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Impact of landfill fly ash on soil contamination with heavy metals in Rabigh Area, Saudi Arabia

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Abstract. This study was carried out to investigate special distribution of micro- and toxic-elements separated from carbon fly ash buried in landfill in Rabigh, Saudi Arabia, comparing between the total micro- and toxic metals and the available metals extracted using the DTPA (diethylenetriaminepentaacetic acid) micronutrient extraction method which is a non-equilibrium extraction for estimating the potential soil availability. The results showed that the highest total and DTPA extractable and available concentrations of sulfur (S), manganese (Mn), zinc (Zn), copper (Cu), iron (Fe), aluminum (AL), cobalt (CO), chromium (Cr), nickel (Ni), vanadium (V) are in the soil inside the landfill, then concentrations decrease with increase in distances 0, 250, 500, 1000 m away from landfill at all locations, north south, east, west. The soil total micro-and toxic-element accumulations are highest at south location, followed by east, then west and the least concentrations are in the soil of the north location. The soil DTPA extractable available micro- and toxic-elements are highest at the east location, then south then north and west location has soil with the least element concentrations. Iron (Fe) as soil total micro-element is the highest (38888.37 mg/kg), but as DTPA available element it is very low (16.46 mg/kg) at all locations and distances. Sulfur (S) comes second to Fe as total soil element with (541.24 mg/kg), then Mn element, while for soil DTPA available micro-elements S is the highest element (193.60 mg/kg) followed by Fe, and Cu is the element with the least concentrations in the soil. For toxic-elements Al dominates total soil concentrations (19173.27 mg/kg), followed by V then Cr, Ni and Co, and for DTPA available soil metals Ni and V gave higher concentrations than Co and Cr at all distances and locations. Then it can be said that sulfur (S) is the most available micro-element, and nickel (Ni) and vanadium (V) are the most available toxic-elements inside and around Rabigh HOFA landfill area. The concentration of soil total Fe is higher than European Standards (2002), Saudi Standards (2020) and Indian Standards (2000), and that of S is higher than Saudi Standards (2020). Nickel (Ni) is higher than Saudi Standards (2020). The rest metal concentrations in landfill soil are below phototoxic concentration standards put forward by EU (2002), Saudi Arabia (2020), and Indian standards (2000). The rest element concentrations in landfill soil are below phototoxic concentration standards put forward by these standards. The aim of this study is to measure the total contents of micro- and toxic-elements and extractable micro- and toxic-elements of the HOFA dumping landfill area at Rabigh district in Saudi Arabia, using the method of diethylene triamine penta acetic acid (AB-DTPA) according to the method of (Soltanpour and Schwab (1977), and study the spatial magnitude of distribution of these toxic elements away from the landfill area, in an attempt to evaluate their hazardous effect on the surrounding soil, plants and ground water.

Keywords: Micro-, toxic-elements, landfill, fly ash carbon, DTPA.

1. Introduction

Saudi Arabia generates huge amounts of liquid and solid waste, estimated at millions of tons per year, and the most important of these pollutants is Fly Ash, which results from burning

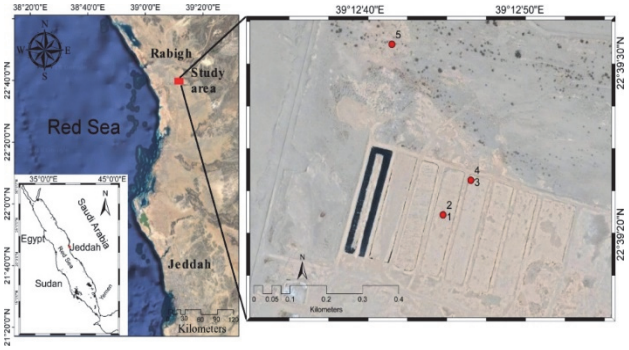
heavy oil and crude oil used as fuel in many facilities, especially power plants, desalination plants, cement plants that consume huge amounts of fuel. Fly ash (FA) oil now is got rid of by dumping it in large landfill areas at Rabigh and in other areas. This leads to contamination and pollution of soil, water, and plants in this region because this FA contains heavy metals and toxic elements. Heavy oil fly ash "HOFA" is considered a hazardous waste because it contains considerable amounts of heavy metals, particularly it contains significant amounts of vanadium "V" and nickel "Ni", (Bakkar, et al. 2023). Heavy oil fly ash landfills are classified hazardous due to the multi-pollutants of heavy metals, soluble salts, and polychlorinated-p-dioxins and furans (PCDD/Fs), (Peng et al., 2020). The high concentration of potentially toxic heavy metals (Cd, Zn, Pb, Cr, Ni, etc.) in HOFA can be easily leached into the surrounding soil around the landfill area (Liu, et al. 2022). The leaching concentrations of Pb and Cd were found to exceed emission standards worldwide, and Zn and Cr were also observed to have high leaching concentrations (Fan et al., 2021; Tian et al., 2021). Lin, et al. (2022) applied the field stabilization/solidification (S/S) treatment for municipal solid waste incineration fly ash (MSWIFA) and multi-step leachate treatment. The method reduced mobility and bioavailability of heavy metals in MSWIFA. The heavy fuel oil fly ash (HFOF) in a landfill was subjected to heavy metals leaching tests in order to investigate its potential environmental hazards, and concentrations of chromium, nickel and vanadium, in the extract, were in the range of 1.89–30.5, 55.9–2113 and 270–6260mg/l, respectively (Al-Malack, et al. (2016).Heavy oil fly ash contains concentrations of heavy oil elements (such as sulfur, which contains high levels of 4-8%, Cd, Co V, Fe, Ni, Zn, Mn, Pb, Cu) (Konist, et al. 2020). Heavy metals, namely Cd, Cr, Pb, Cu and Zn were significant concentrations in the soil within a radius of 2,000 m from the landfill (Chuangcham, et al. 2008). Heavy oil FA has a carbonaceous matrix and contains V, Ni, Zn, Cr, Cu, and Pb in variable amounts (Al-Degs, et al. 2014). Fly ash is usually rich in heavy elements such as (Chromium, Cobalt, mercury, Terbium (Adriano, et al. 1980), and many of the fine elements present in FA, including Mo, S. Se, Sr, As, B, Ca are found in its small molecules. Hence, information regarding the content of these metals in soils and their availability to plants is important (Adriano, 2001). The contents of total as well as extractable Mn and Fe varied widely with extractants and different soil samples (Behera and Shukla, 2014). There is a decrease in the concentration of soil heavy and toxic metals with increase in distance from the landfill, and level of Ni and V in soil of landfill were higher than the permissible level (Al-Otaibi, 2006). Soil heavy metal concentrations inside the landfill are higher than concentrations of soil samples from the sites outside landfill (Makuleke and Veronica, 2020). Landfill leachate is formed when soil becomes moist through rainfall, and through it heavy metals are released and migrate out of the landfills and distribute in the areas around it (Hussein, et al. 2007). Falling rainwater percolates through disposed materials of the landfill, the waste becomes moist and undergoes decomposition and degradation and elements distribute outside the area of landfill (Costa, et al. (2019). The diethylene triamine penta-acetic acid (DTPA) extracting is used predominantly worldwide for extraction of plant-available metals (Lindsay and Norvell, 1978). The aim of this study is to measure and compare between the total contents of micro- and toxic-elements and extractable micro- and toxic-elements of the HOFA dumping landfill area at Rabigh district in Saudi Arabia, using the method of diethylene triamine penta acetic acid (AB-DTPA) according to the method of (Soltanpour and Schwab (1977). Also the aim is to characterize and study the spatial magnitude of distribution of these toxic elements

