Int. J. Environ. Res., 8(3):543-550,Summer 2014
ISSN: 1735-6865

Sources of Cu, V, Cd, Cr, Mn, Zn, Co, Ni, Pb, Ca and Fe in Soil of Aradkooh Landfill

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Received 25 March 2014; Revised 27 April 2014; Accepted 15 May 2014

ABSTRACT: Currently all the waste produced are collected and transferred to the only landfill of Tehran, Aradkooh (Kahrizak), that is located in the south of Tehran. This landfill has been in use for over 45 years that has received over 35 million tons of waste during its life. In the present investigation 40 soil samples were collected from Aradkooh landfill to know about the origin of metals. The samples were acid digested and element concentrations were measured by AAS. Association of metals with different soil phases was brought out and it is shown that a great portion of metal contents possess lithogenous source. The following pattern of geochemical distribution was found in soil samples collected from Aradkooh landfill.
Percentile of lithogenous Portion:-
Fe&V(95%)>Cu(91%)>Cd&Cr(90%)>Mn(89%)>Zn(87%)>Co(81%)>Ni(76%)>Pb(75%)>Ca(51%)
Percentile of Anthropogenic portion:-
Ca(49%)>Pb(25%)>Ni(24%)>Co(19%)>Zn(13%)>Mn(11%)>Cd&Cr(10%)>Cu(9%)>Fe&V(5%).
Based on geochemical studies (bulk and portioning studies) standard concentrations for metals is proposed. Cluster analysis revealed that the intra relationship amongst all studied metals is present (except for organic content, Ca, Fe and Mn). It seems that there is rather a good agreement amongst various pollution indices if unique terminology is used. All the three indices (I_{POLL}, I_{geo} and EF) used in the present investigation show no pollution for Fe, Mn, Zn, Cu and Ni and moderate pollution for Ca. These indices are not consistent in assessment of other elements such as V, Cd, Cr, Co and Pb that could be due to use of different media in formulae (shale values, crust values and background levels).

Key words: Soil, Landfill, Pollution, Metal, Index

INTRODUCTION

In the recent years many studies have been carried out on different aspects of Iran's environment including water, soil and air pollution(Nasrabadi and Abbasi Maedeh, 2014; Tajziehchi *et al.*, 2014; Afkhami *et al.*, 2013; Karbassi *et al.*, 2013; Tajziehchi *et al.*, 2013; Mansouri *et al.*, 2013; Rashtchi *et al.*, 2013; Ghaderi *et al.*, 2012; Fazelzadeh *et al.*, 2012; Noori *et al.*, 2012; Vesali Naseh *et al.*, 2012; Hosseini Alhashemi *et al.*, 2012; Karbassi *et al.*, 2011; Alipour *et al.*, 2011; Babaei Semiromi *et al.*, 2011; Farsad *et al.*, 2011; Parvaresh *et al.*, 2011; Tehrani *et al.*, 2010; Biati *et al.*, 2010; Nasrabadi *et al.*, 2010; Baghvand *et al.*, 2010; Abbaspour *et al.*, 2009; Karbassi *et al.*, 2008; Karbassi *et al.*, 2007). There are also some studies on the landfill that include waste management as well as electricity generation (Abdoli *et al.*, 2014; Abduli *et al.*, 2013; Abbasi *et al.*, 2013; Rashidi *et al.*, 2012; Abdoli *et al.*, 2012; Abduli & Azimi, 2010; Rafee *et al.*, 2008). However, it should be admitted that a very few studies have been carried out on the geochemistry and soil pollution of landfills in Iran. land treatment of leachate was conducted in a slow rate at various speeds that resulted in removal of COD (99.1%), BOD5 (99.7%), TDS (52.4%), TSS (98.8%) and TOC(94.9%) respectively (Pazoki *et al.*, 2014). Statistical analysis shows that Solid waste generation and composition varies from household to household in Iran (Monavari *et al.*, 2012). Safari et al. (2012) used HYDRUS-1D to show that the hydraulic conductivity decreases about three orders of magnitude within 180

