Source Apportionment of Heavy Metal Contaminated Soil Around a Urea Fertilizer Factory and Probabilistic Risk Assessment of Human Health

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Research Article

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Posted Date: June 14th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-418592/v1

Source apportionmentof heavy metal contaminated soil around a Urea fertilizer factory andprobabilistic risk assessmentof human health

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Abstract

The mean concentrations of heavy metals viz: K, Ca, Mg, Ti, Fe, Co, Cu, As, Zn, Rb, Sr, Zr, Pb and Th were measured in soil samples using Energy Dispersive X-ray Fluorescence (EDXRF) technique and sampling sites as a whole were found highly contaminated by Zn, considerably contaminated by Mg and Pb, while moderately contaminated by Fe, Co, Cu, Rb, Sr, As, Rb, Y, Th. The sampling sites are moderate to strongly polluted by heavy metals according to Enrichment factors value, whereas, Pollution Load Index values for 95% of the sample sites were ≥1.5, indicating deterioration of soil quality. Potential Ecological risk (RI) value followed the increasing sequence of Pb>As>Co>Zn>Cu. Non-carcinogenic exposure found higher in children compared to adults,however carcinogenic risk assessment revealed that both groups (adult and children) lied within Grade II category (10^{-5} to 10^{-6}) and considered to be at no risk.

Keywords: Health Risk Index (HRI), Metal Pollution Index (MPI), X-ray Fluorescence (XRF) Spectroscopy, Carcinogenic Risk, Ecological Risk (RI).

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Introduction

Fertilizers are applied to increase and enhance the crop yield and ensure healthy produce by appropriate balance of nutrient to the soil. Exact balance of fertilizer helps in soil quality depletion and hence helps in proper growth of plant. Basically fertilizers are chemical substances that promotes the crop productivity by supplying nitrogen, potassium and phosphorous and enhance the water retention capacity of the soil, increase soil fertility as well.Among different types of chemical fertilizers urea is the most important nitrogenous fertilizer to improve the quality of soil providing nitrogen to increase the yield of crops.Soil is a complex matrix that can absorb pollutants like metals (Hamaker et al.1972 and Thompson et al. 1972), which becomes common across the globe due to increase in geologic and anthropogenic activities. Emission and waste disposal from rapidly expanding industrial areas, coal combustion, use of chemical fertilizer, waste water irrigation, domestic wastes are known to be responsible for the release of heavy metals into the soil, leaving behind lasting effects for years (Fusion et al. 1999), since they are environmentally stable, non-biodegradable, and tend to cause accumulation in soils. In addition to anthropogenic sources, toxic pollutants may be derived from other sources such as the weathering of naturally high background rocks and metal deposits (Senesi et al. 1999).When the surface soils are contaminated, they consequently serve as a transmitter of pollutants to surface water, groundwater, atmosphere, and food. Excessive accumulation of heavy metals in soil may not only result in soil pollution or contamination, but can also lead to elevate heavy metal (HM) uptake by plants, and thus affect food quality and safety (Muchuweti et al. 2006). Therefore heavy metal accumulation in soil is of increasing concern as it ultimately becomes the potential source of human health risks (Singh et al. 2010). This problem has been focused by many researchers and widely reported (Eriyamremuet al.2005; Muchuweti et al. 2006; Satarug et al. 2000).However, heavy metal contaminated soil can affect human health in two ways viz: via food chain or may directly from soil dust. Direct ingestion of particles (ADD_{ing}); inhalation of the suspended particles through mouth and nose (ADD_{inh}); dermal absorption of trace elements in particles adhered to exposed skin (ADD_{dermal}) (Ihediohaet al.2017) are the three major direct human exposure pathway.

The Jamuna Fertilizer Company Ltd. Jamalpur of Bangladesh produces Urea fertilizer, contributing significantly to meet the demand for urea fertilizer of the country from years. The main raw materials used are the natural gas, differentchemicals like Fe_2O_3, Fe_3O_4, Al_2O_3, K_2O, CaO, and SiO_2etc. However the factory dischargesthe

liquidwastes to the nearby lands which finally go to the Jamuna River and to the adjacent agricultural lands. In this way, the soil gets contaminated and causes toxicity to the public thereafter when the land isused for agricultural cultivation. A vast investigation therefore needed to understand the present heavy metal status of that area, their potential sources as well as impact on human health.The present study was sketched to determine qualitatively and quantitatively the concentrations of heavy metals (Mg, K, Ca, Ti, Fe, Co, Cu, Zn, As, Rb, Sr, Zr, Pb and Th)in the near-surface (~0–20 cm) soils around theJamuna Fertilizer Company Ltd., area using Energy Dispersive X-ray fluorescence spectrometry (EDXRF) and to assess the extent of pollution by calculating some contamination indices and ecological risk assessment . To find outthe possible sources statistical analysis like Pearson correlation, Principal Component Analysis (PCA) has been done and the impact on direct human exposure via inhalation, ingestion and dermal contact of soil dust evaluated as well.

Materials and methods

Study Area

The North-East side of 'The Jamuna Fertilizer Co. Ltd.Jamalpur of Bangladesh (geographical coordinates are at 24° 59' 0" North, 90° 6' 0" East), a residential cum agricultural field area,was selected as the study area and soil samples were collected randomly from twenty different points around the Fertilizer factory. There are cultivation lands near the factory site which received huge amount of solid and liquid waste, in addition to the discharge from fertilizer factory; the study area is getting contaminated by a nearby car workshop, from where wastes are frequently dumped.The site map of sampling area is shown in Fig. 1.

Sample collectionand preparation

A total of 20 soilsamples were collectedfrom different places of the sampling siteusing stainless-steel specula at regular intervals of 2 m at specific transects and labeled as soil-1 to soil-20. The soil samples after collection were sieved with a stainless steel sieve to remove dirt and plant materials. Samples were then separately taken into porcelain dishes and placed in an oven at around 70ºC for complete drying. Each driedsample wasgrounded to fine powder using a mortar and pestle and preserved in a distinctly marked plastic vial inside a desiccator. The homogeneous powder was used to prepare pellet (7mm dia. and 1mm thick) using 10 ton pressure by a pellet maker (Specac, UK) for elemental analysis by EDXRF.

Sample irradiation and method validation

The sample irradiation was performed using Energy Dispersive X-ray Fluorescence (EDXRF) Spectroscopy System.

The entire process is done following (Shirin et al. 2019).The X-Ray beam of 22.4 keV from ^{109}Cd point source hits the target sample to produce the characteristic X-rays, the [Si (Li)] detector (Canberra) having the resolution of 175eV at 5.9 keVdetects the characteristic X-rays, which are ultimately converted into voltage pulses and amplified by the spectroscopy amplifier and then finallyprocessed in MCA having16K^{+}channel.The irradiation and spectrum data acquisition are operated and controlled by a software package provided with the system (AXIL). The standard materials were also irradiated under similar experimental conditions for construction of the calibration curves for quantitative elemental determination in the respective samples. The commercial software AXIL has been applied for the qualitative and quantitative elemental determination.

