RESEARCH PAPER

Geo-chemical investigation and health risk assessment of potential toxic elements in industrial wastewater irrigated soil: A geo-statistical approach

Nisar Muhammad*, **Mohammad Nafees**

Department of Environmental Sciences, University of Peshawar, Peshawar 25120, Pakistan

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Abstract

The current study was conducted to identify potential toxic elements (PTEs) concentrations and associated health risk assessment (HRA) in adjacent agricultural soil of Gadoon Amazai industrial estate (GAIE) irrigated with industrial wastewater from last three decades. To achieve the objectives, 32 target and 21 reference soil samples were collected and analyzed for PTEs concentration. Geo-chemical results revealed that all the nine PTEs in target samples were above the permissible limits of different international standards and reference samples, indicating that industrial wastewater is causing potential ecological risk to target agriculture soil. Geo-statistical results revealed that geo-accumulation (I_{geo}), contamination factor (CF), enrichment factor (EF) and pollution load index (PLI) were at significant levels and can cause potential ecological risks. Health risk assessment revealed that hazard quotient ingestion (HQ Ing) in children is the main source of non-carcinogenic risk and can cause significant health risks. This HQ Ing for children contributes to 76% of the total hazard index (HI). The study recommends sustainable treatment of the contaminated soil. Furthermore, residents of the study area should be made aware of the ecological risks associated with the wastewater irrigation and contaminated agricultural soil.

***Corresponding Author:** Nisar Muhammad ✉ nisar5609@gmail.com

Introduction

Urbanization, industrialization, indiscriminate application of chemicals to agricultural fields and irrigation with wastewater has increased soil pollution in both developed and developing countries over the past decades(Micó*et al.,* 2006; Yu*et al.,* 2008). Among these, agriculture soils with PTEs contamination is cry for today (Ma *et al.,* 2015). Contamination of agriculture soils can be both anthropogenic and natural. Among the anthropogenic sources, industrial sector is primary the source of PTEs. Industrial wastewater used for irrigation adds PTEs in excessive amount to the soil. Soil contamination in return pose potential risks to crops grown on these soils by degradation of food quality, reducing crop productivity and potential threats to soil organism (Nagajyoti*et al.,* 2010)as well as affecting groundwater sources and eventually human beings through bioaccumulation (Li*et al.,* 2014), thus causing severe public health concerns over long time periods.

Metals toxicity can lead to various disorders extreme damages due to oxidative stress from free radical formation (Jaishankar*et al.,* 2014). Based on the absorbed dose, route and duration of exposure, PTEs are responsible for many health risks among the general public (Hernández-Bonilla*et al.,* 2016; Jaishankar*et al.,* 2014; Morais*et al.,* 2012; USEPA 1986; Zarei*et al.,* 2018). Previous studied suggest various health risks associated with PTES. For instance, Mn can cause chronic impacts such as nerve damage, hallucination, Parkinson, lungs embolism and bronchitis (Hernández-Bonilla *et al.,* 2016). Cadmium is a universal toxicant and its inhalation and exposure results to chills, fever and muscle pain in acute mode and lungs, bones and kidneys diseases in chronic intake (Vilahur*et al.,* 2015). Cu disturbs thyroid and adrenal glands secretions and also causes mental disorderness, anemia, anxiety and hypoglycemia (Singh *et al.,* 2004). Pb has wide range of toxic effects i.e. cardiac problems, psychopathic effects (disturbance of peripheral and central nervous) and inhibition of blood production

(Morais*et al.,* 2012). Cr causes skin swelling, erythema, chronic pharyng it is and asthma in humans (Ipeaiyeda and Onianwa 2011). Its chronic intake leads to carcinogenesis, gastro-intestion alysis, hepatitis and renal failure (Zarei *et al.,* 2018). Zn harms both plants and humans. In plants it causes chlorosis, stunted growth, shortens internodes and whitens leaves (Brewer 2010). While in humans it have chronic impacts on immunity, neurons growth and body growth and protein synthesis (Wang *et al.,* 2012). Ni has severe health impacts like lung and sinus cancer, disorder of lung function and chronic bronchitis due to human exposures to nickel releasing sources(Zarei*et al.,* 2018) and has chronic impacts on human blood level, protein synthesis and DNA composition(Thyssen*et al.,* 2007). Fe has also reported for dysfunction of DNA chain, hepatic effects and cardiovascular diseases (Brewer 2010). Co is famous for carcinogenic and genotoxic effects in humans. It causes disorder of thyroid glands, cardiovascular system and bronchial asthma (Ahmad*et al.,* 2014).

A variety of public health measures have been adopted so far to control, prevent and treat metal toxicity occurring at various levels, such as occupational exposure, accidents and environmental factors (Jaishankar *et al.,* 2014). HRA tools help in detection of public health problems pertaining to ingestion, inhalation and dermal contact of PTEs(Chen*et al.,* 2013).

