The Comparison of Three Environmental Metrics for Cd, Cu, and Ni in the Agricultural Region of the Mid Continent of USA

Almesleh A.A Najwah [1]*   Goodell Philip [2]*

1. Program of Environmental Science & Engineering, University of Texas at El Paso
2. Department of Geological Science, University of Texas at El Paso

Abstract

Enrichment factor (EF), potential ecological risk assessment (PERI), and geoaccumulation (I geo) were employed to measure degree the of contamination Cd, Cu, and Ni in soils in Iowa (IA), Kansas (KS, and Nebraska (NE). Cd and Cu were measured as minimal enrichment and low risk using EF and PERI indexes. This study aims to study the regional distribution of chemical elements to determine the source of the elements and which evaluation tools may be applied to determine the quality and the health of the soil. The presence of significant concentrations of different biologically active chemical substances, such as agricultural additives can affect the status and functioning of the soil microbial biogenesis, soil fertility, and human health. Nevertheless, Cd measured uncontaminated to moderately contaminated while Cu, and Ni indicated uncontaminated (I geo $\leq$ 0) in the soil. EF of Cd is the highest EF of three heavy metals, Cd > Cu > Ni. The highest value of EF of Cd is observed in KS (1.65) followed by NE (1.25) and IA (1.22). However, enrichment degree of Cu is approximately similar in IA (1.11) and KS (1.01) while enrichment degree of Ni is lowest and its average in NE (1.07), IA (0.76, KS (0.82), and NE (0.92). Igeo showed high value Cd estimated at 0.36 in KS followed by 0.29 in NE and 0.18 in IA, which indicate to the possibility of the soil contamination with the Cd originated from human inputs. In addition, high value of Cu in IA in the soil is sourced from human applications as well. PERI showed serious ecological risk pollution of Ni in the soils of IA, KS, and NE. According to the evaluating standard of PERI, Ni is classified as a very high risk in IA (2784.5), in KS (1883.1), in NE (1154.6) while Cd and Cu are estimated as low risk of soil contamination.

Keywords: soil chemistry, chemical elements, soil contamination, PERI, EF, I geo, geochemical mapping, Regional Geochemical Mapping (RGM).

DOI: 10.7176/JEES/10-6-09

Publication date: June 30th 2020

1. Introduction

The aim of this study is evaluate potential chemical loading of Cadmium (Cd), Copper (Cu) and Nickel (Ni) using various contamination indices: (i) enrichment factor (EF), (ii) potential ecological risk index (PERI), and (iii) geoaccumulation (Igeo), that have been used for determining the most effective tool to evaluate the long-term pollution in the soil. The USA has a National Geochemical Database, and a part of that data (Smith *et al*., 2014) is a soil survey containing samples from different soil horizons.

In this study, three indexes are used and compared to estimate the soil contamination in Mid-Continent of USA. The spatial distribution maps are created to discover the hotspots or anomalies of Cd, Cu, and Ni. Then, observation is made of any relationship between chemical hotspots and independent air and land maps published in the Toxmap website (http://toxmap.nlm.nih.gov).

Regional Geochemical Mapping (RGM) documents and interprets the surface geochemistry of the earth. This knowledge is useful in environmental issues and resource exploration. Data may be acquired at different scales (samples per square kilometer), cover different areas (1. Small target, 2. State size, 3. Country wide), and include different chemicals (40 chemicals is possible).

Environmental scientists search for metrics to determine relative environmental danger, risk, or hazards from chemicals (Dartan, et al, 2015., Chen et al., 2016., Zang, et al., 2017). Numerous parameters or criteria have been proposed to make such measurements, and several are in frequent use (Zhiyuan et al, 2011; Andre, 2012; Edwin, 2013; Naveedullah et al, 2013; Alghobar & Suresha, 2015; Dartan, et al., 2015; Nweke & Ukpai, 2016; Chee Poh & Tahir, 2017; Davoodi et al., 2017). No one parameter has distinguished itself as notably the best, and uncertainty exists as to their relative values.

The present study selects a large area where geologic variables are reduced and where potential impacts by man have minimum variability. Thus, study of traditional environmental issues (Desaules, 2012; Edwn, 2013; Alghobar & Suresha, 2015; Nweke & Ukpai, 2016) can be augmented by comparison of chemical contamination metrics.

2. Study Area

A portion of the mid-continent of the USA consisting of the Iowa (IA), Kansas (KS), and Nebraska (NE) is the study area. The National Geochemical Database presents multielement chemical data of this region which will

here be used to study the results of agricultural and industrial activities (Fig.1). The study area is an agricultural regions and farmland covers 99% of IA and lesser areas in KS and NE.

The intense agricultural productivity in this region results in many agricultural factories and processing plants, specifically one's devoted animals and processing of animals to prepare them to the human consumption. Iowa is one the of agriculturally most industrial areas in USA. In Kansas, food processing is the second activity in the state includes flour-milling, animal feed, meat-packing plants. The largest industry in Nebraska is food manufacturing including meat processing (www.newsmax.com).
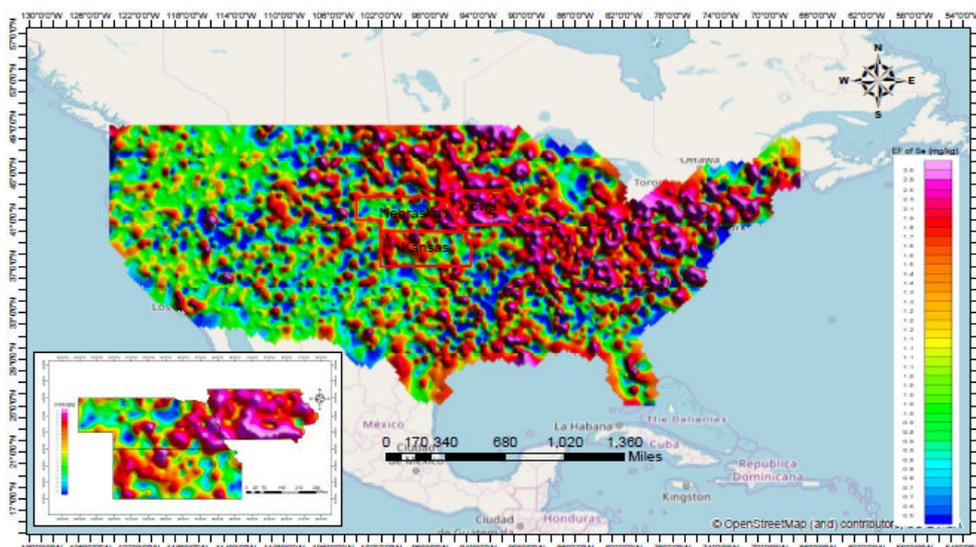

Fig.1 Map shows area of study and soil geochemistry and spatial distribution of chemical concentrations in United States (USGS data project) (Smith et al., 2014).

3. Materials and Methods

3.1 Soil Sampling and Analysis

The data used in this study was extracted from the National Geochemical Database of the United States Geological Survey (www//minerals.usgs.gov/science/soil-geochemical-landscapes) (Smith *et al*., 2014), which includes the chemical methods of analysis of the several chemical elements. The samples were collected from three states: 91 samples from IA, 132 from KS, and 130 samples from NE. These are soil samples which were collected from three horizons (0-5cm, A horizon, and C horizon). The topsoil and C. horizon were used here.

3.2 Statistical Analysis of data

Descriptive statistics and ANOVA multivariate analysis using Tukey was used to estimate the variance between the means of the analyzed EF, I geo, and PERI. Duncan's Multiple Range Test (DMRT) was carried out to test the differences between means (significance level<0.05). The means and the standard deviations (SD) were determined. The standard statistics of metal concentrations are given and compared by analysis of variance (ANOVA) followed by the Tukey's test at the 5% level. Pearsons correlation matrix was employed to identify the relationship between the chemical elements, which indicate a statistically significant difference between the means of the soil elements among the states and within the states (P<0.05).

Chemical spatial distribution maps of each single metal concentration were created to enable the visualization of the data and identify the differences and similarities between the spatial distributions of heavy metals in the soils of the three states. Osais Montaj was the geosoftware used to create the geochemical maps.

3.3 Estimation of Contamination Level

Many methods have been developed to quantify the degree of contamination in environmental studies. In the present study three states in the midcontinent of the USA have been selected to pursue these questions. Numerous methods are in use to quantify soil chemistry quality. Three of them in recently use are employed here, so as to compare results. The current study utilizes three methods for estimating the soil contamination including Enrichment Factor (EF), Potential Ecological Risk Index (PERI), and geoaccumulation (Igeo). Three metals, Cd, Cu, and Ni have been selected for investigation on the basis of their known toxic potential and of having a reported MPL (maximum permitted limit), and past history of contamination. Three states have been selected, IA, KS, and NE. The intense agriculture of Iowa diminishes in western KS and NE; ranchland and less rain become the situation. No mining of these metals has ever taken place in these states.