In EDXRF technique, a simple comparison is appliedfor elemental concentration measurement (Islam et al.2007 and Jolly et al.2007 and Jolly et al.2012).In the present study, three pellets from commercially available soil standard (Soil-7 /IAEA)were used to construct a calibration curve, by plotting the sensitivities of the elements as a function of their atomic number. The calibration curve was validated and checked through analysis of standard reference materials "Montana-1/2710a". The results obtained for elements of interest and certified values for corresponding elements are in good agreement as they are found to vary within the acceptable range of error (±10%). The entire process was describing elsewhere (Jolly et al. 2013).

Assessment of metal contamination

Geo-accumulation index (Igeo)

Geo-accumulation index (Igeo) is measured using the following equation (Abrahimet al. 2008 and Parker et al. 2008):

$$\text{Igeo} = \log 2 \frac{\text{Cx}}{1.5 \times \text{Bx}}$$

Where, $C_x$refers the measured concentration of the metal x, $B_x$is the geochemical background concentration of metal x and 1.5 is the background matrix correction factor due to lithospheric effects. The geo-accumulation index consists of seven grades or classes (Bhuiyanet al. 2010; jolly et al. 2018). Class 0 (practically uncontaminated): Igeo≤0; Class 1 (uncontaminated to moderately contaminated): 0 <Igeo<1; Class 2 (moderately contaminated): 1 <Igeo< 2; Class 3(moderately to heavily contaminated): 2 <Igeo< 3; Class 4 (heavily contaminated): 3 <Igeo< 4; Class 5 (heavily to extremely contaminated): 4 <Igeo< 5; Class 6 (extremely contaminated): 5 <Igeo. Class 6 is an open class and comprises all values of the index higher than Class 5. The elemental concentrations in Class 6 may be hundredfold greater than the geochemical background value (Bhuiyan et al. 2010).

Enrichment factor (EF)

To estimate the anthropogenic heavy metal impact on soil, a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels (Hornung et al. 1989;Dickinson et al. 1996; Abrahim and Parker 2008; Bhuiyan et al. 2010) is necessary. Thus EF can be calculated by using the following equation:

$$EF = \frac{(\text{Metal/Fe}) \text{ Sample}}{(\text{Metal/Fe}) \text{ Background}}$$

Following (Tamim et al. 2016), iron (Fe) was used as the reference element for geochemical normalization in the present study. The EF values close to unity indicate crusted origin (comparable to those of UCC) of the metals, those less than 1.0 suggest a possible mobilization or depletion of metals (Zsefer et al., 1996), whereas EF>1.0 indicates that the element is of anthropogenic origin. EF values EF<2, 2<EF<5, 5<EF<20, 20<EF<40, and EF<40 are the indication of minimal, moderate, significant, very high and extremely high enrichment respectively.

Contamination Factor (CF)

The contamination status of the soil can be determined by calculating contamination factor (CF) following (Thomilson et al. 1980) as below:

$$CF = \frac{\text{Cmetal}}{\text{C background}}$$

Where $C_{metal,}$ $B_{ackground}$are the measured concentration of a specific metal and background value of that metal respectively. World surface rock average proposed by(MartinandMeybeck 1979) is considered as background concentration for the present study.The contamination levels were classified based on their intensities on a scale ranging from 1 to 6 as shown in Table 1. The highest number indicates that the metal concentration is 100 times greater than what would be expected in the crust.

Pollution load index (PLI)

Pollution load index (PLI) is calculated from the Contamination Factors (CF) of the specific heavy metals for a specific sampling site, which can be defined by following(Hakanson Let al. 1980) and categorized by following (Zhao et al. 2012) as low (CF<1), moderate (CF: 1–3), considerable (CF: 3–6) and high (CF>6). Following Tomlinson et al. (1980), PLI can be calculated by the equation bellow:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \text{----------} \times CFx)^{1/x}$$

Where, CF_1 to CFx represents the contamination factors for the specific toxic metals and x is the total number of contamination factors considered. PLI=1 indicates the presence of only baseline levels of pollutants and values above 1 indicate progressive deterioration of the site quality(Mohiuddin et al. 2010).

Degree of contamination (Cd)

Degree of contamination (Cd) is usually calculated to determine the contamination status of the sediment/soil in and defined as the sum of all contamination factors as:

$$Cd = \sum CF$$

Where, Cd<8=Low, 8≤Cd<16= moderate, 16≤Cd<32 =considerable and 32≤Cd = very high degree of contamination respectively.

Nemerow Comprehensive Index (P_N)

Nemerow index method is widely used to assess the integrated and comprehensive pollution status of the heavy metals and metalloids in soil(Chen et al. 2010).The single factor index (Pi) method was applied to measure the pollution degree of a single pollutant in the soil samples. This method could highlight the most important pollutant which influences the most pollution at an individual site easily and clearly. On the other hand the Nemerow pollution index (Pn) was used to evaluate the comprehensive pollution status of soils with all the heavy metals of concern (Chen, 2010). Since different heavy metals might have impacts on one site, this method could provide a reasonable interpretation of the heavy metal pollution at each site as a whole.

The expression of P_i is as follow:

$$P_i = \frac{C_i}{S_i}$$

where Pi is the single factor index of individual metal, Ci represents the actual measured concentration of metals in soil and Si represents the geochemical background content(Kabata-Pendias2011).Pi_{avg} indicates the mean value of Pi whereas Pi_{max} represents the maximum value in an individual sampling site. To evaluate the integrated environmental quality ofthe soil of any particular area of interest it is only necessary to calculate the Pn value and then compare it with the corresponding classification standard (Table 1)(Chen et al. 2008).

However P_N is calculated by following equation:

$$P_N = \frac{\sqrt{(Pi)^2_{mean} + (Pi)^2_{max}}}{2}$$

169 $(P_i)_{max}$ and $(P^i)_{mean}$ refer to maximum and average values of P_i, among the target elements respectively (Li et al.
170 2018).(Zhong et al. 2010) classified P_N as $P_N \leq 0.7$, $0.7 < P_N \leq 1.0$, $1.0 < P_N \leq 2.0$, $2.0 < P_N \leq 3.0$, $P_N > 3.0$ for clean, warning
171 limit, slight pollution, moderate pollution and heavy pollution respectively by individual elements.

172 **Potential Ecological Risk Index**

173 (Hakanson et al.1980) proposed potential ecological risk of individual factors (E_r^i) and the potential ecological risk
174 index (RI)for the evaluation of the potential ecological risk of pollutants in soils by the equation:

175 $$E_r^i = T_{r\times}^i \frac{C^i}{C_n^i}$$

176 $$RI = \sum_i^m E_r^i$$

177 Where $E_r^i$the ecological risk of a single factor is, C^i is the measured concentration of the metal in soil$C_n^i$is the
178 geochemical background in the soil (Chen et al. 1992), m is the analyzed metal concentration, $T_r^i$is the toxicity
179 response coefficient of heavy metals which are 5, 5, 1, 5, 10 for Co, Cu, Zn, Pb and Asrespectively used in the
180 present study. E_r^i is categorized as <40 low risk, 40-80 moderate risk, 80-160 considerable risk, 160-320 high risk,
181 ≥320 very high risk and RI value <100, 100-200, 200-400, ≥400 referred as low, moderate, considerable, high risk
182 respectively.