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days. As a matter of fact the bottom liner of a landfill may not be saturated throughout its life span (Safari, 2006). Heavy metal contents in leachates have been measured by Abduli & Safari (2003) revealing that metals can either remain in dissolved form or being adsorbed onto the suspended solids. It is also possible to increase the removal efficiency of some metals present in leachate (such as Zn and Mn) by addition of lime to bed soil (Safari & Nabi Bidhendi, 2007). Electro-chemical technique is also used to remove Cu and Cr from Kahrizak landfill with an efficiency of 95% and 84% , respectively (Rabbani *et al.,* 2012). Addition of 4% nano-clay can significantly reduce permeability, increases compressive strength and retains mono-valent ions between layers (Kananizadeh *et al.,* 2011). Tehran with a population of more than 10 million is the capital of Iran and is the biggest city in the Middle East. The amount of solid waste generation is about 7000 ton/day. Currently all the waste produced are collected and transferred to the only landfill of Tehran, Aradkooh (Kahrizak), that is located in the south of Tehran. This landfill has been in use for over 45 years that has received over 35 million tons of waste during its life. The aim of present investigation is to bring out association of metals with different soil phases as well as pollution intensity of metals in soils of Aradkooh landfill through geochemical studies. It should be pointed out that Arakkooh landfill is also known as Kahrizak landfill.

MATERIALS & METHODS

About 40 stations were selected for soil sampling around the Aradkooh landfill. Every sample of five stations were grouped together to obtain 8 stations (Fig. 1). The soil samples were collected by an auger from top 50 Cm. They were dried at 40 degree Celsius in oven for about 36 hours (Mollazadeh *et al.*, 2013).

The soil samples were cone and quartered several times and finally about 250g of each sample was sieved through 63μm (Saeedi & Karbassi, 2006). They were finely powdered in an agate mortar and pestle. Bulk geochemical analysis was carried out on 500mg of each soil sample using 7mL aqua regia and 3mL $HClO_4$ and the volume of sample was adjust to 50mL by 1N HCl. One step chemical partitioning technique was used to assess anthropogenic portion of metal contents in soil samples (Karbassi *et al.*, 2005). The accuracy of analysis was approximately ±7 % for all elements. A certified reference material (MESS-3) was analyzed as a quality assurance check (Table 1).

Organic contents of soil samples were measured by the Loss On Ignition (LOI) of samples for 4hrs at 450°C in a muffle furnace (Glasby and Pzefer, 1998). To