The selection of background is a variable and a controversy. Global average shale chemistry is a frequent fallback. The data set under use here sampled three soil horizons at each sample sites, thus it is fortunate that the C horizon data is present and is what will be used as background. Histograms and standard statistic parameters lead towards a better understanding of the data. Multivariant statistical analysis illustrates the geochemical groupings inherent in the samples. The three measures of relative contamination are now presented with equations. Table 1 compares their scales of risky, measurement, and contamination.

3.3.1 Enrichment Factor (EF)

EF is calculated as a ratio of element concentration in the soil, normalized to a reference concentration, Ti. The content of heavy metals is measured on a mass basis. The enrichment factor is calculated to measure the degree of the element enrichment of heavy metals using the formula expressed as:

$$\text{Enrichment Factor (EF)} = \frac{(C_i/C_{Ti})\ sample}{(C_i/C_{Ti})\ background}$$

(C_i/C_{Ti}) sample is the ratio of mean of the target element to Ti concentration (C_{Ti}) in the soil sample, and (C_i/C_{Ti}) background is the ratio in the target element in C-horizon to C_{Ti}. Ti is here considered a conservative element, meaning that it is relatively immobile. Concentrations of the C layer are here taken as the natural background or bedrock value instead of its concentration in the crust or shale as used elsewhere (Barbieri, 2016). The degree of chemical loading is evaluated using the criteria shown in Table 1. Numerical values of EF are then classified into degrees of chemical loading, equivalent to degrees of soil contamination (Jiao et al.,2015).

3.3.2. Potential Ecological Risk Index (PERI)

Potential Ecological Risk Index (PERI) is a tool to estimate the degree of heavy metal loading in soils. The equation of PERI is calculated as a sum of times the concentration the risk index of individual risk indices of heavy metal.

$$\text{PERI} = \sum_{i}^{n}(\text{TRF X CF})$$

What are i and n

CF is the reported concentration, and TRF is toxic response factor that is the environmental response to the contaminant. A weighting factor (Toxic Response Factor) is known also as relative toxicity for heavy metals. Each potential contaminant has its own value, which are As = 10, Co = 5, Hg = 40, Ni = 6 (Darko et al., 2017), Mn = 1 (Xu et al., 2008, Soliman et al., 2015), , Cd = 30, Cr = 2, Cu = 5, Pb = 5, and Zn = 1(Hakanson, 1980, Jiang et al., 2014, Darko et al., 2017). The degree of ecological risk for each element can be determined according to PERI classification as it shown in Table 1 (Darko et al, 2017).

3.3.3 Geoaccumulation (I geo)

The accumulative index "I_{geo}" is a geological assessment that is widely used to measure the magnitude of heavy metal loading related to soils (Muller (1969). I_{geo} was used to measure the extent of heavy metals or indication of extra input by human to the soil. Many researchers applied "I geo" index by Muller (1969) to assess different heavy metal contaminations such as Abrahim and Parker, 2008; Varol, 2011; Nweke and Ukpai, 2016; Izah et al., 2017; Muzerengi, 2017; Huang et al., 2017; Mehr et al., 2017.

The values of geo accumulation (I_{geo}) index are determined by calculating the base 2 logarithm of the metal concentration of metal divided by its background concentration. To quantify the degree of heavy metals contamination, the mathematical equation proposed by Muller (1969) is calculated as follows:

$$I_{geo} = \log_2 \frac{C_n}{1.5\ X\ B_n}$$

C_n is the average concentration of metal in the soil (measured concentration of the examined metal), and B_n is the standard concentration of the metal (geochemical background concentration of given metal in the crust or reference value of the metal "n"). The factor 1.5 is the background matrix correction factor for minimizing the impact of possible variations in the standard values. It is used because of the possible variations in background values for a given metal in the environment as well as very small anthropogenic impacts that may be attributed to lithologic variations or impacts in the soils. As such, it is kind of a correction factor. Muller (1969) categorized geo accumulation index into seven class indicators that are used to classify the degree of metal contamination. According to the criteria, $I_{geo} \leq 0$ indicates the uncontaminated soil. Values 0-1 indicate to un-polluted to moderately polluted soil while values 1-2 indicate moderately polluted soil. Values 2-3 indicate moderately or strong polluted soil. Values 3-4 indicated to strongly polluted soil. Values 4-5 is a sign of strongly to extremely contaminated soil. Values >5 show extremely polluted soil. The classification of Igeo is shown in Table. 1.

Table. 1 Comparison of contamination chemical loading, or degree of contamination for the three metric, enrichment factor (EF), potential ecological risk index (PERI) classes, geo accumulation (Igeo) (EF= Reference: Jiao et al (2015), Igeo= Muller (1969).

EF value	Class	Designation of soil quality (enrichment level)
< 1	0	no enrichment
1-2	1	depletion or deficiency to minimal enrichment
2–5	2	moderate enrichment
5–20	3	significant enrichment
20–40	4	very high enrichment
> 40	5	Extremely high enrichment

PERI value	PERI class	Designation of soil quality (PERI)
<40	0	low risk
≤ 40 < 80	1	moderate risk
80 ≤ PERI < 160	2	considerable risk
160 ≤ PERI < 320	3	high risk
≥ 320	4	very high risk

I geo Value	I geo Class	Designation of soil quality (Pollution Intensity)
≤0	0	Uncontaminated
0-1	1	uncontaminated to moderately contaminated
1-2	2	moderately contaminated
2-3	3	moderately to strongly contaminated
3-4	4	strongly contaminated
4-5	5	strongly to extremely contaminated
≥5	6	extremely contaminated

4. Results and discussion of estimated contamination level

It should be emphasized that the heavy metals can be accumulated in the soil, and then can be absorbed by the plants and passed to human and animals as food sources. For several reasons, long term accumulations of heavy metals in the soil can also affect seriously the soil biota. In some cases, the areas of overloading of heavy metals in the soil are not related to industrial applications, urban activities, and others. Moreover, all these regions have been subjected to intensive agricultural anthropogenic applications. Some of the regions with high concentrations of Cd, Cu, and Ni in the surface soils are mostly far away from the industrial applications, which infer to anthropogenic agricultural sources in these areas. This is evident when point source ToxMaps of the USEPA are discussed below.

In the land use maps of Iowa, Kansas, and Nebraska, the regions are considered as agricultural regions rather than industrial regions, so some heavy metals may be originated from anthropogenic applications specifically overloading of chemo agricultural substances. This study has revealed that there is direct connection between human activities and heavy metal contamination due to metal loading. The soil average we selected is higher than the average of the states, but in each state, there are variabilities. There are high and lower areas in the spatial distribution. Local contamination was investigated.

Table (2) Standard statistics of the chemical data (USGS) used in this study. This input includes soil horizons A, B, and C. Units are ppm. Maximum (Max), minimum (Min), standard deviation (SD)

	IA			KS			NE		
Chemical	Cd	Cu	Ni	Cd	Cu	Ni	Cd	Cu	Ni
Max	0.6	95.2	31.2	2.1	48	42	0.9	48	41.5
Min	0.1	2.9	4.6	0.1	3.7	3.1	0.1	2.3	1.7
Average	0.32	21.08	20.36	0.41	15.78	16.04	0.30	12.96	11.67
SD	0.13	14.13	5.26	0.31	6.24	7.07	0.21	8.13	8.20
N= 348									

4.1 Enrichment Factor (EF)

Discussed above are three frequently used measures of chemical contamination or normality. Numerical values are produced, the range of values is subdivided, and each subdivision is given written numerically destination of soil quality, a quantitative name of degree of contamination. These are given in Table 1. Input data is summarized in Table 2, for our three chemicals of interest Cd, Cu, and Ni, for our three states of interest (different columns), for 348 soil samples sites. The numerical results of the above activities are summarized in Table 3. Figure 2 presents a graphical depiction of three different metric values on vertical axes by state on the X axis, with each chemical designated separately. Special characterization of these data is presented in Figures 2, 3, and 4, and will be discussed subsequently.