away from the landfill area, in an attempt to evaluate the hazardous effect of these toxic metals on the surrounding soil, plants and ground water.

Materials and Methods

Study area

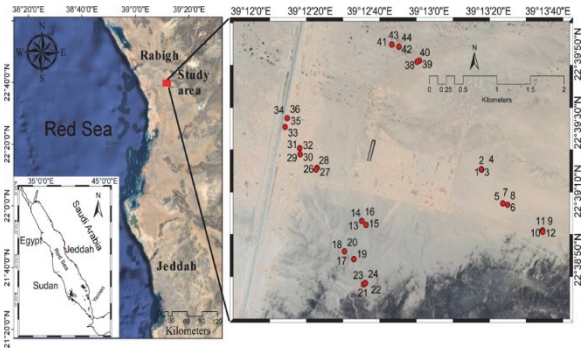
The landfill in Rabigh governate located at N 20° 37 23 and E 39° 56 4.52 (Fig.1).



(Fig. 1). Map of the studied area at Rabigh landfill.

Collection of soil samples

Sixty four surface soil samples were randomly collected from 0 to 30 cm depth from inside the landfill and at three different distances (250m, 500m, and 1000m) and at four locations (North, South, West, East) (Fig2) using stainless steel soil augers and taken to the laboratory for analysis. Collected soil samples were air dried, ground to pass a 2-mm sieve after stone and debris were removed, and then stored in plastic bottles for analysis in laboratory.



(Fig. 2). Map of the studied area at Rabigh landfill (soil sampling).

Determination of Micro and Toxic Elements (Total) and DTPA available:

The pseudo-total content of the studied elements in soils was extracted in triplicates by the acid digestion of a 0.6-g subsample in a Milestone-ETHOS EASY (Germany) microwave system according to US EPA 3051a (2007). From each sample, 0.5 g was used to estimate the concentration of Iron (Fe), Zinc (Zn), Manganese (Mn), Copper (Cu), Lead (Pb), Chromium (Cr), cadmium (Cd) and nickel (Ni) and vandum (V). An atomic absorption device was used. The elements were estimated after extraction by

the digestion method with perchloric acid and nitric acid (Shelton and Harper, 1941) and the concentration of these elements was estimated by use of the atomic absorption spectrophotometer model 5000 Perkin Elmer (device from Chibob). Soil extracts were analyzed in an inductively-coupled plasma optical emission spectrometry (ICP-OES; Ultima 2, Horiba Jobin Yvon, Unterhaching, Germany).

All the PTE analyses were performed at the Laboratory of Soil- and Groundwater Management at Wuppertal University, Germany.

Determination of Micro and Toxic Elements (DTPA)

The potentially available content of the studied elements in soils was extracted in triplicates using 1 M NH4HCO3 - diethylene triamine penta acetic acid (AB-DTPA) according to the method of (Soltanpour and Schwab (1977).

Determination of pH and Electrical Conductivity (EC)

A pH meter was used, which was measured by a glass electrode, and the device was calibrated using two buffer solutions of known concentration. A conductivity meter was used to express the degree of conductivity in millimeters/cm and the device was calibrated with a standard solution of potassium chloride (KCl).

Statistical analysis

Complete randomize analysis of variance (ANOVA) SAS was used based on (El-Nakhlawy, 2010) was used to study differences between different locations, and also between different distances regarding element concentrations.

Results

Landfill Soil Analysis

Soil pH and Electric Conductivity (EC):

Results of the mean values of soil pH, EC (ds/m) (Table 1) show that the soil of the landfill is basic (pH>7) inside landfill and at all distances away from the landfill and at different locations and depths. Soil pH varies between 7.52 in the south location and 7.44 in the east location, and soil EC varies between 973.47 in the south and 905.38 ds/m in the east location. According to distances, the highest pH and EC are in the soil inside the landfill with 7.56 and 984.39, respectively, then pH and EC reduce gradually with the increase of distance from the landfill. As for soil depth, soil pH and EC are high at 15 cm depth with 7.51 and 922.47 ds/m, respectively, compared to 30 cm depth with pH 7.30 and EC 831.39 ds/m.

(Table 1). Means of soil pH, EC (ds/m) under the effects of Location (North, South, West, East) Distance (250m, 500m, and 1000m) and Soil Depth (0-15, 15-30 cm) and their interactions Over the landfill area.

Treatments	pH (mg/L)	EC (ds/m)
Location		
East	7.44 b	905.38 b
West	7.32 c	853.18 c
North	7.33 c	775.70 d
South	7.52 a	973.47 a

Treatments	pH (mg/L)	EC (ds/m)
LSD	0.017	39.83
Distance (M)		
0	7.56 a	984.39 a
250	7.48 b	904.54 b
500	7.36 c	810.32 c
1000	7.20 d	808.48 c
LSD	0.014	33.54
Soil Depth (cm)		
15	7.510 a	922.47 a
30	7.302 b	831.39 b
LSD	0.025	38.56

*: Means followed by the same letter are not significantly different according to RLSD at P≤0.05.

