7 and 84.4 %, respectively. The mobility of Co is strongly related to the kind of organic matter in soils. Organic chelates of Co are known to be easily mobile and moved to soil profile. Co organic chelates may also be readily available to plants. This is especially pronounced at higher pH and in fearly drained soils.

TABLE 5. Heavy metals content in sorghum shoots (mg/kg) as affected by rock phosphate application to industrial sludge-amended soil.

S)d=a	Rock phosphate	Heavy metals content in sorghum shoots (mg/kg)										
Sludge Rate ton/fed	kg / fed	Fe	Mn	Zn	Cu	Co	Cr	Ni	Cd	Pb		
Control	0	389	231	203	21.7	21.2	13.7	23.9	2.6	143		
	100	383	159	182	19.2	19.2	12.3	23.2	2.3	128		
	200	361	137	170	14.9	17.5	10.3	20.7	1.8	116		
	300	332	117	162	12.3	13.6	7.50	17.5	1.3	105		
N	Mean	366	161	1 79	17.0	17.9	11.0	21.3	2.0	123		
20	0	838	469	437	33.7	31.4	24.7	36.3	4.5	225		
	100	823	444	343	31.7	29.4	22.0	34.1	4.2	213		
	200	794	421	337	28.2	27.4	20.0	31.0	3.7	200		
	300	7 77	431	312	23.9	24.1	15.8	28.3	3.1	181		
N	Mean	808	441	360	29.4	28.1	20.6	32.4	3.9	205		
40	0	1061	508	494	38.0	46.5	26.7	39.8	6.4	236		
	100	995	476	469	36.7	33.0	24.6	37.3	6.1	222		
	200	966	458	352	32.8	29.7	22.1	34.5	5.6	211		
	300	942	429	389	26.0	26.1	18.5	31.5	5.1	189		
N	Aean .	991	468	426	33.4	33.8	23.0	35.8	5.8	215		
80	0	1331	533	587	41.8	59.3	31.0	44.9	8.7	251		
	100	1086	520	551	39.6	35.1	29.3	41,9	8.4	232		
	200	984	500	577	34.4	32.3	24.5	38.2	7.8	218		
	300	955	474	527	29.0	27.6	22.1	35.2	7.3	205		
N	Aean	1089	507	561	36.2	38.6	26.7	40.1	8.05	227		
LSD _{.05}												
S		62.2	15.1	26.6	0.70	0.52	0.76	0.57	0.7	3.5		
RP		33.0	12.5	12.2	n.s.	0.68	n.s.	0.75	0.5	4.6		
SxRP		65.9	24.9	53.3	1.40	1.37	1.52	n.s.	1.4	n.s.		

Application of RP significantly decreased the contents of Co. The rates of decrease in Co content of shoots were 26.3, 32.5 and 42.2 %. as a result of applying 100, 200 and 300 kg RP/fed, respectively. The comparable values in roots were 6.6, 14.6 and 27.4 %, respectively. Abdel-Sabour & Rabie (2003) investigated Co-content in ten vegetables plant namely, Abelmashus, Carden, Onion, Jews mallow, Spinach, Radish, Celery, Chard, Rocket, Lettuce and sorghum grown on either normal or contaminated soil of the Mostored area. It is clear from the study that vegetables grown on contaminated soil showed a highest accumulation of Co especially in the leafy plant such as Lettuce, Spinach, Carden, Rocket and Radish. Most of the investigated plants accumulated high amounts of Co, which exceeds very much the normal range. Rocket recorded the highest content of Co (61.3 µg/g) followed by Celery $(39.7 \mu g/g)$, Spinach $(32.3 \mu g/g)$, Jews mallow $(32.1 \mu g/g)$, Onion $(31.5 \mu g/g)$, Lettuce (29.4 μg/g), Chard (28.8 μg/g) and Carden (25.7 μg/g). Though Radish and Abelmashus recorded the lowest contents of Co (11.6 and 13.7 µg/g, respectively), sorghum showed as high Co as 16.8 mg/kg, but these levels exceeds the normal range as reported by El-Sokkary (1988). They found that

under normal conditions, the concentration of Co in the leaves of some plant species ranged between 0.01 and 4.30 mg/kg with an average of 2.16 mg/kg which is similar to those reported by Bowen (1979). He reported that the concentration of Co in edible vegetables ranged between 0.01 and 4.60 with an average of 2.31 mg/kg. Application of RP decreased the uptake of Cr in sorghum shoots and roots by several order of magnitude.