The enrichment factors of heavy metals in the soils of three states are shown in Table 3, they vary as Cd > Cu > Ni. The enrichment degree of Cd is the highest. The highest value of EF of Cd is observed in KS (1.65) followed by NE (1.25) and IA (1.22). However, enrichment degree of Cu is lower than Cd, and it is approximately similar in IA (1.11), and KS (1.01). Enrichment degree of Ni is lowest and its average in NE (1.07), IA (0.76, KS (0.82), and NE (0.92) (Table. 3 & Fig.2a). The maps of EF are shown in Fig. 2a, however, there is very low correlation coefficients between the three heavy metals.

4.2 Potential Ecological Risk Index (PERI)

PERI is a simple and precise method that can be used for evaluating the geographic and environmental features of heavy metals in the soil. There is a serious ecological risk pollution of Ni investigated in the soils of IA, KS, and NE. According to the evaluating standard of PERI, Ni is classified as a very high risk in IA (2784.5), in KS (1883.1),

in NE (1154.6). Cd and Cu are estimated as low risk assessment according to PERI criteria (Table. 3 & Fig.2b). There is no correlation between the three chemicals according to PERI index, which show that these chemicals come from different sources.

4.3 Geoaccumulation (I geo) Index

According to the calculation results of I geo (Table 3), the index of Cd is the highest, its maximum value is 0.36 in KS, followed by 0.29 in NE, and 0.18 in IA (Table 3 & Fig. 2c), which reveals the possibility of the contamination in the soil with the Cd originating from human applications (Table 3). The correlations of three chemicals are very low, which indicate that the sources of these chemicals are different and mostly they are not natural sources.

Table. 3 Enrichment Factor (EF) , potential ecological risk index (PERI), and geo accumulation (Igeo) in Iowa, Kansas, and Nebraska.

| EF						PERI				I geo			
Element Index	State	N	Mean	Std. Deviation	Degree of EF	Element Index	Mean	Std. Deviation	Degree of PERI	Element Index	Mean	Std. Deviation	Degree of I geo
EF_Cd	IA	91	1.2235	0.7461	Minimal enrichment	Cd_PERI	6.3307	4.8361	low risk	Igeo_Cd	0.1840	0.7672	uncontaminated to moderately contaminated
	KS	127	1.6524	1.0887	Minimal enrichment		5.1210	2.0056	low risk		0.3607	0.7220	uncontaminated to moderately contaminated
	NE	130	1.2504	0.6026	Minimal enrichment		6.0683	3.4705	low risk		0.2919	0.6464	uncontaminated to moderately contaminated
	Total	348	1.3901	.8658	Minimal enrichment		5.7912	3.5034	low risk		0.2888	0.7086	uncontaminated to moderately contaminated
EF_Cu	IA	91	1.1181	.5916	Minimal enrichment	Cu_PERI	38.9651	24.0996	low risk	Igeo_Cu	0.0520	0.6185	uncontaminated to moderately contaminated
	KS	127	1.0138	0.2742	Minimal enrichment		48.4621	30.5113	low risk		-0.1072	0.4215	uncontaminated
	NE	130	1.0770	0.4144	Minimal enrichment		40.0530	19.2140	low risk		-.00082	0.6553	uncontaminated
	Total	348	1.0647	0.4286	Minimal enrichment		42.8373	25.3837	low risk		-0.0286	0.5723	uncontaminated
EF_Ni	IA	91	0.7632	0.2191	no enrichment	Ni_PERI	2784.5055	1176.9914	very high risk	Igeo_Ni	-0.3320	0.5382	uncontaminated
	KS	127	0.8220	0.2508	no enrichment		1883.1386	1804.1186	very high risk		-0.3714	0.5202	uncontaminated
	NE	130	0.9264	0.4096	no enrichment		1154.6581	1454.5122	very high risk		-0.1358	0.6895	uncontaminated
	Total	348	0.8457	0.3196	no enrichment		1846.7073	1654.7568	very high risk		-0.2731	0.6014	uncontaminated
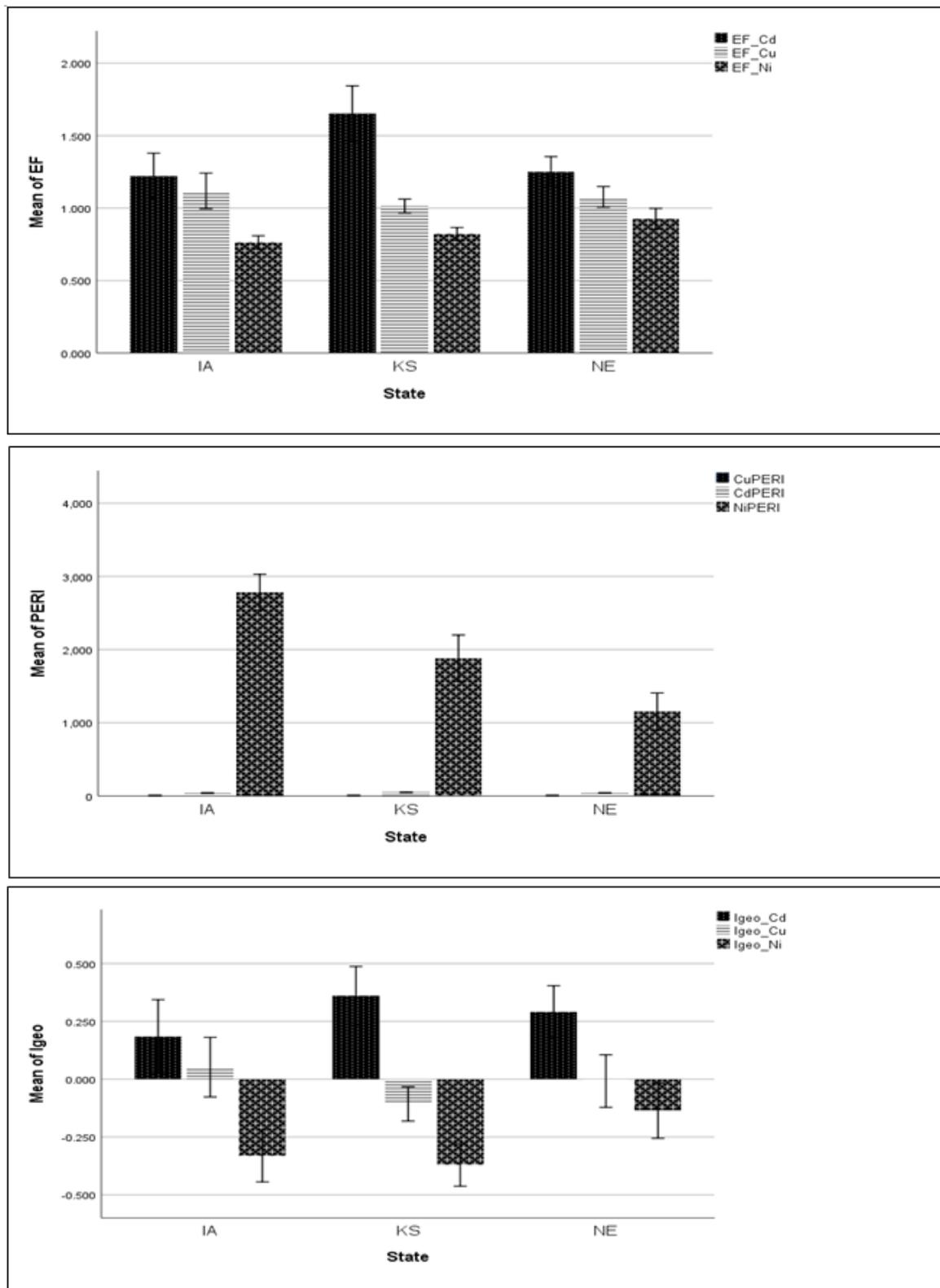
Fig. 2 (a, b, c) Enrichment factor (EF), Geo-accumulation (I geo), Potential ecological risk index (PERI) values of individual heavy metals in surface soil in the study area.

At the initial stage of investigating new data, there are descriptive products which describe the data, and most often there are proposed filters to that data. Histograms and standard statistic parameters, and correlation coefficients, lead towards a better understanding. Multivariate statistical analysis illustrates the paragenetic/geochemical groupings inherent in the samples.