Micro-Elements (S, Mn, Zn, Cu, Fe) and Toxic-Elements of (Al, Co, Cr, Ni, V) in the soil of the landfill area. Total and DTPA Soil Micro-Elements (S, Mn, Zn, Cu, Fe)

The analysis of variance (Table 2) shows highly significant differences (P≥0.01) between the different locations and the different distances regarding the concentration of total and DTPA micro-elements of Sulfur (S), Manganese (Mn), Zinc (Zn), Copper (Cu), Iron (Fe), in the soil of the landfill area. Also, there are highly significant differences (P≥0.01) in the interaction between (Location+Distance) regarding the concentration of these micro-elements in the soil.

(Table 2). Analysis of variance of total Micro-Elements of Sulfur (S), Manganese (Mn), Zinc (Zn), Copper (Cu), and Iron (Fe) under the effects of Location (North, South, West, East) Distance (250m, 500m, and 1000m) and their interactions Over the landfill area.

		Total elements					DTPA elements				
		Mg/kg									
Source of variation	df	S	Mn	Zn	Cu	F e	S	Mn	Zn	Cu	F e
Replicates	2	1477.53	33.52	0.018	0.30	700502.0	2160.97	1.005	0.129	0.016	30.47
Location	3	64470.36 *	14165.92 **	354.672 **	57.30 **	116174341.0 **	52839.71 **	10.646 **	3.999 **	0.329 **	28.09 **
Error (a)	6	1938.97	207.75	0.891	0.35	3666400.2	840.28	0.019	0.062	0.008	0.24
Distance	3	433080.82 **	6953.31 **	237.295 **	86.11 **	76959889.9 **	41512.56 **	23.547 **	9.489 **	0.772 **	5324.35 **
Location*distance	9	89629.12 **	1024.41 **	6.062 **	4.33 **	6785635.5	13595.86 **	1.782 **	0.889 **	0.060 **	8.47
Error (B)	24	15251.62	180.74	1.04	0.402	3215007.2	1562.25	0.214	0.063	0.015	6.61

*: Means followed by the same letter are not significantly different according to RLSD at P≤0.05.

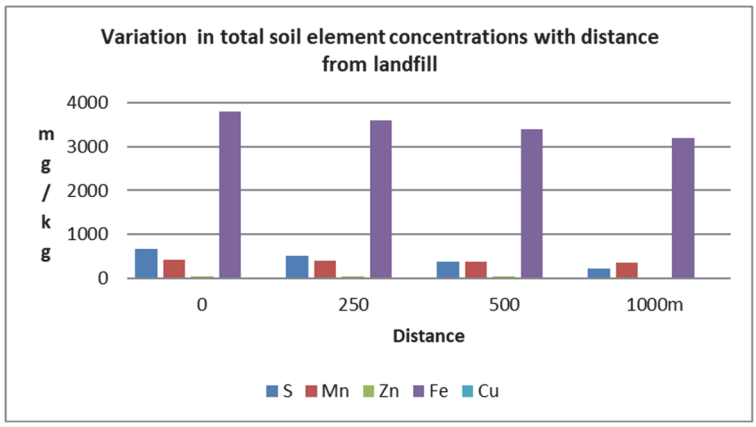
Means of total and DTPA soil Micro- Elements of Sulfur (S), Manganese (Mn), Zinc (Zn), Copper (Cu), Iron (Fe) under the effects of Location (North, South, West, East) and Distance (0m, 250m, 500m, and 1000m) Over the landfill area

Table (3) shows that soil at the south location has the highest total micro-element accumulations, followed by soil in the east, then soil in the west and the least element concentrations are in the soil of the north location. Regarding soil DTPA micro-elements the highest concentrations are at the east location, then south then north and west location has soil with the lowest element concentrations. According to distance from landfill the highest total and DTPA soil micro-element concentrations are in the soil inside the landfill and then decrease with increase in distance 0, 250, 500, 1000 m away from landfill (Figures 3,4,5). Iron (Fe) is the highest soil total concentration followed by S element, while for soil DTPA S is the highest concentration followed by Fe. Total micro-element concentrations and DTPA concentrations in soil inside landfill are (Fe=38205.16 – 47.06, S=677.37 – 240.96, Mn=419.97 – 4.46, Zn=38.35 -2.34, Cu=23.11- 0.760 mg/L respectively). And Cu is the element with the least concentrations in the soil. The concentration of soil total Fe is higher than European Standards (2002), Saudi Standards (2020) and Indian Standards (2000), and that of S is higher than Saudi Standards (2020). The rest element concentrations in landfill soil are below phototoxic concentration standards put forward by these standards.

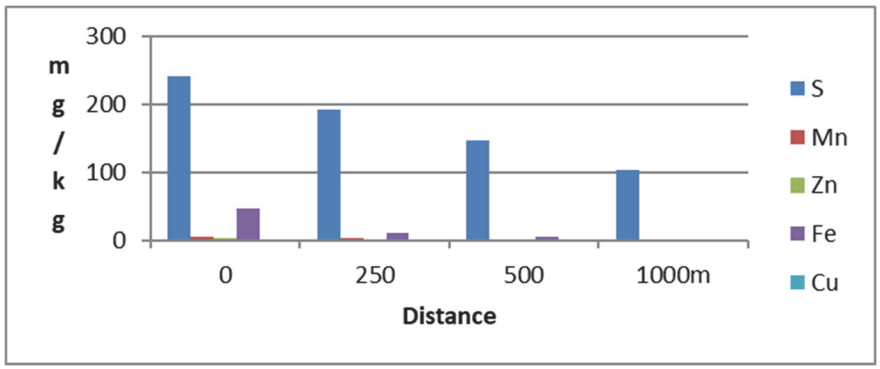
(Table 3). Means of total and DTPA soil Micro- Elements of Sulfur (S), Manganese (Mn), Zinc (Zn), Copper (Cu), Iron (Fe) under the effects of Location (North, South, West, East) and Distance (250m, 500m, and 1000m) Over the landfill area and the phototoxic concentrations according to European Union Standards EU, (2002)*, Saudi Arabia Standard (2020) and Indian Standards (Awashthi, 2000).

