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Geostatistical And Geospatial Distribution Of Multiple Metallic Elements In Agricultural Regions Of The Mid-Continental Usa

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GEOSTATISTICAL AND GEOSPATIAL DISTRIBUTION OF MULTIPLE
METALLIC ELEMENTS IN AGRICULTURAL REGIONS OF THE MID-
CONTINENTAL USA

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By

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2018

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DISSERTATION

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ABSTRACT

Regional geochemical mapping constitute the chemistry of the surface of the earth in a large scale and relatively low sample density. It is widely accepted scientific activity and man uses some cases to identify contamination. In the present study, data present in national geochemical survey database was used to investigate the chemical loading loading of the agricultural soil. In the mid-continent region of the United States. Several traditional parameters were used mainly the enrichment factor (EF), and geoaccumulation index (I_{geo}). Total chemical influence (TCI) maps were used to guide sampling. In addition, regional trace element chemistry of bedrock was created and residual geochemical mapping was initiated. The heavy metals selected for this study include As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn, selected in the basis of toxicity and maximum permitted limit (MPL). Analysis in this study showed that Co, Cu, V, and Zn with high concentrations values (outliers) could be potentially associated with potential anthropogenic applications. Principal Component Analysis (PCA) showed one family has a strong correlation including the elements As, Co, Cr, Ni, and Zn. Maps of loess distribution and glacial encroachment were investigated to test the influence in soil chemistry. Point sourness of chemical emissions were also considered, but except few cases, there were no influences in soil chemical anomalous. The heavy metals in geochemical maps within values 1.4-7.6 investigated anthropogenic outputs from different point sources ranging from moderate to substantially enriched soil EF's.. It is not evident that air releases contributed to heavy metals in soil chemistry. Surprisingly, the results of generated litho-geochemical maps showed different aspects of soil chemistry. The soil chemistry of these states reflects anthropogenic activities. Considering the spatial variations of soil chemistry, approximately 70% of the soil suffered from overloading of heavy metals. Certain biological properties of the soil were determined to test soil fertility. PO_4^{3-} is the most abundant nutrient in

the soil. High values observed in some regions in Midwest of USA implies great chemical inputs by the human rather than natural sources, causing important implications for soil fertility. The results suggest possible long time overloading of fertilizers inputs into the surface soil of agricultural regions in mid-continent of USA.

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LIST OF ABBREVIATIONS

ArcGIS	Arc Geographic Information System
As	Arsenic
B	Boron
BG	Background
C	Carbon
Ca	Calcium
Cd	Cadmium
CF	Contamination factor
CH	C. Horizon
C-horizon	Deep soil layer
Cl	Chlorine
Co	Cobalt
CP	Cumulative Probability
Cr	Chromium
Cu	Copper
Dc	Degree of contamination
DMRT	Duncan's Multiple Range Test
ECDF	Empirical cumulative distribution function
EF	Enrichment Factor
EN	Element name
ER	Enrichment ratio
Fe	Iron
Hg	Mercury
IA	Iowa
ICP-OES	Inductively coupled plasma optical emission spectrometry
I _{geo}	Geoaccumulation
IRGA	Infrared gas analyzer
K	Potassium
K ₂ SO ₄	.Potassium sulfate
KS	Kansas
LGMS	Lithogeochemical Maps
Ls	Limestone
MAC	.Maximum allowable concentrations
Med	.The mean and median
Mg	.Magnesium
Mn	Manganese
Mn	Manganese
Mo	Molybdenum
MPL	Maximum Permitted Limit
N	Nitrogen
NAD1984	North American Datum of 1984
NE	Nebraska
NGS	National Geochemical Survey

NGS	National Geochemical Survey
NH ₄ ⁺	Ammonium
Ni	Nickle
NLM	National Library of Medicine
NO ₃ ⁻	Nitrate
NOAA	National Oceanic and Atmospheric Administration
NPRI	National pollutant release inventory
P	Phosphorous
Pb	Lead
PCA	Principal component analysis
PCC	Pearson correlation coefficients
PCM	Pearson's correlation matrix
PEF	Pedologic EF
PO ₄ ³⁻	Phosphate
ppm	Parts per million or μmol/mol)
ppm	Parts per million
PS	Pseudo sigma .
Q1	One quarter of the data fall below the first quartile
Q2	Second quartile
Q3	Third quartile
RANGRID GX	Random gridding method
RGM	Regional geochemical mapping
RLGM	Residual lithochemical maps
RMD	Robust Mahalanobis distances
S	sulfur
SD	Standard deviation
Se	Selenium
Sh	Shale
SOC	Soil organic carbon
SRR	Soil Respiration rate
SS	Sandstone
T	Time constant
TCI	Total chemical influence
Ti	Titanium
TOC	Total organic carbon
TRI	Toxic release inventory
USDA	United States department of agriculture
USEPA	Environmental protection agency
USEPA	US Environmental protection agency
USGS	United States of geological survey
V	Vanadium
Zn	Zinc

INTRODUCTION

Regional Geochemical Mapping is a scientific endeavor which produces the chemistry of the landscape, that is, the averaged chemistry of a portion of the surface of the earth. Ideally, rock, sediment, and soil samples are taken in the field, and are subjected to multi-element chemical analysis. In the USA, stream sediment data are available for 250,000 samples, excluding Alaska. In that same area, over 8,000 sites were sampled for multiple soil horizons. There are anomalies from both natural and anthropogenic causes and background values are provided for future environmental evaluations. These data bases are rich with information, if you know how to ask the right questions.

Prior work revealed geologically provocative trace element anomalies in stream sediment samples in the mid-west USA (Zumlot et al). When the soil chemistry data became available (Smith et al., 2014) those anomalies were tested (data processed, maps created) again. Anomalies persisted. Why are there widespread anomalies of Y (Yttrium) and several other chemicals in Iowa and throughout the mid-continent of the USA? The regional geology of this area is relatively simple, and there are no known natural mechanisms to concentrate these several chemicals in the types of rocks present in the bedrock, and there are no known mineral deposits. What is the origin of these multiple, large, chemical anomalies? This is the question to which the present study is directed. An additional question is ‘Does this anomalous chemistry effects the soil health, its sustainability? This is a question which can be better understood by using biological parameters.

Answers can be developed by the correct design and execution of a project. The design follows. The biological parameters of interest require the study of actual soil samples, thus

sampling needs to be undertaken. Samples should be taken from the areas of greatest chemical impact, thus the TCI (Total Chemical Influence) parameter is initiated. Chemicals are chosen which have an EPA (Environmental Protection Agency) Maximum Permitted Limit (MPL) so that the concentrations can be normalized. TCI maps can provide sample design, and high and low targets.

Multiple methodologies are present in the study of variations in geochemistry, some suited to particular processes. Sample chemistry is an expression of mineralogy, and human or biological additives. Regional soil and stream sediment geochemical data are amenable and suitable to the use of the Enrichment Factor (EF) and geoaccumulation (I_{geo}). Results are given ranges on a numerical scale with respect to degree contamination. However, caution requires the consideration of the anomaly as naturally occurring feature known as a mineral deposit, or a lesser mineral occurrence, which have specific geochemical fingerprints.

Lacking in the data types of landscape geochemistry is that of bedrock geochemical mapping, particularly when bedrock is deep in the subsurface. In much of the mid-continent of the USA, bedrock is known from water-well and oil field drilling. The stratigraphy is uniform over enormous regions, and the rocks internally contain different facies. Geochemically this results in large ranges of chemical concentrations. Bedrock geologic maps are to be trusted. No database exists on the chemistry of bedrock, thus recourse must be directed to regional geochemical mapping methodology. Global geochemists have arrived at ranges of concentrations of chemical elements for different rock types; combine these values with distributions determined by the geologic distribution of that rock type, a geologic map. These are the bedrock geochemical maps, including trace elements.

The extent to which soil chemistry is derived from the bedrock chemistry can be evaluated by mapping the residual between the bedrock map and soil horizon C. Comparison between soils horizon A and C measure other processes.

Biological parameters are of great importance in the characterization of these samples. It is indeed a challenge to document sustainability. The chapters of this dissertation are integrated within the discussion above. This introduction gives an overview of the problem, and possible steps to find some answers. This is a problem with many variables.

CHAPTER 1

USING ENRICHMENT FACTOR TO EVALUATE THE DISTRIBUTION OF NATURAL AND ANTHROPOGENIC SOURCES OF HEAVY METALS IN KANSAS, IOWA, AND NEBRASKA, MID-CONTINENT, USA

ABSTRACT

Heavy metals in the soil are influenced by the chemistry of natural (crustal) sources with extreme values from the source point of contamination. The heavy metals selected for this study include Arsenic (As), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Mercury (Hg), Manganese (Mn), Nickel (Ni), Lead (Pb), Selenium (Se), Vanadium (V), and Zinc (Zn). Analysis showed that Co, Cu, V, and Zn with high concentrations values (outliers) can be potentially associated with possibly anthropogenic applications. The principal component analysis (PCA) showed that one family has a strong correlation, including the chemical elements As, Co, Cr, Ni, and Zn. Another family showed that Pb and V were significantly correlated. These investigations confirmed that some of the heavy metals originated from anthropogenic activities rather than natural sources. In addition, we used the method enrichment factor (EF) to estimate the native metal concentrations in Iowa (IA), Kansas (KS), and Nebraska (NE). According to the EF indicator, we found that the mean of the moderate EF values were observed in IA only with regards to Se (2.37). However, the mean values of heavy metals in IA, according to the EF value criteria, established by Muller (1969), are minimal enrichments in Se $2.37 > \text{Mn } 1.359 > \text{Pb } 1.336 > \text{Zn } 1.265 > \text{Cd } 1.226 > \text{Cr } 1.22 > \text{Hg } 1.105 > \text{As } 1.014 > \text{Cu } 1.005 > \text{Co } 0.989 > \text{V } 0.861 > \text{Ni } 0.776$ (1.13 ± 0.29). In KS, the calculation of EF showed deficiency or minimal enrichment with values < 2 (1.12 ± 0.44), which indicated $\text{Cd } 1.567 > \text{Hg } 1.389 > \text{Pb } 1.327 > \text{Se } 1.325 > \text{Zn } 1.232 > \text{Mn}$

1.133 > Cu 0.985 > Cr 0.959 > V 0.948 > As 0.901 > Co 0.89 > Ni 0.841. The correlation coefficients of the United States Geological Survey (USGS) surface soil data have highly significant relationship amongst the heavy metals. A significant correlation of As was found with Ni (0.68) and V (0.67). Cd had a strong correlation with Ni (0.60), Se (0.65), and V (0.72). Co was significantly correlated with Ni (0.60), and Cu correlated with Zn (0.61). A significant association was also detected between Ni and Se (0.67) as well as V (0.86). In addition, Se was significantly correlated ($p < 0.01$) with V (0.75). In NE, except for Ni and V ($EF > 1$), the minimal impact of human inputs on soil chemical contents have been observed with all metals as follows: Cd 1.292 > Se 1.405 > Hg 1.122 > Pb 1.140 > Zn 1.121 > Mn 1.092 > Co 1.034 > As 1.005 > Cr 1.003 > Cu 0.989 > V 0.953 > Ni 0.915 (1.09 ± 0.18). The outliers of heavy metals on geochemical maps within values 1.4–7.6 document anthropogenic outputs from different point sources, ranging from moderately to significantly enriched soil EFs. Therefore, the anthropogenic contribution of each metal represents the contribution of point-source contamination at each observation site. Point source contamination has occurred at several sites but is probably associated with agricultural additives rather than other sources, such as industrial activities. However, a negative correlation was clearly observed between the soil anomaly hot spots, when air and land emissions were superimposed on soil geochemical backgrounds. It was not evident if air releases contributed to heavy metals in the soil chemistry.

1. INTRODUCTION

In the last decades, soil contamination by heavy metals has received more attention and become an environmental concern. The soil is a primary component of the ecosystem of the earth and consists of solid phases that involve organic matter and minerals. Additionally, gases and water occupy the phases with pores. Soil represents the interface of the four spheres of the earth, the geosphere, atmosphere, hydrosphere, and biosphere. It is the basis for the growth of various species of plants required for the food chain of living organisms. It is also the home of a large mass of microorganisms. One of the most important properties of soil is the ability to filter, absorb, or precipitate the substances that arrive at the surface. Heavy metals in the soil have been considered and found in low concentrations in rocks and in the soil (Shacklette & Boerngen, 1984, Wilson et al., 2008, & Smith et al., 2014).

Some of these elements, such as As, Se, and others, are found as anions while others, such as Cd, Cr, Cu, Hg, Ni, Pb, and Zn, occur as cations (Wilson et al., 2008). The concentrations of trace elements in soil are small, as compared to the major elements, and are measured in parts per million (ppm) and not percentages. However, there is increase of these concentrations and their accumulation overtime that cause soil pollution. In the global environment, contamination of soil exists due to the accumulation of heavy metals in agricultural soils (Pierzynski et al., 2005). Every geographic region/location has different features, which can determine the nature and the source of the trace elements in that soil type. Concentrations of several chemicals are usually within the normal range, but they can be contaminated or considered geochemically anomalous.

Sustainability of the soil is a huge global concern. The need to identify the contaminated land areas and health risk assessments has given rise to a growing interest in the agricultural

geochemical environment. Non-nutritive and/or metals can accumulate in the soil and food crops overtime if they exceed their permissible concentrations or threshold (Naveedullah et al., 2013 & Nweke and Ukpai, 2016).

Soil properties vary spatially according to many factors, such as the geographic location, the chemical composition, the physical properties, and the climate conditions (Rincon et al., 2013). Soil properties such as soil mineralogy, organic matter content, chemical compounds, pH, moisture levels, and temperature, can also affect the fate of contaminants (Estevez et al., 2008 & Li et al., 2014). In addition, it can be affected by human activities through the intentional addition of chemical substances to the soil such as fertilizer, pesticides, and other modified compounds, which impact its physical, chemical, and biological properties. The concentrations of chemical elements may sometimes exceed the US Environmental Protection Agency (USEPA) recommended concentrations and can cause damage to plants and create problems for both humans and animals.

It is required to understand the differences between the natural sources and the anthropogenic impacts of heavy metals for determining the quality and the health of the soil, and the bioavailability of these heavy elements in it (Pierzynski et al., 2005, Wilson et al., 2008, & Maina et al., 2016). The heavy metals in the soil are deposited directly or indirectly through human applications. The bioavailability of metals varies according to their origin, but it is higher near anthropogenic activities (Kabata-Pendias & Pendias, 2001). The presence of significant concentrations of various biologically active chemical substances, such as agricultural additives, can affect the status and functioning of the soil microbial biogenesis, soil fertility, and human health (Arias et al., 2005, Cycon et al., 2013, & Marcin et al., 2013). Current agricultural practices may reduce soil biodiversity due to the overuse of chemicals, leading to adverse ecological

alterations (Enriqueta et al., 2005). The potential effect of chemical loading and several additives on food chain security has created one of the most important public health issues worldwide. The loading of heavy metal elements is especially risky because of their high toxicity, non-biodegradability, and persistence (Khan, et al, 2013 & Li et al., 2014). The human body may accumulate these chemicals, causing severe health problems (Fu and Wei, 2013). Agricultural soils in mid-continental US are increasingly facing destruction due to the use of additives (Woodruff et al., 2015). The large accumulation of chemicals or additives in agricultural soils may adversely influence the structure and diversity of soil microorganisms. Chemical accumulation in the soil may decrease the microbial biomass and activity, which in effect impacts the structure and the diversity of microbial communities.

There is a difference between the chemistry of the soil and the chemistry of the original lithology, affected because of several environmental factors (Sucharova et al, 2012). The elements in the surface soil (O-horizon) pass into the biosphere through plant uptake, but the deep soil layers are associated to the lithosphere (Sucharova et al, 2012).

The most used general quantitative methods are the enrichment factor (EF), the geochemical index (I_{geo}), the contamination factor (CF), and the degree of contamination (Dc) (Nweke & Ukpai, 2016). The EF and I_{geo} have been used and described below; the CF and Dc have not been used. Ecological risk assessment indexes provide a simple and inclusive tool for measuring the level of soil contamination; moreover, it shows the variances in bioavailability, relative influence ratio, and geographical features (Nweke & Ukpai, 2016). Ecological risk assessment methods, applied to heavy metals in soil, have received more attention in recent years for their ability to discover soil contamination (Nweke & Ukpai, 2016). The I_{geo} is an

environmental tool that has been used for the estimation of the contamination of sediment since the 1970s (Huang et al., 2017). EF is used to describe the minimum factor of the bodies of mineral ores and by what weight percent of mineral in an ore body is greater than its average occurrence in the Earth's crust. High top/bottom-soil ratios or high values of EFs are used as proof for major anthropogenic impact on the geochemistry of the surface of the earth. Reimenn et al., (2008) pointed out that natural mineral deposits can also lead to high EFs and I_{geo} , and that caution should be maintained for their potential influence. There are various methods to calculate EF. One instance involves the normalization of Fe/Mn concentration. Another method is using the ratio of polluted sites normalized to the non-polluted site. I_{geo} has been used to determine the degree of soil contamination since the 1970s and many researchers have used the I_{geo} tool to evaluate the soil and sediment contamination (Huang, et al., 2017).

The overall objective of this study is to determine the spatial patterning of potentially contaminated soils with heavy metals, using various pollution indices. Another goal of this study is to estimate the enrichment of heavy metals, including As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn, in the soil in IA, KS, and NE. The measurement of the potential chemical cumulative loading, performed using EF, can provide the opportunity to evaluate long-term pollution. The data was used for the following: 1) Studying how the surface topsoil reflect the geochemistry of IA, NE, and KS, 2) comparing the distribution and concentrations of the heavy metals, 3) calculating the EF as a proof of soil contamination by anthropogenic applications, 4) quantifying the agreement between the EF of surface soil maps and the surface soil content for each studied element, through a comparison of the products and the spatial distribution, and 5) testing if high EF values can be associated to known sources of pollution.

2. MATERIALS AND METHODS

2.1 Study Area and Site Description

The area of the study is in mid-continental USA. The states of Iowa (IA), Kansas (KS), and Nebraska (NE) (Fig. 1.1 & Fig. 1.2) were the target of this study, to evaluate the chemical loading in the soil. The study area is an agricultural region and farmland covers 99% of IA and some areas in KS and NE. The agricultural grain crops in IA include corn and soy. In KS, the agricultural crops include alfalfa, gollum, sunflowers, black locus, juniper, mulberry trees, amaranth, wheat, and casters. Agricultural activities in NE are corn, wheat, sorghum, potatoes, and sugar beets and the crops include grass, wild rose, sage, prickly pear, cone flower, prickly poppy, sager roses, plantain (mint, vervain, dogbane at batch), trees (locust, ash-leaf maple), and corn.

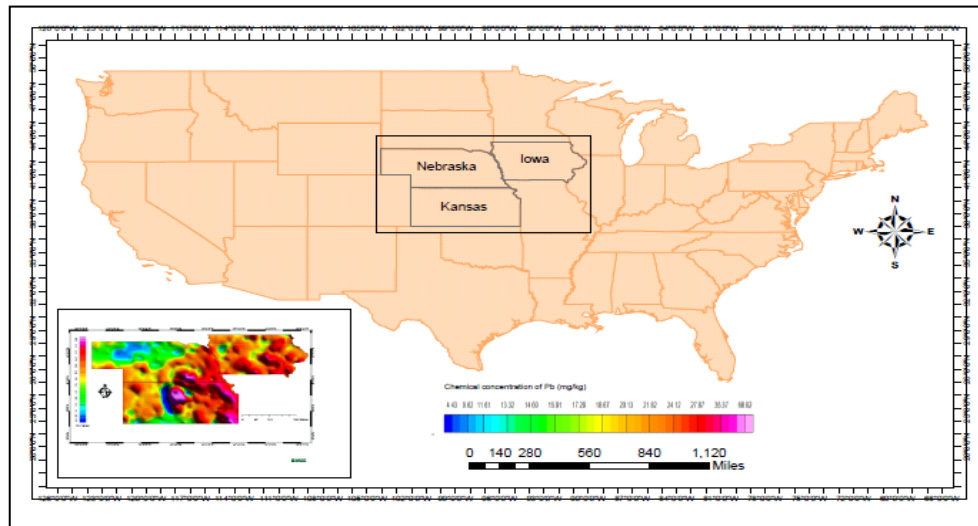


Figure 1.1: Map of study area - The map shows the

area of study and soil geochemistry and the spatial distribution of chemical concentrations of As, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, Se, V, and Zn in the United States (USGS data project) (Smith et al., 2014).