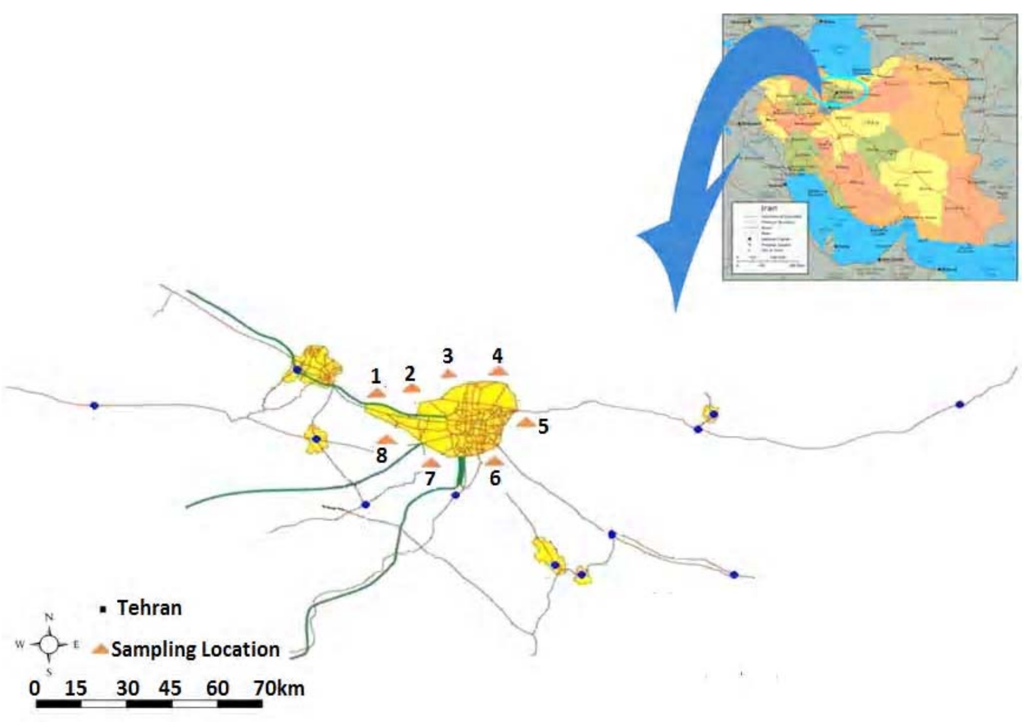

Fig. 1. Soil sampling locations at Aradkooh landfill

Table 1. Published & obtained data for reference sample MESS-3

Element	Unit	Published Data*	Obtained Data	Deviation (%)
Ni	mg/kg	46.9±2.2	43.2	-7.9
Pb	mg/kg	21.1±0.7	22.9	+8.5
Cu	mg/kg	33.9±1.6	33.2	-2.1
Cd	mg/kg	0.24±0.01	0.27	+12.5
Cr	mg/kg	105±4.0	109.7	+4.5
V	mg/kg	243±10.0	253.8	4.4
Co	mg/kg	14.4±2.0	12.9	-10.4
Zn	mg/kg	159±8.0	157.3	-1.1
Mn	mg/kg	324±12	337	+4.0
Fe	%	4.34±0.11	4.29	-1.2
Ca	%	1.47±0.06	1.44	-2.0

*National Research Council Canada (NRCC)

assess the intensity of metal contamination in soil samples, three different indices were used. These are I_{POLL} (karbassi *et al.*, 2008), I_{geo} (Muller, 1979) and EF (Pekey, 2006). To unify the results we have adopted the new scale developed by Pekey (2006). This new scale is given in Table 2. The Weighted Pair Group method (GWP), for its merits, was used to identify relationships amongst the metals (Davis 1973).

$I_{POLL} = Log_2(Cn / Bn)$

Where, Cn is the total elemental content in soil and Bn is the lithogenous portion of element.

$I_{geo} = Log_2(Cn / Bn \times 1.5)$

Where, Cn is the total elemental content in soil, Bn is the concentration of metals in shale and 1.5 is a factor for normalization of background metals concentrations in shale.

EF=[Cnx/Bnx]/[Cny/Bny]

Where, Cnx and Cny are metal content in soil sample and crust respectively and Bnx and Bny are Fe content of soil sample and crust respectively.

RESULTS & DISCUSSION

The bulk metal contents in soil samples of Aradkooh landfill is presented in Table 3. The organic matter (LOI) ranges from about 9 to 18% in soil samples. Many studies show that organic content of soil and sediment in Iran is less 5% (Saeedi & karbassi, 2006; Karbassi *et al.*, 2008, Parvaresh *et al.*, 2011; Mollazadeh *et al.*, 2013). Therefore, the higher organic contents in the soils of Aradkooh might be attributed to the high BOD content of leachate (over 45000 mg/L as reported by Rashidi *et al.*, 2012).