	Total elements					**DTPA element**				
	Mg/kg									
Source of variation	**S**	**Mn**	**Zn**	**F e**	**Cu**	**S**	**Mn**	**Zn**	**Fe**	**Cu**
Location										
South	541.24 a	431.49 a	40.11a	38888.37 a	22.96 a	193.60 b	2.80b	1.549b	16.46b	0.515b
West	426.81 c	384.84 c	32.54c	34245.58 c	19.42 c	95.08 d	1.76d	0.552d	14.30d	0.255d
North	370.30 d	350.38 d	27.14d	31663.56 d	17.83 d	146.98 c	2.02 c	1.069 c	15.22 c	0.387 c
East	481.67 b	406.32 b	35.52b	36659.47 b	20.91b	250.75 a	3.86a	1.876a	17.82a	0.640a
LSD	43.98	14.39	0.94	1912.8	0.59	28.95	0.13	0.25	0.49	0.09
Distance										
0	677.37 a	419.97 a	38.35a	38205.16 a	23.11 a	240.97 a	4.46 a	2.34 a	47.06 a	0.760 a
250	522.78 b	404.01 b	36.37b	36372.73 b	21.58b	193.42 b	2.83b	1.61 b	10.36b	0.520b
500	387.83 c	384.71 c	32.22c	34610.70 c	19.51 c	147.63 c	1.94c	0.67 c	4.95 c	0.354c
1000m	232.03 d	364.34 d	28.37d	32268.39 d	16.93 d	104.40 d	1.21d	0.41 d	1.42 d	0.162d
LSD	104.06	11.32	0.86	1510.8	0.53	33.30	0.39	0.21	2.016	0.010
Phototoxic concentration * (mg/kg)										
EU (2002)	-	-	-	140	300	-	-	-	140	300
Saudi Arabia Standard (2020)	500	-	-	63	200	500	-	-	63	200
Indian Standards (2000)	-	-	-	135-270	300-600	-	-	-	135-270	300-600

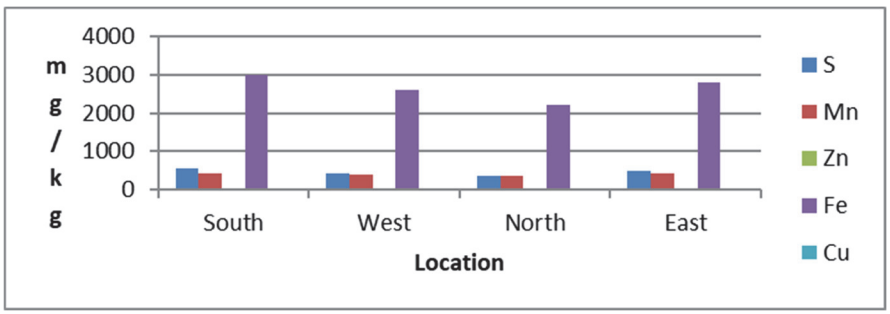
*: Means followed by the same letter are not significantly different according to RLSD at P≤0.05.



(Figure3). Total Micro-elements in soil with distance from the landfill.



(Fig. 4). diethylene triamine penta-acetic acid (DTPA)-extractable micro-elements in the soils with distance from landfill.



(Fig. 5). Total Micro-elements in soil with Location from the landfill.

Means of content of total and DTPA soil Micro- Elements (S), Manganese (Mn), Zinc (Zn), Copper (Cu), Iron (Fe) under the interaction effects of Location (North, South, West, East) and Distance (250m, 500m, and 1000m) Over the landfill area.

Results in (Table 4) show that the highest soil micro-element concentrations are in soils inside landfill for both total and DTPA (available) elements at all locations, then element concentrations decrease gradually with increase in distances away from landfill to 250, 500, 1000m. For total soil micro-element concentrations (Mn, Zn, Cu, Fe) the sequence of element increase based on location

is south>east>west>north, but for S is east>west>north>south. As for soil DTPA (available) elements the sequence of concentrations from high to low based on location is east>south>north>west. For total soil micro-elements best combination for highest concentration in soil for Fe and Mn is at east location 250m away from landfill, for Zn and Cu at south inside landfill, and for S at east location 250m from landfill. As for DTPA soil elements best interaction is at east location in landfill for Fe, Mn, Zn, and south location inside landfill for S and Cu.

Table (4). Means of total and DTPA soil Micro- Elements of sulfur (S), (Fe), Zinc (Zn), Manganese (Mn), Copper (Cu), under the effects of interaction between Location (North, South, West, East) and Distance (250m, 500m, and 1000m) Over the landfill area.

		Total elements					DTPA elements				
		Mg/kg									
Source of variation		S	Mn	Zn	Cu	Fe	S	Mn	Zn	Cu	Fe
Location	Distance										
South	0	555.83	455.63	45.89	26.83	41080.82	309.49	4.77	2.828	0.950	47.96
	250	445.35	468.18	42.44	25.43	41396.96	221.04	4.10	2.788	0.791	10.70
	500	515.49	434.74	38.08	22.08	39028.92	201.90	1.96	0.497	0.252	5.73
	1000	648.29	367.41	34.04	17.52	34046.80	41.98	0.38	0.084	0.067	1.45
West	0	736.64	409.61	37.08	22.44	37383.55	144.43	3.33	1.142	0.513	42.29
	250	601.00	396.43	36.30	21.26	36315.65	106.69	1.61	0.480	0.277	9.17
	500	281.56	365.42	29.72	17.61	32504.39	90.46	1.60	0.523	0.181	4.65
	1000	88.03	367.90	27.06	16.38	30778.74	38.76	0.49	0.065	0.050	1.08
North	0	614.14	377.40	29.66	20.00	33686.27	271.05	4.62	2.570	0.751	46.42
	250	419.75	352.38	28.33	18.45	31622.21	197.17	2.05	1.109	0.394	9.27
	500	338.85	336.25	27.44	17.35	30435.63	87.54	1.02	0.327	0.286	3.83
	1000	108.46	335.51	23.15	15.54	30910.13	32.15	0.41	0.271	0.116	1.36
East	0	802.87	437.23	40.79	23.17	40670.01	238.90	5.13	2.856	0.827	51.57
	250	625.04	399.08	38.42	21.20	36156.10	248.76	3.55	2.074	0.620	12.31
	500	415.43	402.45	33.66	20.99	36473.87	210.62	3.18	1.332	0.698	5.60
	1000	83.34	386.54	29.23	18.27	33337.92	304.71	3.57	1.241	0.417	1.80
LSD	22.65	208.12	22.65	1.71	1.06	NS	66.61	0.779	2.828	0.201	NS

*: Means followed by the same letter are not significantly different according to RLSD at P≤0.05.