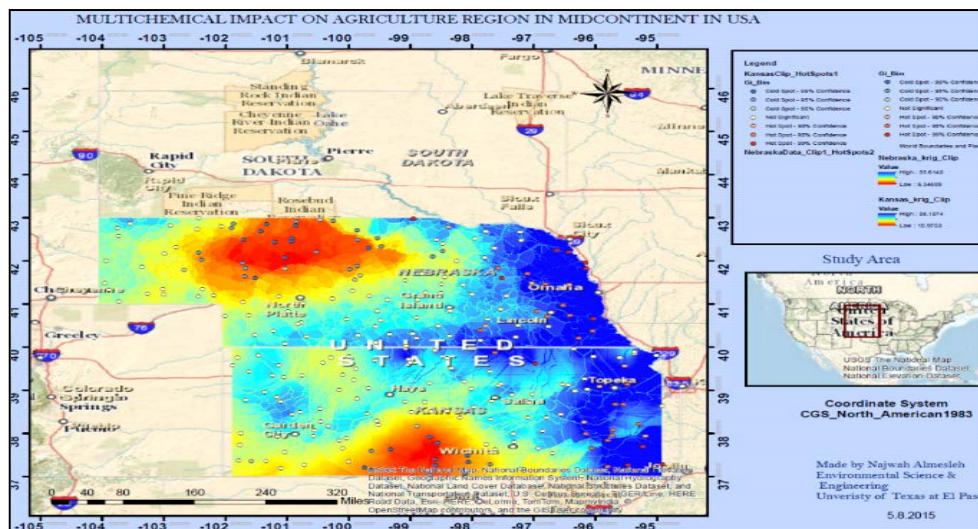


Figure 1.2: Map of study area -The map shows the area of study and soil geochemistry and the spatial distribution of chemical concentrations of As, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, Se, V, and Zn in the United States (USGS data project) (Smith et al., 2014).

2.1.1 Climate of the Area

The area of the state of IA is 56,288 m², with rolling prairies that are located in the middle latitudes between the Mississippi and Missouri rivers. The average high temperature is 60.8°. The average annual temperature is 45° in the north and 52° in the south. Rainfall in the area arrives from the Gulf of Mexico during the warm months. In winter and autumn, the dry Canadian air flows in northwest, beside the air masses that move from the Pacific Ocean, leading to restively dry and cold weather, causing the soils to be frozen and then thawed promoting soil mixing and avoiding compaction. However, in the summer, the high temperature is caused by the hot and dry winds that come in from the desert southwest.

A topographic feature of the area of KS has different elevations, < 900 feet in the southeast and > 3,000 feet in the west. Therefore, the diminished rain shadow influence of the Rocky Mountains, with elevation difference, creates a wide variation in the annual rainfall of the state. The summers are warm while the winters are cold. In KS, the annual mean temperatures are 58° in the south and southeast and 52° in northwest. The average low temperature there is 36.6°. The precipitation in terms of forceful rainfall in winter can be associated with high winds and heavy snow, and it takes place during spring and summer (National Oceanic and Atmospheric Administration, 2018). The area of the state of NE is 77,227 m², with 705m² being water, and the elevation in the southeast ranges from < 900 feet above sea level to 1,200 feet in the northeast. The Sand Hills contains some lakes around it (Fig. 2) as well as valleys and basins that are located in the north, central, and high plains of the western portion of the state; the prairie is located in eastern part of the state, formed from sandy loam or slit loam soils. There are fluctuations in the seasonal temperatures; in general, the weather is hot in the summer and cold in the winter. Some of the

moisture comes from the Pacific Ocean but the air passes over the Rocky Mountains, which causes a decrease in moisture, and the air becomes warm. The average temperature in Nebraska is 48.7 °F (National Oceanic and Atmospheric Administration, 2018). Temperatures increase to above 100° F, especially in June through September. The rainfall is formed by warm air thunderstorms during summer and spring that may occasionally cause flooding (National Oceanic and Atmospheric Administration, 2018).

2.1.2 Soil Sampling and Chemical Analysis

The data used in this study is extracted from the United States of Geological Survey (USGS) (Smith et al., 2014). The analyzed published data and the chemical methods of analysis of several heavy metals are available on the USGS website (Smith et al., 2014). According to these datasets, some of the chemicals have been found in high concentrations, which could reflect possible soil contamination from anthropogenic activities (Smith et al., 2014 & Woodruff et al., 2015). From this point, the study uses these datasets to estimate if there is anthropogenic chemical loading into the soil to produce chemical maps that can be applied for interdisciplinary research. Smith et al., (2014) collected samples from a total 4,871 sites; the sampling data from the three states was analyzed and interpolated into this study: 91 samples from IA, 132 from KS, 130 samples from NE were a part of the National Geochemical Survey (NGS) (Smith et al., 2014).



Fig. 2.1: Location of the Sand Hills in Nebraska (Nebraska Sand hills Randonneurs, 2018)



Fig. 2.2: Location of the Sand Hills in Nebraska (Nebraska Sand hills Randonneurs, 2018)

2.2 Data Analysis

The typical method of analyzing geochemical data involves the description of the single element and spatial distribution. Data analysis for this study includes the use of geostatistical methods (Reimann et al., 2008). These are performed using the R Studio Version 0.98.1091. Three points of analysis are applied, including data integration, analysis, and validation. The surface soil data is arranged into two modules and plotted in histograms and cumulative frequency diagrams, based on the concentration of elements. While the mean, median, absolute deviation, and coefficients of variation are calculated for the studied elements. The samples are analyzed to determine the concentration of the target heavy metals in the soil (Smith et al., 2014). In this study, the selected chemical subsets consisting of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn in ~353 samples are used to conduct the geostatistical analysis in IA, KS, and NE. The geostatistical methods program called lognormal software is used because the statistical analysis in this study was a multi-variate one. The graphs, histograms and empirical cumulative distribution functions were produced. Spatial distribution analysis is performed to graphically display the distribution of the studied heavy metals to identify their origins. The PCA is employed to conclude the hypothetical sources of the chemical elements, whether they are natural or anthropogenic. The heavy metals spatial distribution maps were generated using the R program and the EF distribution maps were created using the Oasis Montaj software.

2.3 Assessment of Soil Chemical Loading Based on Enrichment Factor (EF)

Evaluation of anthropogenic activities on the topsoil is more commonly studied and can be investigated using more complex ratios, such as the EF (Sucharova et al, 2012). Since the soil

developed from various background parent materials, the variability of the geochemical background can be reduced through the normalization of the heavy metals to the reference element (Bourennane et al., 2010).

The data used for the estimation of the chemical loading was carried out using EF, as reported by Muller (1969), to estimate the potential contamination hazards intensity for the heavy metals in the agricultural soil. The EF index is used for contamination assessment in soils. This index is achieved by dividing the content of a trace element by uncontaminated reference values. Several studies have used different techniques or equations to estimate EFs in the soil (Bourennane et al., 2010; Desaulles, 2012; Sucharova et al., 2012; Szolnoki et al., 2013; Sun et al., 2017, & Tepanosyan et al., 2017), and others have used off-site references (Dragovic et al., 2008, Hasan et al., 2013, Naveedullah et al., 2013, Zhang et al., 2015, Dartan et al., 2015, Kumar et al., 2015, & Chee Poh & Tahir, 2017). Some of these researchers also used on-site references. The off-site references do not have parent material (crustal average values) data because this method does not match the actual location as a background for screening soil pollution. This is a point of consideration that the heavy metal content, in each natural regional background, is different (Anderson & Kravitz, 2010). In general, the data is normalized to conservative on-site reference elements because the topsoil and deep soil layers are not 1:1 comparable (Desaulles, 2012). In an off-site reference, using the mean of the element content in the parent earth crust, for the normalization of EF calculations, cannot provide the accurate background values for EF evaluation. Values of the deep soil layer (C-horizon) are the most suitable on-site references of the same soil profile (Bourennane et al., 2010 & Oliveira et al., 2011). The samples collected from the topsoil are developed from the same parent materials as the deepest horizons at the same site since,

the EF ratio can cancel the elemental segregation process during rock formation, and directly be influenced by weathering (Bourennane et al., 2010).

2.3.1 Enrichment Factor (EF)

The median metal content found in the earth's soils is close to the elemental composition of the crust, and drops within the ranges perceived in the soil, excluding a few rare exceptions (Essington, 2004). Geochemical background is defined as a relative measure to distinguish between natural elements or compound concentrations and anthropogenically influenced concentrations in real samples (Matschullat et al., 2000). There are several indexes used to identify anthropogenically contaminated soils, the calculation of EF is based on exchangeable fraction that presents the actual bioavailable fraction (Barbieri, 2016). EF is a significant indicator for determining the degree of anthropogenic contamination of heavy metals in topsoil through the calculation of the ratio of the element concentration to its concentration in deep, uncontaminated soil layers (Sucharova et al, 2012). It is a quantitative value of the relative enrichment or depletion of heavy metals in the surface soil as compared to the deep soil. C-layer represents the component of parent geological bedrock. The geogenic background estimation of the metals' sources whether it is natural or has been introduced through anthropogenic activities can be an effective tool. The EF is used to distinguish and assess the relative contributions between heavy metal inputs of a natural and/or anthropogenic manner, into soils and the accumulation or depletion of the elements there (Bourennane et al., 2010, Nweke & Ukpai, 2016, & Muzerengi, 2017). If the EF value of the element is < 1 , it probably means that it has been leached (Muzerengi, 2017).

The EF equation parameter was used for the evaluation of soil chemical loading in IA, KS, and NE; it mapped the properties or chemical variations in the data. The soil samples were collected from the surface soil (0–5 cm) while the C-horizon samples were collected from a depth 18–167cm in IA, 10–100cm in KS, and 10–153cm in NE (Smith et al, 2014). The EF is used to evaluate soil contamination by connecting the abundance of a target element in the examined soil (material source), to a reference metal originating from the Earth's crust (enrichment) (Uduma and Awagu, 2013, Edwin, 2013, & Naveedullah et al., 2013). Element normalizers are typically required as the standard to calculate EF. This parameter depends on using Titanium (Ti) as an immobile chemical element (Krauskopf & Bird, 1995 & Kabata-Pendias, 2001). If the element normalizer is conventional, it means that it originates from the Earth's crust. The section of the element normalizer is based on the assumptions that it is not easily impacted by weathering (conservative element), it is very abundant in the earth's crust, and it does not contain anthropogenic enrichment (Maina et al., 2016). Consideration of element ratios is more due to the changes in the geochemical processes than for using the single element concentration (Desaules, 2012). The most common element normalizers used for EF calculations are categorized into two groups. The first group includes Zr, Sc, and Ti. The second group includes Al, Mn, and Fe (Reimann and Decarital, 2000, Blaster et al., 2000, Sucharova et al, 2012, Naveedullah et al, 2013, Szolnoki et al., 2013, Maina et al, 2016 , & Nweke Ukpai, 2016).

The natural background values of the normalizing element, Ti, were used in this study. It is one of the most common reference elements used to calculate EF. The concept is that EF is the standardization of the target heavy metal level in the surface soil to the reference metal, using local background values (Tepanosyan et al., 2017). It is calculated as the elemental concentration in the

soil normalized to the reference (Ti) as the qualified normalization element. Ti is used because of the following reasons: 1) It is an immobile element that has low existence availability; 2) It has little variability of mobility in the soil (particularly stable) (Desaules, 2012), 3) Common rock forming elements are resistant to weathering in the soil (Szolnoki et al., 2013), 4) They are not influenced anthropogenically. Several authors have reported that Ti is an efficient element to be used for measuring the degree of anthropogenic or geogenic accumulated loads, such as Reimann & Decaritat (2000), Maine et al. (2016), & Tepanosyan et al. (2017). Ti was used as a geochemical immobile normalizer for each element under question. The EF was calculated as a ratio of element concentrations in the soil normalized to a reference Ti. The content of heavy metals is measured on a mass basis and the EF is calculated to measure the degree of the element enrichment of heavy metals in IA, NE, and KS, using the formula expressed as:

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

Where, $(C_i/C_{Ti})_{\text{sample}}$ is the ratio of the mean (-1) of the target element to Ti concentration (C_{Ti}) in the soil sample, and $(C_i/C_{Ti})_{\text{background}}$ is the ratio in the reference (conservative element) in C-horizon. Ti concentrations in the soil of the C-layer were considered as the natural background value instead of its concentration in the crust; that make for more reliable findings for evaluating the level of anthropogenic sources in the environment (Barbieri, 2016). Moreover, the concentration of the element of interest and reference in the soil depth of C-horizon can be used if their values are not available in the crust (Bourennane et al., 2010, Sucharova et al, 2012, & Maina et al., 2016). Oliveira et al. (2011) & Desaules (2012) stated that the deep soil layer values are

more convenient on-site references of the same soil profile. Moreover, using the concentration of the element and the normalizer in the topsoil, as compared to their concentrations in deep soil at the same site, can minimize the natural variation (biogeochemical and localized lithogenic processes).

The basic concept is that any change of the dominator ratio at the soil surface is due to an additional source (human input) and the ratio is around 1 in the absence of an external source. Five contamination categories were used in this study and the interpretation of the EF is therefore shows an increase and/or decrease. Therefore, this increase can indicate to anthropogenic applications as a source of the contamination in the soil (Sutherland, 2002). Values of EF less than 1 indicate the likelihood of mobilization or depletion of metals respective to the reference, while EF values more than 1 propose that the element level in the soil is of anthropogenic origin (Nweke & Ukpai, 2016). The classifications of the contamination indicators, based on the EF, range from $EF < 2$ to $EF > 40$, and are described in Table 1. (Uduma and Awagu, 2013, Jiao et al., 2015, Barbieri, 2016, Nweke & Ukpai, 2016, & Muzerengi, 2017). As EF values increase, according to its suggested six classes, the probable anthropogenic inputs increase (Edwin, 2013) as it shown in Table 1.

Table 1 Classification of enrichment factor (EF) and the degree of soil chemical loading in terms of the five enrichment categories

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

Reference: Jiao et al. (2015)

2.3.2 Statistical Analysis

The statistical analysis of the experimental data was performed to determine human influence on a spatial scale and the correlation between the heavy metals. The experimental data included heavy metals in the soils (Smith et al., 2014). The probability and statistical data analyses of the study were carried out to interpret the results by using the SPSS 24 software (IBM SPSS statistics). Descriptive statistics and ANOVA multivariate analysis, using Boxplots, was used to estimate the variance between the means of the analyzed EF. Duncan's Multiple Range Test (DMRT) was carried out to test the differences between the means (significance level<0.05). The means and the standard deviations (SD) were determined. The heavy metal concentrations were achieved and compared in terms of the analysis of variance (ANOVA) followed by the Tukey's post-hoc test at the 5% level. Pearson's correlation matrix was employed to identify the relationship between the chemical elements. Thus, differences between values at significance level were $P < 0.05$, which is indicative of a statistically significant difference between the means of the soil heavy elements, among the states and within the states.

3. RESULTS AND DISCUSSION

The statistical analysis using R-studio was applied to generate univariate, bivariate, multivariate, and robust PCAs and multivariate outlier plots to compare the metal concentrations and their relations. Multivariate outliers were detected using a modified version of the Mahalanobis distances, and the variation matrices analysis. Heavy metal concentrations and multivariate outlier maps were created to facilitate the visualization of the data. The logarithm transformation was carried out using a lognormal distribution to estimate the original and transformed data (Reimann et al., 2008). In the exploratory data analysis, univariate statistics was the starting approach (Kurzl, 1988). These univariate non-compositional calculations were plotted using raw data for the variables then compared to transform log ratio plots. (Fig. 3 & Fig. 4). The values are plotted on X and Y-axes in stacked and one-dimensional scatterplots, presenting every single point of the data set using logarithmic scales. The results presented high values of the X-axis of the data set range (Reimann et al., 2008).

Histograms, cumulative frequency diagrams, one-dimensional scatterplots, and Tukey boxplots are presented with the empirical cumulative distribution function (ECDF) plot (Reimann et al., 2008). The original dataset was plotted in two forms of ECDF, with a log-boxplot and a log transformed plot. Heavy metals concentrations and multivariate outlier maps were created to facilitate the visualization of the data and detect the differences and similarities between the spatial distributions of heavy metals on the surface soil as well as to determine where anthropogenic inputs are dominant, as compared to geogenic factors. The data analysis showed visual variances with high and low concentrations of heavy metals in the depth range of 0–5cm.

3.1 Heavy Metal Concentrations in the Topsoil of Iowa, Kansas, and Nebraska

The spatial distribution of samples showed anomalies with high concentrations of some heavy metals associated with outliers. Concentrations of all trace elements are spatially plotted on maps of the three states. The element concentrations were located in different regions in the east and northeast of IA, northeast and southeast KS, and eastern NE. Thus, the plotted histograms for the variables showed a correlation between potential heavy metals and their possible anthropogenic sources (Fig. 8). The observations of high concentrations of the elements Co, Cu, V, and Zn are outliers, probably related to anthropogenic applications. The extreme data values (outliers) were investigated differently for each state. The visualization of the histograms of the ECDF-plot establishes very high values for some elements, as compared to others. An interpretation of these different family groups suggests various sources for each element (Fig 3 & Fig. 4). Geochemical mapping was applied and plotted to identify the spatial distribution regions for each element, which show the point source of the chemical concentration values in the states. No obvious pattern in the distribution of the multivariate outliers and the concentration maps show the same spatial correlation depicted in the robust PCA plot. The study was performed also to establish a relationship between fertilizer use and soil contamination on the other side. The PCA was also used to reduce dimensionality and is presented as biplots for non-compositional statistics. Univariate statistics were the starting approach applied to these derivative results. These univariate, non-compositional calculations were plotted using raw data and then compared to log ratio plots. The summary of the statistical analysis is shown in Table 2. Massive variances have been investigated in heavy metals' concentrations in the surface soil, with different numbers of outliers. (Fig. 3 & Fig. 4). The original geochemical maps also presented different distribution

patterns. A comparison between the raw data and log ratio transformed data eliminates the possibility of outliers on the upper end. As all the univariate plots are analyzed, it can be concluded that all trace elements are multimodal. Only three trace elements, Mn, Pb, and Se, show bimodality. Elements include As, Co, Cu, Hg, Ni, V, and Zn exhibit trimodality. An interpretation of these different family groups suggests various sources for each element. Some of the geochemical maps of heavy metals distribution highlighted the natural geological features and the others presented anthropogenic inputs

Table 2 A summarized exploratory data analysis showing different calculated values. The measures for central value is represented with element name (EN), the mean and median (Med), spread with the standard deviation (SD), pseudo sigma (PS), and quartile (Q).

EN	Min	Q_0.05	Q1	Med	Mean-log	Mean	Q3	Q_0.95	Max	SD	Mad	PS	CV %	CV R %
As	0.9	1.4	4	6	5.2	6.1	8.1	11	19.3	3.04	3.11	3.04	49.7	51.9
Cd	0.1	0.1	0.2	0.3	0.3	0.3	0.4	1	2.1	0.23	0.15	0.15	65.2	49.4
Co	0.7	1.7	5.8	8.2	7.1	8.3	10.9	15	21.1	3.90	3.86	3.78	47.2	47.0
Cr	2	8.0	23	33	28.3	32.3	42	52	88	13.86	13.34	14.08	43.0	40.4
Cu	2.3	4.7	10.8	15.7	14.0	16.1	19.7	27	95.2	9.06	6.52	6.60	56.2	41.6
Hg	0.01	0.0	0.01	0.02	0.0	0.0	0.03	0	0.1	0.01	0.01	0.01	56.5	74.1
Mn	54	135.0	317	470	451.6	558.9	694	1114	7780	505.50	259.50	279.50	90.5	55.2
Ni	1.7	3.4	10	14.8	13.2	15.5	20.6	28	42	7.70	7.86	7.86	49.5	53.1
Pb	8.4	11.5	17.7	20.6	20.7	22.9	23.9	34	450	24.26	4.60	4.60	106.1	22.3
Se	0.2	0.2	0.2	0.3	0.3	0.4	0.5	1	2.6	0.22	0.15	0.22	59.4	49.4
V	8	15.6	46	67	56.9	64.4	82	103	194	27.79	25.20	26.69	43.2	37.6
Zn	9	18.0	47	61	56.7	64.1	79	116	270	30.42	25.20	23.72	47.5	41.3

The concentration of the As is an example of how the chemical concentrations in the study areas are highly varied. A comparison between the raw data and the log ratio transformation eliminates the possibility of outlier on the upper and lower ends. The Tukey box plot for As demonstrates that the median has a small skew toward the left, which may suggest the use of

fertilizers. Therefore, in the histogram and the density trace of the ECDF, no high significant values of As have been identified. The exceptions are four outliers in the scale between 15–20 ppm on the plot, as shown in Fig.1.1. This value is far from the central group of the data set, through a limited range of the whole data set. The plotted maps (Fig.3.1) showed that the As concentrations are variable within the three states. The highest concentrations of As (10.7–19.3 mg/kg) are located in all the three states. In IA, the elevated concentrations are found in the northwest, Midwest, and the southern portion of the state, as shown in Fig. 3.1. However, no correlation was reported between the O-horizon and the B-horizon for heavy metals (Sucharova et al., 2012). Gypsum mining is the only mine located near the center, specifically in northwest IA.