Spatial analysis is initially different. Description, when necessary, initially mimics or is the description of an

anomaly map. Description may be carried out in a fashion similar to a topographic map, describing hills, valleys, etc. From this perspective, the following terms are defined for the generalized description of this special variable, in geology, these interests are called geomorphology. Background = 0 (zero), it is important for there to be an area where zero or close to zero chemical concentrations are present. This was the case in the Dunes in northwest Nebraska. This large region of wind-blown sand in largely quartz and clay and is not and never has been under cultivation. It serves as a region of near zero values for most chemical constituents. However, sometimes unexplained anomalies exist, such as Se. Regional plateaus are regions of broad non-zero, relatively uniform, and anomalies are interpreted to be of agricultural origin, from fertilizers and additives. Ridges and basins are linear anomalous features of positive (ridges) or negative (basins) values. Grabens and horsts are alternative parallel valleys and uplifts. Moreover, embayments are entries into a regional plateau or other feature, which may merge with the other features. Dimples are site specific, circular anomaly, in addition, on a fertilizer derived regional plateau dimples may be towns, within which fertilizer nor additives are not applied (negative anomaly). Otherwise, dimples as positive anomalies are point sources due to industrial activity. However, boundaries may consist of large value changes over short distances, as measured in general perpendicular to trend of boundary. Alternatively, perpendicular to the trend of the shape the rate of change of the measurement is relatively slow.

Table. 4 Comparison between correlations of EF, I geo, and PERI of the Cd, Cu, and Ni.

EF - Correlations		Cd	Cu	Ni
N = 348				
Cd	Pearson Correlation	1	0.094	0.097
	Sig. (2-tailed)		0.080	0.072
Cu	Pearson Correlation	0.094	1	.473**
	Sig. (2-tailed)	0.080		0.000
Ni	Pearson Correlation	0.097	0.473**	1
	Sig. (2-tailed)	0.072	0.000	
**. Correlation is significant at the 0.01 level (2-tailed).				

PERI - Correlations		Cu	Cd	Ni
Cu	Pearson Correlation	1	0.281**	-0.161**
	Sig. (2-tailed)		0.000	0.003
Cd	Pearson Correlation	0.281**	1	-.088
	Sig. (2-tailed)	.000		0.101
Ni	Pearson Correlation	-0.161**	-0.088	1
	Sig. (2-tailed)	0.003	0.101	
**. Correlation is significant at the 0.01 level (2-tailed).				

I geo - Correlations		Cd	Cu	Ni
N = 348				
Cd	Pearson Correlation	1	.276**	0.253**
	Sig. (2-tailed)		.000	0.000
Cu	Pearson Correlation	0.276**	1	0.704**
	Sig. (2-tailed)	0.000		.000
Ni	Pearson Correlation	.253**	0.704**	1
	Sig. (2-tailed)	.000	.000	
**. Correlation is significant at the 0.01 level (2-tailed).				

5. Spatial distribution of heavy metals using Enrichment factor (EF)

The distribution maps of the three metrics Cd, Cu, and Ni are presented in Figures 3, 4, and 5. Some of these zones with high metric values may be related to agricultural, anthropogenic inputs. These areas have been subjected historically to intensive agricultural inputs. The distribution maps of Cd show moderate value of 4.8 in eastern of IA and KS, while in NE, the high value was observed in southern part of the state (Fig. 3a) that indicate an anthropogenic source. The low value (0.6) was concentrated in the west of IA, KS, and NE, in addition to northern NE (Fig. 3a). An extended two domains are in the north of NE and south of KS (in the border), indicated that high Cd values are attributed by human inputs.

One of the major anthropogenic sources of Cd is phosphate fertilizers applications. The main deposited of Cd into the soil are atmospheric deposition and phosphate fertilizers inputs that include up to 300 mg Cd/kg (Alloway and Steinnes, 1999). The main sources of Cd released from the air are industrial applications, which increase the amount of Cd from emissions released from anthropogenic applications (IARC, 1993). Direct emissions of Cd are phosphogypsum and other byproduct gypsums, soil waste, residual ashes of combustion, and mine waste dumps (Alloway and Steinnes, 1999). Specifically, Cd sourced mainly from phosphate fertilizers deposited into the agricultural soils (EPA, 1985). It is important to note that high fertilization rate of the soil using triple super phosphate for 36 years caused increasing of Cd content estimated 14-fold in the surface soil (Singh 1994). Phosphate fertilizer is a source of Cd accumulation in the agricultural soil, and there does not appear to be an association between the Cd levels in the surface soil and local geological features in KS and NE.

Significant high values of EF of Cu was investigated with high-calculated values of 5.4 that lay in the range of EF indicator 5-20 (class 3) (Table.1). Three hotspots of EF of Cu extended vertically from north to south in IA. Moreover, two small spots are located in northeast and northwest of IA (Fig.4a). However, there are two regions affected with the metal located in southern NE that continuing to north of KS. Besides this, there are high spots distributed in the north of NE. Furthermore, one high spot is presented in southeast of KS (Fig. 4a). EF values of Ni between 0.4-1.8 in IA, KS, and NE. The EF map of Ni displayed two individual domains in IA, one located in upper half of IA (north), and another located in lower half (south) of the state, surrounded with lower values areas with values of 1.8 (Fig. 5a). The EF calculation showed deficiency or minimal EF the study area. However, two minimal enriched EF regions have been observed in north and south of NE, in addition, one area located in east and south of KS, and one area located in south of IA (Fig. 5a).

6. Spatial distribution maps of heavy metals using geoaccumulation (Igeo)

The soil Igeo values varied in geochemical distribution in different sites, as it was evaluated by Igeo calculation. The maximum geochemical value of Igeo of Cd was 1.12 in the study area. According to I geo spatial maps, the most polluted regions are in west of IA, extended to the east of NE, and in the north of KS (Fig. 3b, 4b, and 5b). An extended two hot spot domains are located in west of IA and east NE (in border connected regions) that

indicated that high Cd concentration is attributed to human activities. Therefore, the agricultural soils in these regions are potentially influenced by Cd loading as it shown in Fig. 3b. Igeo values indicate that the soil was more contaminated than other locations with Cu (Fig. 4b). Significant enriched Igeo of Cu was determined with high calculated values of 1.18 that fall in the range of Igeo signs 1-2 (class 2). Three hotspots of Cu were observed in east of IA (one spot), and west of NE (two spots) (Fig. 4b). The Igeo values lie in the class 2 of the indicators and are interpreted as unpolluted to moderately polluted soils. Most of IA regions have been affected by moderately contaminated soils (Fig.4b). Ni is one of the heavy metals that presented negative inputs into the soil with weakly deepened areas with lower value range in the study area. I geo values of Ni fall in range -2.24 - 0.16. Class 0 in Igeo refers to un-contaminated soil in IA, KS, and NE (Fig.5b). The spatial pattern of anthropogenic applications revealed that hot spots in ToxMaps are not associated with the geochemical maps (Fig. 7a, 7b, 7c). To estimate the anthropogenic inputs in the soil, the point sources of soil and land maps are overlapped with spatial chemical maps to identify the anomalous metal contributions (Fig. 7).

For many, most of Iowa landscape is intensively farmed agricultural regions (Iowa Association of Naturalists, 1998). Some of the chemicals are used for improving and increasing the crops have had remarkable impact on the environment. The impacts of the fertilizers depend on the chemical type and species of the plant, besides other environmental factors such as geographical and physical factors that can be changed yearly from one region to another.

7. Spatial distribution maps of heavy metals using potential ecological risk index (PERI)

The data analysis of PERI showed visual variances with high and low values of the heavy metals in the surface soils. The unique spatial distribution was observed at the local scale categorized by the localized hotspots.

Moreover, high values of Cd PERI were observed (114.3-180) in the soils (Fig. 3c). A massive Cd massive anomaly or plateau is in half of Kansas. These features are potentially related to the anthropogenic applications. For Cu, there are two anomalies, one in Nebraska, Iowa, and another in Dunes in northwest of Nebraska (Fig. 4c). Generally, broad diffuse anomalies and undulations occur except in central Nebraska. An unusual area of low values exists at the north border, and there is a band/zone in the east to southeast across Iowa.

Ni has the highest values of the heavy PERI (1,096.42–12,198.9) that are shown in the chemical spatial maps that trend in some regions mostly across the study area, which are located in most of Iowa and east of Nebraska and Kansas (Fig. 5c).