Analysis of variance of total and DTPA (available) Soil Toxic Elements aluminum (Al), cobalt (Co), chromium (Cr), nickel (Ni), Vanadium (V) under the effects of Location, Distance and their interactions over the landfill area.

The analysis of variance (Table 5) shows very high significant differences (P≥0.01) between the different locations and the different distances regarding the concentration of toxic elements of Al, Co, Cr, Ni, and V in the soil of the landfill area. Also, there are highly significant differences (P≥0.01) in the interaction between (Location + Distance) regarding the concentration of these toxic elements in the soil.

(Table 5). Analysis of variance of Toxic Elements of Aluminum (AL), Cobalt (CO), Chromium (Cr), nickel (Ni), Vanadium (V), in the soil under the effects of Location (North, South, West, East) and Distance (250m, 500m, and 1000m) and their interactions Over the landfill area.

		Total elements					DTPA elements				
		Mg/kg									
	df	Al	Co	Cr	Ni	V	Al	Co	Cr	Ni	V
Replicates	2	325470.25	0.610	176.09	17.75	11.35		0.00010	0.0008	7.30	0.044
Location	3	16504062.42 **	15.558 **	1357.28 **	759.36 **	3188.84 **		0.00120 **	0.0252 **	9.87 **	8.433 **
Error (a)	6	492140.80	0.011	14.63	1.49	13.94		0.00001	0.0001	0.18	0.081
Distance	3	10841595.06 **	34.484 **	1271.85 **	571.21 **	1565.66 **		0.00600 **	0.1170 **	235.07 **	200.398 **
Location*distance	9	2764243.42 **	2.424 **	48.55	20.08 **	59.03 **		0.00042 **	0.0058 **	3.72	3.591 **
Error (B)	24	388300.3	0.205	32.10	5.61	9.64		0.000033	0.00022	1.63	0.104

Means of total and DTPA Soil Toxic Elements AL, Co, Cr, nickel (Ni) and Vanadium (V) under the effects of Location (North, South, West, East) and Distance (250m, 500m, and 1000m Over the landfill area.

Results in (Table 6) show that the significantly higher concentrations of the total and DTPA soil toxic elements AL, Co, Cr, nickel (Ni), Vanadium (V) are in the south location, followed by the east location, and the north is the location with the least soil concentrations. Also concentrations of the total and DTPA soil toxic-elements are significantly the highest inside landfill soil, then gradually decrease with increase in distance away from landfill at all locations (figures). Al

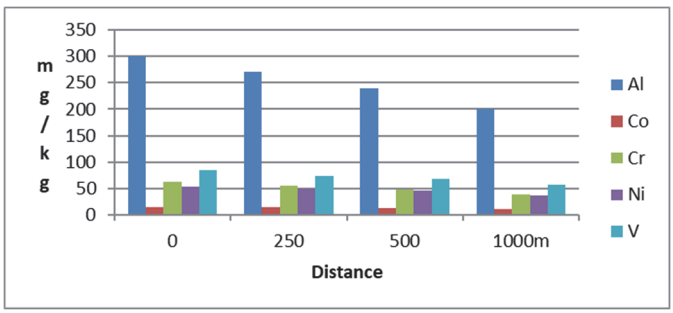
dominates the total toxic-element concentrations, giving the highest concentration (18916.32 mg/L), followed by V (84.67 mg/L), then Cr (63.26 mg/L), Ni (53.81 mg/L), Co (15.07 mg/L) (Figure 4). For DTPA soil metals Ni and V gave higher concentrations than Co and Cr at all distances and locations. Nickel (Ni) is higher than Saudi Standards (2020). The rest metal concentrations in landfill soil are below phototoxic concentration standards put forward by EU (2002), Saudi Arabia (2020), and Indian standards (2000).

(Table 6). Means of total and DTPA Toxic Elements Aluminum (AL), Cobalt (CO), Chromium (Cr), nickel (Ni), Vanadium (V), under the effects of Location (North, South, West, East) and Distance (250m, 500m, and 1000m) and the phototoxic concentrations according to European Union Standards EU, (2002)*.

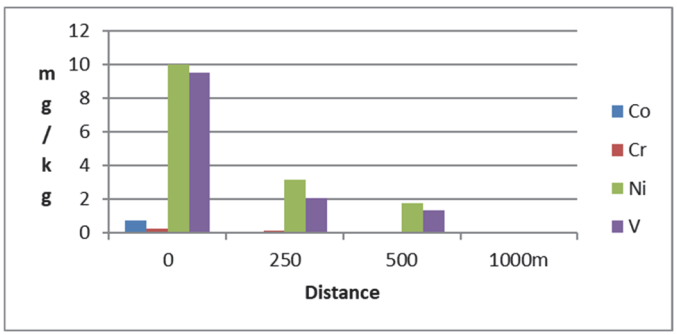
	Total elements					**DTPA elements**			
	Mg/kg								
Source of variation	**Al**	**Co**	**Cr**	**Ni**	**V**	**Co**	**Cr**	**Ni**	**V**
Location									
South	19173.27 a	14.59 a	63.92 a	54.58 a	90.41 a	0.038 b	0.104 b	3.91 b	3.80 b
West	17360.38 c	12.70 c	47.38 c	45.35 c	64.39 c	0.024 d	0.049 d	2.50 d	2.32 d