The Cd boxplot shows various families, due to the different element concentrations, with a maximum value of 2.5 ppm. They show a possibility of three families. The concentrations present single variables at log scale in three families that are outliers around 0.6–2.5 ppm (Fig. 3.2). There were anomalous concentrations of Cd in the study area; however, few significant concentrations have been shown for Cd in NE except in the northeast and southeast sides of the state. High concentrations for Cd were recognized in south and northwestern IA and northeastern and southeastern KS (Fig.3.2). Concentrations of Co in the plot present single variables at concentrations of 16–21 ppm on a log scale, as shown in (Fig.3.3). This supports the hypothesis that there are different point sources of the chemicals. The Tukey box plot also exhibits a skew toward the right. However, the ECDF plot of the original data shows almost a bell-shape. The Co Tukey box plot demonstrated that the median is skewed toward the right and has a small skew toward the left, which may be due to the use of fertilizers. Outlines and the areas of Sand Hills are clear, with either zero or very low concentrations of Co (Fig. 3.3). In IA, the analyzed data

demonstrates that most of the Co is in the central-southeast area, with few outliers at the far northwest region where some lava flows. In NE, there is a trend of Co extending from the southern-southeast part of NE to IA. This area represents agricultural areas where fertilizers are extensively used, which may have led to this trend. In KS, most of the Co is concentrated in the central-southern part of the state but with low concentrations; most of the state is free of Co (Fig.3.3). These observations may indicate that the anthropogenic sources in these regions are causing these variations. The behavior of Co in the study area is similar to V (Fig. 3.3 & Fig.6.2). The comparison of the two elements shows single groups of outliers. Cr graphs showed single families at log scale with concentrations between 52.4–88 ppm. These are indicators for anthropogenic applications in the study areas. Cr plots show a possibility of three families. An interpretation of these different family groups suggests various sources for each contaminant (families in the range of 30 are considered, as compared to two families within the range of 0–10 and 40) (Fig.4.1). The mean of Cr in the soil is 32.2 ppm. There exist several suggested industrial sources of Cr such as polythene bags, Pb-Cr batteries, and plastic wastes (Edwin, 2013). The distribution of Cr is presented in Fig. 4.1, the two plot-log scale diagrams (one dimensional scatter plot (left), and ECDF plot (right), include the cumulative frequency. The element concentrations show two outliers between 60–85 ppm, as seen in Fig.1c. The plotted maps show variation of the hotspots between 52.4–88 ppm, located in all regions of IA except the north central portion of the state. However, the hotspots containing a higher concentration of Cr are in the east of KS and NE (Fig. 4.1).

Cu concentration families are classified into three groups, and the outliers are investigated in the log scale of 27–95 ppm, as shown in Fig. 4.2. Moreover, multiple Cu values have been observed at 4, 90, 95 ppm. The investigation of the distribution of Cu concentration by ppm is

shown in Fig. 2.1). In Fig. 4.2, the high Cu concentrations are distributed through the scales at 27.4–95.2 ppm in the plotted maps. A majority of IA has all the hotspots, except for in the north, while in NE and KS; they are located in the eastern portions of the state (Fig. 4.2).

The Hg plots show association with various families due to the lack of significant figures provided by the chemical assay. Therefore, no significant values have been observed (Fig.4.3). The plotted map shows low concentrations of Hg, within the range 0.04–0.10 ppm (Fig.4.3). It is expected that Mn is the most abundant element in nature. The observation has been confirmed in this study, with one outlier in the study area at a very high concentration in the plot (800 ppm). The ECDF plot presents two families only and 1000–23000 ppm is estimated for some outliers in the scale. The ECDF plotted data showed normal distribution of Mn in the log scale, > 1000ppm, (Fig.5.1). This suggests that there are some anthropogenic activities that are not related to the geological aspects. Moreover, in the maps produced in this study, elevated concentrations of more than 1114–7780 ppm of Mn were identified in all the regions of IA. In NE, a small area in the northeast with high concentrations of Mn is observed; other than that some anomalous values are located on the east side of KS (Fig. 5.1).

Ni concentrations present single variables at a log scale of 30–45 ppm. The outliers were identified in the histogram as well. This is an issue probably related to the anthropogenic activities in the study area. Ni plots show a possibility of three families (Fig, 5.2). An interpretation of these different families suggests various sources for each metal (family in the scale 10 and 20 is considered, compared to the other families with a scale of 0–5, and 25–30 ppm). The investigation of the distribution of Ni in data analysis plots are shown in Fig. 5.2. The maps of the states show the similarity points of high concentrations of Ni in all the regions of IA. However,

there are high concentrations of Ni in the east and south of NE. In KS, the element is concentrated in the east and north (Fig. 5.2). Histograms of Pb show very high concentrations in the soil, evidenced by three outlier points at the log scale 80, 100, 400 ppm (Fig. 5.3). Moreover, the outliers are shown in the scale between 33.9–450 ppm in the plotted maps. The investigation of the distribution of Pb is shown in Fig. 5.3. There are higher concentrations of the Pb, possibly from anthropogenic sources, in the farms of both eastern and northern IA. According to the statistical analysis of Se, five outliers have been identified in the study area, within the range of 1–2.5 ppm, which suggests that low concentrations of Se with no apparent contamination source can be considered (Fig.6.1). In the scatter plot, two points of outliers are observed with the values 1.5 and 3 ppm, respectively (Fig.6.1). In the V histogram, three families have been observed at the scale 0–200 ppm, with a high peak between 50–100 ppm. The observation of high V concentrations has been identified in the soil, in the range of 150–200 ppm in the histogram, which indicates contamination points in this area (Fig. 6.2). The maps of IA, KS, and NE show high concentrations of V, mostly in the east and south of IA and only in eastern NE. Furthermore, significant concentrations were shown in almost all of KS, including the southwestern part of the state being in the range of >103–194 ppm. However, lower concentrations of V were observed in northwestern KS (Fig.6.2).

The concentrations of Zn showed single values at 116 and 270 ppm (log scale), indicating a contamination point source in the study area. Zn plots showed a possibility of three families, while two outliers are presented in the maps. An interpretation of these different family groups suggest various sources for each contaminated site (family in the range 116 and 270 are considered as contamination points as compared to other two families within the range of 0–100 ppm). The

investigation of the distribution of Zn is shown in the histogram and CP plots (Fig. 6.3).

The distribution of Zn, in the plotted maps, showed the highest concentrations in IA and KS with a range of > 116–270 ppm, which includes some amount of Zn located in the east region (Fig.6.3).

Zn was also spatially correlated with Co, Cr, and Ni, as shown in the chemical maps (Fig.9). A spatial correlation has been also observed between the chemical elements Hg, Mn, and Se, as shown in Fig. 9. Another spatial correlation was investigated, between the chemical elements Pb and V, as shown in Fig. 9.

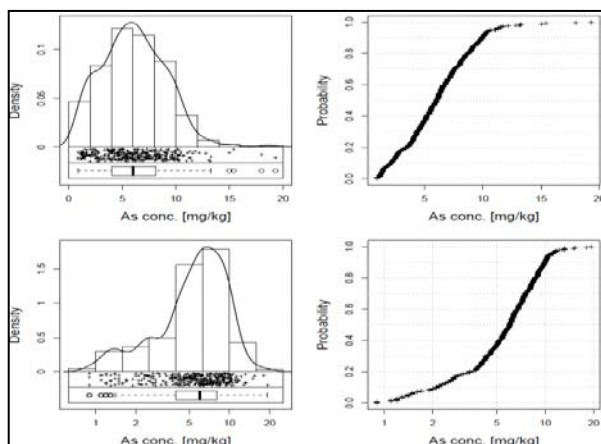


Fig. 3.1

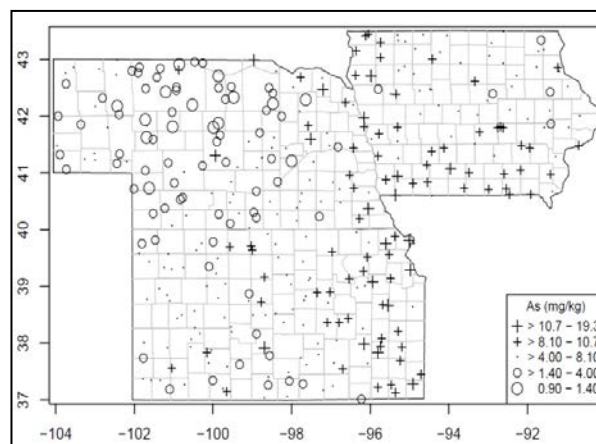


Fig.3.2

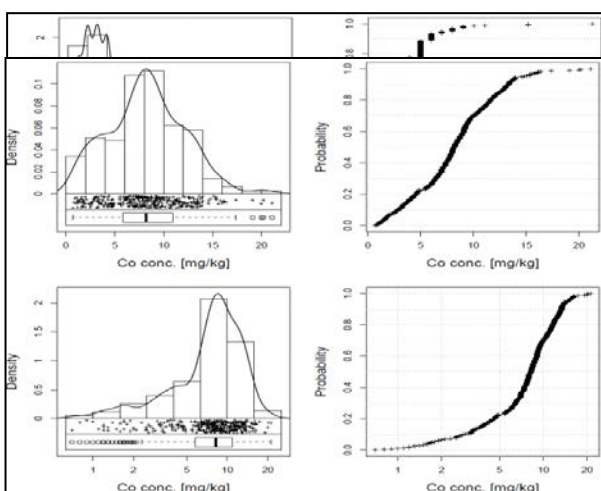


Fig. 3.3

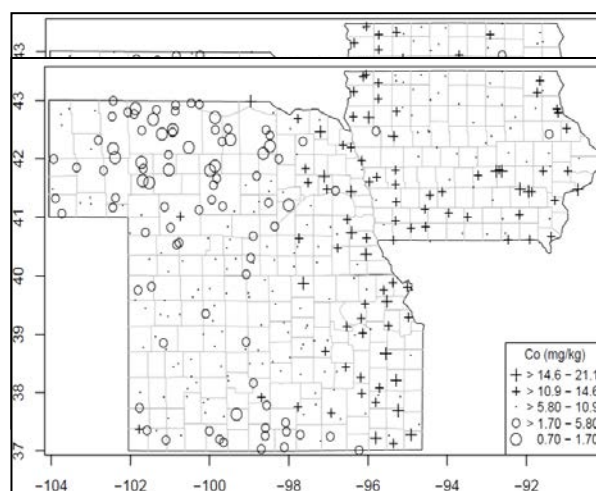


Fig.3.4

Fig. 3.5

Fig.3.6

Fig. 3 1-6 Histogram, density trace, one-dimensional scatterplot, and Tukey box plot in just one display, combined with the ECDF-plot for As, Cd, and Cr. Diagrams above: Original data (with log-box plot). Diagrams below: Log-transformed data.

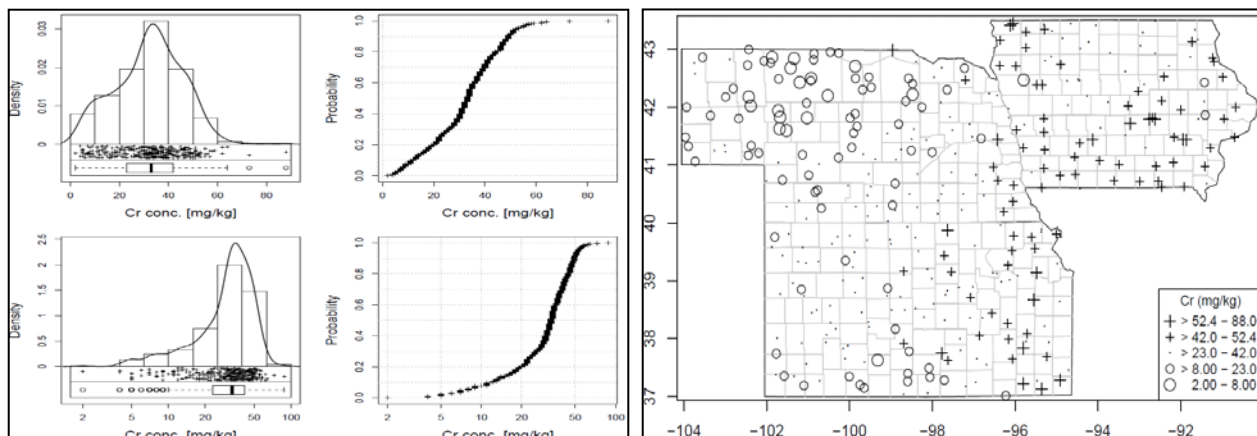


Fig. 4.1

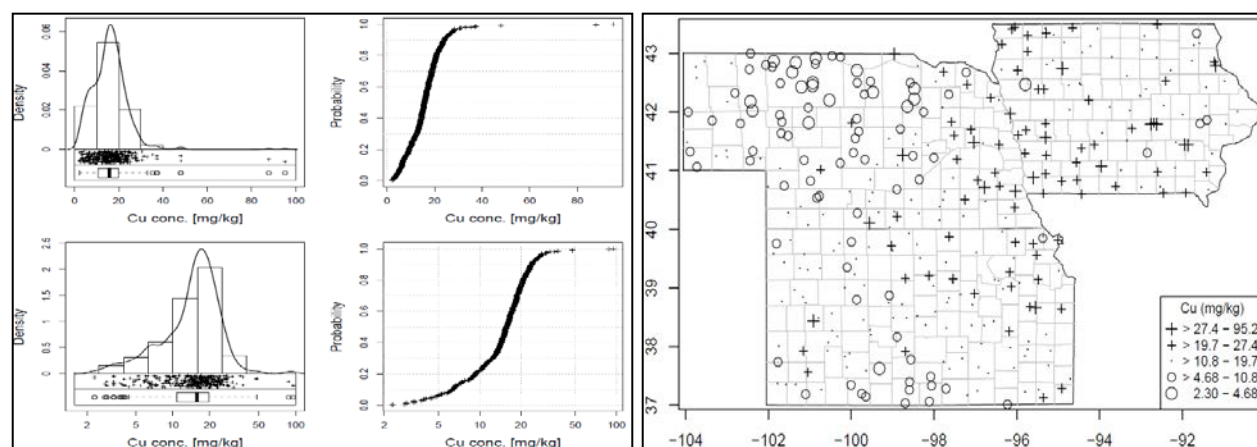


Fig.4.2

Fig. 4.3

Fig.4.4

Fig. 4.5

Fig.4.6

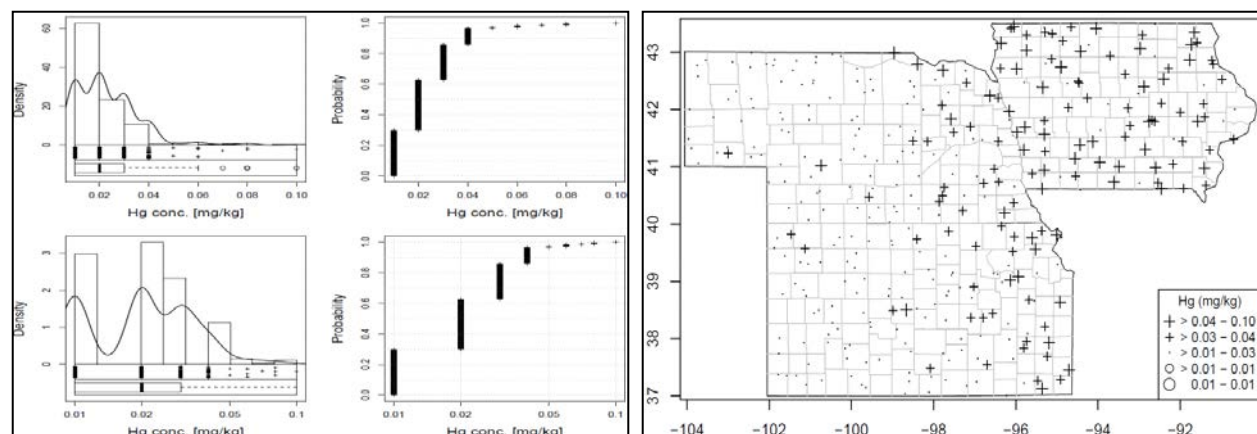


Fig. 4.1-6 Histogram, density trace, one-dimensional scatterplot, and Tukey box plot in just one display, combined with the ECDF-plot for Co, Cu, and Hg. Diagrams above: Original data (with log-boxplot). Diagrams below: Log-transformed data.

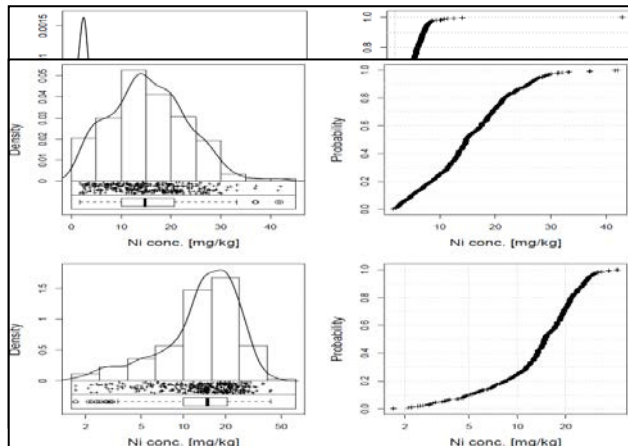


Fig. 5.1

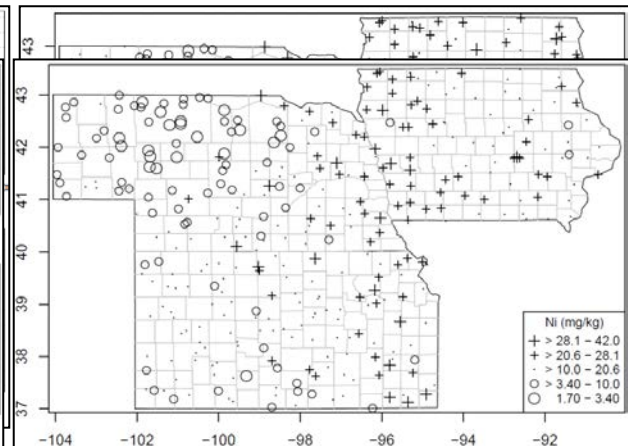


Fig. 5.2

Fig. 5.3

Fig. 5.4

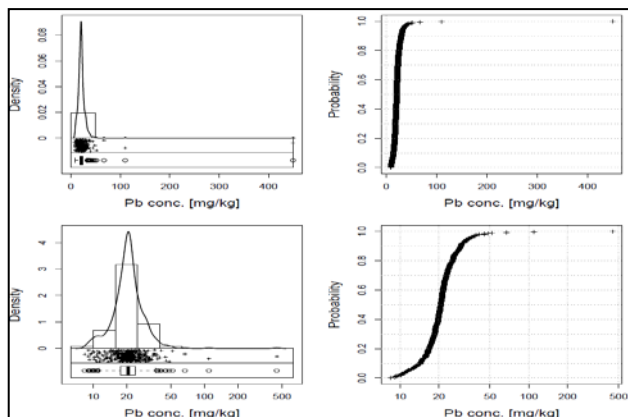


Fig. 5.5

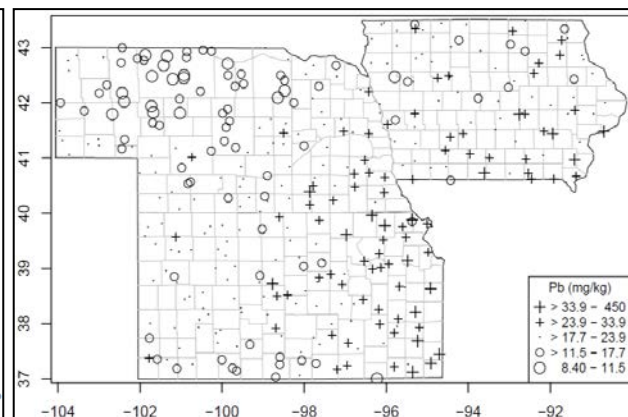


Fig. 5.6

Fig. 5.1-6 Histogram, density trace, one-dimensional scatterplot, and Tukey box plot in just one display, combined with the ECDF-plot for Mn, Ni, and Pb. Diagrams above: Original data (with log-boxplot). Diagrams below: Log-transformed data.