The higher Ca contents (as high as about 9%) might be due to use of lime in landfill. The lower Fe contents (as low as 1.9%) could have been resulted as dilution by higher organic contents as well higher Ca contents (addition of lime to bed soils; Safari & Nabi Bidhendi, 2007).It is also evident that mean Mn content of soil samples (484 mg/kg) is much lower than the mean crust (850 mg/kg). Manganese is mobile in nature and could easily be transferred in dissolved phase under anoxic condition of landfill leachate (Safari & Nabi Bidhendi, 2007; Karbassi *et al.*, 2008). Cadmium, Pb and Cr contents of soil samples are rather higher than the mean crust. The higher concentration of these metals (except for Pb) cannot be attributed to anthropogenic source since their share as shown be chemical partitioning study is not significant. The pattern of lithogenous and anthropogenic share of various studied metals as revealed by chemical partitioning is as follows:

Percentile of lithogenous Portion:-

Fe&V(95%)>Cu(91%)>Cd&Cr(90%)>Mn(89%)>Zn(87%)>Co(81%)>Ni(76%)>Pb(75%)>Ca(51%)

Percentile of Anthropogenic portion:-

Ca(49%)>Pb(25%)>Ni(24%)>Co(19%)>Zn(13%)>Mn(11%)>Cd&Cr(10%)>Cu(9%)>Fe&V(5%)

Chemical partitioning clearly shows that while Ca, Pb, Ni, Co and to lower extent other metals are partially derived from anthropogenic sources. Therefore, comparison of metal contents with mean crust values may not be a logic practice. Though, the concentration of many studied metals is lower than the mean crust values but some parts of them are derived from non-lithogenous sources. It should be noted that the presence of Ca (as high as 49% of its total concentration) in the anthropogenic could be due to their readily dissolution in weak acids such as HCl that is used in partitioning studies. Therefore, it might be inferred that 49% and 51% of Ca is inorganic and organic respectively. Some studies have concluded that about 10% of any metals' content could naturally be present in anthropogenic fraction (Karbassi *et al.*, 2008; Saeedi & karbassi, 2006). Therefore, in the present investigation the anthropogenic portion of metals such

Table 2. Terminologies for contamination classes on single and integrated indices

Indices	unpolluted	low polluted	moderately polluted	strongly polluted	extremely polluted
I_{POLL}*	<0.42	0.42–1.42	1.42–3.42	3.42–4.42	>4.42
EF	<2	2–4	4–16	16–32	>32
I_{geo}	<0.42	0.42–1.42	1.42–3.42	3.42–4.42	>4.42

*same terminology used for Igeo is adopted.

Table 3. Metal contents in soils of Aradkooh landfill

Sampling stations	%			mg/kg								
	LOI	Ca	Fe	Mn	Zn	Co	V	Cr	Cd	Cu	Pb	Ni
1	9.2	8.0	2.3	423	66	12	90	99	1	32	22	65
2	16.1	6.2	2.2	430	64	12	87	97	1	28	22	63
3	16.4	7.4	2.1	540	77	17	99	115	2	37	29	73
4	12.5	8.6	2.3	478	69	11	92	100	1	23	23	70
5	11.5	7.5	2.2	490	66	10	90	87	1	32	22	68
6	10.6	6.0	2.2	500	65	12	90	92	1	32	23	63
7	18.2	7.0	2.3	478	68	12	92	97	2	28	23	65
8	9.3	7.2	2.0	530	82	16	98	111	3	42	28	74
Min.	9.2	6.0	2.0	423	64	10	87	87	1	28	22	63
Max.	18.2	8.6	2.3	540	82	17	99	115	3	42	29	75
Mean	13.0	7.2	2.2	484	70	13	92	100	1.5	32	24	68
STD(±)	4.8	1.3	0.1	61	9	4	6	16	1	6	3	7
Mean Crust	-----	3.3	4.72	850	95	19	130	90	0.3	45	12	80

Table 4. Percentile of lithogenous and anthropogenic portion of metals in soils of Aradkooh landfill