The spatial distribution patterns showing elevated values are observed in Fig. 5c with values (18.56 – 31.57) in northeast of Iowa and northwest of Nebraska. The unique observation is that the lowest possible levels of Ni in northwest of Nebraska (where the Sand Dunes are located), and western Kansas too. East of 97 18 broad plateau of 2500 with broad 100 mile diameter anomalies. One board anomaly in southeast of Kansas where Zinc is mining is located. Moreover, a negative anomaly is observed in northeast of Iowa.
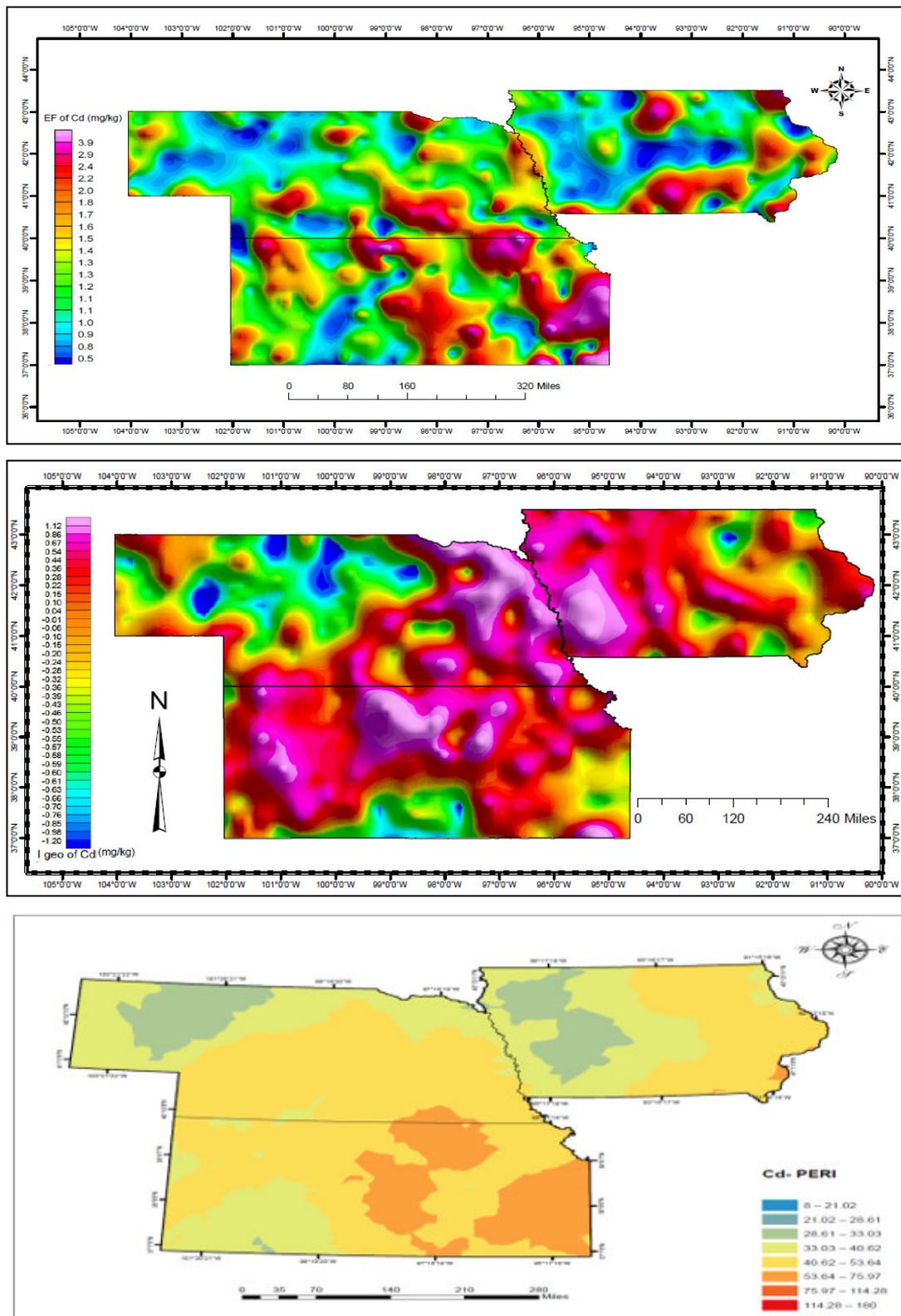
Fig. 3 Spatial distribution maps show (a) EF, (b) I geo , (c) PERI values of Cd in the surface soil in study area.
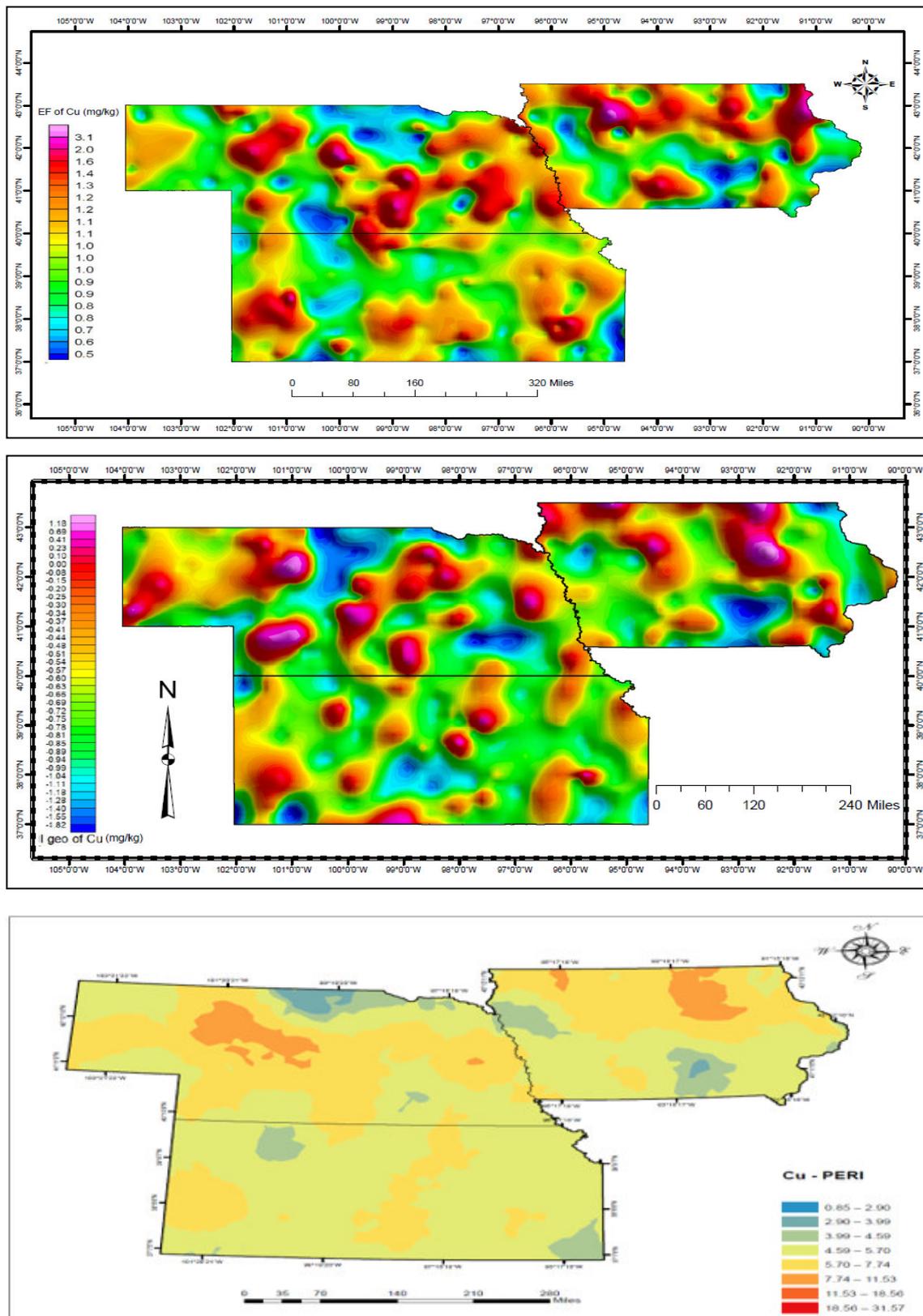
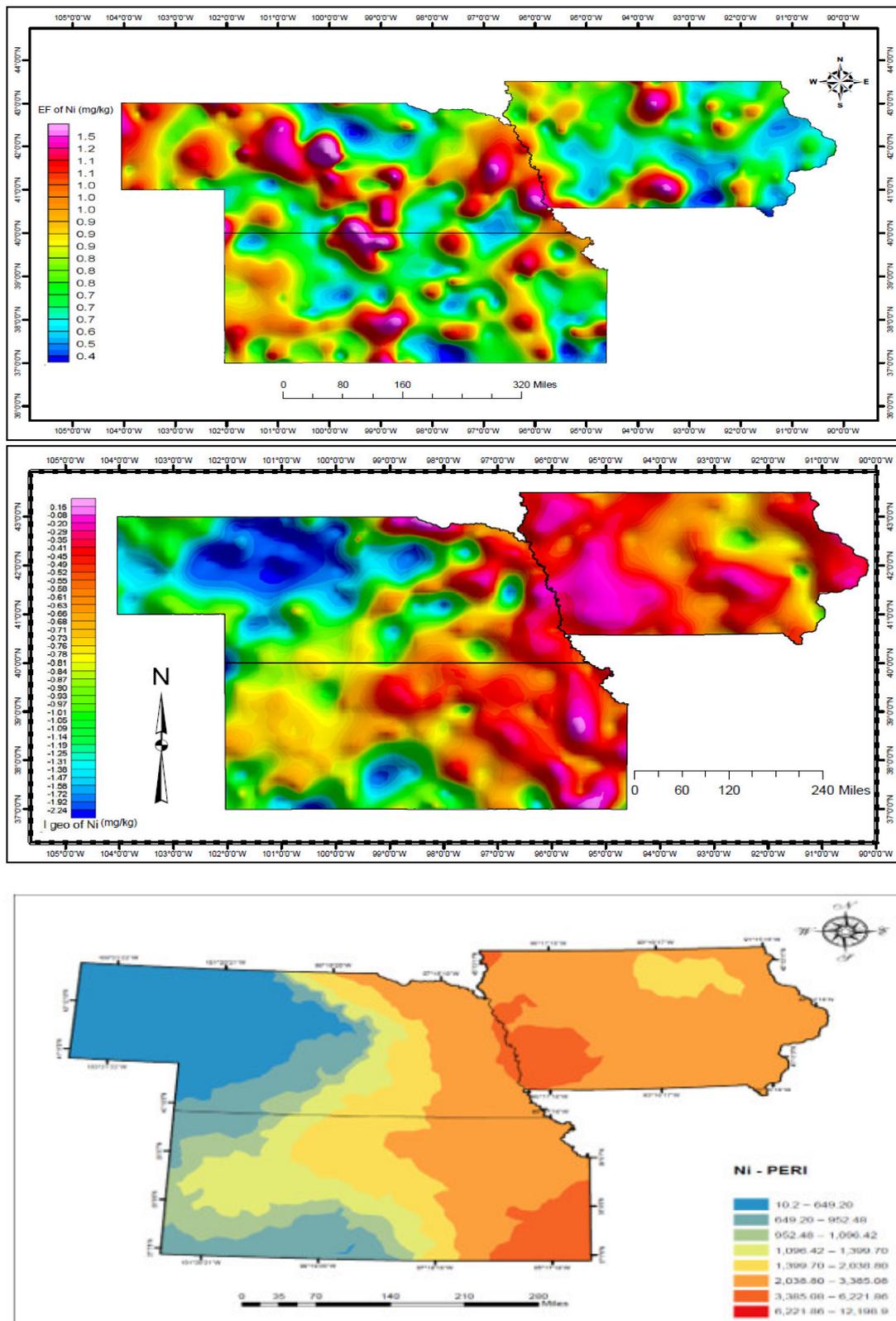Fig. 4 Spatial distribution maps show (a) EF, (b) I geo, (c) PERI values of Cu in the surface soil in study area.