TABLE 6. Heavy metals content in sorghum roots (mg/kg) as affected by rock phosphate application to industrial sludge-amended soil.

Sludge	Rock	Heavy metals content in sorghum roots (mg/kg)									
Rate ton/fed	phosphate kg/fed										
1011/100	ng/ tea	Fe	Mn	Zn	Cu	Co	Cr	Ni	Cd	Pb	
Control	0	530	284	257	24.7	22.5	16.7	28.3	3.9	151	
	100	521	215	238	23.2	20.0	15.1	26.9	3.5	129	
	200	502	186	220	20.0	18.5	12.7	24.8	3.1	119	
	300	492	157	183	15.2	14.9	9.33	22.1	2.4	110	
N	Лean	511	211	225	20.8	19.0	13.5	25.5	3.2	127	
20	0	1331	485	324	38.9	33.0	28.3	40.2	5.5	259	
	100	1170	398	300	35.1	31.4	26.4	38.4	5.2	225	
	200	997	373	280	31.9	29.0	23.3	35.6	4.6	216	
	300	969	338	270	27.3	27.6	20.4	32.6	4.1	207	
N	/lean	1117	399	294	33.3	30.3	24.6	36.6	4.85	227	
40	0	1461	518	396	41.8	37.9	32.3	47.3	7.8	267	
	100	1262	429	372	37.9	36.0	30.7	45.7	7.5	234	
	200	1083	410	345	33.7	33.1	25.8	43.1	6.9	227	
	300	976	382	332	29.3	29.9	23.0	38.3	6.3	211	
N	⁄lean	1196	435	361	35.7	34.2	28.0	43.6	7.13	235	
80	0	1940	610	521	48.1	41.4	36.0	54.2	9.7	288	
	100	1760	525	493	44.4	38.4	32.5	52.3	9.3	248	
	200	1511	511	467	38.8	34.6	30.4	48.6	8.9	236	
	300	1270	494	450	33.4	25.5	25.9	43.5	8.3	226	
N	1ean	1620	535	483	41.2	35.0	31.2	49.7	9.05	250	
	LSD ₀₅										
	S	137	5.94	19.3	0.99	1.32	1.04	0.80	0.7	2.7	
	RP	97.2	5.36	7.79	n.s.	1.75	n.s.	1.06	0.6	3.6	
SxRP		194	10.7	38.7	1.98	3.5	2.08	n.s.	_ 1.5	7.6	

Data obtained in Table 5 show that IS application positively affected Ni content in sorghum shoots. It was $44.86~\mu g^{-1}$ (under application of 80 tons IS per fed in absence of any application of RP). Increasing the rate of applied IS was occulted with an increase in Ni content in shoots. The rate of increase was 51.5, 64.1~and~87.4~% due to the application of 20, 40 and 80 tons IS/fed, respectively in absence of application of RP. The rate of increases in roots Ni were 42.0.~67.1~and~91.3~%, respectively. Application of RP decreased Ni content in plant. The rate of decrease in Ni-content in shoots due to applying 100, 200~and~300~kg~RP/fed~was~5.6, 14.1~and~22.3~%, respectively. The values for the response in roots were 3.9,~10.5~and~19.7, respectively.

Data obtained in Tables 5 and 6 show that IS application positively affected Cd content in sorghum shoots and roots. Cd concentrations in tested samples were higher than normal levels reported for Egyptian field crops (< 0.3 mg/kg according to Aboulroos *et al.*, 1996). Cadmium uptake by plants depend on: (a) plant species, (b) chemical form of the element in soil (Koeppe, 1977), (c) occurrence of other elements notably competing heavy metals, and of complexing legends, and adsorption sites associated with the solid phase, (d) available Cd in soil solution, and (e) soil and weather conditions. Abdel-Sabour *et al.* (1998) investigated ten vegetable plant species, collected from field at industrial area northern greater Cairo city. The soils at this location have been subjected to prolonged industrial wastewater irrigation (more than 35 years). Results revealed that vegetable plant species varied in their affinity to accumulate metals in their edible parts.