183 **Human health risk assessment**

184 **Hazard Quotient (HQ)**

185 The exposure risks of soil metals posed to the public are calculatedfollowing the United States of Environmental
186 Protection Agency suggestive formula for health risk assessment (US Environmental Protection Agency 1989; US
187 Environmental Protection Agency 2001).Ingestion of particles (ADD_{ing}); inhalation (ADD_{inh}); dermal absorption of
188 trace elements via skin (Ihediohaet al.2017)are the three major direct pathway for human exposure. Presently Cu,
189 Zn, Asand Pbweretaken as the subject for calculating the health risk assessment via soil dust, where As and Pbposed
190 a carcinogenic risk, and other are non-carcinogenic. Populationgroup: adults and children are considered and the
191 doses calculated for each element and exposure pathway are subsequently divided by the toxicity threshold value,
192 which is referred to as the reference dose (RfD), of a specific element to yield a non-carcinogenic Hazard quotient
193 (HQ), whereas the Hazard index (HI) is the total non-carcinogenic risk of all exposure pathways to a variety of
194 pollutants (USEPA 1989; Li et al. 2014). For carcinogens, the dose is multiplied by the corresponding slope factor

(SF) to produce a level of carcinogenic risk (Ferreira-Baptista2005)which is regarded as the probability of an individual developing any type of cancer in their whole life time due to exposure to carcinogenic hazards .

Hazard Quotient (HQ) implies the Non-carcinogenic hazards, expressed as the probability of an individual suffering an adverse effect. It is defined as the quotient of ADI or dose, divided by the toxicity threshold value, which is referred to as the chronic reference dose (RfD) in mg/kg-day of a specific heavy metal**.**It is an exceedance of ingested pollutant when ingested exposure dose is compared with the oral reference dose and when the value of HQ is less than 1, then the exposed population (consumers) is safe but HQ equal to or higher than 1, means the human health is not safe, therefore potential health risk occurred, and related interventions for protective measures are required. However, HQ parameter does not estimate the risks; it only indicates a risk level associated with pollutants exposure. The non-carcinogenic risk was estimated using HQ calculated for heavy metals by using the following equation:

Hazard Quotient (HQ) = $HQ = \frac{ADD}{RfD}$ ……. (1)

Where, ADD is the Dose due to the exposure of heavy metals and RfD is the oral reference dose. The oral reference dose is the dose of a substance that can be taken in daily without identifiable risk for lifetime exposure or the daily oral exposure for the human population, which does not cause deleterious effects during a life-time.

Ingestion of Heavy Metals through Soil was calculated thus;

$$ADD_{ing} = C \times \frac{IngRXEFXED}{BWXAT} \times 10^{-6} \ldots\ldots (2)$$

Where, ADD_{ing} is the average daily intake of heavy metals, ingested from the soil, in mg/kg-day, C indicates the concentration of heavy metal in mg/kg for soil. IngRis the soil ingestion rate in mg/day; EF, the exposure frequency in days/year; ED the exposure duration in years; BW, the body weight of the exposed individual in kg; and AT, the time period over which the dose is averaged in days. Also CF is the conversion factor inkg/mg.

Inhalation of Heavy Metals via Soil Particulates was calculated thus;

$$ADD_{inh} = C \times \frac{IngRXEFXED}{PEF \times BWXAT} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where, ADD_{inh}intake of heavy metals, inhaled from the soil in mg/kg-day, C indicates the concentration of heavy metal in soil in mg/kg, and IngRand PEF are the soil inhalation rate in $mg.day^{-1}$ and the particulate emission factor in m^3/kg, respectively. EF, ED, BW, and AT are as defined earlier in Equation (2) above.

Dermal Contact with Soil is calculated thus;

$$ADD_{dermal} = C \times \frac{SAXSLXABS \times EF \times ED}{BWXAT} \times 10^{-6} \ldots\ldots\ldots (4)$$

Where, ADD_{dermal} is the exposure dose via dermal contact in mg/kg/day. C represents the concentration of heavy metal in soil in mg/kg, SA stands for exposed skin area in cm^2. SL, adherence factor in $mg.cm^{-2}day^{-1}$; and ABS, the fraction of the applied dose absorbed across the skin, unitless. EF, ED, BW, CF, and AT are as defined earlier in Equation (2). Table 2 shows the exposure parameters, used for health risk assessment of standard residential exposure scenario through different exposure pathways.

For n number of heavy metals, the non-carcinogenic effect on population is as a result of the sum of all HQ's due to individual heavy metals, which is referred to as another term called Hazard Index (HI), as described by (USEPA 1989). Equation (5) shows the mathematical representation of this parameter

$$HI = \sum HQ_i = HQ_{ing} + HQ_{inh} + HQ_{der} \ldots\ldots\ldots\ldots\ldots (5)$$

For carcinogens, the risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to potential carcinogens. The equation to calculate excess lifetime cancer risk is:

$$\text{Cancer risk} = \text{ADD X SF}$$

Final calculation for the total excess lifetime cancer risk for an individual from the average contribution of the individual heavy metals for all pathways are done using the following equation:

$$Risk_{Total} = Risk_{ingestion} + Risk_{inhalation} + Risk_{dermal} \ldots\ldots\ldots\ldots (7)$$

For the Risk factor calculation the dose is multiplied by the corresponding slope factor to produce a level of carcinogenic risk. If the risk is $<10^{-4}$ then it is said to be the acceptable carcinogenic risk value range(Gu, Y G, Gao, Y P,& Lin, Q 2016).

Result and Discussion

Heavy metal abundance in and around fertilizer factory soil

The results of heavy metal concentrations for each sampling site in soil presented in Table 3 ranged over the following intervals; Mg: 7812-24257 (mean14712), K: 5631-15115(mean 11828), Ca: 4906-12408(mean 8607), Ti: 2874-5886(mean 4378), Fe: 20470-62465(mean 47358), Co: 3.25-22.90 (mean 10.93), Cu: 10.22-27.54 (mean 17.04), Zn: 61.55-282.09 (mean 151.57). As: 5.63-13.08 (mean 8.65), Rb: 114.91-258.32 (mean 191.08), Sr: 132.73-287.46 (mean 191.42), Zr: 206.62-337.14 (mean 263.64), Pb: 61.77-132.24 (mean 88.69), and Th: 9.46-25.43 (mean 17.55) mg kg^{-1} respectively. The mean concentrations of Mg, Fe, Cu, Zn, Rb, Sr, Th, As, Co and Pb were higher and

K, Ca, Ti and Zr were lower compared to world average values as reported by Taylor and Francis group LLC, 2011.Heavy metals occur in many fertilizers and pesticides (Ahmed and Goni 2010, Aucejo et al. 1997 and Facchinelli et al.2001) suggested that wastewater is the main source for metal in agricultural soil. The mean concentrations of Znand Pb in agricultural soil in the present investigation were found higher than reported by (Ratul et al. 2018).The mean concentrations of Co andAs were found lower but Cu and Zn concentrations were higher than reported by(Kkodomet al. 2012). The mean concentrations of Cu, As and Pb in some sites were higher than the Dutch soil quality standard (VROM 2000)except Zn, indicating metals in soil might pose adverse effect on humans, plants and animals.