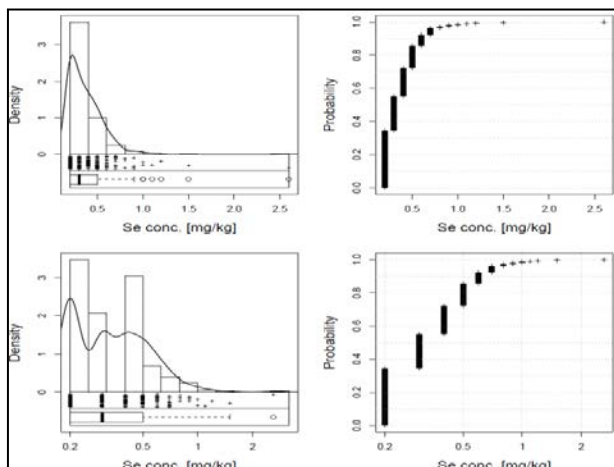


Fig 6.1

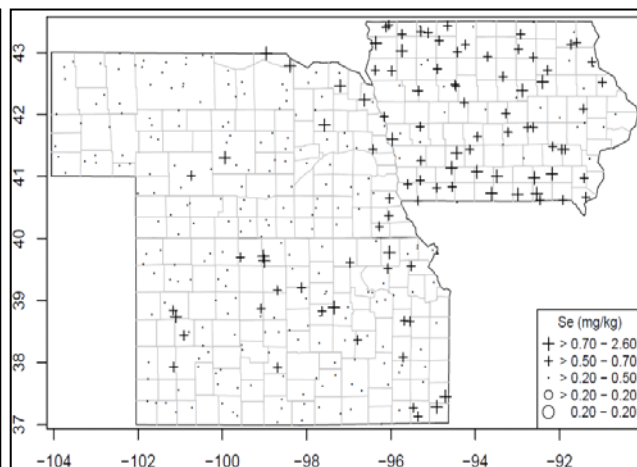


Fig. 6.2

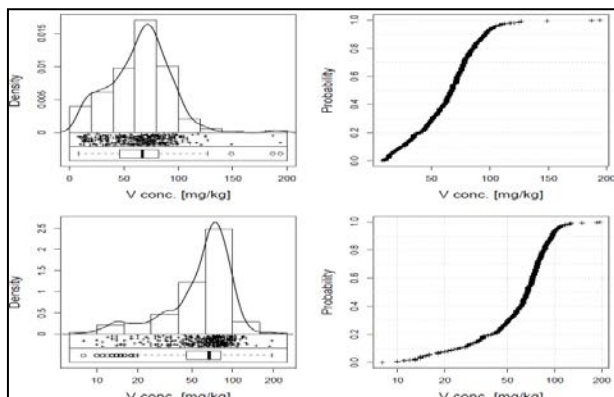


Fig 6.3.3

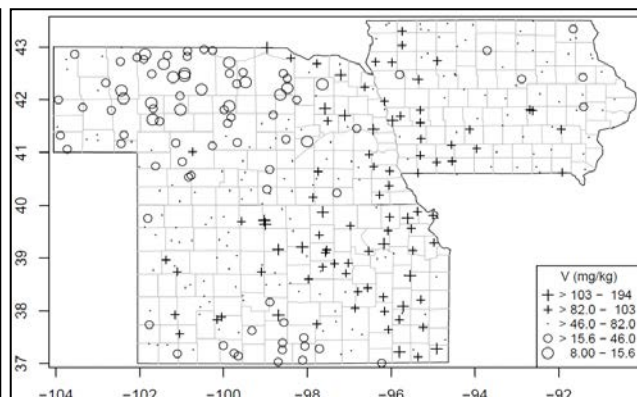


Fig.6.4

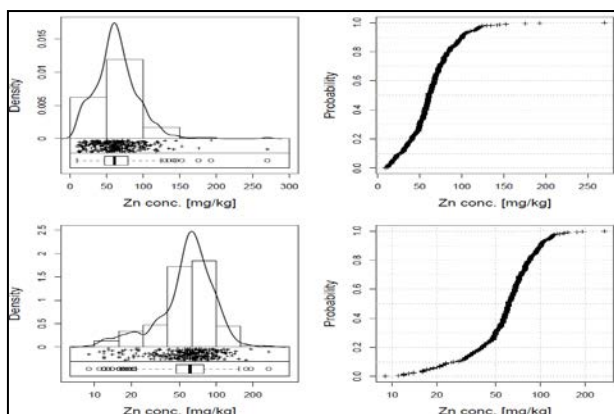


Fig 6.5

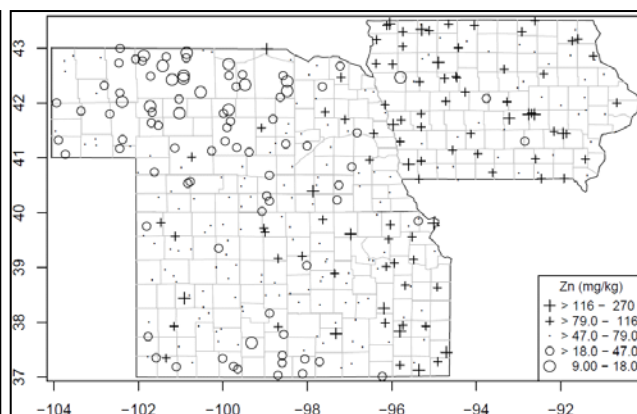


Fig.6.6

Fig. 6.1-6 Histogram, density trace, one-dimensional scatterplot, and Tukey box plot in just one display, combined with the ECDF-plot for Se, V, and Zn. Diagrams above: Original data (with log-boxplot). Diagrams below: Log-transformed data.

Robust Mahalanobis distances (RMD) showed outliers for all the heavy elements, illustrated in Fig. 7.1 & Fig. 7.2. The log ratio transformations were applied to the raw data. The correlation coefficient is shown in the scatterplot to compare to the calculated Pearson and Spearman correlation matrices.

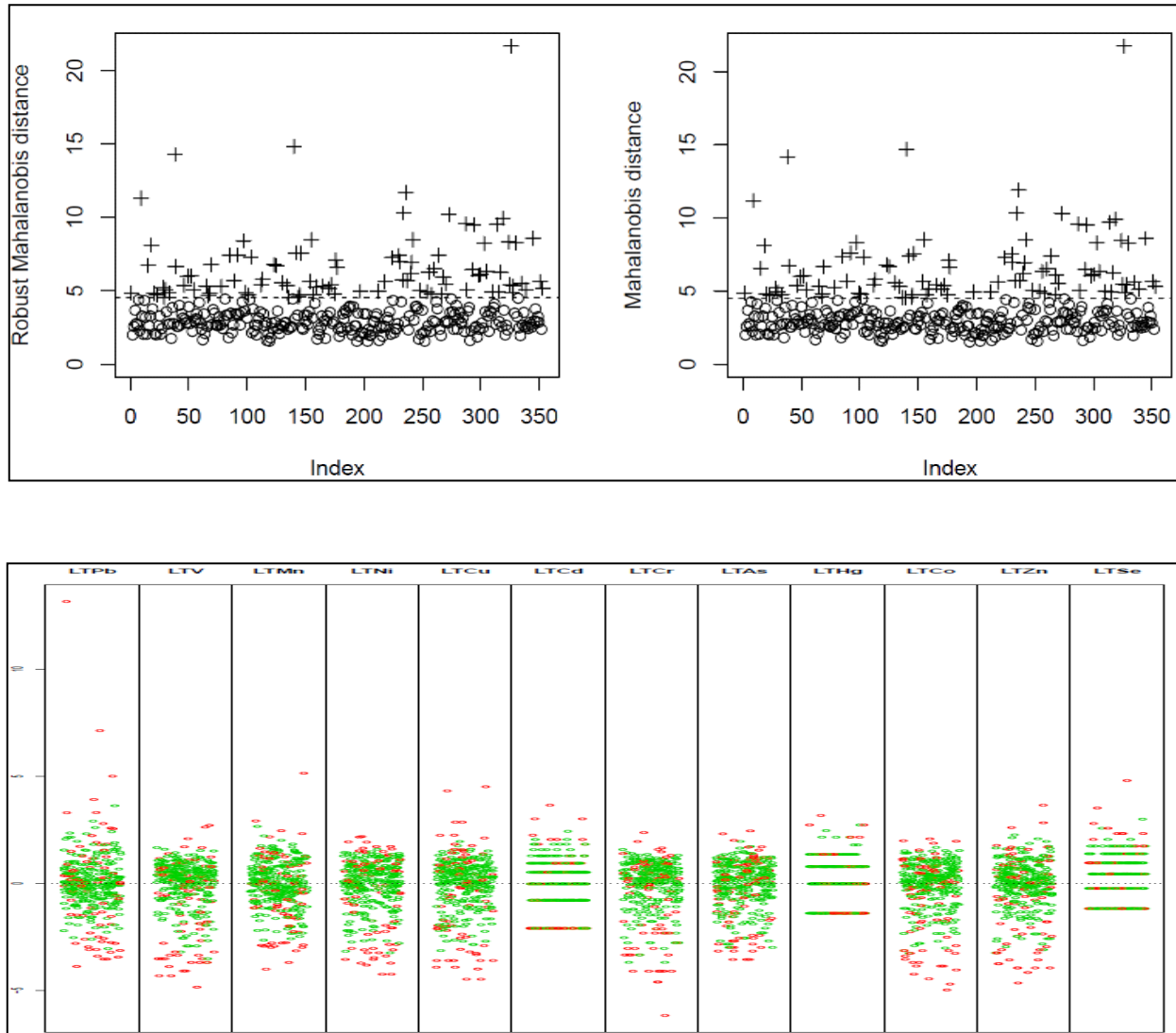


Fig. 7.1 The robust Mahalanobis distances show outliers of the data in IA, KS, and NE.

Fig. 7. 2 The univariate scatterplot analysis shows a plot of each single element for the outlier's identification. LT= log transformation. (red = outliers and green = non-outliers)

3.2 Correlation between Heavy Metals of Soil Samples

Through the multivariate analysis, many outliers have been observed in the maps of IA, KS, and NE, as shown in Fig. 7.1 & Fig. 7.2. A hierarchical cluster analysis was calculated to determine the similarity in behavior of each of the elements. This information was presented as a dendrogram (Fig. 8). The correlated distinctive relationships between the chemicals have been strongly investigated (Fig. 9). The multivariate statistical method was used to distinguish the relationship between the chemical variants by determining the directions of the elements, for translating the group chemical analysis (Fig. 9).

The PCA was performed to detect the relationships between the metals. The analysis presented different groups, with axes 1 and 2 demonstrating the cumulative percentage PC1 of the first element, explaining 72.1% of the total variance, contrasted with PC2 of the second group of elements, with 7.42%. This chemical analysis investigated significant spatial variability between the chemical elements. Some variables indicate trends related to others with high concentrations. One family of trace elements shows parallel linear directions that include the elements As, Co, Cr, Cu, Ni, and Zn. These same elements show a strong correlation in bivariate analysis. Moreover, the other chemical family that includes Pb and V are strongly correlated (Fig. 9). The third family of chemicals includes Mn and Se and they are significantly correlated (Fig.9). Another family is Zn, Cd, Pb, of the PC2.

Fig. 9 PCA for non-compositional biplot for showing the contaminants. Biplot of PC1 (72.1%) is plotted on the x-axis versus PC2 (7.42%) on the y-axis for a robust PCA.

3.3 Topsoil Pollution Assessment Using the Enrichment Factor (EF)

Enrichment or depletion of the heavy metals in the soil can be determined in relation to their content in the crust, using enrichment ratio (ER). It is calculated by dividing the median element concentration in the soil over its mean concentration in the earth's crust content (Essington, 2004). The values of $EF < 1$ on the scale indicates the possibility of consumption or/and depletion of the elements, which takes priority above their accumulation in the soil (Uduma & Awagu, 2013).

The EF parameter normalized the concentration of heavy elements with respect to the element normalizer (Ti). The summary of the descriptive statistics of EFs, corresponding to twelve heavy metals measured in agricultural soils in IA, KS, and NE are given in Table 3.

The calculated range of EF is 0.25–4.76. The mean values of the EFs were less than or close to 1 for the elements As, Co, Cu, Ni, and V, proposing neither enrichment nor impoverishment in the topsoil's average with these heavy metals. In contrast, the mean EF values for Cd, Hg, Pb, and Zn were greater than 1.1, demonstrating a deficiency to minimal soil contamination with these heavy metals. EF values of Se present to be more than 1.5 (Fig.10).

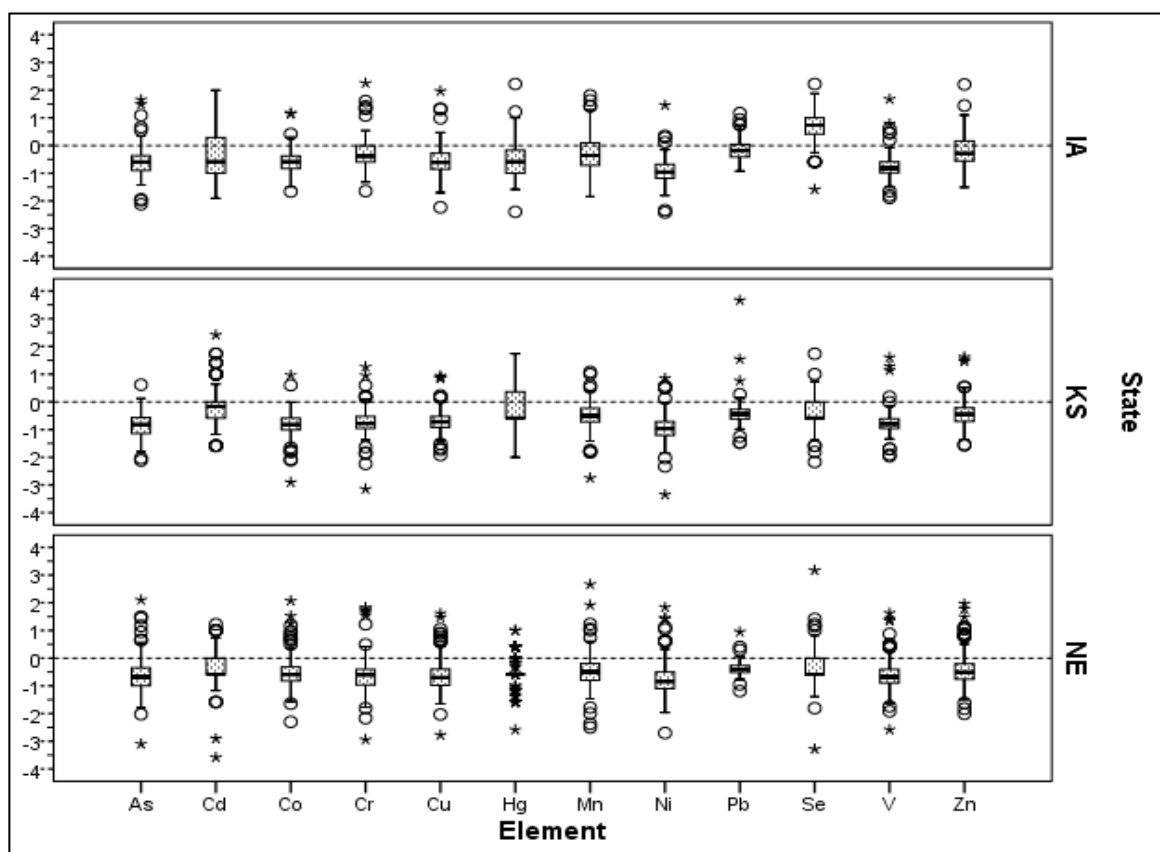


Fig. 10 EF mean of heavy metals in IA, KS, and NE

Table 3 Summarized exploratory data analysis of the enrichment factor (EF) in IA, KS, and NE, element name, showing different calculated values using Ti as element normalizer.

EN	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
N	348	348	348	348	348	348	348	348	348	348	348	348
Min	0.25	0.1	0.25	0.21	0.4	0.16	0.28	0.11	0.44	0.19	0.5	0.45
Max	4.76	13.71	2.06	2.4	2.57	5.83	5.25	4.09	19.07	8.57	5.65	3.69
Mean	0.97	1.37	0.97	1.04	0.99	1.21	1.18	0.85	1.26	1.63	0.93	1.2
Std.	0.43	1	0.26	0.31	0.3	0.66	0.57	0.36	1.02	1	0.3	0.42

In the EF criteria, a range of 1 to 40 indicates elemental enrichment (Edwin, 2013; Ismaeel and Kusag, 2016; Barbieri, 2016; Izah et al., 2017; & Tepanosyan et al., 2017). EF values were interpreted using the methods of Varol (2011), Sakan et al. (2015), Edwin (2013), Ololade (2014), Kumar (2015), Dartan et al. (2015), & Alghobar (2015). EF values < 1 indicate no enrichment, likely due to biological processes and/or leaching and natural weathering (Chee Poh and Tahir, 2017). EF = 1 can be considered as no increase or loss of the heavy metal in the soil with respect to the normalizer, while EF values > 1 (< 2) indicates additional anthropogenic inputs of heavy metals in the soil (Chee Poh and Tahir, 2017). Different classes exist and are defined as the following; EF < 3 (2) is little enrichment, 3–5 indicates moderately enriched, 5–10 is moderately severe enrichment, 10–25 is severe or significant enrichment, while, 25–50 indicates significant severe enrichment, and > 40 is exceptionally severe (Chee Poh and Tahir, 2017 & Sun et al., 2017).

The assessment of soil quality is done according to these criteria. Most of the EF values were estimated in the range 1.0–2 including for As, Cd, Cr, Cu, Hg, Mn, Pb, and Zn (Fig. 10), which must be interpreted as indicating no significant depletion or enrichment (Muller, 1969). All EF values were at more than 0.5 for the selected states. However, for the elements Co and V, the EF was less than 1, which indicated significant depletion or no enrichment. In terms of the levels of all three states, the significant moderate enrichment value was observed with Se at 2.37 in IA, pointing towards it being an enriched element in the surface soil, relative to the deep soil, especially compared to the other two states as shown in Table 4 and Figure 10. This finding shows that Se is a significant anthropogenic addition to the soil, contributing to the increased concentrations of heavy metals in the soil with significant difference ($p < 0.05$). EF of As concentration was 1 in IA and NE, while it was observed close to 1 (0.99) in KS. (Table 4). EF = 1 indicates that As is minimally enriched or depleted (Fig.10). EF mean values of Cd fall in the range of 1–2. EF investigated values are 1.23, 1.29, and 1.57 in IA, NE, and KS, respectively. The maximum EF value was recorded in KS. EF values of Cd indicate minimal enrichment, relative to C-horizon in IA, KS, and NE (Fig.10 & Table 4). EF of Cd in KS was more than its values observed in IA and NE. EF values of soil Co indicate that there is no enrichment or depletion. The observed values in the study areas were 0.99, 1.03, and 1.23 in IA, NE, and KS, respectively (Fig.11 & Table 4). EF values calculated for soil Cr were 0.96, 1.00, and 1.22 in KS, NE, and IA, respectively, and that indicates minimal occurrence or depletion of this element in the soil (Fig.11 & Table 4). EF values of Cu observed in KS, NE, and IA (0.99, 0.99, and 1.00, respectively) represent no significant enrichment in the surface soils (Fig.11 & Table 5). EF calculated values of Hg were estimated at 1.11, 1.12, and 1.39 in IA, NE, and KS, respectively (Fig.10, Table 4). These observations agree

with the EF of this element and with the values of Cd and Co. EF calculated values of soil Mn lie in the range of 1.09–1.36, indicating enrichment in the topsoil. The values were assessed in NE, KS, and NE being 1.09, 1.13, and 1.36, respectively (Fig.10 & Table 4). The observed of EF values of soil Ni were 0.78, 0.84, and 0.92 in IA, KS, and NE, respectively (Fig.11 & Table 4). The bioavailability and mobility of Ni may increase under acidic and neutral conditions (Kabata-Pendias and Pendias, 2001). EF of Pb was within the range 1–1.5. The estimated EF values of Pb were 1.14, 1.33, and 1.34 in NE, KS, and IA, respectively, which shows significant enrichment. The highest values of EF in the study area were for Se. EF of Se was moderately enriched in IA (2.37), as compared to EF values in KS and NE (1.33, 1.41), respectively (Fig.11 & Table 4). Chronic Selenosis in horses has been identified in western IA and has been attributed to Se in loess soils, however, no chemical data was presented for Selenium soil contents, and no other such situations have been reported (Witte and Will, 1993). The values of EF for soil V in IA, KS, and NE showed insignificant enrichment, calculated at less than 1 (0.86, 0.95, 0.95, respectively) (Fig.11 & Table 4). Zinc is one of the most necessary elements for organisms, but it could be toxic if it exceeds the permitted limit. The results of EF calculation of Zn concentration in NE, KS, and IA were 1.12, 1.23, and 1.27, respectively, demonstrating minimal enrichment (Fig.11). A strong association of pollution with heavy metal can be addressed with its distribution through industrial applications, agrochemicals, such as fertilizers and pesticides, and mining of regions.