Station/Fraction		%										
		Ca	Fe	Mn	Zn	Co	V	Cr	Cd	Cu	Pb	Ni
1	Lithogenous	52	96	95	88	92	97	95	100	94	86	77
	Anthropogenic	48	4	5	12	8	3	5	0	6	14	23
2	Lithogenous	52	95	93	89	83	97	93	100	93	77	79
	Anthropogenic	48	5	7	11	17	3	7	0	7	23	21
3	Lithogenous	57	95	79	84	65	90	81	50	86	62	71
	Anthropogenic	43	5	21	16	35	10	19	50	14	38	29
4	Lithogenous	49	96	92	91	82	93	90	100	91	74	80
	Anthropogenic	51	4	8	9	18	7	10	0	9	26	20
5	Lithogenous	48	95	91	88	90	97	93	100	97	86	82
	Anthropogenic	52	5	9	12	10	3	7	0	3	14	18
6	Lithogenous	48	95	87	94	83	98	90	100	94	78	78
	Anthropogenic	52	5	13	6	17	2	10	0	6	22	22
7	Lithogenous	51	96	93	88	83	98	92	100	96	83	75
	Anthropogenic	49	4	7	12	17	2	8	0	4	17	25
8	Lithogenous	51	95	84	80	69	92	85	67	79	57	69
	Anthropogenic	49	5	16	20	31	8	15	13	21	43	31
Mean	Lithogenous	51	95	89	87	81	95	90	90	91	75	76
	Anthropogenic	49	5	11	13	19	5	10	10	9	25	24

as Cd, Cr, Cu, Fe and V might be considered as natural. However, other metals such as Pb, Ni, Co and to lower extent Zn and Mn are partially derived from anthropogenic sources. Cluster analysis (Fig. 2) shows that except for LOI, Ca and Fe all other studied metals (V, Cu, Cd, Cr, Mn, Zn, Co, Ni and Pb) are positively clustered to each other. This might show that behavior these metals are somehow alike. On the other hand organic matter (LOI), iron bearing rocks (Fe as an indicator) and biogenic materials (Ca as n indicator) do not play any important role in distribution abundance of V, Cu, Cd, Cr, Mn, Zn, Co, Ni and Pb in soils of Aradkooh landfill.

As mentioned in material and methods section, three different indices were used to quantify the pollution intensity in soils of Aradkooh landfill. It was also mentioned that Pekey (2006) method was used to unify the results of various pollution indices. While using the new scale developed by Pekey (2006), we have added I_{POLL} index to Table 2. Pollution intensity

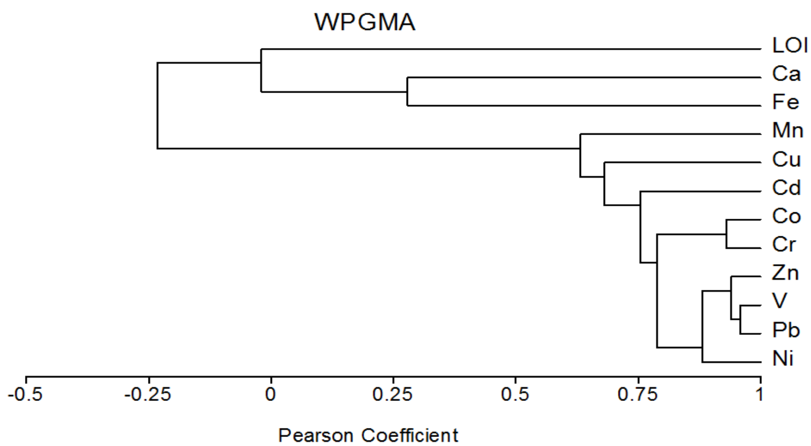

Fig. 2. Dendrogram of cluster analysis for metals in soils of Aradkooh landfill

Table 5. Pollution intensity in soils of Aradkooh landfill

Station/Index		%										
		Ca	**Fe**	**Mn**	**Zn**	**Co**	**V**	**Cr**	**Cd**	**Cu**	**Pb**	**Ni**
Mean of 8 stations	I_{POLL}	2.06	0.07	0.17	0.19	1.25	1.05	0.15	0.2	0.13	0.37	0.39
	I_{geo}	1.46	0	0	0	0	0	0	1.72	0	0.14	0
	EF	4.68	1.00	1.22	1.58	1.47	1.65	2.38	10.73	1.53	4.29	1.82