Possible source identification

Pearson correlation matrix analysis

The Pearson correlation matrix in different elements in order to identify the correlation among the heavy metals in the soil sample are given in Table 4.The strength that associated in between different elements,indicating by p value refers 0.01 and 0.05 as strong and significant correlations respectively. Present study reveals that Mg, Al, Si, Ca, Zr possess positive correlations with each other and Al & K possess significant correlation with Fe, Ti, Rb, Y, Pb& Th. All the alkali and alkali earth metals correlate positively with Si. Al correlates with Fe in weathered materials and can be an indicator of mafic rocks. Cu, Zn, Pb&Th also possess significant correlation with each other. Similarly Zr, Th, Y &Pbare significantly correlated with each other. In nature, thorium occurs in the +4 oxidation state, together with Yttrium and other heavy metals.Zr and Y generally considered as immobile elements for mass balance evaluation, are mobile in some cases under extreme climatic conditions. Zr exhibits strong positive correlation with Si and hence Zircon is a mineral belonging to the group of silicates. Zr also shows significant correlation with Ca, however traces of Zr also exist in limestone (Kabata-Pendias1993). It also noted that As possesses very weak or negative correlation with other metals. The strong positive correlation could indicate similar source origin of heavy metal in different soil sample.

Principal component analysis

The total variance in each factor was calculated as the sum of the squared loadings for the given factor. The scree plot (Fig.2) is used to identify the number of PCs to be retained to understand the underlying element structure.In this study six factors which represents 90% of the total variance referred as PC1, PC2 PC3, PC4,PC5& PC6 explain more than 42%, 17%, 9%, 7%, 7% & 5% of variance respectively and the Eigen values are 8.117, 3.282, 1.885,

1.459, 1.359, 1.024 for each component (Fig.3). The first principal component PC1 is highly loaded with Rb, Ti, Fe, K, Al, Y, Pb, Sr and all of these elements are mostly exist in soilgeogenicaly. The second principal component PC2 is strongly loaded with Zr, Ca, Mg and weakly loaded with Si. The long-established agricultural practice and liming are the sources of Ca; cement factories, fertilizers, and dust can also be sources of Ca& Mg. The third principal component PC3 is strongly loaded with Cu, Zn, Th and moderately loaded with Pb. In nature, Pb is originated as progeny of radioactive thorium andvehicle brakes and tire wear as possible sources of Zn &Cu.The fourth principal component PC4 is strongly loaded with only Sr and can be released from industrial waste, disposal of coal ash, and incinerator ash (Reimann and de Caritat1998). The fifth principal component PC5 is strongly loaded with P and moderately loaded with Si, complies the major anthropogenic sources of phosphate containing fertilizers. The sixth principal component PC6 is strongly loaded with As.PCA correlation circle for the studied elements based on Pearson correlation matrix is shown in Fig.4.

Assessment of pollution status

Geo-accumulation Index (I_{geo}) and Enrichment factor (EF)

The Enrichment Factor (EF) and Geo-accumulation Index (I_{geo}) are indicators used to assess the presence and intensity of anthropogenic contaminant deposition on surface soil. The calculated mean geo-accumulation index I_{geo}(Mulleret al.1979)value ofJamuna fertilizer factory area soils at different sampling points (Fig.5) for the elements Mg, K, Ca, Ti, Fe, Co, Cu fall in Class 0 (practically uncontaminated): $I_{geo} \leq 0$ and for the elements Zn, As, Rb, Sr, Y, PbTh in Class 1 (uncontaminated to moderately contaminated): $0 < I_{geo} < 1$. The I_{geo} value reveals that the proposed site is moderately contaminated by toxic elements As, Pb,Th .Mean EF values of K, Ca, Ti, ,Fe, Co, Cu, Zn, As Rb, Sr, Y,Zrand Pbfollowed the decreasing order of Ca(0.08)<Pb(0.39)<As(0.47)<Zn((0.64)<Y(0.95)<K(1.07)<Co(1.18)<Zr(1.23)<Rb(1.32)<Sr(1.38)<Fe(1.39)<Cu(1.83)<Ti(2.18) but EF value of Th (Thorium) is not included in this study as of reference values are not available. The EF value of all heavy metals were reported to be<2 at all sampling sites (Fig.6) but Ti showed moderate enrichment in the area as it remains between 2 and 5 thus can be severe in the near future so regular monitoring is necessary.

Contamination factor (CF)

Sampling point Soil-1is moderately contaminated by Mg, Fe, As, Zn. Cu, Sr Y, Thbut the contamination level of Al, K, Ca, Co, Ti and Co is very low (Table 5). Similarly, sampling point Soil-2 is moderately contaminated by Mg, Co, Zn, As, Y, Rb,PbThwhile contamination level is low for Al, K, Ca, Co, Ti, Fe, Cu , Sr.Soil-3 is considerably

contaminated by Rb and Pbbut moderately contaminated by Mg, Fe, Co, Cu, and Zn, As, Sr, Y,Th. Soil-4 is considerably contamination by Mg, Zn,Pbbut moderately contamination by Al, Fe, Co, Cu, As, Rb, Sr Y, Th. Considerable contamination is observed by Mg,Zn and moderate contamination by Fe, Co, Cu As, Rb, Sr, Y, Pb, Th in sampling point Soil-5. Moderate contamination is found in sampling point Soil-6, but the considerable contaminants are Co, Zn, Rb and Pb. Similarly Sampling points soil-7,soil-8,soil-9,soil-10,soil-11,soil-12,soil-13soil-14,soil-15,soil-16,soil-17, soil-18, and soil-20 are considerably contaminated by Mg, Pb, Zn, Rb, Co; moderatelycontaminated by Fe, Co, Zn, As, Rb, Sr,Y,Th and low contamination factor indicative of low contamination by Al, K, Ca, Ti, Co, Cu, . Finally, sampling point Soil-19 is highly contaminated by only Zn,considerably contaminated Mg, and Pb and moderately contaminated by Fe, Co, Cu, Rb, Sr, As, Rb, Y, and Th. It is evident from Table5that the contamination factor for Pb, Cu Mg, Fe, Co, As, Rb, Th , Y and Zn were higher than other study (Abdullah al zabir et al ,2016), which indicates that Pb, Rb, Mg and Zn were the major pollutants in those soils.The degree of contamination(Cd) in the studied area at different points reveals that sampling point soil-16 is very highly contaminated ; soil-1, soil-2, soil-3, soil-4, soil-5, soil- 6,soil-7, soil-8, soil-9, soil-10, soil-11,soil- 12,soil-13, soil-14, soil-15 soil-17,soil-18,soil-19 and soil-20 - all are at considerable degree of contamination .

Pollution Load Index (PLI)

The Pollution Load Index (PLI) shown in (Fig.7) suggests thatall the sampling points, except Soil-7, are polluted and deteriorating progressively by different toxic heavy metals with the indication that the middle part of the study area is less polluted than northern and eastern parts of the study area.The highest PLI (2.28) was observed at sampling point (Soil -16) indicates heavily contaminated compared to other sites.