Table 4 EF values calculated for IA, KS, and NE

State ID	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
Iowa	1.01	1.23	0.99	1.22	1.00	1.11	1.36	0.78	1.34	2.37	0.86	1.27
Kansas	0.90	1.57	1.23	0.96	0.99	1.39	1.13	0.84	1.33	1.33	0.95	1.23

Nebraska	1.01	1.29	1.03	1.00	0.99	1.12	1.09	0.92	1.14	1.41	0.95	1.12
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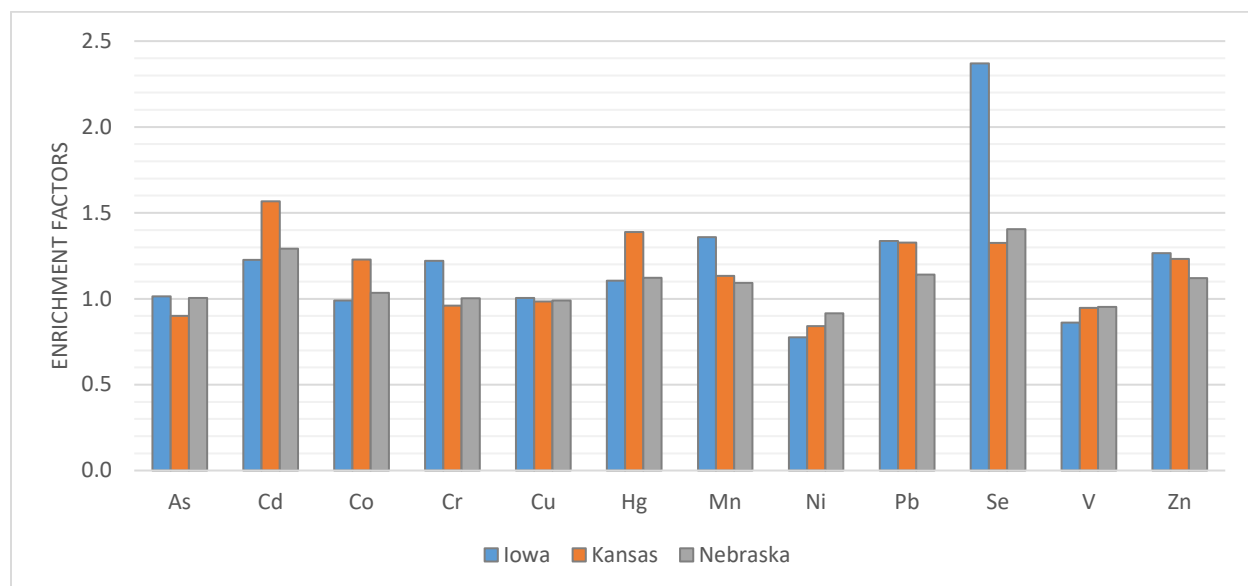


Fig. 11 The EF of various metals in surface soil of IA, KS, and NE, using Ti reference.

Zhang and Liu (2002) indicated that EF values falling between 0.05–1.5 showed that the source of the metal is due to natural processes; however, when the values are > 1.5 , the source is probably anthropogenic activities. It was also investigated by Kraepiel et al. (2015) that the element behavior in the surface soils, including of Al, Fe, V, Co, and Cr, where there was little to no enrichment in the surface soils, their concentrations were determined mostly by soil production fluxes with little effect on atmospheric inputs or biological activity. However, P, Cu, Zn, and Cd were moderately enriched in topsoil layers because of atmospheric deposition and biological elevation. Zhang et al. (2015) studied the farmland soil contamination with selected chemicals in China. The results investigated that the highest contamination rate was that of Cd (7.75%) while Hg, Cu, Ni, and Zn had lower contamination rates ($< 1\%$). Cd had exceeded the maximum allowable concentrations (European standard), moreover, Cd and Zn showed safer limits at $> 95\%$

in the cultivated soil. The elements that were sensitive to the variations in the atmospheric deposition fluxes included Cu, Zn, and Cd. Meanwhile, Mo and Mn indicated a strong enrichment in the surface soils, which may reflect past anthropogenic inputs (Kraepiel et al., 2015). Mn has a longer residence time in the soil because it can be returned to the surface soils through biological activities (Kraepiel et al., 2015). Hasan et al. (2013) stated that the high values of Cd in the sediment samples collected from the ship breaking regions of Sitakund Upazilla in Chittagong, Bangladesh, probably comes from the agricultural runoffs, containing Cd due to phosphate fertilizers. Izah et al. (2017) investigated the heavy metals contamination in soils associated with the Cassava mill effluents in the Niger Delta region of Nigeria, and these metals were associated with anthropogenic activities. Jiao et al. (2015) indicated that there was a strong relationship between moderately enriched concentrations of the metals As, Cu, and Pb, reaching an EF value of 2, also from anthropogenic inputs from industrial and mining activities. The accumulation of heavy metals could be due to direct or indirect anthropogenic application (Izah et al., 2017 & Tepanosyan et al., 2017). $EF > 2$ indicated non-crustal materials, therefore, these metals are delivered from point or/and non-point contamination sources (Barbieri, 2016). EFs calculated by Edwin (2013) showed moderately enriched values of Cd and Cr in the soil but showed deficiency to minimal enrichment for Cu, Mn, Ni and Zn. Aiman et al. (2016) reported that some metals have not biodegraded and are bound to the soils. The calculated EF values and their minimum and maximum points for individual heavy metals in agricultural soils in IA are presented in Fig. 15, 16, 17, and 18. The concentrations of metals were variable and many of the mean data have suggested chemical loading. Comparing the concentration of the heavy metals showed that some elements accumulate in the soil and fall within the values 2–5 of the EF indicator, such as As, Cd,

Hg, Mn, Pb, Se, and Zn, which indicate moderate enrichment (Table 5 & Fig. 12). The range of EF's for soil samples of IA lie between 0.29–5.25 (Table 5). The surface soils were enriched, in some regions, with the metals As, Cd, Hg, Mn, Pb, and Se (3.74, 3.42, 3.96, 5.25, 3.09, and 4.93, respectively), indicating a significant anthropogenic contamination with high values (1.13 ± 0.29).

Table 5 EF in IA calculated using Ti as element normalizer. Element name (EN), number (N), minimum (Min), maximum (Max), standard deviation (Std).

Element	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
N	91	91	91	91	91	91	91	91	91	91	91	91
Min	0.34	0.37	0.45	0.76	0.40	0.30	0.31	0.30	0.65	0.63	0.50	0.55
Max	3.75	3.43	2.00	2.00	1.69	3.97	5.25	1.84	3.10	4.94	1.34	2.89
Mean	1.01	1.23	0.99	1.22	1.01	1.11	1.36	0.78	1.34	2.37	0.86	1.27
Std	0.43	0.71	0.27	0.25	0.27	0.53	0.91	0.25	0.42	1.01	0.16	0.43

In IA, the mean of very high-enriched EF values was observed only in the case of Se (2.37). The EF maximum values of the metals As, Cd, Hg, Pb, Se, and Zn (3.74, 3.42, 3.96, 3.09, 2.88, respectively), observed in the present study, did not exceed the moderately enriched level with the EF values being < 5 . In contrast, Mn is the only element that has been observed with significant enrichment (5.25). The results of this investigation showed the mean EF of heavy metals in the soil being minimally enriched, except Se (Table 6). The regions in IA have excessive agricultural

activities and the accumulation of the heavy metals in the soil is due to anthropogenic impacts. The correlation matrix was conducted in order to explore the association between the heavy metals. According to the correlation analysis, some of the metals were significantly correlated to one another. The summarized results are shown in Table 6. A significant correlation ($p < 0.01$) was detected between Cd, correlated to Mn (0.67). A significant correlation of Co was also detected with Ni (0.70). Cu was significantly correlated to Zn (0.74). Also, a correlation was detected between Ni and V (0.68). The mean EF values for the metals in IA are shown using the boxplot in Fig 11. It presents the outliers of EFs that have been observed in the boxplot, reflecting the possibility of a unique source of contamination.

Table 6 Pearson's correlation matrixes of EF of heavy metals in IA, using Ti as reference
(**Correlation is significant at the 0.01 level.*Correlation is significant at the 0.05 level)

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
As	1											
Cd	.119	1										
Co	.244*	.375**	1									
Cr	.177	-.185	.179	1								
Cu	.466**	.065	.268*	.539**	1							
Hg	.434**	.265*	.204	.108	.381**	1						
Mn	.086	.677**	.588**	-.034	.006	.210*	1					
Ni	.353**	.290**	.704**	.301**	.422**	.286**	.500**	1				
Pb	.301**	.374**	.326**	.018	.290**	.384**	.256*	.140	1			
Se	.103	.051	.215*	.059	.152	.063	.208*	.198	.311**	1		
V	.453**	-.074	.479**	.503**	.568**	.260*	.066	.689**	.148	.204	1	
Zn	.425**	.274**	.258*	.377**	.749**	.391**	.114	.304**	.536**	.076	.440**	1

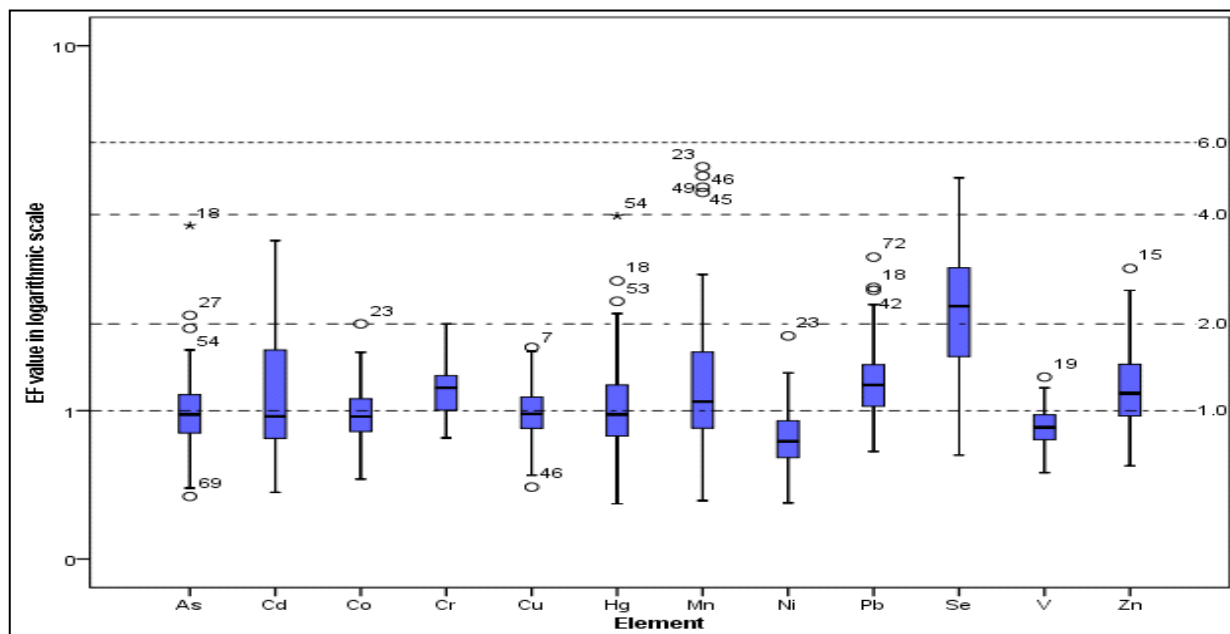


Fig.12 Boxplot showing EF values of individual heavy metals in Iowa

For KS, the calculation of EF values showed deficiency or minimal enrichment < 2 (Table 7). The calculated EF values and their minimum and maximum points for individual heavy metals in agricultural soils in KS are presented in Fig. 15, 16, 17, and 18. Comparison of the concentrations of the heavy metals showed that some elements with the maximum values of the elements are ranged within 1.49–19.07 ppm and are included in Table 7. The lowest two values of EF (1–2) are for Co and Cr. Conversely, the remaining heavy metals are accumulated in the soil and fall within the values 5–20 of the EF indicator for As, Cd, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn (2.80, 13.71, 2.41, 5.83, 4.23, 3.82, 19.07, 8.57, 5.65, 3.69, respectively), which indicates significant enrichment (Table 7). The mean values of EF's for KS soil samples lies between 0.084–1.56 (Fig. 13). The surface soils were minimally enriched or depleted in some regions with the metals Cd, Hg, Mn, Pb, Se, and Zn (1.56, 1.38, 1.13, 1.32, 1.32, and 1.23, respectively) that

indicates significant anthropogenic contamination with high values (1.12 ± 0.44) (Fig.

13). The outliers of heavy metals presented in Fig.13, within values 2–20, investigate anthropogenic outputs from different sources, ranging from moderate to significantly enriched soil EF's.

Table 7 EF in KS calculated using Ti as element normalizer. Element name (EN), number (N), minimum (Min), maximum (Max), standard deviation (Std).

Element	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
N	127	127	127	127	127	127	127	127	127	127	127	127
Min	0.25	0.45	0.25	0.24	0.45	0.16	0.28	0.11	0.44	0.24	0.56	0.46
Max	2.80	13.71	1.50	1.73	2.41	5.83	4.23	3.82	19.07	8.57	5.65	3.69
Mean	0.90	1.57	0.89	0.96	0.99	1.39	1.13	0.84	1.33	1.33	0.95	1.23
Std.	0.32	1.39	0.20	0.25	0.28	0.82	0.39	0.34	1.62	0.83	0.45	0.50

The correlation analysis results showed a significant relationship between some of the heavy metals. A significant correlation of As was found with Ni (0.68), V (0.67). Cd has a strong correlation relationship with Ni (0.60, Se (0.65), and V (0.72). Co was significantly correlated with Ni (0.60), and Cu correlated with Zn (0.61). The significant association of Ni was detected with Se (0.67) and V (0.86). In addition, Se was significantly correlated ($p < 0.01$) with V (0.75) as it shown in Table 8.

Table 8 Pearson correlation matrixes of enrichment factor (EF) of heavy metals in Kansas using Titanium (Ti) as a reference (** Correlation is significant at the 0.01 level.* Correlation is significant at the 0.05 level).

As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn	
As	1											
Cd	.435**	1										

Cr, Cu, Hg, Mn, Ni, Pb, Se, and Zn ranged between 2-5 indicated to significant EF's in NE (Table 9). All maximum values of heavy metals EF's were ≥ 2 (4.75, 4.05, 2.06, 2.40, 2.57, 2.75, 2.37, 4.09, 3.90, 5.55, and 2.34 respectively), except V (1.82). The calculated means of EF's of all heavy metals in NE falls within 0.91- 1.40 including As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn (1.00, 1.29, 1.03, 1.00, 0.98, 1.12, 1.09, 0.91, 1.14, 1.40, 0.95, and 1.12) respectively, which indicating to no significant enrichment (1.09 ± 0.18) (Table 9) (Fig. 14). The outliers are presented in Fig.14.

Table 9 Enrichment Factor (EF) in Nebraska calculated using Ti as element normalizer. Element name (EN), number (N), minimum (Min), maximum (Max), standard deviation (Std).

EN	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
N	130	130	130	130	130	130	130	130	130	130	130	130
Min	0.414	0.103	0.627	0.214	0.398	0.250	0.309	0.433	0.458	0.190	0.591	0.537
Max	4.756	4.050	2.064	2.400	2.572	2.750	2.372	4.094	3.906	5.559	1.823	2.343
Mean	1.005	1.292	1.034	1.003	0.989	1.122	1.092	0.915	1.140	1.405	0.953	1.121
Std	0.509	0.631	0.277	0.353	0.340	0.543	0.346	0.425	0.362	0.884	0.174	0.310

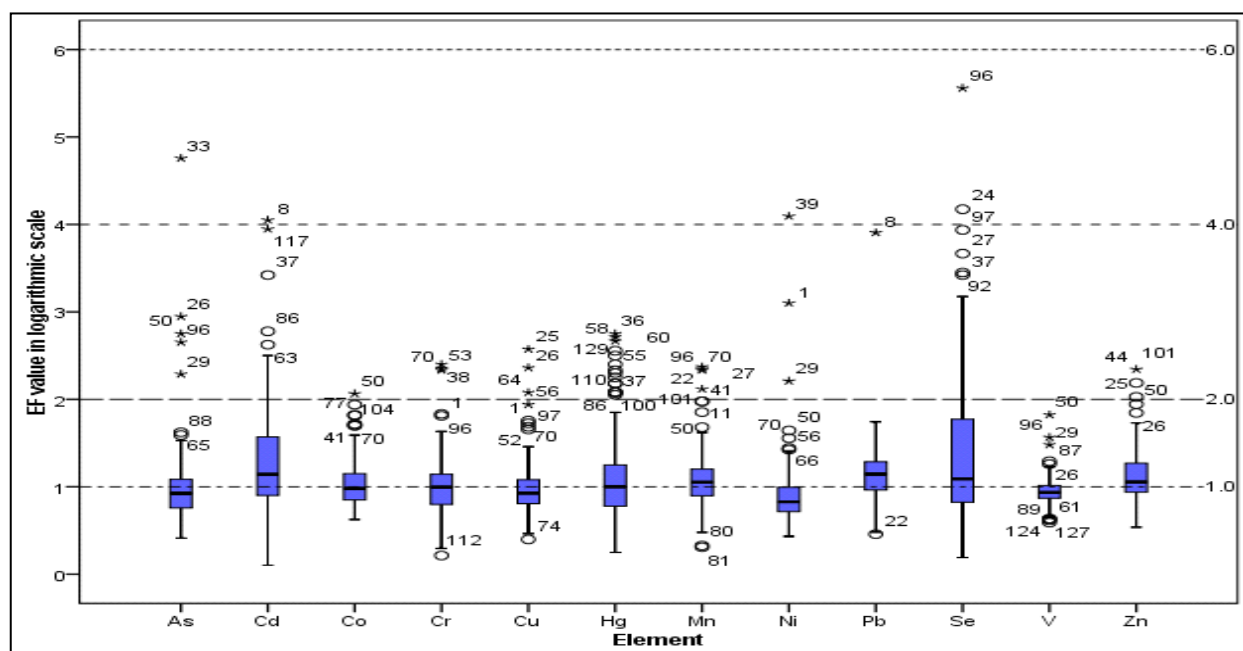


Fig.14 Boxplot showing EF values of individual heavy metals in Nebraska

3.4 Mapping of Enrichment Factor of the Heavy Metals

Geochemical maps were produced to show the single element geochemical distribution. These methods are beneficial indicators to identify the actual sources of chemicals and the activities leading to contamination. The maps were generated for the EF for 12 studied elements for the three states (IA, KS, and NE) that provide a baseline data regarding to distribution and accumulation of the selected elements. The spatial distribution of the soil heavy metals concentrations as projected by Kriging is mapped in Fig. Fig. 15, Fig. 16, Fig. 17, & Fig. 18. Point maps of these data show spatial variation patterns of EF and showed difference from site to site suggesting that the surface soil is affected by human inputs according to the source of the element

in the study areas. The interpretation of EF was based on the deviation of the ratio between the target metal and the immobile and conservative normalizer in the localized soil. High concentrations of metals may be caused by external anthropogenic inputs such as agricultural overflow atmospheric inputs, and industrial wastewater release. The results showed different potential sources of high EF values of As, Cd, Co, Cu, Cr, Hg, Mn, Pb, Se, and Zn (2.6, 4.8, 2.1, 5.4, 2.5, 7.6, 7.5, 4.3, 3.6 and 3.6) (Fig. 15, 16, 17, and 18). Most of the individual EF values as sampling points were 2-5, indicating moderate enrichment. The maximum values in the spatial chemical distribution of EF maps show the differences between elemental concentrations.