	Total elements					DTPA elements			
	Mg/kg								
Source of variation	**Al**	**Co**	**Cr**	**Ni**	**V**	**Co**	**Cr**	**Ni**	**V**
North	16471.96 d	11.92 d	39.06 d	36.35 d	52.49 d	0.030 c	0.077 c	3.25 c	3.18 c
East	18336.91 b	13.46 b	55.16 b	51.04 b	76.87 b	0.047 a	0.157 a	4.63 a	4.26 a
LSD	700.79	0.106	3.82	1.22	3.72	0.044	0.013	0.42	0.28
Distance (M)									
0	18916.32 a	15.07 a	63.26 a	53.81 a	84.67 a	0.065 a	0.224 a	9.940 a	9.46 a
250	18215.43 b	13.83 b	55.28 b	49.78 b	74.34 b	0.036 b	0.124 b	3.126 b	2.04 b
500	17512.66 c	12.70 c	47.78 c	46.11 c	67.65 c	0.025 c	0.029 c	1.176 c	1.36 c
1000	16698.11 d	11.08 d	39.19 d	37.62 d	57.50 d	0.013 d	0.010 d	0.067 d	0.70 d
LSD	525.05	0.38	4.77	1.99	2.61	0.005	0.012	1.07	0.27
Phototoxic concentration * (mg/kg)									
EU (2002)	-	100	250	-	-	٩٩	150	100	-
Saudi Arabia Standard (2020)		45	63	20	130	45	63	20	130
Indian Standards (2000)	-	75-150	-	-	-	-	20	1.5	-

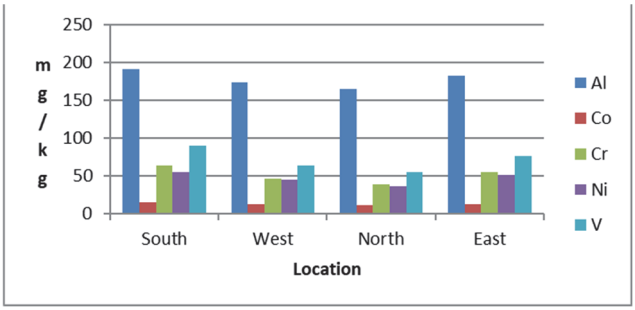
*: Means followed by the same letter are not significantly different according to RLSD at P≤0.05.



(Fig. 6). Total Toxic-elements in soil with distance from landfill.



(Fig. 7). diethylene triamine penta-acetic acid (DTPA)-extractable micro-elements in the soils with distance from landfill.



(Fig. 8). Total Toxic-elements in soil with distance from landfill.

Means of total and DTPA Soil Toxic-Elements of AL, Co, Cr, nickel (Ni) and Vanadium (V) under effects of

interaction between Location (North, South, West, East) and Distance (250m, 500m, Over the landfill area.

The results in (Table 7) indicate that the highest soil concentrations of the total and DTPA toxic elements dominate at the south location, then the east, west and north with the least concentrations, except Al, where the highest total soil concentration in the south is at 250 m away from landfill, and the highest concentration inside landfill is at the east location. The highest soil concentrations of the total and DTPA toxic elements are inside the landfill at all locations, then concentrations gradually decrease with increase in distance away from landfill at all locations. Al has the highest total soil concentration at all locations at all distances away from landfill, followed by V, then Cr, Ni and Co. Soil DTPA toxic-elements Ni and Cr dominate at all locations and distances.

(Table 7). Means of total and DTPA Toxic Elements Al. Co, nickel (Ni), Cr, Vanadium (V) under the interaction effects of Location, (North, South, West, East) and Distance (250m, 500m, and 1000m Over the landfill area.

Source of variation		Total elements					DTPA elements			
		Mg/kg								
Location	Distance	Al	Co	Ni	Cr	V	Co	Ni	Cr	V
South	0	18822.21	17.91	63.80	76.38	101.30	0.072	10.138	0.238	10.714
	250	19789.96	15.54	58.61	71.68	91.58	0.051	4.569	0.143	3.350
	500	18876.20	13.91	53.87	60.98	86.07	0.029	0.930	0.028	0.957
	1000	19204.72	11.02	42.05	46.64	82.69	0.003	0.021	0.010	0.206
West	0	19010.43	14.33	53.49	59.40	78.78	0.049	7.086	0.122	6.493
	250	17581.61	13.90	49.77	52.93	71.38	0.021	1.834	0.057	1.288
	500	16184.88	12.11	41.31	41.14	59.56	0.019	1.079	0.014	1.190
	1000	16664.59	10.46	36.83	36.04	47.84	0.007	0.028	0.004	0.327
North	0	17692.88	13.24	41.24	47.83	63.44	0.078	9.914	0.184	9.848
	250	16280.67	12.23	38.05	39.24	53.26	0.030	2.496	0.090	1.903
	500	16799.02	11.47	35.91	35.29	50.18	0.012	0.597	0.025	0.788
	1000	15115.28	10.76	30.19	33.88	43.11	0.003	0.029	0.009	0.208
East	0	20139.76	14.80	56.71	69.43	95.16	0.064	12.622	0.355	10.822
	250	19209.48	13.63	52.70	57.30	81.14	0.042	3.607	0.208	1.634

	500	18190.55	13.33	53.35	53.70	74.81	0.042	2.100	0.049	2.507
	1000	15807.85	12.10	41.40	40.21	56.37	0.041	0.191	0.017	2.080
LSD		1050.14	0.76	3.99	NS	5.23	0.009	NS	0.025	0.54