Many evaluation methods are used for the determination of PTEs in soils including but not limited to enrichment factor (EF) (Atgin*et al.,* 2000; Ho*et al.,* 2010; Lăcătuşu 1998), geo accumulation index (Igeo) (Çevik *et al.,* 2009; Liu *et al.,* 2015; Muller 1969) pollution load index(Amin*et al.,* 2009), potential ecological risk index (Er) (Cao *et al.,* 2009), combined pollution index (GPI)(Abrahim and Parker 2008);comprehensive pollution index (Wei-Xin *et al.,* 2008), Nemerow comprehensive index (Pn) (Cheng *et al.,* 2007)and secondary phase enrichment factor (Bhattacharya *et al.,* 2006).

Various studies in different areas of Pakistan have been carried previously to assess PTEs toxicity in agricultural soil, such as Lahore (Mahmood and Malik 2014), Islamabad (Malik *et al.,* 2010), Gilgit (Khan *et al.,* 2010), Mardan (Hussain *et al.,* 2013), Kohistan (Muhammad *et al.,* 2011), Sialkot and Wazirabad (Khan *et al.,* 2013; Malik *et al.,* 2010), Hyderabad (Jamali *et al.,* 2007). It can be concluded from these studies that agriculture soils have contaminated due to application of wastewater from industrial and other sources, and subsequently the food grown on these soils, posing a great threat to public health.

The current study targets agricultural lands, irrigated by GAIE wastewater. Due to water scarcity in the area, application of industrial wastewater to agriculture lands is common and is practiced since the last four decades (Khan *et al.,* 2009). Industrial units of various nature are functional in the industrial estate (SDA 2009), releasing wastewater without treatment through combined effluent drains

irrigating adjacent agriculture fields (Khan *et al.,* 2009). These irrigation practices are providing a pathway for PTEs to get accumulated in the soil and subsequently entering the human bodies through ingestion, inhalation and dermal contact (Fytianos *et al.,* 2001; Singh *et al.,* 2010). The objectives of this study covers (a) geo-chemical assessment of PTEs (Mn, Cd, Cu, Pb, Cr, Zn, Ni, Fe and Co) concentration in industrial wastewater irrigated soil (b) geo-statistical assessment of possible potential ecological risks via ingestion, inhalation and dermal contact and (c) health risk assessment for the inhabitants (adults and children) of the study area.

Materials and methods

Description of study area

GAIE is situated in Swabi district of Khyber Pakhtunkhwa (KP) province of Pakistan. It is situated at 33o5'20" N and 72o32'45" E at an altitude of 328 m from sea level. GAIE is bordered Baisak in the north, Topi in the south, Gandaf in the east and Maini at west (Khan *et al.,* 2009).
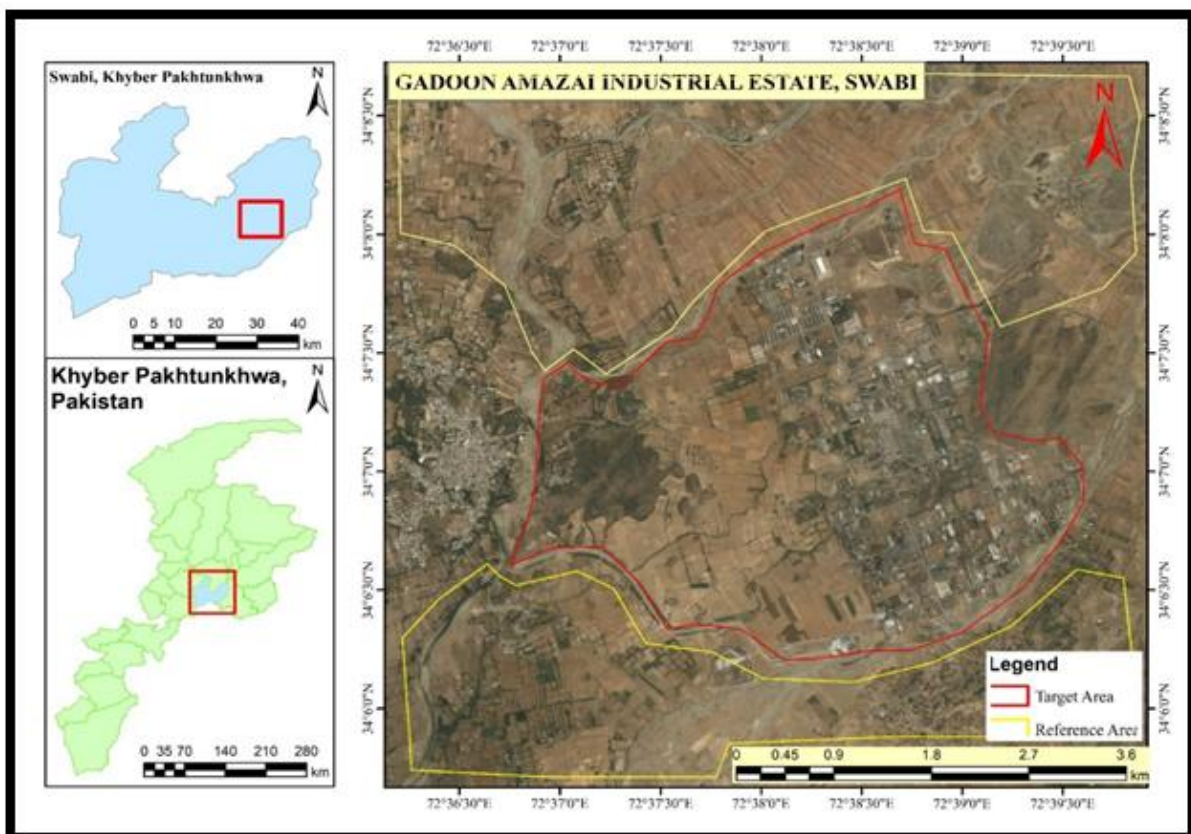