Fig. 5 Spatial distribution maps show (a) EF, (b) I geo, (c) PERI, values of Ni in the surface soil in study area.

8. Pollution source identification of individual heavy metals

For further source identification and assessment of the chemical elements in the soil, the database of heavy metals released into the environment was extracted from the toxic release inventory (TRI) including the toxic chemical releases information and the waste management activities (www.epa.gov/toxics-release-inventory-tri-program,

2017). All industrial group and federal facilities report this information annually to Environmental Protection Agency (EPA). ToxMap is a Geographic Information System (GIS) database, which is operated by EPA. ToxMap provides data on point airborne sources and surface industry sources. ToxMap is from the division of specialized information services of the US National Library of Medicine® (NLM). ToxMap uses maps of the USA to help users visually explore data from the US Environmental Protection Agency (USEPA), Toxics Release Inventory (TRI), National pollutant release inventory (NPRI), and superfund programs with visual projection and maps (http://toxmap.nlm.nih.gov). It helps researchers to generate regional information that show the TRI chemicals released on site into different environments (air, land, water, and by underground injection). The release data are measured in pounds per year. In addition, the toxic chemical amounts are reported which are sent for waste management. These data facilitate identification and color coded release quantities and chemical release data for many years. Moreover, it provides the National Priorities List (NPL) of all chemical contaminants in Superfund sites on the agency for toxic substances and disease registry (http://toxmap.nlm.nih.gov). ToxMap hot spots were compared with the anomalous areas of maps produced here of surface soil chemistry metrics to explore alternative sources of chemicals. Since all the toxic chemicals released are reported for the industrial activities, the other possible sources such as transportation, farming, and households are not involved (http://toxmap.nlm.nih.gov). The consideration of the chemical sources may be from many possible human activities or natural processes. For this reason, the geochemical metric maps were compared with the Toxmap distribution maps of air emission, and soil contamination was considered to help figure out the source of the chemical elements. The geochemical maps using USGS data of the surface soil metric have been created for overlapping these maps with ToxMap as it shown in Fig.6a, 6b, and 6c.

The distribution maps show that no significant air pollution data have contributed to observation here. Many factors have been considered to find out the source of the chemical anomalies. The number of high emissions, the anomalies spots is one. Another factor is the number of the sites varies for each chemical. They are not necessarily to be the same sites. The source of the chemical is different because there are different industrial processes that the sites will vary with chemistry, such as in eastern Kansas. In the consideration of the negative and positive anomalies, in general, all the maps indicated that most of the ToxMap results are close to zero (Figure. 7a, b, c). In the air release map of Cd, the number of Cd releases to air and land are very low. For instance, in the three states Cd release into the air there are only two reported sites. For Cd release into the land, there are also two reported sites. Those sites do not correlate to with any of high values indicated in the maps produced here (Figure. 7 a, b, c). Generally, there are no releases of Cd in the land except only one-point source with value 1 pound. located in the west of IA. No significant Cd releases have been observed in NE and KS (Fig. 7a). The soil anomalies (Fig. 7a) are not associated with the Cd released that is estimated 2-7 pound in the study area into the air. It may be considered that the source of Cd in the soil is anthropogenic land activities fertilizers three slight points are present of Cu released from the air to the soil, and the value of lowest subset increases no more than 6% of the site numbers. These regions are located in southeast of IA and correlated with dominant high Cu regions in geochemical map (Fig. 7b). Cu released into air is 0 - 420 lbs. and 0- 5 lbs. in the land (Fig. 7b).
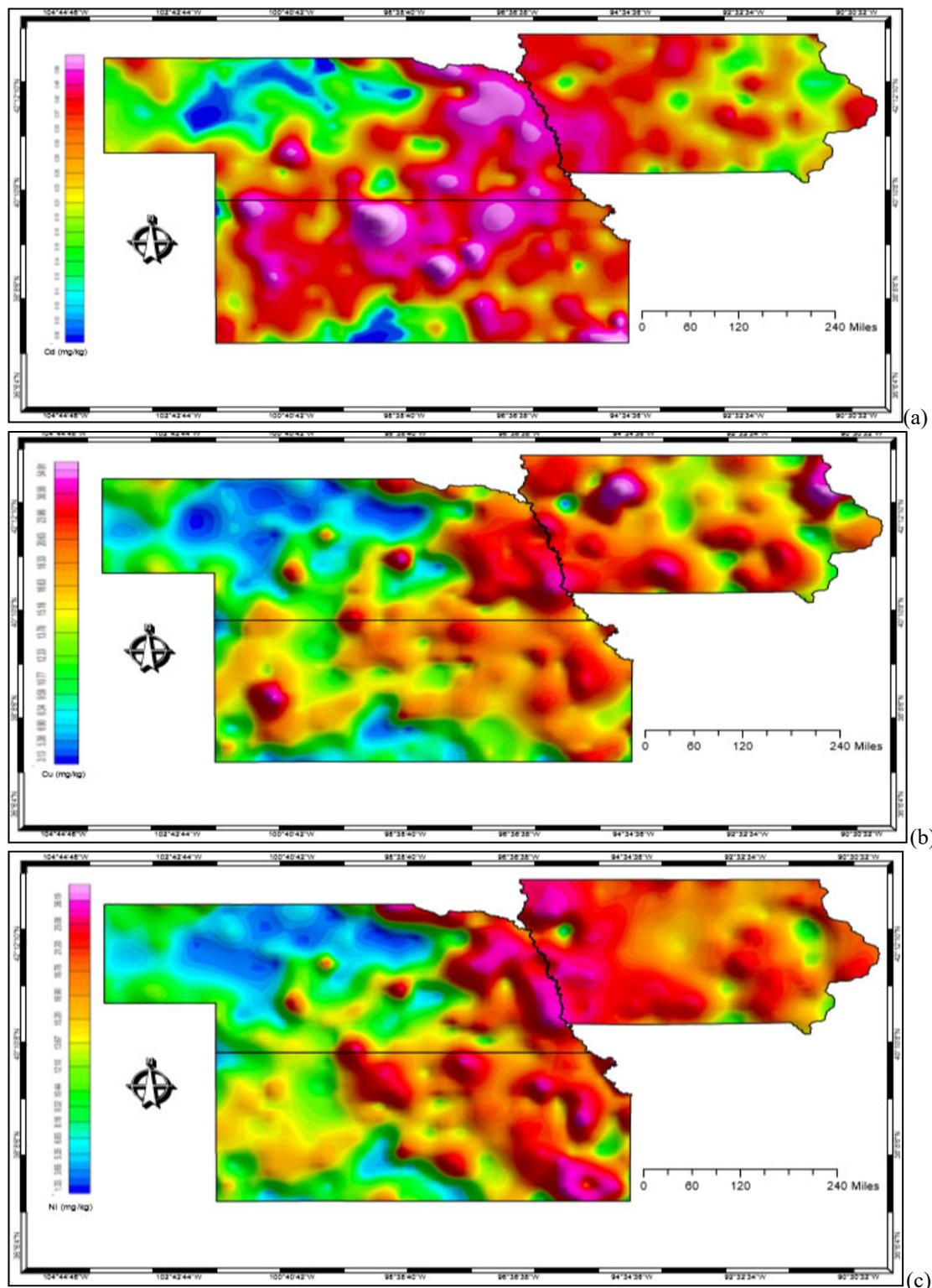
(a)