CONCLUSION

Investigation on geochemistry metals in soils of Aradkooh landfill that has received over 35 million tons of solid waste in the past 45 years is scanty. The present study presented basic data on the metal contents in soils of Aradkooh landfill. Association of metals with different soil phases was brought out and it is shown that a great portion of metal contents possess lithogenous source. The following pattern of geochemical distribution was found in soil samples collected from Aradkooh landfill:-

Percentile of lithogenous Portion:-
Fe&V(95%)>Cu(91%)>Cd&Cr(90%)>Mn(89%)>Zn (87%)>Co(81%)>Ni(76%)>Pb(75%)>Ca(51%)
Percentile of Anthropogenic portion:-
Ca(49%)>Pb(25%)>Ni(24%)>Co(19%)>Zn(13%) >Mn(11%)>Cd&Cr(10%)>Cu(9%)>Fe&V(5%).
Based on geochemical studies (bulk and portioning studies) standard concentrations for metals is proposed (Table 6).

Table 6. Proposed background levels (soil metal standards) for Aradkooh landfill

Proposed Standards for Metal Contents in Soil	%		mg/kg								
	Ca	**Fe**	**Mn**	**Zn**	**Co**	**V**	**Cr**	**Cd**	**Cu**	**Pb**	**Ni**
	3.5±0.6	2.0±0.1	420±22	62±4	10±1	86±3	87±6	1.5±0.25	28±4	18±2	53±3

was computed using I_{POLL}, Igeo and EF (Enrichment Factor) for all stations; however, the mean of these stations is presented in Table 5.

Comparison of the figures in Table 5 and Table 2 show that Ni, Pb, Cu, Cd, Cr, Mn and Fe are unpolluted when using I_{POLL}. Except for Cd and V, Igeo also show similar results as I_{POLL} does. Based on I_{POLL} Ca is moderately polluted and Co & V stand in low pollution. Igeo shows moderate and low pollution of Ca and Cd respectively. While EF (Enrichment factor) shows no pollution for Fe, Mn, Zn, Co, V, Cu and Ni, it does show low pollution for Cr and moderate pollution for Ca, Cd and Pb. All the three indices are alike for Ca, Fe, Mn, Zn, Cu and Ni showing no pollution.

Cluster analysis revealed that the intra relationship amongst all studied metals is present (except for organic content, Ca, Fe and Mn). It seems that there is rather a good agreement amongst various pollution indices if unique terminology as proposed by Pekey (2006) is used. All the three indices used in the present investigation show no pollution for Fe, Mn, Zn, Cu and Ni and moderate pollution for Ca. These indices are not consistent in assessment of other elements such as V, Cd, Cr, Co and Pb that could be due to use of different media (shale values, crust values and background levels).we strongly suggest to develop back-ground levels of metal contents based on chemical partitioning techniques. once such back-ground data are in hand, pallution intensity indices should eventually be revised. For instance I_{POLL} developed by karbassi et al. (2008) can be mentioned as an example. This index is developed based on back-ground levels of metal contents and hence can be more reliable. However, it seems that neither the original scale proposed by karbassi et al.(2008) nor the revised one by pekey (2006) is appropriate. For instance, Pb that possess highest anthropagenic propotion amongst studied metals still falls within " no-pollution" scale.

ACKNOWLEDGEMENT

Authors would like to sincerely thank Dr. A. R. Karbassi, Dean of Faculty of Environment, University of Tehran for his critical review. We also thank Mr. M. Sohrabi for assisting us in sample collection. We appreciate great help from Mr. M. Esmaeeli (Sanat Azmoon Co.) for determination of metal contents.

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