Fig. 1. Location map and soil sampling points of GAIE and adjacent area.

The area population is 390, 312 (DCR 2017). Gadoon Amazai industrial estate was established in 1987 and covers total area of 1119 acres (Hussain *et al.,* 2015). At present, GAIE has 310 operational units consisting of textile, chemical, plastic, steel, pharmaceutical, and paper mills etc. These operational units release wastewater without treatment through 10 effluent drains with a flow of ≈290 L/s primarily used for irrigation in the adjacent agriculture fields. Industrial effluents irrigate nearly 450 acres area due to limited supply of irrigation water (Khan *et al.,* 2009). GAIE is currently employing 15345 persons, which is helping in economic uplift of the area.

Samples collection

Representative target soil samples were collected (0-20 cm) depth by auger from agriculture fields irrigated by industrial wastewater and reference soil samples (0-20 cm) from agriculture fields irrigated with ground water. Locations of samples were recorded with global positioning system. All the collected samples were stored in Kraft paper, sealed and labelled (Yang *et al.,* 2011b).

Geo-chemical analysis

The collected soil samples were air dried, sieved (with 2 mm sieve), homogenized and quartered. A representative quarter was selected and pulverized to 200 mesh size. The powdered samples were dried in oven at 110°C for two hours and cooled in desiccator (Yang *et al.,* 2011b). For determination of PTEs 1g from each of the prepared samples was taken in Teflon beaker and 15 ml Aqua Regia (1HNO$_3$:3HCl) was added. The samples were heated till complete evaporation. Then 20 ml of 2 N hydrochloric acid (HCl) solution was added and heated. Finally these were diluted to 30 ml with deionized water and filtered (Hutchison and Jeffrey 2012).This filtrate was used for determination of PTEs concentration using atomic absorption spectrophotometer.

Geo-statistical analysis

Two types of indices are used for depicting pollution load i.e. single and integrated index. As the name indicates, single pollution load index represents pollution caused by a single pollutant while the latter shows multiple pollutants (Caeiro *et al.,* 2005; Qingjie *et al.,* 2008).

Geo-accumulation index

Geo-accumulation index (I$_{geo}$) is used for quantification of the accumulated pollution load (both anthropogenic and natural) in soil. I$_{geo}$ was calculated by equation;

$$\text{I}_{geo} = \log_2\left[\frac{C_n}{1.5 \text{ x } B_n}\right]$$

Where C$_n$ and B$_n$ are same to the CF equation. While 1.5 is expected variation of anthropogenic contamination in reference samples as discussed by (Fagbote and Olanipekun 2010; Lokeshwari and Chandrappa 2006). Pollution level of I$_{geo}$ ≤0 is considered as non-pollution, 0<I$_{geo}$ ≤1 slightly pollution, 1<I$_{geo}$ ≤2 moderate pollution, 2<I$_{geo}$ ≤3 moderate to heavily pollution, 3<I$_{geo}$ ≤4 heavily pollution, 4<I$_{geo}$ ≤5 heavily to extreme pollution and I I$_{geo}$>5 as extreme pollution(Aiman *et al.,* 2016; Ali *et al.,* 2017; Wei *et al.,* 2015).

Enrichment factor

Enrichment factor is used for assessment of affected soil due to elemental pollution from geogenic or anthropogenic activities and was calculated by the following equation (Atgin *et al.,* 2000; Ho *et al.,* 2010).

$$\text{EF} = \left(\frac{C_n}{C_m}\right)\bigg/\left(\frac{C_b}{C_x}\right)$$

Where Cn is the elemental concentration and Cm is lowest (rare) concentration in target area while Cb is the elemental concentration and Cx is the lowest (rare) concentration in reference area. Enrichment factor of 2-5 is considered as moderate, 5-20 as significant, 20-40 as very high and > 40 as extremely high enrichment (Sinex and Helz 1981; Sutherland 2000).