Results in Tables 5 and 6 show that industrial sludge application increased significantly Pb content in sorghum plant. As it could be seen that Pb tend to accumulate in roots than in shoots. Greater content in roots than shoots may reflect a limited translocation of Pb from roots to shoots. This finding is in agreement with those obtained by Kabata-Pendias & Pendias (1984). Maize (Zea mays) and sesame (Sesamum indicum) were grown in field plots to evaluate crop uptake of selected heavy metals as affected by heavy metals from industrial sludge compost in Egypt (Abdel-Sabour & Abo El-Seoud, 1996). The effect of rate of application was investigated to assess the potential heavy metals entry into the food chain, and their possible adverse effects on the capacity of sandy soil to sustain the growth of the growing crops. Based on the results from these set of experiments, industrial sludge compost application to sandy soil significantly increased Pb levels in both plant samples.

For the application of rock phosphate, it was significantly decreased the content of Pb in plant, particularly as the rate of application increased up to 300 kg/fed. Basta & Gradwahl (1998) reported that treatments of soil with RP reduced plant available Pb (Ma & Rao, 1997) demonstrated that RP has a potential to cost-effectively treat Pb-contaminated soils. Ma et al. (1997) reported that rock phosphates were effective in immobilizing Pb from aqueous solutions and considerable reduced its water-soluble contaminated soils by 56-100 %, respectively. Previous studies have shown that the interactions of apatite with dissolved Pb are caused by the dissolution of apatite grains concomitant with the precipitation of lead orthophosphates (pyromorphites). Inducing the formation of lead phosphate compounds [e.g., pyromorphite Pb5(PO4)3-(X) where X = OH, F, or CI] in contaminated soils may reduce the bioavailability and chemical lability of Pb in soil. Laperche et al. (1997) investigated apatite amendments to control the bioavailability of Pb in contaminated soill. A Pb-contaminated soil was treated with natural and synthetic apatites, and the bioavailability of Pb was determined in plant uptake studies with sudax (Sorghum bicolor). The Pb content in shoot tissue decreased as the quantity of added apatite increased. However, Pb and P contents in the plant roots increased as the quantity of added apatite

increased. In the absence of apatite amendments, Pb content in the shoot was 170 mg/kg dry weight; apatite decreased the shoot Pb concentration to 3 mg/kg.

References

- Abdel-Sabour, M. F. and Mohamed, A. R. A. G. (1994) On the optimum use of municipal waste water, organic waste for ameliorating sandy soils. Final report, project No C-3-10, NARP, US-AID project 263-0152, Cairo, Egypt.
- Abdel-Sabour, M. F. and Zohny, E. (2003) The impact of industrial activities on total chromium in alluvial Egyptian soils as determined by delayed neutron activation analysis technique. *Proc.* 3rd African Res. Reactors Conf. 17th march, 2003, Rabat, Morocco.
- Abdel-Sabour, M. F.; Rabie, F. H.; Mostafa, T. and Hassan, S. A. (1998) Impact of industrial wastewater disposal on surface water bodies in industrial area north greater Cairo. Proc. 4th Int. symp. Aug. 9-13, pp. 872-887, On Environ. Geotech. And Global Sustainable Development, Boston, Mass., USA.
- **Abdel-Sabour, M. F. and Rabie, F.H.** (2003) Accumulation of heavy metals in vegetable plants grown in Mostorod area. Egypt. J. Soil Sci. 43 (1): 63-76.
- Abdel-Sabour, M. F. and Abo El-Seoud, M.A. (1996) Effect of organic waste compost addition on sesame growth, yield and chemical composition. *Agric. Ecosy. And Environ.* 60: 157-164.
- **Aboulroos, S.A.; Holah, S.H. and Badawy, S.H. (1996)** Background levels of some heavy metals in soils of Egypt and associated corn plant. *Egypt. J. Soil Sci.* **36** (1-4).
- Abouiroos, S.A.; Holah, S. H. and Badawy, S.H. (1989) Influence of prolonged use of sewage effluent in irrigation on heavy metal accumulation in soils and plants. *Z. Pflanzener. Boodenk.* 152: 51-55.
- Alloway, B. J. (1990) "Heavy Metals in Soils", Blackie Academic and Professional, U.K.
- Andriano, D.C. (1986) "Trace Elements in the Terrestrial Environment", Springer Verlag, Berlin, Heidelberg, New York, Tokyo.
- Aitken, M. N.; Cummins, D. I.; Hayes, M. H. B. and Wilson, W. S. (1997) The effect of long-term annual sewage sludge applications on the heavy metal content of soils and plants. Health and Environmental Aspects, 425-437.
- Basta, N.T. and Gradwahl, R. (1998) Remediation of heavy metal contaminated soil using rock phosphate. Better Crops with Plant Food 82 (4): 29-31.
- Chaney, R. L. (1992) Land application of composted municipal solid waste: Public Health Safety and Environmental Issues, pp. 61-83, *Proc. of National Conf. of Solid Waste Composting Council*, Alex: VA. 22314.
- Bowen, H. J. M. (1979) "Environmental Chemistry of the Elements", Academic Press, New York, 333.