Nemerow Comprehensive index (PN)

The single factor index of heavy metals of the studied samples showed that the average pollution degree was decreased in the givenorder: Pb> Zn>Ti>Fe>Co>As>Cu. Pb had the highest single factor index value and few stations are suffered from severe Zn pollution according to the single factor index(Table 6). The results of the Nemerow pollution index (P_N) indicated the sampling site soil-7 and soil 17 had low pollution and fall in the pollution class III, whereas sampling site soil-6, soil-9, soil 16 and soil-19 showed severe heavy metal pollution and fall in the pollution class V and rest of the sites displayed moderate pollution and fall pollution class IV. Therefore,

in the study area, measures must be taken to avoid the potential trace element contamination of soils to protect environmental health.

Potential Ecological Risk (PERI)

In this study, Potential Ecological Risk (PERI) for the elements Co, Cu, Zn, Pband As have been calculatedand presented in Table 7. All the sampling site (soil-1 to soil-20) showed high PERI value for the element Pb and As, while the lowest PERI value varied from element to element and site as well.Thus cobalt (Co) showed lowest value for soil-1, Cu showed lowest value for soil-3, Soil-4, soil-8, soil-9, soil-10, soil-15, soil-20 and Zn showed lowest value for soil-2, soil-5, soil-6, soil-7, soil-11, soil-12, soil-13, soil-14, soil-16, soil-17, soil-18 and soil-19 respectively.The maximum and minimum value was found 10.133, 3.540, 4.030, 24.488, 19.147 and 1.438, 1.313, 0.879, 11.438,8.3243 for Co, Cu, Zn, Pb and As respectively. The estimated Potential ecological risk (RI) found highest forPb (16.425) and lowest for Zn (2.165).

Non -Carcinogenic Hazard quotient (HQ)

Non carcinogenic risk calculationhas been done for the elements Zn, Cu, Pb and As for both adults and children presented in Table 8, where the HQ value for adults followed the sequence of Pb>As>Cu>Zn and for children it was As>Pb>Zn>Cu.The exposure rate due to As, Pb, Cu and Zn is higher in children than the adults. Regardless of age, the HQ and Hazard Index (HI) values of the analyzed metals by different exposure pathways were less than 1, which as a whole indicates that the risk is small and negligible and could cause no obvious health hazards on the surrounding population. From Table8, it may be appraised thatthe direct oral ingestion of soil particles is the highest, followed by dermal absorption of elements in soils adhered to exposed skin, and inhalation of resuspendedsoil particulates by nose or mouth minimization. Again from the calculated result it can beconcluded that direct oral ingestion of soil particles is highest in case of children population. Children exposure risk to arsenic (As)on this note is the highest: HQ reached to 0.1893, by direct oral ingestion of soil particles. Hazard Index (HI) followed the sequence as Pb>As>Cu>Zn and As>Pb>Zn>Cu for adult and child respectively.

Thecarcinogenic risk due to the four heavy metals Cu, Zn, As and Pb has been calculated for both the adults and children population (Table 9), from where it is evident that children are more vulnerable than adults and the risk factor of As is much higher than Pb in case of children.The total carcinogenic risk factor for children is 7.762×10^{-6} which is less than the acceptablecarcinogenic value range (Risk$<10^{-4}$) and as the risk value lies within (10^{-6}to10^{-5}), according to (Li et al.2017) it has been considered as Grade II (Low risk) and hence there is no need to wary about

the risk.The total carcinogenic risk factor for adults is 3.326×10^{-6} which is within the acceptable range (Risk<10^{-4}) and did not pose a carcinogenic risk to the population group.

Conclusion

Thestudy presents a detailed investigation of heavy metal pollution inanthropogenically and geogenically impacted soils of a Urea fertilizer factory area.The mean concentrations of metals (Fe,Mg, K, Ca, Ti, Zr, Sr, Rb, Zn, Pb, Th, Cu, Co, As) inthe vicinity of the area varied location to location; however, soil-4,soil-6,soil-9,soil-11,soil-13,soil-14,soil-15,soil-16,soil-17, soil-19 of the study area are slightly contaminated by Mg, Zn and Pb, whereas other sampling points are either uncontaminated or moderately contaminated by Mg, Zn and Pb, and uncontaminated by all other elements studied.The EF values for K, Fe, Zr, Rb, Sr, Cu, Co, Pb, Zn,Y, and Ca showed that these metals were derived mainly fromnatural processes or geogenic sources and were related to the exposure of the Earth's crustmaterial, with no evidence of the tailings dump impacts. However, Ti indicated moderateenrichment with maximum EF values of 2 and 5respectively. Zinc showed very high contamination in soil and made contribution to contamination of the soilexpressed by contamination factor, CF (CF>4). Only sampling point Soil-19 is highly contaminated by Zn, considerably contaminated by Mg and Pb, and moderately contaminated by Fe, Co, Cu, Rb, Sr, As, Rb, Y, and Th. Besides, all the sampling points are contaminated, though low in concentration, by Al, K, Co, Ca and Sr. The degree of contamination at different points reveals that sampling point soil-16 around Jamuna Fertilizer is very highly contaminated.Mean Ecological Risk Assessment value (RI) followed a sequence of Pb>As>Co>Cu>Zn. The calculated RI values indicate moderate ecological risk by Pb, As and low ecological risk by Co, Cu & Zn in the particular area.Nemerow pollution index indicated 10% sampling sites have low pollution, whereas 20% are severe and 70% are moderately polluted. Human health risk assessment showed that non-carcinogenic risk by the element Cu, Zn, Pb and As in the fertilizer area soil is negligible for both population groups and carcinogenic risk assessment for Pb&As for both population groups (adult and children) lies within Grade II group (10^{-5} to 10^{-6}) and are considered to be at no risk.

Multivariate statistical analysisrevealed source of all the elements are mostly geogenicaly and affected by agricultural practice, liming, wastes from cement factories and use of excessive fertilizers and dust particle etc.Vehicle- break and tire- wear are also the source of some elements (Pb, Zn) in the soil of that particular area.

Acknowledgement

The authors would like to express their thanks and gratitude to all the staff members of Atmospheric and Environmental Chemistry laboratory, Atomic Energy Centre, Dhaka to carry out this research work.

Ethical Approval

All the authors of this research work gave their consent to publish the article.

Consent to Participate

N/A

Consent to Publish

N/A

Authors Contribution

ShirinAkter: samplecollection and analysis, data calculation; MehediHasan, SaifulIslamTushar: statistical analysis of data, Mottalib Hossain Sarkar, Khan Mohammad Mamun, Mohammad JamiulKabir: sample preparation and analysis, Mohammad Obidur Rahman, Mohammad Safiur Rahman, Mohammad JoynalAbedin, and BilkisAra Begum :Writing, YeasminNahar Jolly: writing, editing and final approval of the manuscript.

Funding

The present work didn't receive any fund from any government or non-government organization.

Competing of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this research paper.