Discussion

This study is an analysis of a landfill soil used for dumping off of heavy oil fly ash (FA) in Rabigh, Saudi Arabia. The soil analysis comprised determination of five micro-elements sulfur (S), Manganese (Mn), Zinc (Zn), Copper (Cu), Iron (Fe), and five toxic-elements Aluminum (AL), Cobalt (CO), Chromium (Cr), nickel (Ni), Vanadium (V). The objectives of this research is to study the spatial distribution pattern of these micro- and toxic-elements in soil inside the landfill and the soil around it, to sea to what extent these elements migrate outside the landfill and to what extent they polluted the soil. The DTPA (diethylene triamine pentaacetic acid) micronutrient extraction method is used to determine these micro- and toxic-elements, together with determination of the total micro- and toxic-elements. The DTPA soil test was developed by Lindsay and Norvell (1978) as a non-equilibrium extraction for estimating the potential soil availability of micronutrients and trace elements. The obtained results show that the concentrations of total as well as DTPA extractable micro- and toxic-elements varied widely with locations and distances away from landfill area. Regarding locations soil total micro- and toxic-element accumulations are the highest at south location, followed by soil in the east, then soil in the west and the least element concentrations are in the soil of the north location. According to soil DTPA extractable micro- and toxic-elements the highest concentrations are at the east location, then south then north and west location has soil with the lowest element concentrations. For distance away from landfill the highest total and DTPA extractable and available soil micro- and toxic-element concentrations are in the soil inside the landfill, and then concentrations decrease with increase in distance 0, 250, 500, 1000 m away from landfill at all locations, north south, east, west. It is observed that DTPA extractable elements do not follow the same trend of distribution of the total soil elements, which suggest that DTPA available elements are affected by intrinsic factors. This highest concentrations of the DTPA elements at east and lowest concentrations at west location may be related to the nearness of west location to the Red Sea water effects, while east location is far away from Red Sea effects. And this emphasizes the fact that DTPA extractable elements are vulnerable to the intrinsic factors which agrees with finding of (Behara and Shukla 2014) who made comparative study between total and DTPA extracted soil elements in India. Element concentrations varied widely with extractants, total contents are higher than DTPA extractable contents. Iron (Fe) total concentration is very high (38888.37 mg/kg) but DTPA extractable available Fe is very low (16.46 mg/kg). This correlates with results of (Lindsay, 1979), who admitted that the solubility of Fe in soil decreases by 1000 fold for each one unit increase of soil pH in the range of 4 to 9, as compared to a 100- fold decrease for Mn, Cu and Zn. However, total Fe has higher range values in all the soils at all locations and distances than DTPA-extractable Fe, indicating the vulnerability of the DTPA-extractable Fe to the influence of external factors. This is in line with the findings of (Behara and Shukla 2014) who found higher values in total Fe than DTPA extractable Fe in some soils in India. Iron (Fe) total concentration is (Behara and Shukla 2014) Regarding locations soil total micro-element accumulations are the highest at south location, followed by soil in the east, then soil in the west and the least element concentrations are in the soil of the north location. According to soil DTPA extractable micro-elements the highest concentrations are at the east location, then south then north and west location has soil with the lowest element concentrations. The highest total and DTPA extractable and available soil micro-element concentrations are in the soil inside the landfill, and then concentrations decrease with increase in distance 0, 250, 500, 1000 m away from landfill at all locations,

north south, east, west. Element concentrations varied widely with extractants, total contents are higher than DTPA extractable contents. Iron (Fe) total concentration is very high (38888.37 mg/kg) but DTPA extractable available Fe is very low (16.46 mg/kg). This correlates with results of (Lindsay, 1979), who admitted that the solubility of Fe in soil decreases by 1000 fold for each one unit increase of soil pH in the range of 4 to 9, as compared to a 100- fold decrease for Mn, Cu and Zn. However, total Fe has higher range values in all the soils at all locations and distances than DTPA-extractable Fe, indicating the vulnerability of the DTPA-extractable Fe to the influence of external factors. This is in line with the findings of (Behara and Shukla 2014) who found higher values in total Fe than DTPA extractable Fe in some soils in India. Fe is followed by S element as total element, while for soil DTPA S is the highest concentration followed by Fe. Cu is the element with the least concentrations in the soil. Al dominates the total toxic-element concentrations, giving the highest concentration, followed by V then Cr, Ni and Co. For DTPA extractable soil metals Ni and V gave higher concentrations than Co and Cr at all distances and locations. Landfill is the place where municipal wastes are dumped, and through rainfall effects that penetrates these waste materials the dumped matter is subjected to decomposition and degradation and many element are released particularly heavy metals. These results correspond with the findings of (Al-Otaibi, 2006) who found decrease in soil heavy and toxic metal concentrations with increase in distance from the landfill. Makuleke and Veronica, (2020) found that heavy metals concentrations of the soils inside the landfill are higher than concentrations of samples from the sites outside landfill. Generally, special heterogeneity of soil micro- and toxic-elements at Rabigh landfill soils correlate with findings of (Li et al. 2011), who reported these variations in some soils in China. Hussein, et al. (2007) reported that leachate is produced in landfills, and through it heavy metals are released and migrate out of the landfills and distribute in the areas around it. Costa, et al. (2019), mentioned that rainwater percolates through dumped materials of the landfill, the waste becomes moist and undergoes decomposition and degradation and elements distribute out. The water drifts out of the landfill in all directions north, east, west and south, carrying with it heavy metals to distances away from the landfill area (Makuleke, and Veronica, 2020). This hypothesis justifies the gradual reduction in concentration of micro- and toxic-elements in the soil away from landfill. Many studies mentioned migration of heavy metals away from landfill, (Gelly, et al. 2019) reported migration of Pb, Zn and Cu away from landfill, and detected Pb at 7 km away from landfill. The concentration of soil total Fe is higher than European Standards (2002), Saudi Standards (2020) and Indian Standards (2000), and that of S is higher than Saudi Standards (2020). The rest element concentrations in landfill soil are below phototoxic concentration standards put forward by these standards. Nickel (Ni) is higher than Saudi Standards (2020). The rest metal concentrations in landfill soil are below phototoxic concentration standards put forward by EU (2002), Saudi Arabia (2020), and Indian standards (2000).