- Chang, A. C.; Warneke, J. E.; Page, A. L. and Lund, L. J. (1984) Accumulation of heavy metals in sewage sludge-treated soils. J. Environ. Qual. 13: 87-91.
- **El-Gamal, I.M.I.** (1980) Evaluation of Cairo liquid sewage sludge applied to soil with special consideration to its heavy metals contents. *M.Sc. Thesis*, Fac. Agric., Ain. Shams Univ., Cairo, Egypt.
- El-Leithi, A.A. (1986) Pedological studies of heavy metals in the vicinity of some industrial and highway areas in soils of Nile Delta. pH. D. Thesis, Alexandria Univ., Alexandria, Egypt.
- El-Nashar, M.B. (1985) Effect of sewage water on soil properties of the Egyptian soil. *Ph.D. Thesis*, Fac. of Agric., Monofia Univ., Egypt.
- El-Sabbagh, T.A. (1991) "Environmental impact of industrial area "Mostorod" on the concentrations of some elements in water, soil and plant. M. Sc. Thesis, Inst. of Environmental Studies and Res., Ain Shams Univ., Egypt.
- El-Sokkary, I.H. (1988) Yield and elemental composition of plant crops grown on sewage sludge amended calcareous soil. VDLUFA-Schriftenreihe 28, Kongressband, TEIL II.
- Gomez, K.A. and Gomez, A.A. (1984) "Statistical Procedures for Agriculture Research", p. 680, John Willey and Sons, New York.
- Hassan, S.A. (1997) Heavy metals soil pollution in the industrial area north of greater Cairo, M. Sc. Thesis, Institute of Environmental Studies and Research, Ain Shams Univ., Egypt.
- Isac, R.A. (1990) "Officials Methods of Analysis of the Association of Official Analytical Chemists", AOAC, Inc. Arlington, VA.
- Kabata-Pendias, A. and Pendias, H. (1984) "Trace Elements in Soils and Plants", 2nd CRC Press, Inc. Boca Raton, USA.
- Kandil, LA. (1994) Impact of some trace metals on some forage crops in desert soils., M.Sc. Thesis, Inst. Environ. Studies & Res., Ain Shams Univ., Egypt.
- King, L.D. and Hajjar, L.M. (1990) The residual effect of sewage sludge on heavy metal content of Tobacco and Peanut. J. Environ. Qual. 19: 738-748.
- Koeppe, D.E. (1977) The uptake, distribution and effect of Cd and lead in plants. "The Science of the Environment", 197-206, Ellsevier Sci. Publ. Comp., Amstrerdam.
- Kukier, U. and Chaney, L. (2000) Remediating Ni-phytotoxicity and hydrous iron oxide. Canadian J. Soil Sci. 80: 581-593.
- Laperche-V.; Logan-TJ.; Gaddam-P. and Traina-SJ. (1997) Effect of apatite amendments on plant uptake of lead from contaminated soil. *Environmental-Science-and-Technology* 31 (10): 2745-2753.