The EF spatial maps of As showed the range values between 0.5-2.6. The maximum value of 2.6 suggesting moderate enrichment as it was described by Jiao et al. (2015) in some regions especially in the east of IA, northwest, middle, south of NE, and north, southwest of KS (Fig.15.1). However, the minimum value of EF was 0.5 was observed in some areas in IA, KS, and NE as it is shown in (Fig. 15.1). The distribution maps of Cd showed a significant value of 4.8 in eastern of IA and KS, while in NE the highest values were observed in southern part of the state (Fig. 15.2) indicating an anthropogenic point source. The low value (0.6) was concentrated in the west of IA, KS, and NE, in addition to northern NE (Fig. 15.2). An extended two domains are located in the north of NE and south of KS (in the border), indicating that high Cd concentration is attributed to human inputs. The spatial pattern of anthropogenic EF's values of Co in agricultural soil falls within range 0.5-2.1 (Fig. 15.3). The hotspots points of EF soil Cd identified in southern of IA and northern of NE. In KS, few moderate EF areas have been observed (Fig. 15.3). Higher anthropogenic EFs regions of Cr were identified in most of IA with values 2.5 especially in the middle areas of IA. In NE the high EF regions were determined with one hotspot located in

northwest side and one hotspot in the middle (Fig.16.1). The range of EF of Cr was 0.6-2.5 in three states. However, the high EF was observed in southwest of KS. The interesting areas additionally were identified as straight line located in northern, and triangle points in the middle of KS (Fig.16.1). Significant enriched EF of Cu was investigated with high-calculated values 5.4 that lie in the range of EF indicator 5-20 (class 3) indicating point source. Three hotspots of EF of Cu extended vertically from north to south of IA. Moreover, two small spots are located in northeast and northwest of IA (Fig.16.2). However, there are two regions affected with the metal located in southern in 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.16.2). Greater anthropogenic EF of Hg estimated value 7.6 indicating to significant hotspot enrichment observed through many regions in KS especially in east side. In IA, EF of Hg determined in northeast and southeast, and one hotspot located in south of the state (Fig. 16.3). Interestingly, EF points of Cu values presented areas that were extended to north of KS. This observation detect a close spatial correlation with the Cu high EF points in south of NE (Fig. 16.2 & Fig.16.3). The lower EF values (0.5) were investigated in the different locations in IA, KS, and NE ((Fig. 16.3). Interestingly, several high EF values were disappeared in north of NE (Sand Hills) similar to EF map of Pb. The spatial behavior of EF map of Mn showed the highest value (7.5) in the north and southeast of IA. Nevertheless, the surface soils in the rest of the area seems less enriched (Fig. 17.1). Moreover, the interesting point, the hotspot located in particular area in the north of IA is surrounded with weakly enriched areas with lower value range (0.5-1) (Fig. 17.1). Likewise, this area is isolated from high area in located in south of IA, this could be due to the following factors: i) the high average of Mn input by geochemical processes in the earth surface. (ii) It could be referred to

anthropogenic applications. The evidence can be possibly considered that Mn source may be non-natural is that several high EF values in the maps of NE and KS parts were discovered. EF values of Ni ranged 0.4-1.8 that is categorized with no significant enrichment in IA, KS, and NE. The EF map of Ni displayed two split 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 1.8 (Fig. 17.2). The EF calculation showed deficiency or minimal EF the study area. However, two minimal enriched EF regions have been observed in northern NE and in addition one area located in north of KS (Fig.17.2). EF values of Pb fluctuated according to the region under concern and the range of calculated EF of Pb was 0.7-4.3. The smooth aspect of the map presented hotspots of Pb located mostly in middle of KS with high value 4.3 (Fig. 17.3). EF map of IA showed a moderate enrichment in extended points in east, north and south of the state. The high anomaly of EF values did no longer exist in most areas of the EF map especially in north of NE (Sand Hills). However, one small hotspot was perceived only in southeast of NE (Fig.17.3). The distribution frequency of anthropogenic EF values of soil Se revealed influenced regions in most of IA and has continuously extended to the east of NE with high value (3.6). It is important to note that there is linear region of anomalous concentrations extending along south of IA has high value (3.6) that is classified as moderate enriched (Fig. 17.3). Furthermore, Se and Zn exhibited similar high values (3.6) (Fig. 18.1 & Fig.18.3). Some of diffused areas also have been observed in different areas in NE and KS (Fig. 18.1). These observations indicating possibly the contribution of anthropogenic activities of Se increasing Se content in the soil rather than natural geological processes. The distribution of EF maps of V showed great spatial variations along three states. The most affected area was among of KS. The range of EF of V was estimated 0.5-1.4

(Fig.18.2). NE and KS revealed similar patterns compare to IA. These multidimensional variations of EF of V observed in NE and KS are independent. The distribution of chemical loading of EF maps of Zn with values ranging from 0.6-3.6 that is classified as significantly moderate enriched. The pattern of high Zn enrichment was recorded with closer zones in the EF of V concentration maps, especially in the east of IA, which may stating to different potential anthropogenic sources of Zn, (Fig. 18.3). This is evident from Fig. 16.2, Fig. 16.3, & Fig. 17.1) that show significant element intensity of Cu, Hg, and Mn that exceed the normal range indicated in EF classes.

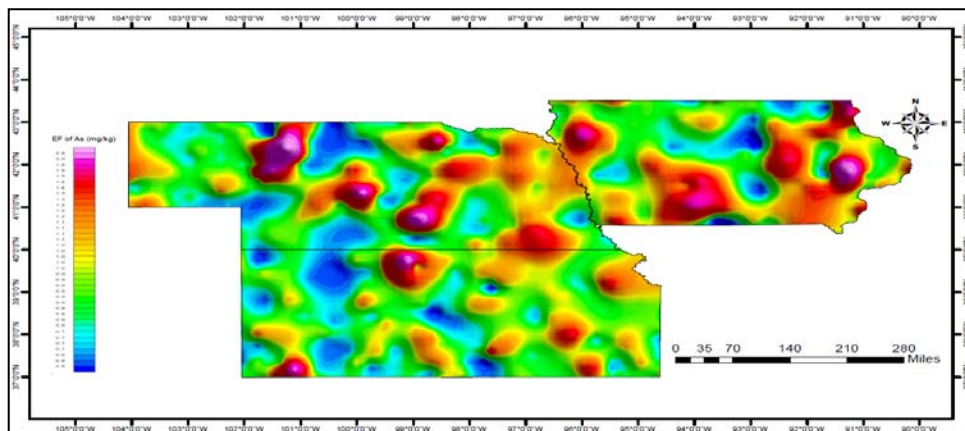


Fig.15.1

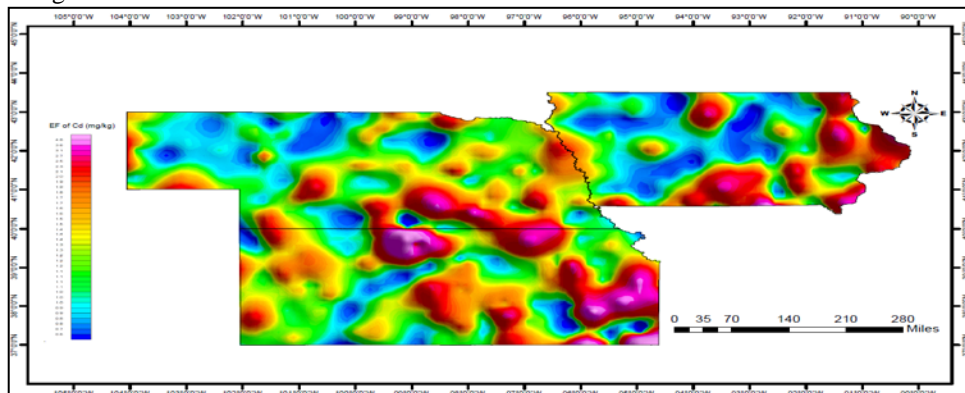


Fig.15.2

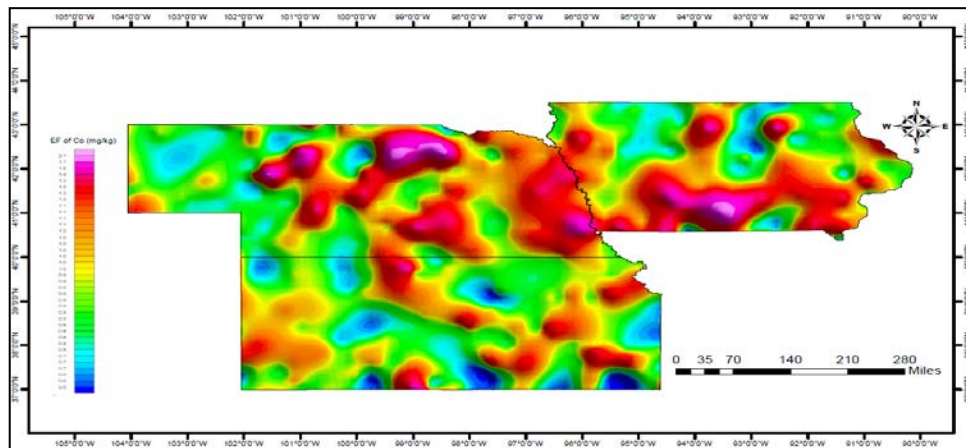


Fig.15.3

Fig. 15. 1-3 (As, Cd, and Co) Distribution maps of enrichment factor values of heavy metals in the study area.

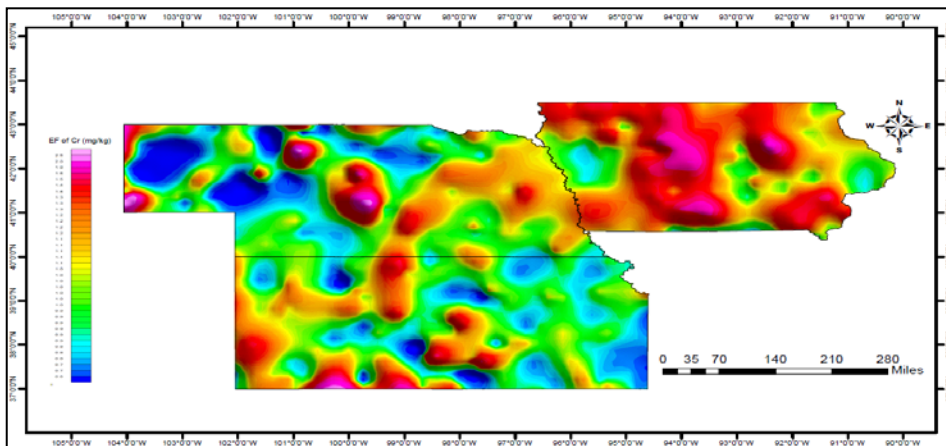


Fig.16.1

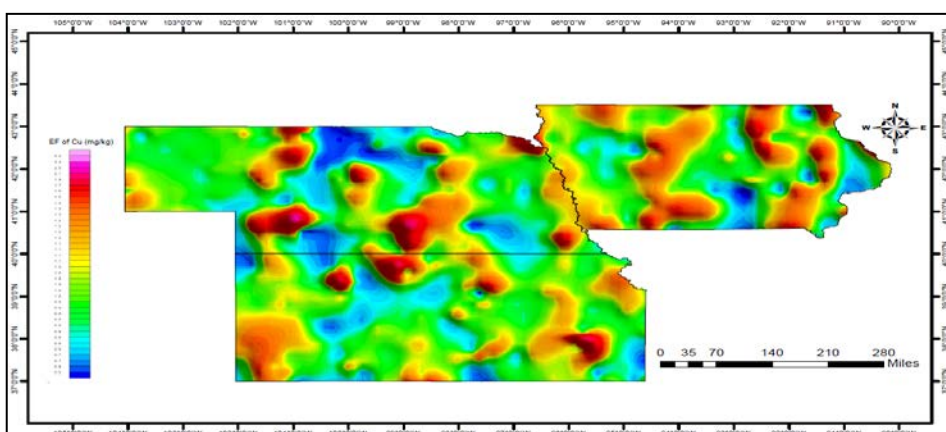


Fig.16.2

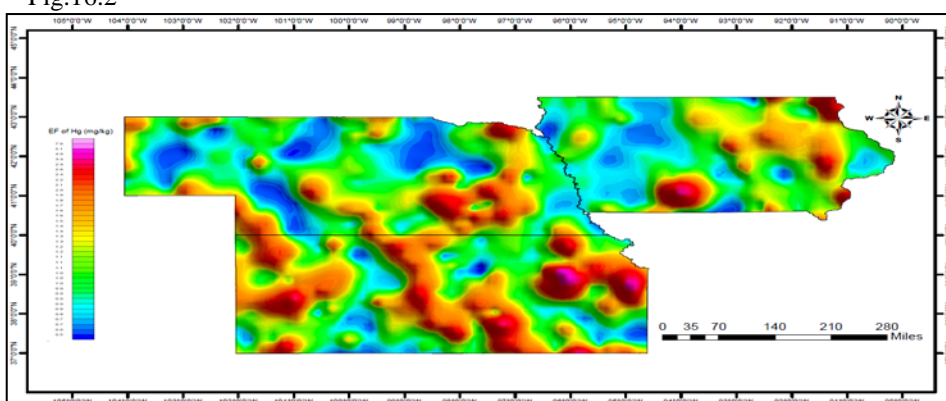


Fig.16.3

Fig. 16. 1-3 (Cr, Cu, and Hg) Distribution maps of enrichment factor values of heavy metals in the study area.

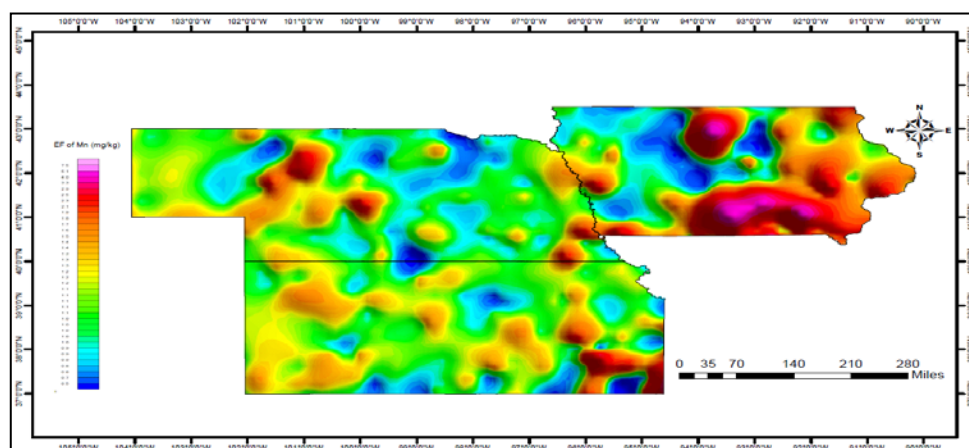


Fig.17.1

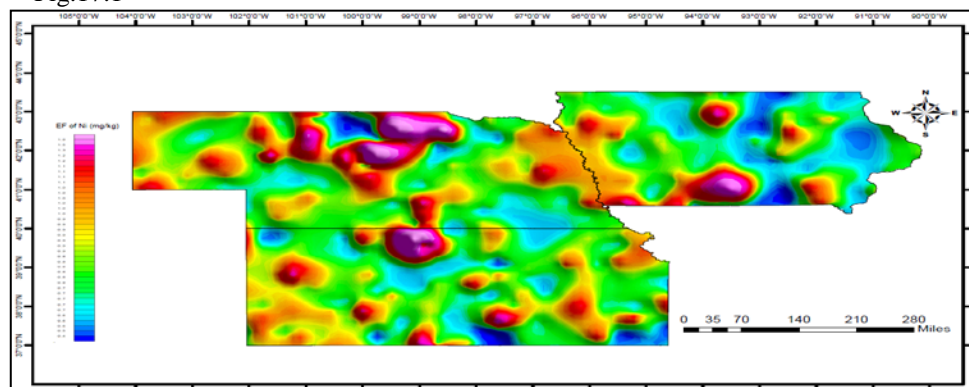


Fig.17.2

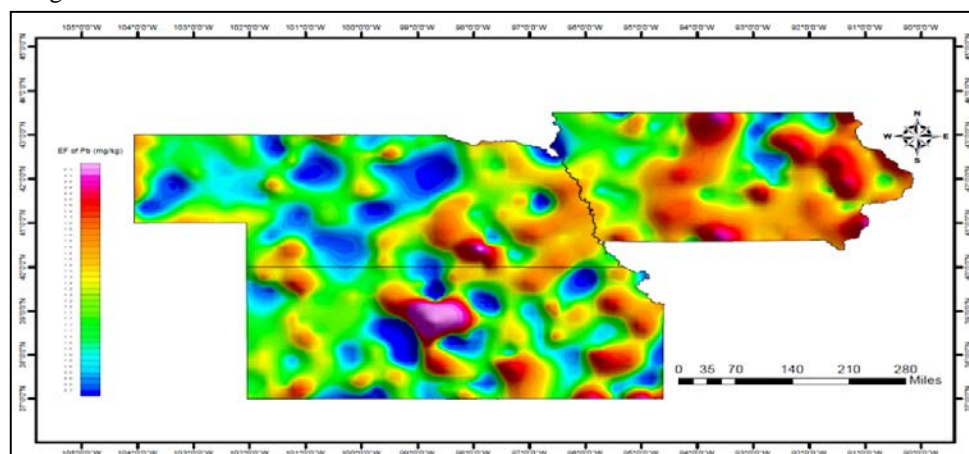


Fig.17.3

Fig. 17. 1-3 (Mn, Ni, and Pb) Distribution maps of enrichment factor values of heavy metals in the study area.

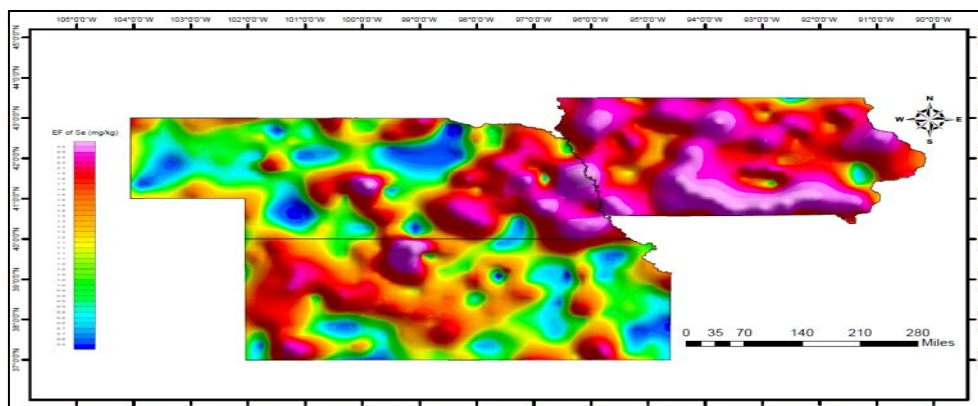


Fig.18.1

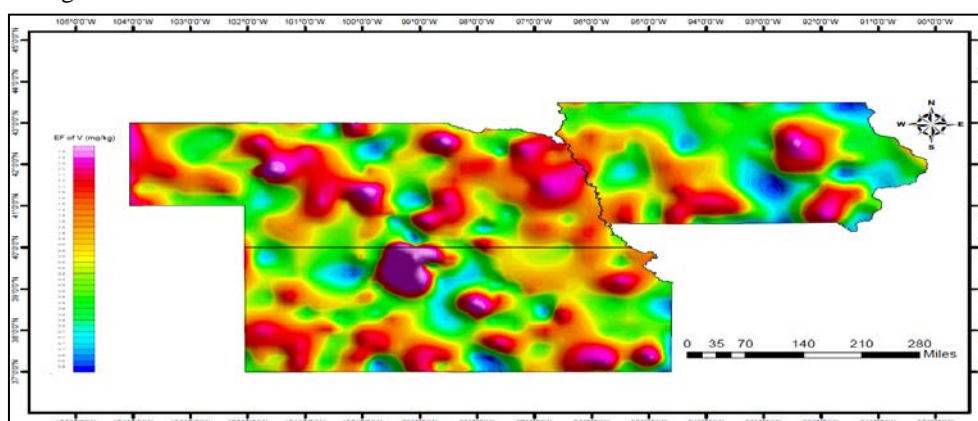


Fig.18.2

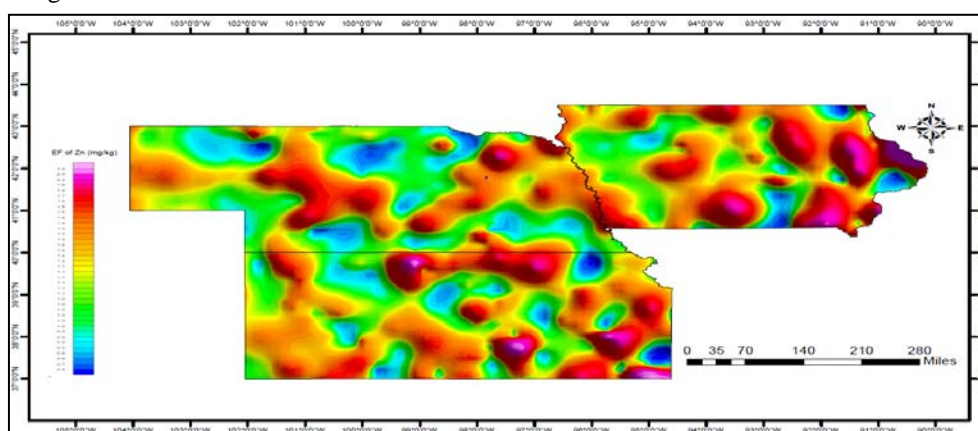


Fig.18.3

Fig. 18. 1-3 (Se, V, and Zn) Distribution maps of enrichment factor values of heavy metals in the study area.