Conclusion

The results showed that the highest total and DTPA extractable and available concentrations of soil micro- and toxic-elements sulfur (S), manganese (Mn), zinc (Zn), copper (Cu), iron (Fe), and five toxic-elements aluminum (AL), cobalt (CO), chromium (Cr), nickel (Ni) , vanadium (V) are in the soil inside the landfill, then concentrations decrease with increase in distances 0, 250, 500, 1000 m away from landfill at all locations, north south, east, west. The soil total micro-and toxic-element accumulations are highest at south location, followed by east, then west and the least element concentrations are in the soil of the north location. The soil DTPA extractable available micro- and toxic-elements are highest at the east location, then south then north and west location has soil with the lowest element concentrations. Iron (Fe) is the highest soil total micro-element at all locations and distances followed by S, then Mn element, while for soil DTPA

available micro-elements S is the highest element followed by Fe, and Cu is the element with the least concentrations in the soil. Regarding toxic-elements Al dominates total soil concentrations, followed by V then Cr, Ni and Co, and for DTPA available soil metals Ni and V gave higher concentrations than Co and Cr at all distances and locations. The concentration of soil total Fe is higher than European Standards (2002), Saudi Standards (2020) and Indian Standards (2000), and that of S is higher than Saudi Standards (2020). Nickel (Ni) is higher than Saudi Standards (2020). The rest metal concentrations in landfill soil are below phototoxic concentration standards put forward by EU (2002), Saudi Arabia (2020), and Indian standards (2000). The rest element concentrations in landfill soil are below phototoxic concentration standards put forward by these standards. Then it can be said that sulfur (S) is the most available micro-element, and nickel (Ni) and vanadium (V) are the most available toxic-elements inside and around Rabigh HOFA landfill area. It is recommended to direct further research to increase the recovery and extraction of the heavy metals from heavy oil fly ash landfills in Saudi Arabia through different extraction methods like water extraction, toxicity characteristics leaching procedure (TCLP) and leaching sand columns.

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تأثير رماد مكبات النفايات على تلوث التربة بالمعادن الثقيلة في منطقة رابغ، المملكة العربية السعودية

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المستخلص. أجريت هذه الدراسة للتحقيق في التوزيع الخاص للعناصر الدقيقة والسامة الناتجة عن الرماد الكربوني المتطاير المدفون في مكب النفايات في رابغ، المملكة العربية السعودية، والمقارنة بين إجمالي المعادن الدقيقة والسامة والمعادن الميسرة المستخلصة باستخدام طريقة DTPA (حمض ثنائي إيثيلين ثلاثي أمين خماسي الأسيتيك) وهي طريقة استخلاص غير متوازنة لتقدير احتمالية توافر العناصر بالتربة. أظهرت النتائج أن التربة داخل مكب النفايات احتوت على أعلى تركيزات إجمالية وميسرة وقابلة للاستخلاص بواسطة DTPA للكبريت(S) والمنجنيز(Mn) والزنك(Zn) والنحاس(Cu) والحديد(Fe) والألمنيوم(AL) والكوبالت(CO) والكروم(Cr) والنيكل(Ni) والفاناديوم(V)، ثم تقل التركيزات مع زيادة المسافات من ٠ و٢٥٠ و٥٠٠ و١٠٠٠ متر بعيدًا عن مكب النفايات في جميع الاتجاهات، شمال جنوب وشرق وغرب. كما وجد أن تركيزات العناصر الدقيقة والسامة الكلية في التربة كانت أعلى في الموقع الجنوبي، يليه الشرق، ثم الغرب، في حين أن أقل التركيزات موجودة في تربة الموقع الشمالي. ووجد أن تركيزات العناصر الدقيقة والسامة الميسرة القابلة للاستخراج بواسطة DTPA أعلى في في تربة الموقع الشرقي، ثم الجنوب ثم الشمال والغرب حيث تحتوي التربة على أقل تركيزات للعناصر. التركيز الكلي للحديد(Fe) في التربة كان هو الأعلى (٣٨٨٨٨.٣٧ مجم/كجم)، في جميع المواقع والمسافات ولكن كعنصر ميسر بواسطة DTPA فهو منخفض جدًا (١٦.٤٦ مجم/كجم). يأتي الكبريت(S) في المرتبة الثانية بعد Fe كتركيز كلي في التربة بـ (٥٤١.٢٤ مجم/كجم)، ثم عنصر المنغنيز، أما بالنسبة للعناصر الدقيقة الميسة في التربة فإن S هو أعلى عنصر (١٩٣.٦٠ مجم/كجم) يليه Fe، والنحاس هو العنصر الأقل تركيزًا في التربة. بالنسبة للعناصر السامة فإن Al يهيمن على تركيزات التربة الكلية (١٩١٧٣.٢٧ مجم/كجم)، يليه V ثم Cr وNi وCo، وبالنسبة للمعادن الميسرة في التربة أعطى Ni وV تركيزات أعلى منCo وCr في جميع المسافات والمواقع. ومن ثم يمكن القول أن الكبريت(S) هو أكثر العناصر الدقيقة توفرًا، وأن النيكل(Ni) والفاناديوم(V) هما أكثر العناصر السامة توفرًا داخل وحول منطقة مكب النفايات في رابغ. كان التركيز الكلي للحديد في التربة أعلى من المعايير الأوروبية (٢٠٠٢) والمعايير السعودية (٢٠٢٠) والمعايير الهندية (٢٠٠٠)، وتركيز S أعلى من المعايير السعودية (٢٠٢٠). النيكل(Ni) أعلى من المعايير السعودية (٢٠٢٠). تركيزات المعادن المتبقية في تربة مكب النفايات أقل من معايير تركيز السمية النباتية التي وضعها الاتحاد الأوروبي (٢٠٠٢) والمملكة العربية السعودية (٢٠٢٠) والمعايير الهندية (٢٠٠٠). تركيزات

العناصر المتبقية في تربة مكب النفايات أقل من معايير تركيز السمية النباتية التي وضعتها هذه المعايير. تهدف هذه الدراسة إلى قياس المحتوى الكلي للعناصر الدقيقة والسامة والعناصر الدقيقة والسامة القابلة للاستخلاص في منطقة مكب النفايات في محافظة رابغ في المملكة العربية السعودية، باستخدام طريقة ثنائي إيثيلين ثلاثي أمين خماسي حمض الأسيتيك(AB-DTPA) وفقًا لطريقة (Soltanpour and Schwab, 1977)، ودراسة الحجم المكاني لتوزيع هذه العناصر السامة بعيدًا عن منطقة المكب، في محاولة لتقييم تأثيرها الخطير على التربة المحيطة والنباتات والمياه الجوفية.

الكلمات المفتاحية: العناصر الدقيقة السامة، مكب النفايات، الرماد الكربوني المتطاير، DTPA.