Contamination factor

Contamination factor is obtained by dividing target sample concentration by reference sample concentration. CF was calculated by following equation(Harikumar *et al.,* 2009).

$$CF = \frac{C_n}{B_n}$$

Where C_n is the target sample concentration and B_n is the reference sample concentration. Contamination level is considered as CF <1 low, 1≤ CF <3 moderate CF, 3≤ CF <6 considerable CF and CF >6 very high CF (Ahdy and Khaled 2009; Hakanson 1980).

Pollution load index

Pollution Load Index is used to investigate contents of elements in soil beyond the reference concentration. PLI was calculated according to the equation (Tomlinson *et al.,* 1980; Yang *et al.,* 2011a).

$$PLI = (CF_1 X CF_2 X CF_2 \dots \dots)^{1/n}$$

Where CF is the contamination factor and *n* is the number of elements.PLI=0 is considered as perfection, PLI =1 as baseline pollution and PLI >1 as progressive deterioration (Tomlinson *et al.,* 1980).

Ecological risk factor

Ecological risk factor used to determine pollution load in soil as well as risk factor in soil was calculated by the equation;

$$Er = Tr \ x \ CF$$

Where Errepresentsecological risk potential, Trtoxicresponse factor and CFcontamination factor. Values for toxic response factor values of some elements are: Mn=Zn=Fe=1, Cd=30, Cu=Pb=Ni=Co=5, and Cr=2(Hakanson 1980). Er of <30 is considered as low risk, 30-60 as moderate risk, 60-120 as considerable risk, 120-240 as high risk and >240 as significantly high risk (Hakanson 1980; Wei and Yang 2010).

Health risk assessment

For non-carcinogenic HRA models, all the inhabitants including adults and children of a particular area should be considered for PTE sexposure that occurs mainly through ingestion, inhalation and dermalpath ways (Chen *et al.,* 2013).

The HRA models are designed as per united states environmental protection agency guidelines(USEPA 1986;2001a). For cumulative non-carcinogenic risk, the three exposure ways designated models were combined. ADD was determined using exposure factors handbook (USEPA 1997)and USEPA technical report (EPA 1996)through following equations.

$$ADD \ Ing = C_{Soil} \frac{IngR * CF * EF * ED}{BW * AT}$$

$$ADD \ Inh = C_{Soil} \frac{InhR * EF * ED}{PEF * BW * AT}$$

$$ADD \ Derm = C_{Soil} \frac{SA * CF * AF * ABF * EF * ED}{BW * AT}$$

Where ADD Ing is the average daily dose exposure via ingestion, ADD Inhvia inhalation and ADD Derm via dermal contact. Furthermore, C is concentration of PTE in soil (mg/kg), IngR is ingestion rate of soil (100 mg/day for adults and 200 mg/day for children)(ESAG 2009; USEPA 2001a;b;c;d)and ED is exposure duration of 24 and 6 years for adults and children respectively(USEPA 2002). BW is body weight of 72 and 15 kg for adults and children (ESAG 2009; Lu *et al.,* 2010; Zheng *et al.,* 2010)and AT is average time of 365 x ED for both adults and children (EPA 1989). InhR is inhalation rate of soil which is 12.8 and 7.63 m^3/day for adults and children respectively, PEF is particular emission factor of 1.36 x 10^9 m^3/kg(USEPA 2001b;c;d;2002).SA is surface skin of skin exposed of 4350 and 1600 cm^2 for adults and children respectively(ESAG 2009; Zheng *et al.,* 2010). AF is adherence factor of skin of 0.7 mg/cm^2 for adults and 0.2for children (USEPA 2011, Man 2010) and ABF is adsorption factor of derm 0.001 as stated by (USEPA 2000;2001c;d; Wei *et al.,* 2015). For evaluation of HRA (non-carcinogenic risk) models, the HQ and HI were calculated in both adults and children through following equations (Chen *et al.,* 2012; EPA 1989).

$$HQ = {^{ADD}}/_{RfD}$$

$$HI = \sum HQ_i$$

Where HQ is hazard quotient and ADD is the all the three exposure ways determined separately. RfD is the reference dose defined as "the maximum permissible risk (s) to human population by conserving a sensitive group during a life time (Wei *et al.,* 2015). HQ will be considered a significant risk when its value is >1(USEPA 1986) while HI is hazard index defined as "the sum of all expected non-carcinogenic risks (Lim *et al.,* 2008; Mohmand *et al.,* 2015). Similarly HI>1 will be considered as significant non-carcinogenic risk(USEPA 2001b;c;d).