(b)

(c)

Fig. 6 (a, b, c) Geochemical maps of Cd, Cu, Ni in the surface soil of USGS data (Smith, 2014).

   Partly, by the process of elimination, agricultural practices are what is left. What is the trace element chemistry of fertilizers and additives? No practical interpretation can be made of relationship of Cu anomalies in soil versus the emissions on the land. No correlation has been observed with Ni except minor correlation between soils with air contribution in the southeast and middle of IA, east of KS and NE (Fig. 7c). No soil anomaly and air emissions of Ni have been observed in the west of KS and NE (Fig. 7c). In general, Ni released into the air is 0-1180.9 pounds while it is 0-5 pounds. in the land (Fig. 7c). There is a slight contribution from two air points to the soil anomaly in southeast of IA and KS, however, one point located in east of NE (Fig. 7 ec). Few positive correlations of Ni are observed in south of IA, east of NE and KS ranged 560 – 1180.9 pounds. (Fig. 6c). However,

no correlation has been observed between soil anomalies and land concentrations. A big soil anomaly was observed with Ni in the south of IA (99.3 - 1180.9 lbs.), KS (151-560 lbs.), and NE (9.5- 425 lbs.), but small contribution from the air with low metric values were located in most of IA (0-14 lbs.) and in east of KS (0-10 pounds) and NE (0.01-1 lbs.) and (Fig.6c). These observations show that the source of the chemicals may come from soil anthropogenic activities more than natural sources. There is air contribution and there is no soil anomaly (5.35-6.85lbs) as observed in the south of KS. There were high soil anomaly and low air anomaly regions were observed in southeast, northeast of IA, and east of NE. Point source maps of the three chemicals are given in Figure. 6a, 6b, and 6c had a little to zero influence on the maps generated here. The maps derived from the soil chemistry (www//minerals.usgs.gov) will be described in a manner similar to topographic maps; that is hills valleys and other features. The data must be considered with the histograms at hand. The most important features in the present work are regional plateaus. These plateaus can be interpreted as agricultural additions to the soil because of the wide spread elevated uniform properties.
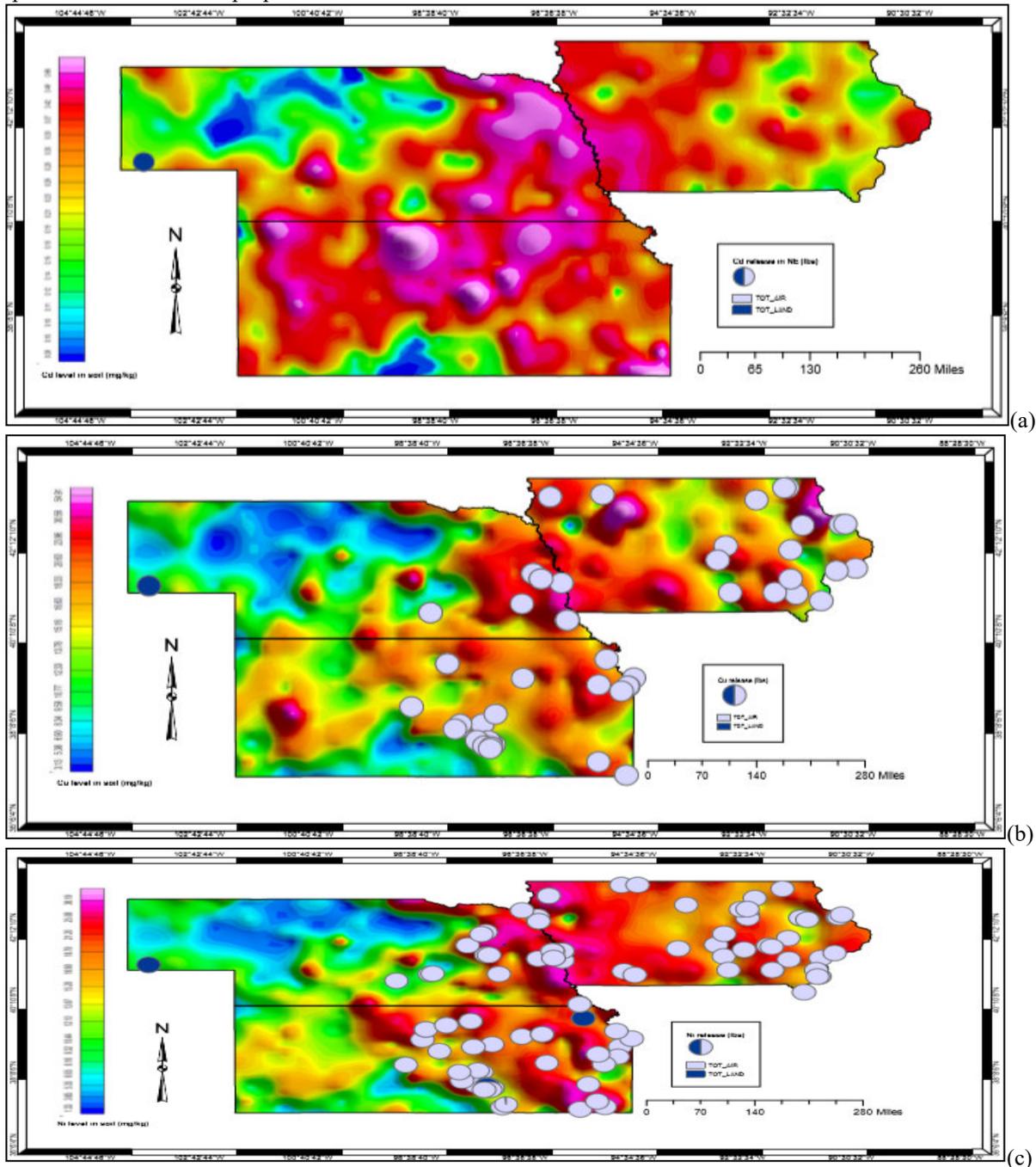

Fig. 7 (a, b, c) Air and land emissions super composed on soil geochemical background maps of Cd, Cu, Ni.

9. Conclusion

1) These results emphasize the multielement character of agricultural applications. Extreme caution is necessary in considering the long-term impacts on the agricultural regions. There is a little research on the overall ecological impacts of the over loading of the chemical fertilizers in the soils. So many techniques can be used for control overloading of the chemicals into the soils, which include the cultural, mechanical, biological, and chemical control in the soils. One method is through reducing the chemical doses used in the soil.

2) Results achieved in this work according to PERI criteria correspond to environmental risk categorized very high risk of Ni and lowest risk of Cd and Cu. However, results show that Ni appeared to be strongly contaminated in the study area especially in Iowa and eastern Kansas and Nebraska. 2) The general pollution degrees of Ni are in the order of PERI in IA (2784.50) > KS (1883.13) > NE (1154.6). Cd and Cu are categorized as low risk according to PERI criteria in the order with low grades while Ni is classified with very high-risk pollution produced by the human activities. According to PERI criteria, Ni has high risk to the soils in the study area. Therefore, the overall risk degrees of PERI of heavy metals are in the order Ni (2784.50) in IA and Cu (48.46) in KS.