Availability of data and materials

N/A

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Figures

Figure 1

Jamuna fertilizer area Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

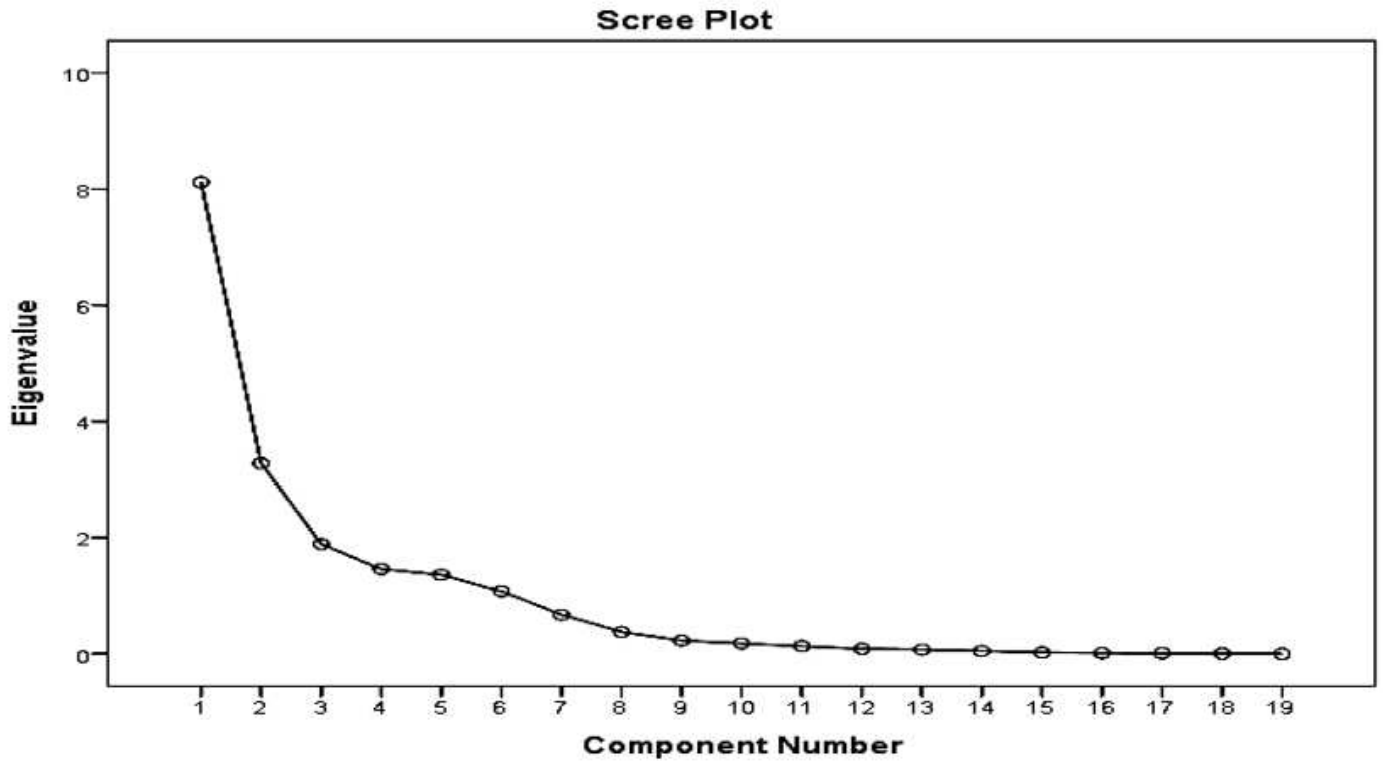

Figure 2

Scree plot of the characteristic roots

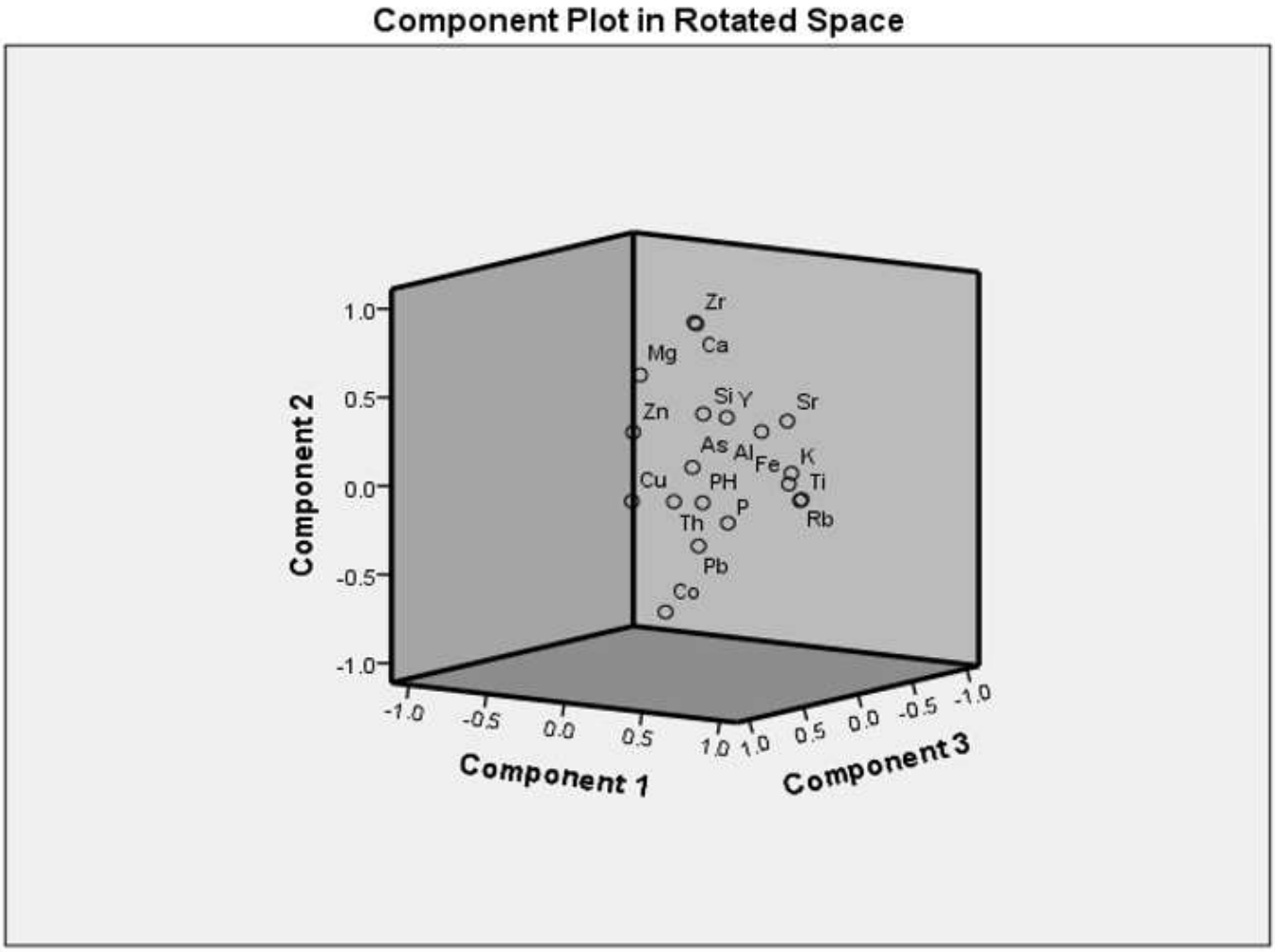

Figure 3

Component plot in rotated space of Principal component analysis.