Results and discussion

Geo-chemical analysis

Results of geo-chemical analysis for PTEs concentration in both target and reference soil samples are summarized in Table 1. PTEs concentration in all the target samples were found greater than the reference samples. Among PTEs, Mn was found with highest concentration while Cd concentration lowest in target soil samples. The order of the PTEs was Mn>Fe>Zn>Cu>Cr>Pb>Ni>Co>Cd with a mean concentration of 3398.00 >2801.23 >1951.65>312.12>295.53>275.06>75.50>62.52>17.61 (mg/kg) (Table 1).

Table 1. Geo-chemical analysis of target and reference soil of GAIE (EPAA. 2012, Bohn. 2001, CME. 2009, EPMC. 2014, EEA. 2007, USEPA. 2002, VROM. 2000).

PTEs	Target soil samples n=32				Reference soil samples n=21				a/b % variation	Permissible limits of different countries						
	Min	Max	Mean[a]	SD	Min	Max	Mean[b]	SD		Australia 2012	Bohn 2001	Canada 2009	China 2014	UK 2007	US 2002	VROM 2000
Mn	994.15	7352.25	3398.00	231.30	161.70	663.73	231.20	27.74	14.7 93	500	774	-	0.07	-	-	-
Cd	1.92	42.70	17.61	1.80	0.68	3.25	1.80	0.83	9.8 90	3	0.06	3	0.40	2	1	1
Cu	14.55	784.15	312.12	8.55	4.85	128.63	52.55	2.64	5.9 83	100	20	150	200	57	270	36
Pb	67.50	613.55	275.06	12.57	4.97	92.78	38.72	2.13	7.1 86	300	10	200	80	50	200	85
Cr	94.87	565.40	295.53	17.05	3.85	110.63	43.81	5.74	6.7 85	50	20	250	250	8	11	100
Zn	670.63	4081.56	1951.65	42.06	21.35	184.83	86.12	73.23	22.7 96	200	50	500	300	221	1100	140
Ni	24.93	248.60	175.50	14.85	7.36	68.42	24.46	1.84	7.1 86	60	40	100	60	230	72	35
Fe	649.87	6873.25	5201.23	28.25	128.00	763.73	366.57	18.37	14.1 93	-	40350	-	3	-	80	-
Co	12.65	143.27	72.52	3.64	1.13	19.63	6.23	1.56	11.6 91	50	-	-	13	-	-	9.00

a= Mean concentration of target soil. b= mean concentration of reference soil.

The results show that concentration of PTEs were higher from their permissible limits of different international standards. PTEs concentration in target samples were many times greater than the reference samples i.e. 14.7, 9.7, 5.9, 7.1, 6.7, 22.7, 7.1, 14.1 and 11.6 for Mn, Cd, Cu, Pb, Cr, Zn, Ni, Fe and Co respectively. Furthermore, PTEs concentration in target samples showed more than 80% variation from their reference samples values (table 1). PTEs found in elemental and compound forms, ultimately taken up by plants grown and becomes highly toxic to humans(Adakole and Abolude 2009; WHO 2004).

Table 2 Comparison of PTEs risk indexes analyzed for soil of the study area.

PTEs	I$_{geo}$	CF	EF	Er	PLI
Mn	Heavily pollution	Very high CF	Low enrichment	Low risk	Progressive deterioration
Cd	Heavily pollution	Very high CF	Low enrichment	High risk	
Cu	Heavily pollution	Considerable CF	Low enrichment	Low risk	
Pb	Heavily pollution	Very high CF	Low enrichment	Moderate risk	
Cr	Moderate to heavily pollution	Considerable CF	Low enrichment	Low risk	
Zn	Heavily pollution	Very high CF	Low enrichment	Low risk	
Ni	Moderate pollution	Moderate CF	Low enrichment	Low risk	
Fe	Heavily pollution	Very high CF	Low enrichment	Low risk	
Co	Heavily pollution	Very high CF	Low enrichment	Moderate risk	

Geo-statistical analysis

Geo-statistical analytical results for I_{geo}, CF and EF are presented in Figure 2. Fe show maximum I_{geo} value while Ni show minimum value. I_{geo} value were found in order of Fe>Co>Zn>Pb>Mn>Cd>Cu>Cr>Ni with mean values of 3.52>3.51> 3.47>3.41> 3.26>3.24>3.15>2.40>1.72.

PTE with a maximum value of CF was Fe while Ni was found with a minimum value. The decreasing order of PTEs for CF was Fe>Co>Zn>Pb>Mn>Cd>Cu>Cr>Ni and found similar order to that of I_{geo}.

The mean decreasing order value were 7.64>7.59>7.42>7.10>6.40>6.30>5.94>3.53>2.19.

Maximum EF value was found for Cd while minimum value found for Cr. EF value of PTEs was found in an order of Cd>Cu>Fe>Mn>Zn>Co>Ni>Pb>Cr with a mean value of 2.24>1.98> 1.51>1.04>0.90> 0.68> 0.65>0.52>0.14. PLI is the accumulative CFs product square route for all the PTEs determined and its value was 2376.90 (Fig. 2).