3.5 Pollution Source Identification for Individual Heavy Metals

For further source identification and assessment of the chemical elements in the soil, a database was extracted from toxic release inventory (TRI), which is a public database including the toxic chemical releases information and waste management activities. Certain industrial groups and federal facilities report this information annually. ToxMap is a Geographic Information System (GIS) database, which includes EPA. ToxMap provides data on point and airborne sources

of anthropogenic influence. ToxMap is a GIS map from the division of specialized information services of the US National Library of Medicine (USNLM). 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 (TOXMAP Environmental Health Maps, 2018). 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 released data are measured by pound. In addition, the toxic chemical amounts are reported which are sent for waste management. These data facilitate identification and color codes 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 (TOXMAP Environmental Health Maps, 2018).

In this study, ToxMap hot spots were compared with the anomalous areas of USGS soil maps of surface soil chemistry produced in this study to explore alternative sources of chemicals. Since all the toxic chemicals released are reported from industrial activities, the other possible sources such as transportation, farming, and households are not involved ((TOXMAP Environmental Health Maps, 2018). According to the heavy metals associated with the human inputs through air pollution, metals are transported through the air and deposited onto the surface soils, depending on the soil properties. This probably reflects variation in natural concentrations between the locations. The consideration of the chemical sources may be from many possible human activities or natural processes. For this reason, comparison between two environmental factors including air emissions and soil contamination was considered to figure out the source of

the chemical elements. The investigations showed that no significant air pollution data have been investigated with some of the elements compare to others. Many factors have been considered to find out the source of the chemical anomalies. The numbers of high emissions, the anomalies spots are one. Another factor is the number of the sites varies for each chemical. They are not necessary to be the same sites. The sources of the chemical are different because there are different industrial processes that the sites will vary with chemistry also. The other variable is the concentration of the chemical by pound shown in the scale. In the consideration of the negative and positive anomalies, in general, all the maps indicated to that most of the results are close to zero.

From the As air emissions distribution maps , it is clear to observe a negative correlation between the soil anomaly hot spots and air and land emissions at all. There were not any recorded high values of the air releases , however, the only low value of As was observed in the far west of IA (4.7 lbs) in the low value area in soil distribution map (Fig.19.1 & Fig. 19.2). In the air release map of Cd, the number of Cd releases to air and land are very low. For instance, in three states Cd release into the air there is 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 (Fig.19.3 & Fig. 19.4). Consequently, the source of Cd looks like from fertilizers.

Generally, there are no releases of Co in the land except only one point source with value 1 lb, located in the west of IA and no significant Co releases have been observed in NE and KS (Fig. 19.5, Fig. 19.6). The range of Cd in the air is 0-7 lbs. while in the land is 0-1 lbs. It is important point to note that Cd is one of the elements that have very low concentrations in all three states. The whole soil anomalies are not associated with the Cd released that is estimated 2-7 lbs. into the air (Fig.19.3) It can be clear that the source of Cd in the soil is anthropogenic land activities (Fig.19.

4). Similar to Co, the three low areas in Cr soil geochemical maps are surrounded by high points have been observed and not interrelated to air emission values (Fig. 20.1 & Fig. 20.2). 1- 328 lbs. of Cr released into air. However, 0-5 lbs of Cr is released into land (Fig. 20 & Fig. 20.2). Only three significant high values are associated to soil anomaly in south of IA. Three anomalies of low concentration in Cr geochemical map have been noted, three points located in east and west of IA and one point in east of KS, which is from farming and windblown deposits (Fig. 20.1). The concentrations of Cr emissions range is 0-752.7 lbs. in the air compared to 0-750 lbs. on the land (Fig.19.2). Air may contribute a little bit to the soil with some dominant values of Cr in south of IA and eastern KS and NE, and are correlated positively with geochemical hotspots in soil (Fig. 20.2). The releases of Cr were 0-145 lbs in IA, 0-30- lbs. in KS and 0.03-250 lbs. in NE (Fig.20.1). In general, the amount of Cr released in the air was 0- 19 lbs. while on the land was 0 lbs. The low concentrations of Cr were negatively correlated with soil anomalies in the study area (Fig. 20.1). According to air emission map of Cr, the highest values recorded in IA was 146-374 lbs. while was in KS and NE (126-370 lbs.), (250-752 lbs.). The only highest point source of Cr in IA was located in the middle of the state. However, the highest source of the air emission of Cr in KS was located in the southeast of the state, while in NE was located in northeast and southeast of the state (Fig. 20.1). These observations determine no correlation between soil anomaly and air emission of Cr in IA and NE, however, one strong correlation was investigated between a soil hotspot and Cd released in northeast of KS. For Cu, three slight contribution point releases from the air to the soil and greater the 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. 20.3 & Fig. 20.49). Cu released into air are 0-420 lbs. and 0-5 lbs. on land (Fig.20.3). No practical

interpretation can be made of relationship of Cu anomalies in soil versus the emissions in the land (Fig. 20.4). No significant regional geochemical background values of Hg have been observed with maximum value 0.11 mg/kg. All the areas showing high concentrations of Hg released into the air (44-298 lbs.) are not associated with the soil anomaly except one point located in southeast of IA (Fig.20.5 & Fig. 20.6). The land release amounts are not correlated with soil anomalies at all (negative correlation) (Fig.20.6). Though it is usual that Mn concentrations in the soil are naturally high, some of the observations from the map reflect some of anthropogenic applications that probably cause an increase of the metal concentrations in the soil, rather than natural deposits. The general concept of Mn overlay map present interesting features where there is no strong relationship between air releases and high values of Mn in soil. In the air, emissions values of Mn are located between 0-3015.5 lbs. and 0-491.6 lbs. In general, 5% of the total 95 sites of air releases correlate with soil anomalies (Fig. 21.1 & Fig. 21.2). No significant amount of Mn is deposited on the land except at one point in the center of IA and a point in east of KS (Fig. 21.2). Most of the study area presents high soil concentrations of Mn located in low air and land emission areas of this element. For Ni, no correlation has been observed except minor correlation between soils with air contribution in the southeast and middle of IA, east of KS and NE (Fig. 21.1). No soil anomaly and air commissions of Ni have been observed in west of KS and NE (Fig. 22.3 & Fig. 21.4). In general, Ni released into the air is 0-1180.9 lbs. while it is 0-5 lbs. in the land (Fig. 22.3). Slight contribution from two air points to the soil anomaly was observed in southeast of IA and KS. However, one point located in east of NE (Fig. 22.3). Few positive correlation of Ni are observed in south of IA, east of NE and KS ranged 560 – 1180.9 lbs. However, no correlation has been observed between soil anomalies and land concentrations (Fig.22.4). 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 concentrations values were located in most of IA (0-14 lbs.) and in east of KS (0-10 lbs.) and NE (0.01-1 lbs.) (Fig. 21.3). This observation shows that the source of the chemical may come from soil anthropogenic activities more than other natural sources. Slight air contribution but no soil anomaly (5.35-6.85mg/kg) was observed for Ni 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. In general, there is only a small correlation if any between the soil concentrations and air emissions. Lack of a soil anomaly means there is a trivial emission. Released values of Pb into air were 0-645 lbs. while the metal values released into land is 0 – 931.3 lbs. The emissions of Pb in the air were low in most of the states' regions compared to the soil except of one point located in southeast of IA, two points located in east and southwest of KS, one point in northeast of NE (Fig.21.5 & Fig. 21.6). The results show that the highest values of Pb distribution in the air in IA (34.40-2180.0 lbs.), KS (7.58- 130.00 lbs.), and NE (150.0 -1714.00 lbs). The largest values in the soil distribution map are not correlated with the air releases points. The only point source of air emissions of Pb correlated with soil anomaly was located in east of KS (7.580-40.000 lbs). Lower concentrations were dominant in most of the study areas include IA (0.00-2.50 lbs.), KS (0-1.06 lbs.), and NE (0-4.10 lbs.). There is an unusual Pb anomaly in center of KS of broad region of those values against the high peak was noted in early explanation in the the text. In general, the lowest value is 0-10 lbs. of Pb released into the air while the highest value is 301-645 lbs. (Fig. 21.5). In the land, the lowest value is 0-0.04 lbs. while is highest is 4.12 – 931.3 lbs. (Fig. 21.6). One high point of Pb is located in the southeast of IA that could correlate to soil anomalies in this area. It is observed that the

superimposed emissions of Pb and there is no relationship of the emissions to Pb soil properties. In general, there is no correlation between soil anomalies and air releases into the environment in IA and NE. However, one point source was correlated with an anomaly in the southeast of KS. The most important interesting point to note is that there is a linear region of very low concentration of Pb located in the center of KS extending more to north, showing negative values next to the positive values (Fig. 21.5). The positive value area located in the center of KS is next to the negative value area of Pb in the produced geochemical map in this study. There is a widespread geochemical background with low concentrations of Se in IA, east and center of NE, and east and north of KS. These low regions are not correlated with low Se concentrations in the air and land. These changes probably indicate the absence of the anthropogenic applications that contributing Se into the air or soil. The only identified high point of Se released into the air was observed in north of IA (6 lbs.) and east of KS (10-750 lbs.) (Fig. 22.1). Another low Se released point was observed in east of NE (5 lbs.) having a slight correlation with a soil anomaly (Fig. 22.1). In the northeast of KS and eastern NE, there is a group of high Se releases and another with low Se levels and they do correlate with high spots of soil (Fig.22.1). Nevertheless, the soil is very broad and uniform and it seems that there is little correlation between soil and air. There is no proof for the emission causing the soil anomalies (Fig.21.1 & Fig. 22.2). V is one of the chemicals that have high geochemical background in most of the study area. The amount of V released into the air is 16-7500 lbs. while in land is 0-750 lbs. (Fig. 22.3 & Fig. 22.4). The only two points of high V released into the air are located in the east of KS and NE (Fig. 22.3). Three highlighted areas located in northeast of IA, south of KS and NE have low concentrations of V that could be natural, or no human activities in these regions. There was a strong correlation between soil

anomaly and air emission of V in southeast of IA, east of KS and NE. The highest values were 131-7500 lbs. in IA, 281-750 lbs. in KS, and 556-1050 lbs. in NE (Fig. 22.3). On the opposite, one point of V released into the air was associated with low concentrations of the metal in the soil located in southwest of NE, which means that there is no correlation between air emission of V and high anomalies of the element (Fig. 22.3). It is document that there is no V correlated with soil anomalies in the study area (Fig. 22.4). Zn is the chemical that has a large population of emission sites into both the air and land. Zn values released into the air ranged 0–34005 lbs, however, the metal concentrations in the land ranged 0–45622 lbs. (Fig. 22.5 & Fig. 22.6). In the southeast corner of KS, there was mining, which is the only place on any, these states where there was mineral production of mine of Zn and Pb. Consequently the soil anomalies seen in southeast of KS probably come from mining. Neither the land nor the air emission maps for Zn have a large elevated population above the first subdivision of the concentration range. The potential release site of Zn is wide spread and mainly in the eastern part of the maps. However, none of the sites is very strong or high concentrations. Those two points that have high concentrations in the land and are not located in the area of soil anomalies (Fig. 22.6). Consequently, the correlation between the air emissions and the soil maps is very low. No sensible interpretation can be made of associations of anomalous soil values in the maps versus the emission concentrations given by the sites. On the land, four sites are elevated and no more than 5% of the sites numbers are elevated by greater than the low subset. Only two sites are elevated with Zn that correlates with soil anomalies. Generally, there is not a lot of heavy land or air contamination from factories and industrial activities. The high values of air emission were 14,272-34,005 lbs. in IA, 1,042-1,898 lbs. KS, and 9,016-34,005 lbs. in NE (Fig.22.5). There are few of high concentrations of Zn in the

air emission maps that contributing to high concentrations of the element in the soil in some extensive regions. One point source of Zn contributing to soil anomalies was observed in the east and the other in the middle north of IA. In KS, the strong positive correlation was observed in one point in the northeast of the state. However, one point was recorded of Zn released into air contributing to soil abnormality in NE (Fig.22.5). Nevertheless, there are some areas may the air contributing to small parts to the soil hotspots such as in east of KS and NE (Fig. 22.5). Some of the low concentrations of the metal in the air were found in some of the soil anomalies, which showed negative correlation of Zn sources in air and soil in most of IA and east of KS and NE (Fig. 22.5 & Fig. 22.6). There is a Zn anomaly in regional geochemical background where is the region of Zn and Pb mining located and in southeast of KS.

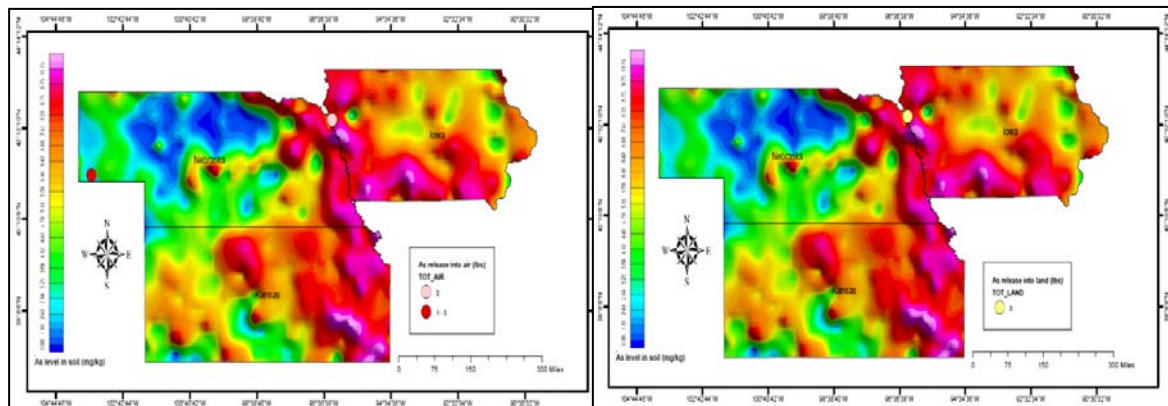


Fig.

19.1

Fig. 19.2

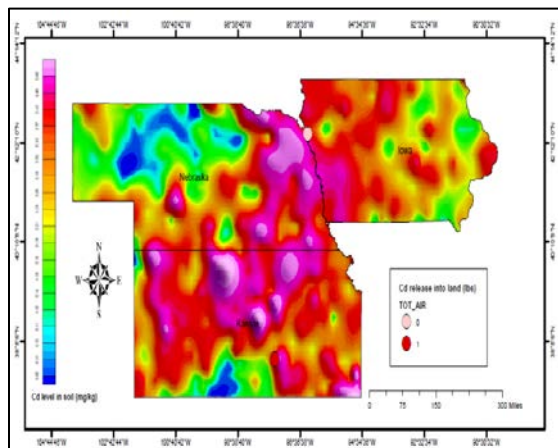
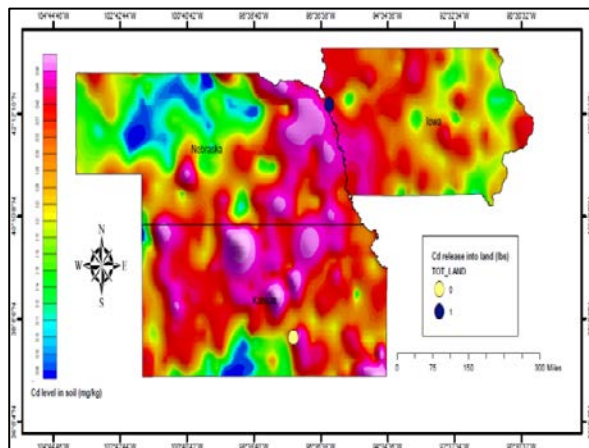


Fig. 19.3



19.4

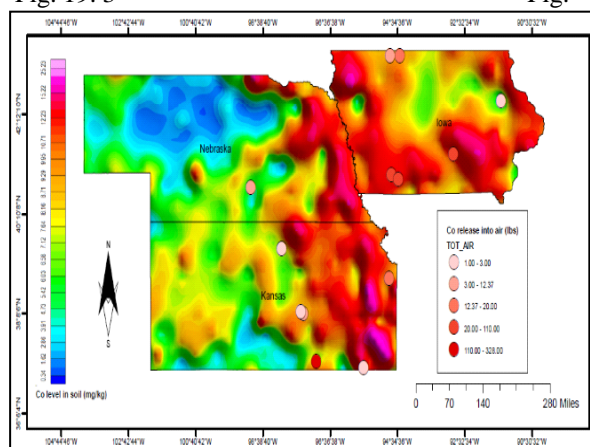


Fig. 19.5

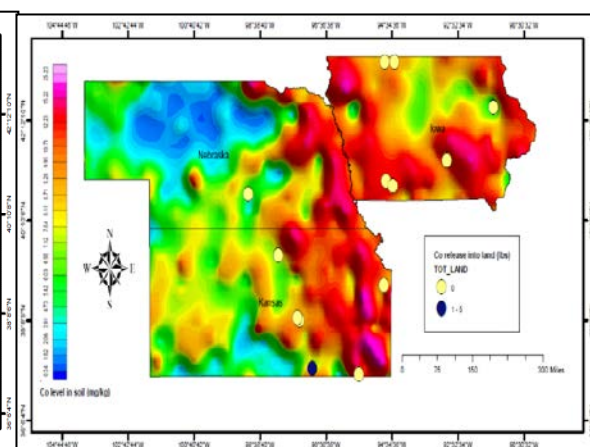


Fig. 19.6

Fig. 19. 1-6 (As, Cd, and Co) Air and land emissions super composed on soil geochemical background maps.

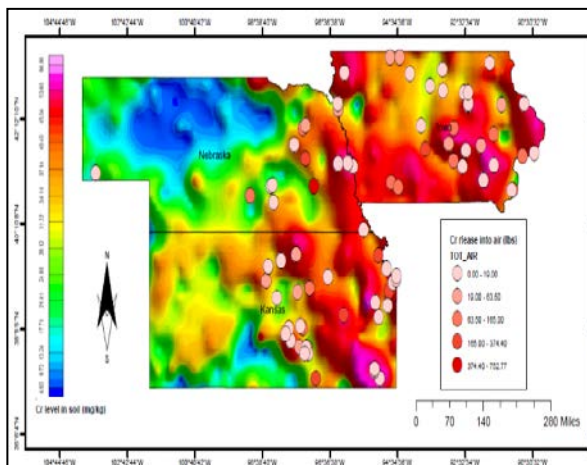


Fig. 20.1

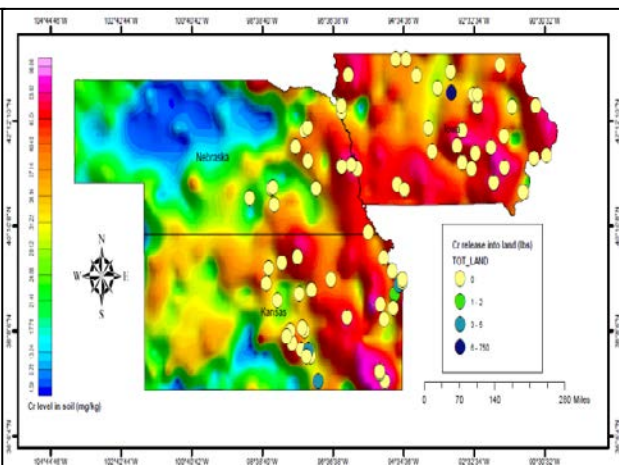


Fig.20.2

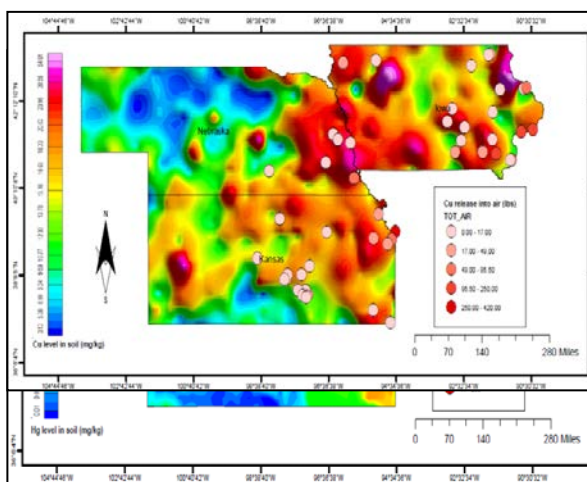


Fig.20.3

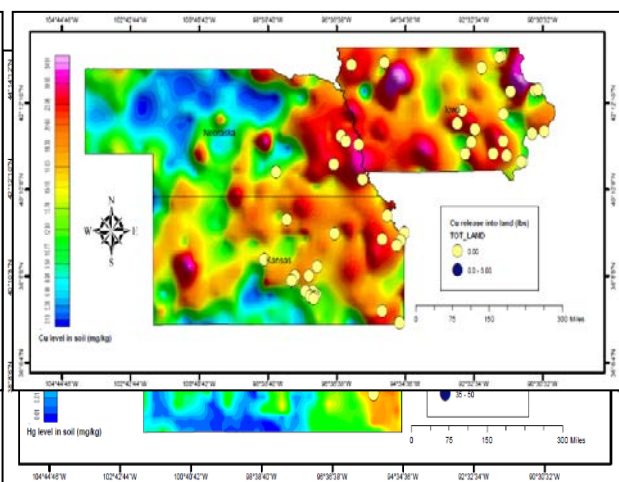


Fig.20.4

Fig.20.5

Fig.20.6

Fig. 20. 1-6 (Cr, Cu, and Hg) Air and land emissions super composed on soil geochemical background maps.