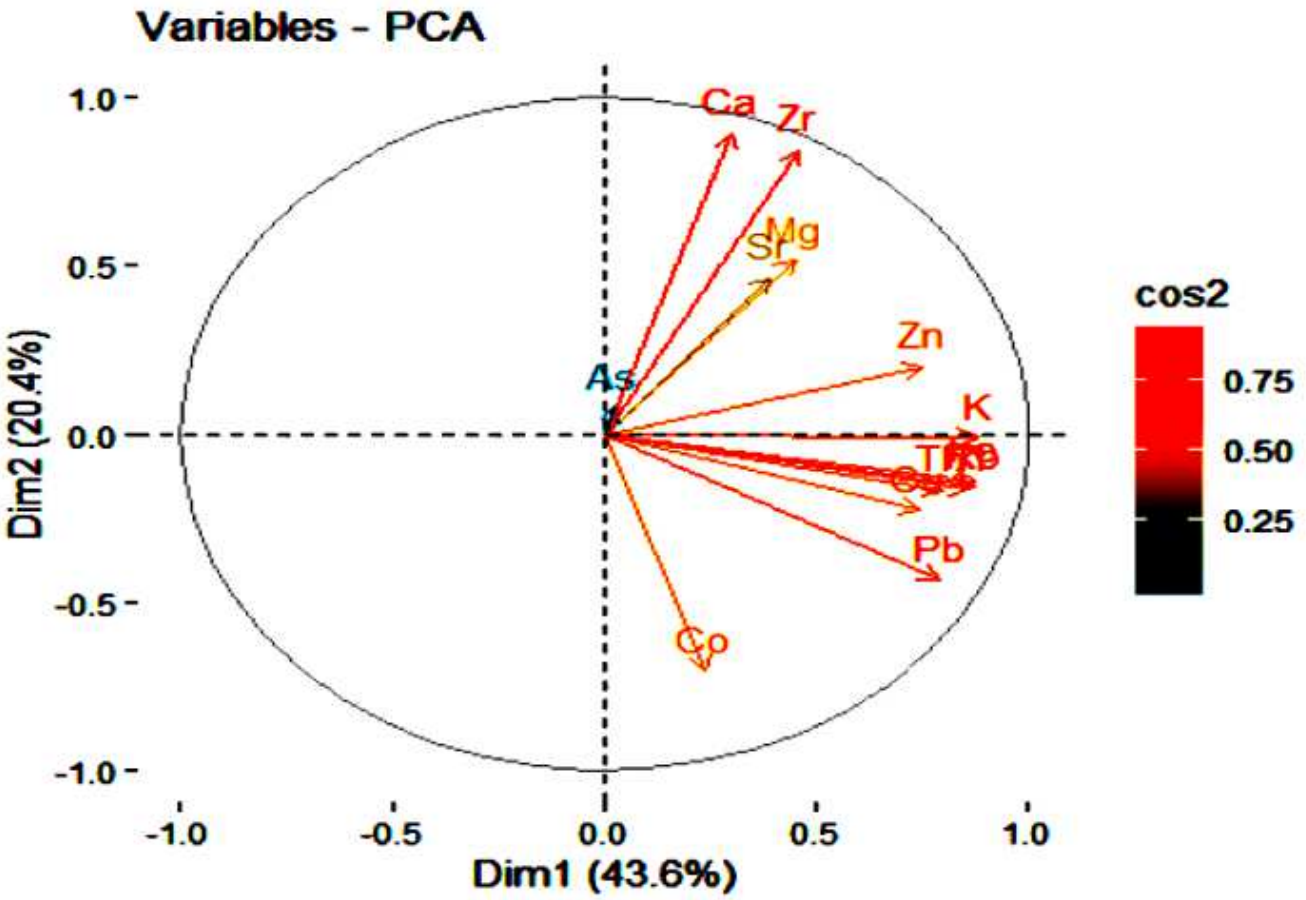

Figure 4

PCA correlation circle for the studied elements

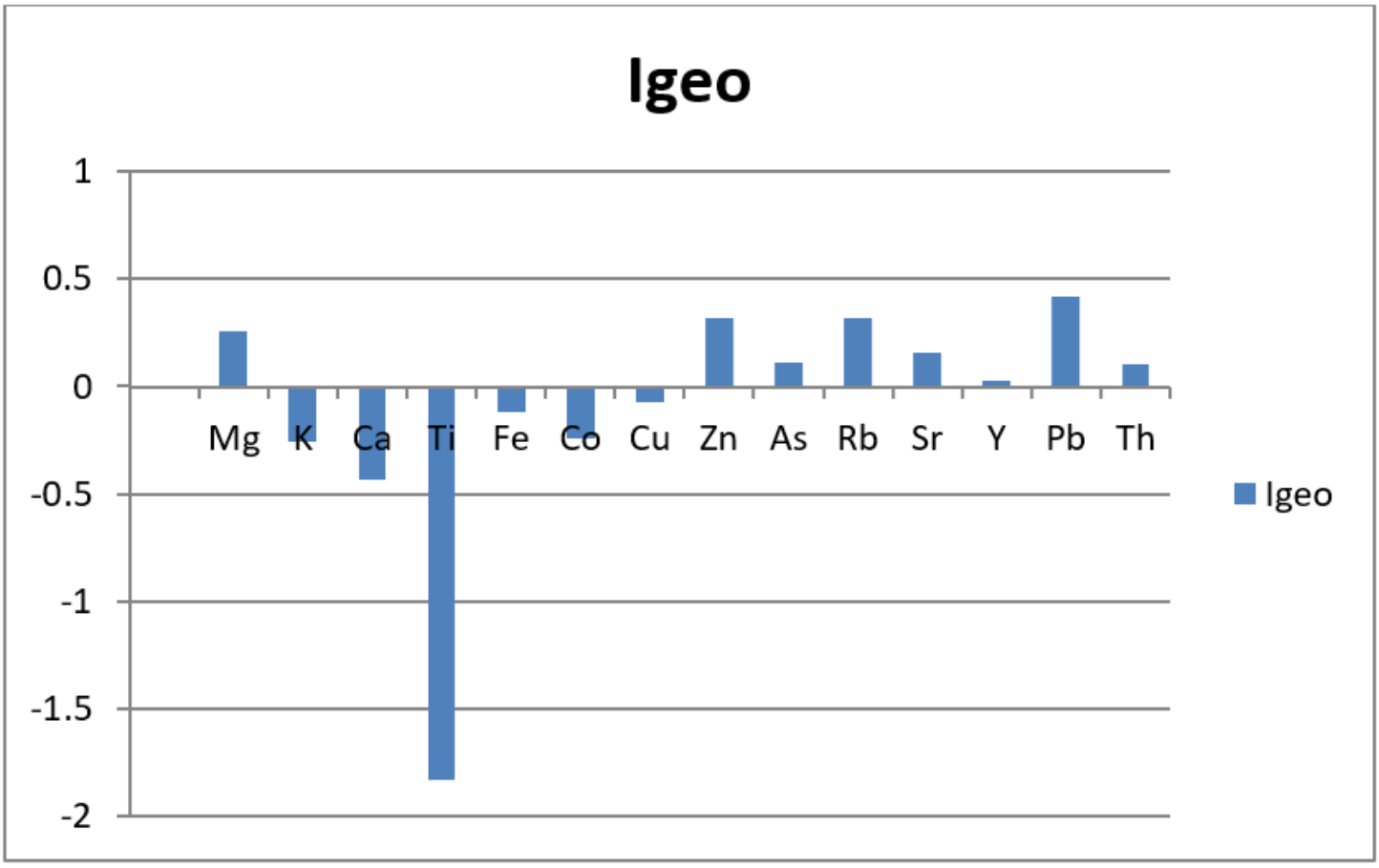

Figure 5

The degree of metal pollution of soil samples according to the Geo-accumulation index (Igeo).