According to the classification of Aiman *et al.,* 2016; Ali *et al.,* 2017; Wei *et al.,* 2015, pollution degrees were evaluated for geo-accumulation and was found in the category of heavily pollution for all the nine PTEs except Cr, which found in the category of moderate to heavily pollution degree.

Table 3. Results of ADD for adults and children of the study area.

PTEs	ADD Ing		ADD Inh		ADD Derm	
	Adults	Children	Adults	Children	Adults	Children
Mn	4.72E-03	4.53E-02	4.44E-07	1.27E-06	1.44E-04	7.25E-05
Cd	2.45E-05	2.35E-04	2.30E-09	6.59E-09	7.45E-07	3.76E-07
Cu	4.33E-04	4.16E-03	4.08E-08	1.17E-07	1.32E-05	6.66E-06
Pb	3.82E-04	3.67E-03	3.60E-08	1.03E-07	1.16E-05	5.87E-06
Cr	4.10E-04	3.94E-03	3.86E-08	1.11E-07	1.25E-05	6.30E-06
Zn	2.71E-03	2.60E-02	2.55E-07	7.30E-07	8.25E-05	4.16E-05
Ni	1.05E-04	1.01E-03	9.87E-09	2.82E-08	3.19E-06	1.61E-06
Fe	3.89E-03	3.73E-02	3.66E-07	1.05E-06	1.18E-04	5.98E-05
Co	8.68E-05	8.34E-04	8.17E-09	2.34E-08	2.64E-06	1.33E-06

These results revealed that there is strong and significant geo-accumulation index for the soil of GAIE. For CF, overall the degree of pollution classification was very high CF, considerable CF and moderate CF (Ahdy and Khaled 2009; Hakanson 1980). In Mn, Cd, Pb, Zn, Fe and Co high degree of CF were founded. In considerable CF, Cu and Cr were exist while in moderate CF in Ni was found. Cumulative results shows a significant CF values for the PTEs in study area. Enrichment factor index showed "low enrichment degree of classification (Sinex and Helz 1981; Sutherland 2000)(Fig 2). According to Tomlinson *et al.,* 1980the PLI value was found in the progressive deterioration degree of pollution which further strengthens the revealed results of CF. The higher PLI value indicates that cumulative higher level of contamination exist in the study area.

Ecological risk

Ecological risk of the PTEs are shown in Fig 3.Cd showed maximum Er value (188.86) while Mn showed minimum (6.40). PTEs with decreasing order of Erare Cd>Co>Pb>Cu>Ni>Fe>Zn>Cr>Mn with mean values of 188.86>37.96> 35.52>29.70> 10.95> 7.64>7.42>7.05>6.40.According to the classification of Hakanson 1980; Wei and Yang 2010,Er lies in three degrees of risk i.e. high risk, moderate risk and low risk. In our case, Cd was found with high risk, Pb and Co with moderate risk while Mn, Cu, Cr, Zn, Ni

and Fe with low risk. These results dictates significant ecological risk for some of the PTEs while growing from low to high in nearby future for others as shown in Fig 3.

Correlation of geo-statistical risks and ecological risk

The geo-statistical analysis for I_{geo}, CF and Er showed strong correlation while EF showed weak correlation according to their classification methodology. Cumulative results of the fourgeo-statistical

techniques (I_{geo}, CF, Er and EF) showed that Cd is found at significant levels contributing to heavy pollution, very high CF, low enrichment, high risk and progressive deterioration values of Igeo, CF, EF, Er and PLI respectively. Second and third level of the significant resulted PTEs werePb and Co. It lies in the category of heavy pollution, very high CF, low enrichment, moderate risk and progressive deterioration risk for I_{geo}, CF, EF, Er and PLI respectively. Fourth, fifth and sixth PTEs are Mn, Zn and Fe.

Table 4. Results of HQ and HI (HRA) for adults and children of the study area.