3) The spatial distribution maps showed point source contamination of Ni, Cd, and Cu, which can indicate significant anthropogenic applications in the study area. Further study is needed to be understanding the sources and extent of accumulation of heavy metals in agricultural soils in mid-continent of USA to reduce metal loading and avoid long term accumulation of heavy metals.

4) of the three metrics used EF and PERI are more reliable. Igeo contain assumptions which are less realistic.

5. The results from this study can be disseminated in many ways such as examine the influence of geology in the soil elemental concentrations, examine crop type being planted in agricultural soils, estimate the concentration of Cd in the fertilizers in agricultural soils. Moreover, further develop recommendations to study health risk assessment in the midcontinent regions of USA.

10. Reference

Abrahim, G.M.S; Parker, R.J. (2008). Assessment of Heavy Metal Enrichment Factors and the Degree of Contamination in Marine Sediments from Tamaki Estuary, Auckland, New Zealand (2008). Environmental Monitoring and Assessment 136(1-3):227-38.

Alghobar, M.A; Suresha, S. (2015). Evaluation of Nutrients and Trace Metals and Their Enrichment Factors in Soil and Sugarcane Crop Irrigated with Wastewater (2015). Journal of Geoscience and Environment Protection, 3, 46-56.

Alloway, B.J; Steinnes, E. (1999). Anthropogenic Additions of Cadmium to Soils. Cadmium in Soils and Plants pp 97-123.appointment and health risk assessment of trace metals in surface soil of Beijing metropolitan, China. Chemosphere 144 (2016) 1002-1011.

Chen, H; Teng, Y; Lu, S; Wang, Y; Wu, J; Wang, J. (2016). Source

Darko, G; Dodd, M; Nkansah, M.A; Aduse-Poku, Y; Ansah, E; Wemegah, D.D; Borquaye, L.S. (2017). Distribution and ecological risks of toxic metals in the topsoils in the Kumasi metropolis, Ghana. Cogent Environmental Science (2017), 3: 1354965.

Dartan, G; Taspinar, F; Toroz, I. (2015). Assessment of heavy metals in agricultural soils and their source appointment: a Turkish district survey. Environment Monitoring Assessment (2015) 187:99.

Davoodi, H; Garibreza, M; Negarestan, H; Mortazavi, M.S; Lak, R. (2017). Ecological Risk Assessment of the Assaluyeh and Bassatin Estuaries (Northern Persian Gulf) Using Sediment Quality Indices.

Desaules, A. (2012). Critical Evaluation of Soil Contamination Assessment Methods for Trace metals. Science of the Total Environment. 426 (2012) 120-131.

Edwin, A. (2013). Distribution and Enrichment of Heavy Metals in Soils from Waste Dump Sites Within Imoru And Environs, Southwest Nigeria. Journal of Environmental and Earth Science. Vol.3. No.14, 2013.

Essington, M.E. (2004). Soil and Water Chemistry, An Integrative Approach. CRC Press LLC.

Hakanson L. (1980). An Ecological Risk Index for Aquatic Pollution Control, a Sediment-Ecological Approach. Water Res, 1980, 14:975-1001.

Hooda, P. H. (2010). Trace Elements in Soils. John Wiley & Sons Ltd.

http://mrdata.usgs.gov/soilgeochemistry/assets/Lead/OFR-2014-1082-Pb.pdf

http://pubs.usgs.gov/sir/2017/5118/sir20175118_element.php.

http://toxmap.nlm.nih.gov.

https://pubs.usgs.gov/sir/2017/5118/sir20175118_geo.php.

Huang, S.H., Yang, Y., Yuan, C.Y., Li, Q., Ouyang, K., Wang, B., Wang, Z.X. (2017). Pollution evaluation of Heavy Metals in soil near smelting area by index of Geoaccumulation (I_{geo}). Earth and Environmental Science 52 (2017), China.

Izah, S.C., Bassey, S.E., Ohimain, E.I. (2017). Geoaccumulation Index, Enrichment Factor and Quantification of concentration of heavy metals in soil receiving Cassava Mill Effluents in A Rural Community in the Niger Delt Region of Nigeria. Molecular Soil Biology. 2017, Vol.8, No.2, 7-20.

Jiang, X., Lu, W.X., Zhao, H.Q., Yang, Q.C., Yang, Z.P. (2014). Potential ecological risk assessment and prediction of soil heavy metal pollution around coal gangue dump. Natural Hazards and Earth System Science, 14 1599-1610, 2014.

Jiao, X., Teng, Y., Zhan, Y., Wu, J., Lin, X. (2015). Soil heavy metal pollution and Risk Assessment in Shenyang Industerial District, Northeast China. PLOS ONE 10 (5).

Kabata-Pendias, A (2011). Trace Elements in Soils and Plants. Fourth edition. CRC Press, 2011 Taylor and Francis Group, LLC. p.505.

Mehr, M.R., Keshavarzi, B., Moore, F., Sharifi, R., Lahijanzadeh, A., Kermani, M. (2017). Distribution, source identification and health risk assessment of soil heavy metals in urban areas of Isfahan province, Iran. Journal of African Earth Sciences 132 (2017) 16-26.

Muller (1969). Index of geo accumulation in sediments of the Rhine River. Geojournal, 2, pp.108-118.

Muzerengi, C. (2017). Enrichment and Geoacculmualtion of Pb, Zn, As, Cd, and Cr in soils near New Union Gold Mine, Limpopo Province of South Africa. Mine Water and Circular Economy. Lappeenranta, Finland, IMWA 2017. P: 720-727.

Naveedullah, M, Z.H., Chunna, Y., Hui, S., Dechao, D., Chaofeng, S., Liping, L., Yingxu, C. (2013). Risk Assessment of Heavy Metals Pollution in Agricultural Soils of Siling Reservior Watershed in Zheiiang Province, China. Hindawi Publishing Corporation. Vol 2013.

Naveedullah; Hashmi, M.Z; Yu, C; Shen, H; Duan, D; Shen, C; Lou, L; Chen, Y. (2013). Risk Assessment of Heavy Metals Pollution in Agricultural Soils of Siling Reservoir Watershed in Zhejiang Province, China. Hindawi Publishing corporation, BioMed Rsearch International. Vol 2013.

Nweke, M.O., Ukpai, S.N. (2016). Use of Enrichment, Ecological Risk and Contamination Factors with Geoaccumulation Indexes to Evaluate Heavy Metal Contents in the Soils around Ameka Mining Area, South of Abakaliki, Nigeria. Journal of Geography, Environment and Earth Science International. 5 (4): 1-13.

Singh B.R. (1994). Trace element availability to plants in caricatural soils, with special emphasis on fertilizer inputs. Environ Rev 2:133 – 146.

Smith, D.B., Cannon, W.F., Woodruff, L.G., Solano, Federico, and Ellefsen, K.J., 2014, Geochemical and mineralogical maps for soils of the conterminous United States: U.S. Geological Survey Open-File Report 2014–1082, 386 p.

Soliman, N.F; Nasr, S.M; Okbah, M.A. (2015). Potential ecological risk of heavy metals in sediments from the Mediterranean coast, Egypt. J Environ Health Sci Eng. 2015; 13: 70.678 QSD-4

Sumner, M.E. (2000) Hand book of Soil Science. CRC Press LLC.

Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. Journal of Hazardous Materials 195 (2011) 355–364.

www.epa.gov/toxics-release-inventory-tri-program, 2017.

www//minerals.usgs.gov/science/soil-geochemical-landscapes

Xu, Z.Q; Tuo, X.G; Ni, Shijun; Zhang, C.J. (2008). Calculation of heavy metal's toxicity coefficient in the evaluation of Potential Ecological Risk Index. Environmental Science and Technology 31(2):112-115.

Zang, F; Wang, S; Nan, Z' Ma, J; Zhang, Q; Chen, Y; Li, Y. (2017). Accumulation, spatio-temporal distribution, and risk assessment of heavy metals in the soil-corn system around a polymetallic mining area from the Loess Plateau, northwest China. Geoderma 305 (2017) 188-196.

Zhiyuan, W; Dengfeng, W; Huibing, Z; Zhiping, Q. (2011). Assessment of Soil Heavy Metal Pollution with Principal Component Analysis and Geoaccumulation Index. Procedia Environmental Sciences 10 (2011) 1946-1952.