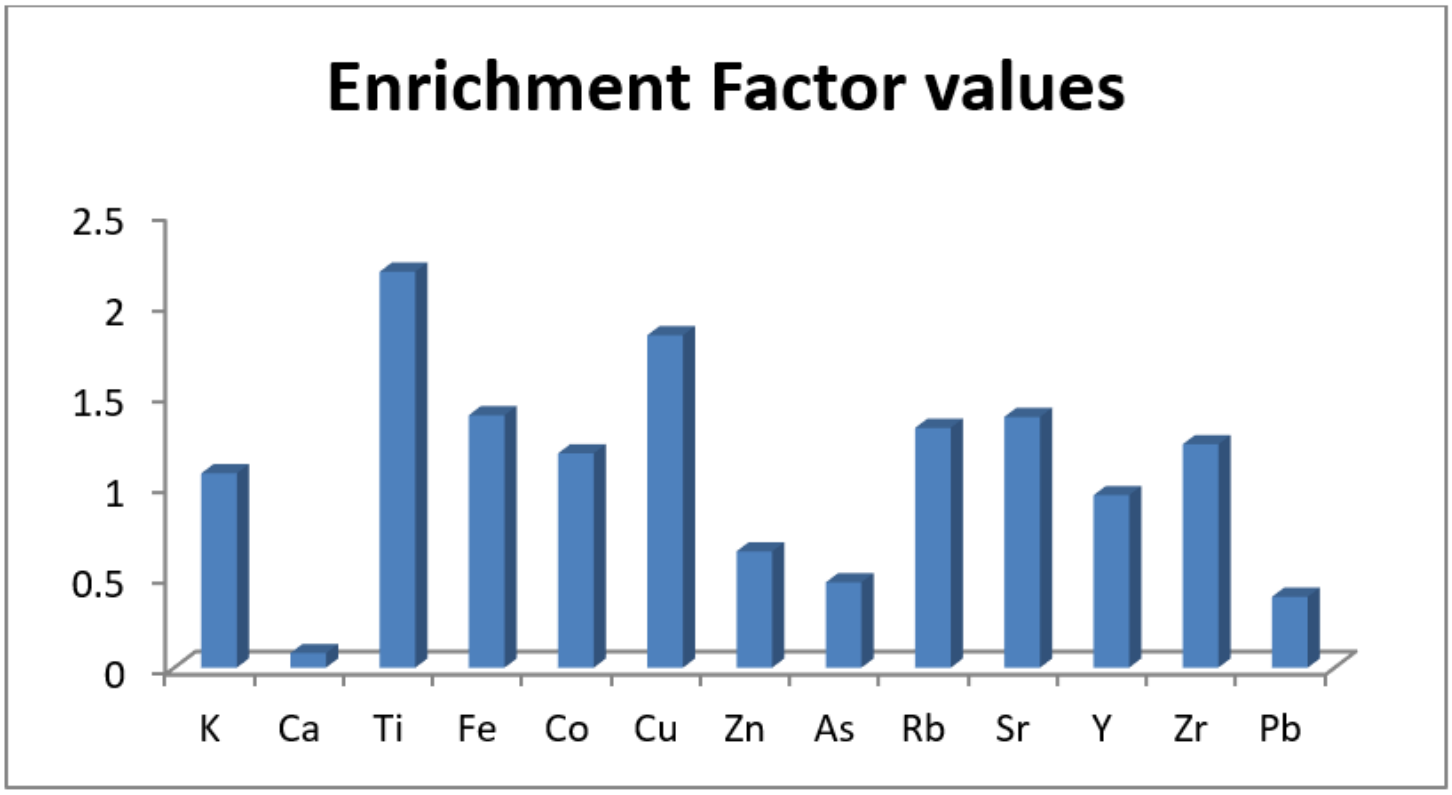

Figure 6

Enrichment Factor value (EF) for Soil Samples of Jamuna fertilizer area

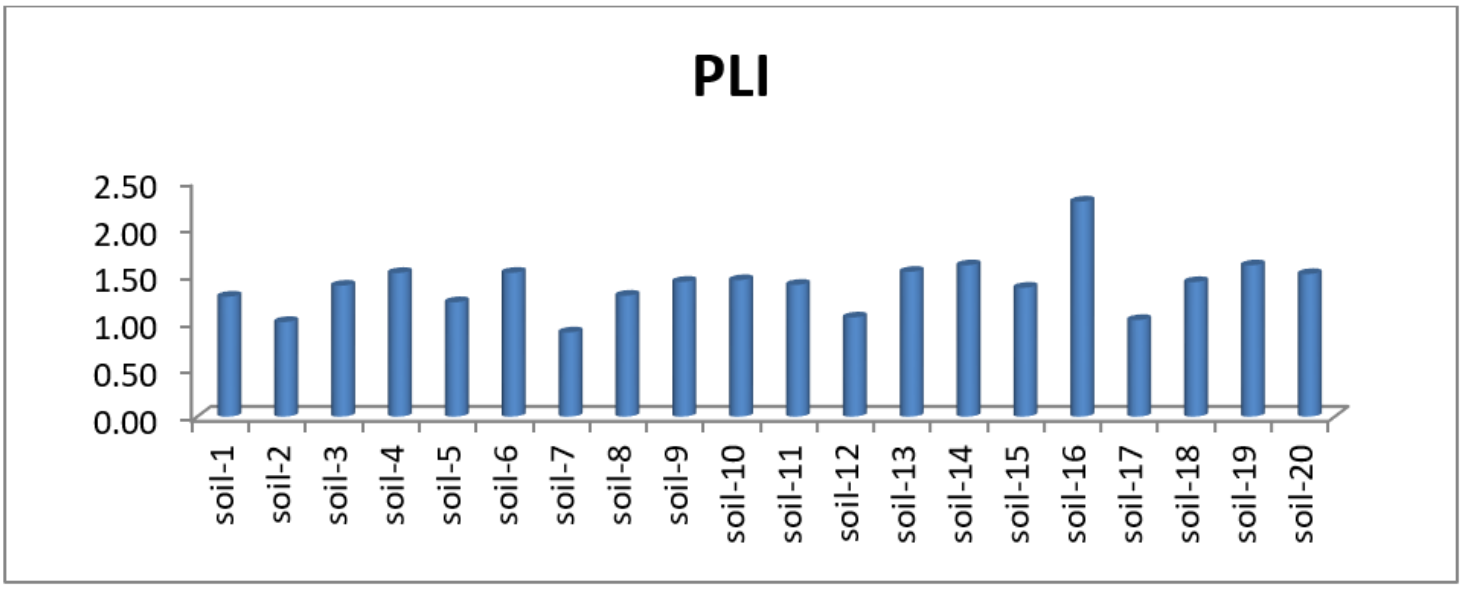

Figure 7

Pollution Load Index (PLI) of soil of Jamuna fertilizer area