PTEs	HQ Ing		HQ Inh		HQ Derm		Rf DIng	Rf DInh	RfD Derm
	Adults	Children	Adults	Children	Adults	Children			
Mn	1.00E-01	9.64E-01	3.11E-02	8.89E-02	7.81E-02	3.94E-02	4.70E-02	1.43E-05	1.84E-03
Cd	2.45E-02	2.35E-01	2.30E-06	6.59E-06	7.45E-02	3.76E-02	1.00E-03	1.00E-03	1.00E-05
Cu	1.08E-02	1.04E-01	1.01E-06	2.90E-06	1.10E-03	5.55E-04	4.00E-02	4.02E-02	1.20E-02
Pb	1.09E-01	1.05E+00	1.02E-05	2.91E-05	2.22E-02	1.12E-02	3.50E-03	3.52E-03	5.25E-04
Cr	1.37E-01	1.31E+00	1.36E-03	3.88E-03	2.50E-01	1.26E-01	3.00E-03	2.86E-05	5.00E-05
Zn	9.04E-03	8.67E-02	8.50E-07	2.43E-06	1.38E-03	6.94E-04	3.00E-01	3.00E-01	6.00E-02
Ni	5.24E-03	5.03E-02	4.79E-07	1.37E-06	5.91E-04	2.98E-04	2.00E-02	2.06E-02	5.40E-03
Fe	4.63E-04	4.45E-03	1.66E-03	4.76E-03	1.69E-03	8.54E-04	8.40E+00	2.20E-04	7.00E-02
Co	4.34E-03	4.17E-02	1.43E-03	4.10E-03	1.65E-04	8.34E-05	2.00E-02	5.71E-06	1.60E-02
HI	4.01E-01	3.85E+00	3.55E-02	1.02E-01	4.30E-01	2.17E-01			
% contribution	8 %	76 %	1 %	2 %	9 %	4 %			

These PTEs lies in the category of heavily pollution, very high CF, low enrichment, low risk and progressive deterioration for I_{geo}, CF, EF, Er and PLI respectively. In the seventh position of this classification Cu contributes to heavy pollution, considerable CF, low enrichment, low risk and progressive deterioration for I_{geo}, CF, EF, Er and PLI respectively. Second last is the Cr that have the pollution status of Moderate to heavily pollution, Considerable CF, Low enrichment, Low risk and progressive deterioration for I_{geo}, CF, EF, Er and PLI respectively. Out of all the nine PTEs, Ni was found with the lowest pollution status of moderate pollution for I_{geo} moderate CF, low enrichment for EF, low risk for Er and progressive deterioration for PLI. The overall significant risk (s) of pollution order was Cd>Pb=Co>Mn=Zn=Fe>Cu>Cr>Ni as shown in

Table 2. Similar results have been reported by Hussain *et al.,* 2015; Shabbaj *et al.,* 2017.
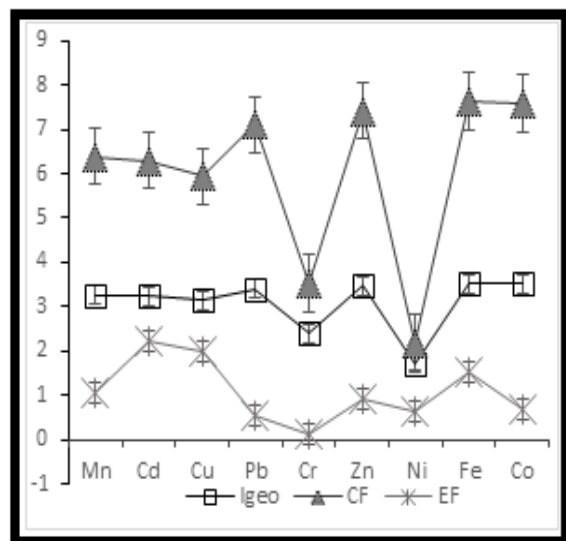

Fig. 2. Geo-accumulation index, contamination factor and enrichment factor of PTEs.

Health risk assessment

Average daily dose

The ADD in all the three exposure ways was measured for adults and children. In adults, ADD Ing with a maximum value of 4.72E-03 was found for Mn and minimum value of 2.45E-05 for Cd. Similarly, in children maximum value (4.53E-02) was found for Mn with while minimum (2.35E-04) for Cd. ADD Ing values were found in order of Mn>Fe>Zn>Ni> Pb> Cr>Cu>Cd>Co for both adults and children. For ADD Inh Maximum values of 4.44E-07 and 1.27E-06 were found for Mn and minimum values of 2.30E-09 and 6.59E-09 for Cd in adults and children respectively.
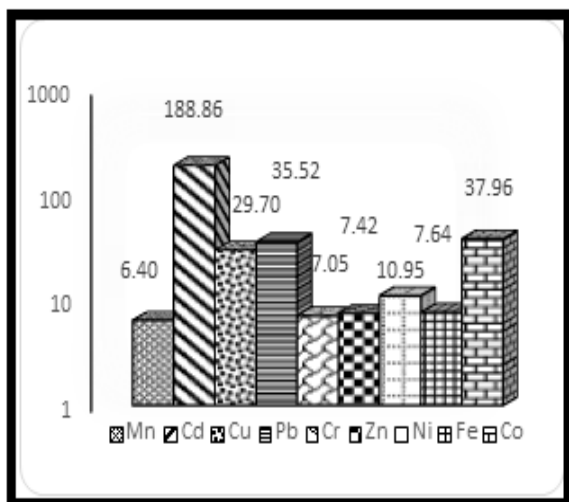
Fig 3 Ecological risk of PTEs for soil of GAIE.