- Lindsay, W. L. and Norvell, W. A. (1978) Development of a DTPA soil test for zinc. iron, manganese, and copper. Soil Sci. Soc. Am. Proc. 42: 421-528.
- Lund, L.J.; Betty, E.E.; Page, A.L. and Ellott, R.A. (1981) Occurrence of naturally high cadmium levels in soi! and its accumulation by vegetation . J. Environ. Qual. 10: 551-556.
- Ma-L. Q. and Rao, G. N. (1997) Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. *J. Environmental-Quality* 26 (3): 788-794.
- Ma-L. Q.; Choate, A. L. and Rao, G. N. (1997) Effects of incubation and phosphate rock on lead extractability and speciation in contaminated soils. *J. Environmental-Quality* 26 (3): 801-807.
- Mehana, T.A. and Farag, F.M. (1999) Effect of sewage sludge application on some soil properties and mineral composition of maize and wheat plants. *J. Agric. Sci. Mansoura Univ.* 24 (9): 5217-5228.
- Mohamed N.A. (1998) A study on some trace metals as related to soil environment. *Ph.D. Thesis*, Fac. Agric., Ain Shams Univ., Egypt.
- Page, A. L.; Miller, R. H. and Keeney, D. R. (1982) "Methods of Soil Analysis Part II. Chemical and Micrbiological Properties", 2nd ed., Amer. Soc. of Soil Sci., Inc. Madison, Wisconsin, USA.
- Power, P. (1985) Users guide to MSTAT (Ver. 3.0), Michigan States Univ. USA.
- Purves, D. (1977) Trace-element contamination of the environment; fundamental aspects of pollution control and environment science; I. Elsevier Scientific Publishing Company, New York.
- Rabie, F.; Rashad, I. F.; Khader, M. Y. and Hussein, W. (1996) Content of biogenic non biogenic heavy metals in El-Saff soils are related to different pollution sources. Egypt. J. Soil Sci. 36: 165-177.
- Ramadan, M.A. (1995) Studies on the pollution of the agricultural environment in Egypt. Ph.D. Thesis, Fac. of Agric., Cairo Univ., Egypt
- Rashad, I. F.; Abdel-Nabi, A.O. and El-Hemely, M. E. (1995) Background levels of heavy metals in the Nile Delta Soils. *Egypt. J. Soil Sci.* 35: 239-252.
- Sedky, L.E. (1995) Chemical mobility and reactivity of some soil components and their impact on crops in the western desert ecosystems. *Ph.D. Thesis*, Inst. Environ Studies Res., Ain Shams Univ., Egypt.
- Yousry, M. and El-Sherif, A.F. (1977) A contribution to lead content in roadside soil and plants. *Egypt. J. Soil Sci.* 17: 115-23.
- Yousry, M.; El-Leboudi, A. and Nofal, M. (1982) Hydrocarbons emulsions from petrogas factories as a source of air pollution on the growth and nutrient uptake of plant. Annals Agric. Sci. 27 (1-2): 260 - 317.

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معالجة العناصر الثقيلة في الاراضى الرملية المعاملة بالمخلفات الصناعية الصلبة باستخدام الصخر الفوسفاتي

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اجريت دراسة لأختبار مقدرة الصخر الفوسفاتي كمحسن فردي لمعالجة العناصر التقيلة مثل Pb, Cd, Ni, Cr, Co, Cu, Zn, Mn, Fe والتي الها تأثير سام على النبات في الاراضى الملوثة بالمجاري الصناعية الصلبة وهي تجربة حقلية استخدمت فيها ارض بكر في محطة التجارب بهيئة الطاقة الذرية المصرية . وكانت العوامل المختبرة هي مخلفات المجاري الصناعية الصلبة (٤ مستويات ١٠٠٠ ٢٠٠ ٢٠٠ ٢٠٠ كجم/لادن) وربع نبات السورجام (٣٠١ ٢٠٠ ٢٠٠ كجم/لادن) وزرع نبات السورجام (Sorghum volgare) كمؤشر وبعد فترة النمو ٧٠ يوم اخذ سوق وجذور النباتات وجفف على ٧٠ درجة منوية وسجلت المادة الجافة واجريت عملية الهضم بالحرق الجاف لسوق وجذور النبات لتقدير محتواها من العناصر التقيلة.

وقد اوضحت النتانج المتحصل عليها ان اضافة مخلفات المجارى الصناعية الصلبة ادت الى زيادة فى المادة الجافة لكل من السوق والجذور وان هذه الزيادة تكون واضحة مع اضافة الصخر الفوسفاتى وذلك بالمقارنة بالنباتات الغير معاملة . وأن محتوى نبات السورجام من العناصر الثقيلة زادت مع الزيادة فى مستويات الاضافة بمخلفات المجارى الصناعية بينما قل محتواها من العناصر الثقيلة عند كل من مستويات الاضافة للصخر الفوسفاتى فى معظم الحالات وقد وجد ان زيادة معدل اضافة مخلفات المجارى الصناعية الصلبة ادى الى زيادة شاذة فى عنصر معدل اضافة مخلفات المجارى الصناعية الصلبة ادى الى زيادة شاذة فى عنصر النيكل فى اعضاء النبات المختلفة واضافة الصخر الفوسفاتى ادى الى نقص معنوى فى مستوى CO الممتص فى سوق وجذور نبات السورجام وقد بينت النتانج بوضوح ان النباتات تنمو افضل فى وجود الصخر الفوسفات ولا يحدث بها تراكم للعناصر الثقيلة تحت الدراسة بنفس درجة معاملة النباتات بالمخلفات الصناعية الصلبة.