The decreasing order of Ing Inh was Mn>Fe>Zn>Cu>Cr>Pb>Ni>Co>Cd in both adults and children. ADD Derm was found maximum (1.44E-04) for Mn and minimum(7.45E-07) for Cd in adults while in children it is was maximum (7.25E-05) for Mn and minimum (3.76E-07) for Cd. ADD Derm decreasing order is same for both adults and children and was Mn>Fe>Zn>Cu>Cr>Pb>Ni>Co>Cd as shown in Table 3.

Hazard quotient

For analysis of HRA, in all the exposure ways, HQ was determined for adults and children. In adults, HQ Ing with a maximum value of 1.37E-01 was found for Cr and minimum of4.63E-04 for Fe. Similarly, in children it was 1.31E+00 (maximum) for Cr and minimum (4.45E-03) for Fe. HQ Ing values were

found in the order of Cr>Pb>Mn>Cd>Cu>Zn>Ni>Co>Fe for both adults and children. For HQInh, maximum values of 3.11E-02 and 8.89E-02 were found for Mn while minimum of 4.79E-07 and 1.37E-06 for Ni in adults and children respectively.

The decreasing order of IngInh was Mn>Fe>Co>Cr>Pb>Cd>Cu>Zn>Ni in both adults and children. HQ Derm was 2.50E-01 at maximum for Cr and 1.65E-04 at minimum for Co for adults while in children it is 1.26E-01 at its maximum level for Cr and 8.34E-05 at its minimum level for Co. ADD Inh decreasing order is same for both adults and children and was Cr>Mn>Cd>Pb>Fe>Zn>Cu>Ni>Co. Calculated HI for HQ Ing was 4.01E-01 and 3.85E+00 for adults and children respectively. HQ Inh was 3.55E-02 for adults and 1.02E-01 for children. Similarly, HQ Derm was 4.30E-01 and 2.17E-01 for both adults and children respectively as shown in Table 4.

Regarding HRA for PTEs, no PTE separate nor in conjugation with others showed non-carcinogenic risk except for HQ Ing in children which carried the 3.85E+00 value and showed non-carcinogenic risk of >1. Which ultimately pose significant threat to children of the selected group. The HQ Ing for children contributes to 76% of the total HI. Second and third significant groups but with no no-carcinogenic risk are HQ Derm and HQ Ing of adults which have contribution part of 9% and 8% respectively. The overall non-carcinogenic risk among the three exposure ways was in the pattern of HQ Ing> HQ Derm>HQ Inh. Similarly, it was found same (HQ Ing> HQ Derm>HQ Inh) for the children While for adults it was HQ Derm> HQ Ing>HQ Inh. These results revealed that ingestion is the main source of potential non-carcinogenic risk for children as shown in Table 4. Similar results have been reported by Ali *et al.,* 2017; Li *et al.,* 2017; Mohmand *et al.,* 2015; Shabbaj *et al.,* 2017; Wang *et al.,* 2012; Wei *et al.,*2015.

Besides this, in children HQ Derm and HQ Inh was 4 % and 2% while in adults HQ Inh was 1% which shows no significance comparatively. It is noteworthy, that in adults the HQ Ing and HQ Derm should be limited as these concentration may leads to significant level in nearby future as stated by Mohmand *et al.,* 2015.

Furthermore, special attention should be paid to the children of HQ Ing group, indicating that these children are vulnerable and would face potential significant effects via the contaminated soil of GAIE. Studies with similar results have been reported by Mohmand *et al.,* 2015.

This study results concluded that there is no non-carcinogenic risk from a single PTE but this is noteworthy that HI for HQ Ing in children is >1 and can cause a significant non-carcinogenic risk that can leads to different pathological diseases. Furthermore, HQ Derm and HQ Ing in adults' percentage contribution states bio-accumulation and persistence of PTEs in human bodies and can contributes to various disease in this group nearby future.

Conclusion

In this study PTEs concentrations, its single pollution load, cumulative pollution and HRA through three (Ing, Inh and Derm) exposure pathways were determined in soil of GAIE, irrigated from industrial wastewater from last three decades. The Geo-chemical results revealed that the PTEs concentration were many times above the permissible limits of different international standards in target soil samples. Moreover, geo-statistical results indicated that I_{geo}, CF, EF and PLI are at significant levels and can cause potential ecological risks. Also, HQ Ing in children is the main source of non-carcinogenic risk for children and can cause significant health risks (in term of diseases).HQ Ing and HQ Derm should be limited in adults, as they are expected to significantly elevate in near future. Special attention should be paid to the children of HQ Ing group, indicating that these children are vulnerable and would face potential

significant health effects via the contaminated soil of GAIE. The study recommends sustainable treatment of the contaminated soil and adoption of CP policies for GAIE. Furthermore, the residents should be made aware of the possible ecological risks associated with the wastewater irrigation and contaminated agricultural soil.

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