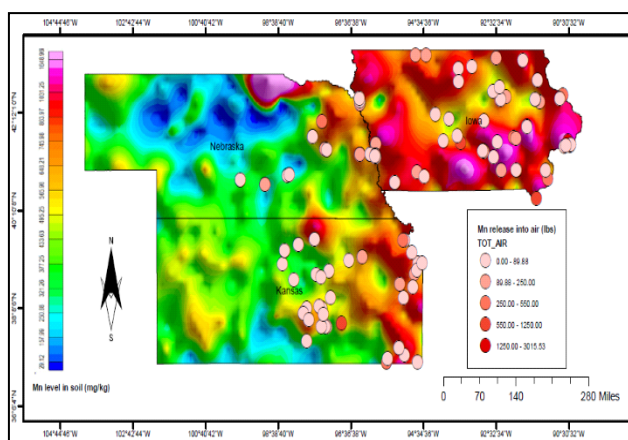


Fig.21.1

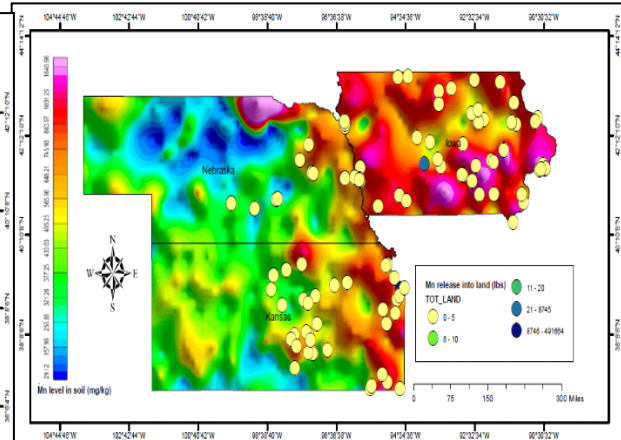


Fig.21.2

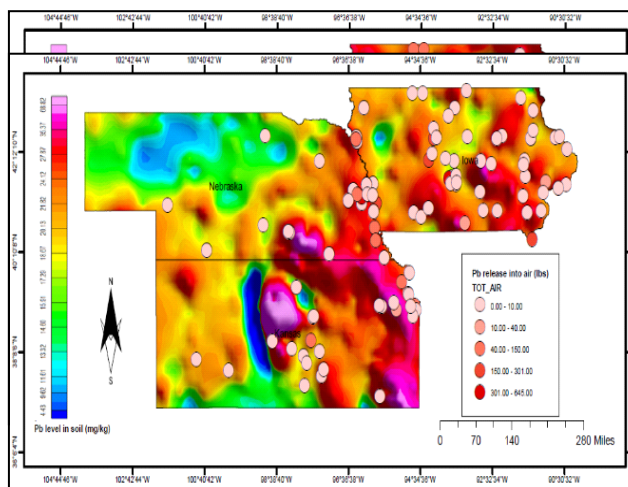


Fig.21.3

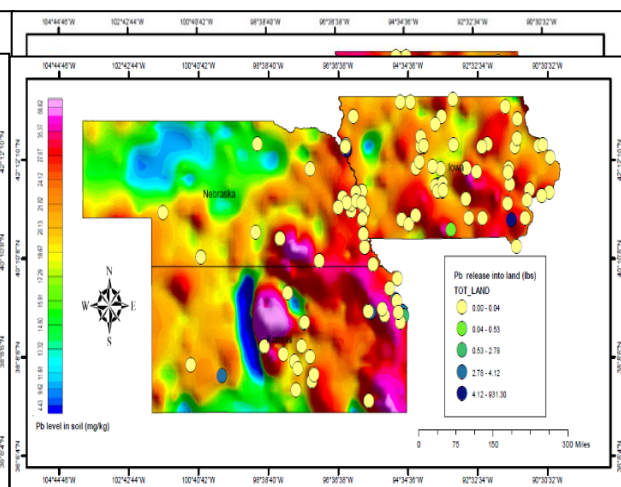


Fig.21.4

Fig.21.5

Fig.21.6

Fig. 21. 1-6 (Mn, Ni, and Pb) Air and land emissions super composed on soil geochemical background maps

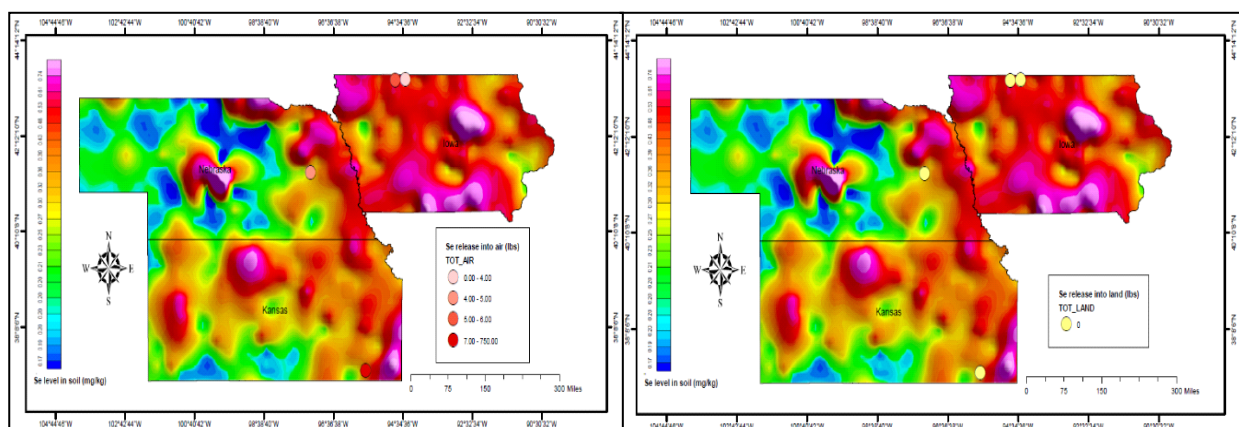


Fig.22.1

Fig.22.2

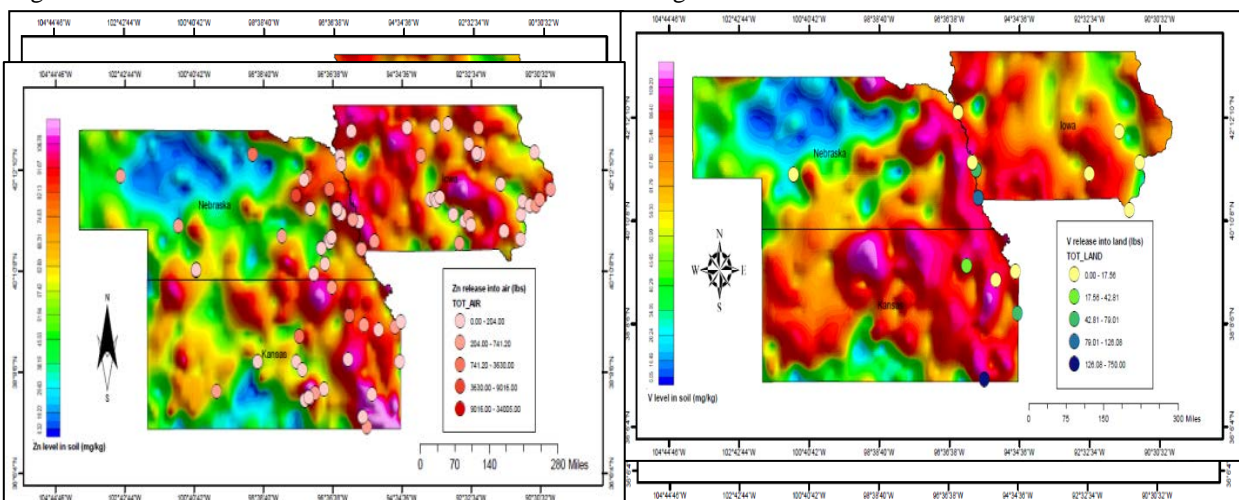


Fig.22.3

Fig.22.4

Fig.22.5

Fig.22.6

Fig. 22. 1-6 (Se, V, and Zn) Air and land emissions super composed on soil geochemical background maps.

4. DISCUSSION

It is significant to identify the chemical element sources to evaluate anthropogenic input. It is noticeable that most of the high concentrations of the chemical elements were recorded in most of IA and eastern KS and NE. There is a significant intensive farming in IA. Therefore, the results of the current study indicate a significant enrichment in most of agricultural areas in

geochemical soil background maps. Therefore, it is suggested that these elements with high EF values are probably due to human applications. United States Department of Agriculture (USDA) divides IA into 23 soil regions, including soils of southern, eastern, and western IA that is loess derived; soils of northern and central IA are till derived. Most of IA regions have soils well-suited for agriculture, which make this state one of the most productive farming areas in the world. The most important crops in IA, KS, and NE are corn, soybeans, and wheat, thus are given the largest region to cultivate.

Sucharova et al. (2012) reported that As, V, and Se were higher in abnormality in northwestern region of the Czech Republic in the O-horizon soil compare to the other regions, which marked with lignite mining and burning activities. Bourennane et al., (2010) reported that Cd has high enrichment in the surface soil because of human industrial applications and urbanization, however, highly enriched Cd is here ascribed to using intensively phosphate enriched fertilizers and urban sludge in agricultural regions in Nord-Pas de Calais (Kabata- Pendias, 2001). In addition, high EF values were observed for Cu, Bi, and Sn in the north compared to the south area that reflect contamination diffusion (Bourennane et al., 2010). The results obtained from this study agree with the results obtained by Szolnoki et al. (2013) suggesting that these metals can originate from organic and inorganic fertilizers and pesticides.

EF was lower compared to high pedologic EF (PEF) of Cu, Zn, and Pb (>2) reported by Szolnoki et al., (2013) in the topsoil in the outskirts of Szeged (Bakto), which is dominated by anthropogenic applications. Sun, et al., 2017 showed that EF's of heavy metals in soil were slight and uncontaminated. The area located in southeast of KS has high values of Zn and Pb that are

located with the same area of mining sites that show the source of those elements comes from the anthropogenic mining activity (Fig. 5.3 & Fig. 6.3).

The mining drainage water that has high concentrations of the chemical elements can be released into the agricultural regions through irrigation, which cause soil contamination. Some of the areas that have high geochemical backgrounds are cities that have produced very much chemical releases into the air, land, and/or as a wastewater. Most of agricultural fertilizers are made from factory wastes. Other sources can contribute the element inputs in the soil is natural weathering processes. One of the most important observations in 2018 is the hypoxic area “dead zone” observed in gulf of New Mexico where is the oxygen depleted water increasing toward to the gulf surface from the sea floor. Nutrients and nitrogen fluid down the Mississippi river.

5. CONCLUSION

Sources of heavy metals contamination can be from natural (lithogenic origin) as well as anthropogenic features. Some of the soils act as sink of chemical overloading, which causes contamination with specific chemicals. Various human activities such as industrial applications and intensive cultivation can change directly and indirectly the soil physiochemical properties. The study focused on evaluate and mapping heavy metals enrichment in the surface soil and using EF and I_{geo} indices to measure the chemical loading in surface soil using statistical programs include R studio and SPSS with ANOVA test and Oasis Montaj geosoftware. Statistical analysis combined with mapping of chemical distribution of metals of 12 elements was carried out. The results of the study reflected different potential effects of heavy metals in the soils of IA, KS, and NE using combination of various methods to identify anthropogenic source: univariate, multivariate, statistical analysis, PCA, t. test (ANOVA), and spatial distribution of metals visualized by

geosoftware. Univariate and multivariate methods were used to investigate geogenic and anthropogenic contributions of baseline values in IA, KS, and NE.

Multivariate statistical analysis and distribution maps revealed high significant overloading regions with heavy metals. Some of these sources may be industrial activities, agricultural applications, through overusing chemicals for soil fertilization, waste materials, mining, and untreated sewage. Non-compositional PCA biplots showed most elements are part of a “group” with similar characteristics. Hg, Mn, As, and Pb can be grouped. V and Cd seem to show a relationship as well. The remaining elements seem to also be grouped together. Cluster analysis revealed Cr, Co, Ni, and V can form the first cluster, and As, Cu, and Zn create the second cluster. Se and Cd create the third cluster. Hg and Pb seem to be independent of the other variables. The second cluster seems to be reasonable in relation to our hypothesis since it is expected to have a relationship between Zn and Cu; also, concentrations of the metals include Cd, Cu, Pb, and Ni. Sites were considered as anthropogenically influenced or non-anthropogenic based on probability of pollution by agricultural, industrial, or urban applications.

The most useful data used to derive conclusions were spatial maps with data that had undergone log-ratio transformation. These maps show that there are homogenous high concentrations of contaminants in Iowa and in eastern of Kansas. In general, the plotted maps in Iowa, Kansas, and Nebraska show obvious anomalies spatial pattern in the outlier distribution with high concentration of some of the elements analyzed in this study. The greatest concentrations are mainly located in the east and northeast of Iowa, east of Nebraska, and northeast and southeast of Kansas.

The statistical plotted histograms for the variables showed correlation between the potential heavy metals and additive sources. These outliers' sources suggest some possibilities such as geological processes, river transport from other sources, the water being used for irrigation is "contaminating" the soils, types of the fertilizers used in agricultural regions, and type of crops planted.

Relative variability needs to be considered in greater depth in order to conclude more investigations. In order to estimate the similarities in accumulation of the heavy metals in the mid-continent of USA, EF was evaluated using statistical analysis and spatial chemical distribution maps that were generated. From the analysis performed on data from the study area, the soils had ranged from no enrichment to significant enrichment in the topsoil compared to other regions. EF investigated minimal to significant polluted soils with respect to Ti as normalizer (element reference). The soils had no influenced by anthropogenic applications in some regions compared to others. The variation of metal accumulation exists among three states and EF values originated from different natural, anthropogenic activities, or mixed sources. The results revealed un-contamination for I_{geo} to significant contamination for EF. Based on geochemical indices of studied heavy metals, the soils are highly enriched in Iowa, Kansas, and Nebraska. A significant proportion of the soil samples collected from the area of the study have been classified as high chemical loading areas. Future work should be directed for more detailed study of this data. Finally, anthropogenic applications in the study areas may need to be more regulated and controlled. There are air emissions that are very low in most parts of the states, but there are some higher areas. Nevertheless, most of these areas are not associated with the high geochemical anomalies in the soil. Generally, there is a small relationship of air emission and high spots of the chemicals in the soil.

CHAPTER 2

MULTI-ELEMENT CHEMISTRY, STATISTICS AND GEOSPATIAL DISTRIBUTION OF MID-CONTINENT SAMPLES, WITH SITES SELECTED BY TOTAL CHEMICAL INFLUENCE (TCI) ANALYSIS

1. INTRODUCTION

In recent years, environmental contamination is the greatest and most serious threat to all living organisms and human health. Heavy metals are a potential human health concern when the levels are high in the agricultural soils (Enriqueta et al., 2005). Extensive application of agrochemicals in farmlands and rapid industrialization can increase the soil contamination rate. Human applications such as mineral processes, industrial wastes, and phosphate fertilizers are some of the main factors responsible for a dramatic increase of heavy metal levels in the soil, which cause serious risks in the environment and human health (Dartan et al., 2015; Jiao et al., 2015).

Soil geochemistry is a critical factor for evaluating the distribution, chemical processes, and reactions of the chemical elements in the biosphere, geosphere, atmosphere, pedosphere, and hydrosphere, and for tracking those chemical processes (Sposito, 1989 & Kabata-Pendias, 2011). The geochemical mapping of the soil reflects the state of the soil horizons in the environment. Recently, the geochemical analyses of trace and major elements have provided essential data for soil researchers in a variety of areas (Vila and Martinez-Llado, 2015, Reimann, et al., 2005). This study attempts to assess the possible contamination sources in Iowa (IA), Kansas (KS), and Nebraska (NE). These states, located in the nation's Corn Belt, are three out of the top nine states responsible for approximately 50% of the nation's fertilizer use. In this study, assessment of concentrations of potential long-term chemical loading in agricultural soils was performed as well

as mapping using different data analysis methods. The source of these concentrations may be natural or anthropogenic processes such as geological applications, geochemical sources, or human activities. Quantifying variations in spatial distribution of soil geochemistry requires geochemical mapping standardized by a geochemical reference network to differentiate the natural and anthropogenic inputs (Darnley, 1997). Outlier concentrations of elements include significant information to be considered and a multivariate approach to detect the values is superior (Riemann et al., 2005).

Soil chemistry is not determined only by the bedrock geochemistry. However, bedrock geochemistry, also known as lithochemisrtry must be determined. It is important to understand the contaminated regions with heavy metals and their potential sources on a national scale.

The main objectives of the present study are as follows: 1) to investigate the distribution of heavy metals and identify their potential sources in soils of the midwest USA using geostatistical analysis combined with spatial distribution mapping, 2) to evaluate and map heavy metals using the index of TCI to address the possible common sources of natural and/or metal anthropogenic inputs, 3) perform a lithologic study by generating lithochemisrtry maps (LGM) and residual geochemical maps (RGM) of the bedrock of the three states investigated to find out the parent or potential anthropogenic sources of heavy metals.

2. MATERIALS AND METHODS

2.1 Data Collection and Characterization

The National Geochemical Survey (NGS) (Smith et al., 2015) has been carried out over the USA. In this project, the United States Geological Survey (USGS) produced a geochemical database of soils. Smith et al. (2014) produced geochemical maps using the reported data.. From

these datasets, a growing awareness of anthropogenic applications in soils is considered. NGS is a unique survey that provides data on the complete series of elemental distribution combined with mineralogical and physiochemical characterization. The USGS collected the samples for the soil geochemical and mineralogical survey between 2007 and 2010. All the samples were analyzed mineralogically and chemically and reported by Woodruff et al. (2015). The low-density geochemical and mineralogical survey of soil of the conterminous United States (US) was part of the North American Soil Geochemical Landscapes Project. Woodruff et al. (2015) present large-scale soil geochemical patterns that are suitable for a wide range of environmental biology and geological applications.

2.2 Heavy Metal Loading Assessment Using Total Chemical Influence (TCI)

In this study, total chemical influence (TCI) as a first step was calculated to characterize and evaluate the chemical loading or possible anthropogenic sources into agricultural soils. Soil sampling and chemical analysis were performed as a second step to establish the concentrations of heavy metals that exceed the threshold or maximum allowable concentrations (MAC) (Weinheim, 1999 & Kabata-Pendias, 2011). Total chemical influence is the tool used to test anthropogenic inputs. In addition, lithogeochemical maps were compared with recent soil geochemical data using several measures. The chemical concentrations documented by the USGS (Smith et al., 2014) show some chemical elements increasing from the surface to depth while other chemicals decrease from the surface to deeper soil. From the data shown by USGS (Smith et al., 2014), it is also evident that the concentrations of the chemicals differ from surface to the depth. With some elements there is no difference between the soil layers. In this study, three states were selected for

study, which are IA, KS, and NE. In formulating an index, TCI was selected based on soil potentially contaminated with twelve elements. These elements are presented in all geochemical datasets that include Arsenic (As), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), Selenium (Se), Vanadium (V), and Zinc (Zn). Specifically elements were analyzed for which the EPA has designated a value for the MAC or maximum contaminant level (MCL) in soil (Sadurski, 2004; Kabata-Pendias, 2011). The EPA does not report additive toxicities of multiple chemicals. These twelve chemicals have different toxicities, different levels of MAC and have different health effects (Jiang et al., 2017). Hakanson (1980) suggests relative toxic responses (numbers increasing with toxicity) of Hg=40, Cd=30, As=10, Pb=Cu=Ni=5, Cr=2, and Zn=1. It is not known if toxicities are additive in a linear or exponential fashion, thus the summation of normalized concentrations is a conservative assumption.

The data for the research locations in this study is all in ppm units and concentrations at each x,y point were loaded into the software package, where a gridded representation of the data was assembled. The gridding was done using a minimum curvature approach. The contoured data were then exported to ArcMap for mapping purposes. All elements were statistically analyzed using Exploratory Data Analysis by Tukey (1977). The data was incorporated into GIS software to generate the maps as shown in Fig. 2 and Fig. 3. The concentrations of the chemicals were normalized or divided by MAC or MCL.

The data used in this study was downloaded from the USGS (Smith et al., 2015). The analyzed data in detail and the chemical methods of analysis are available (Smith et al., 2014). Results of TCI calculations were analyzed using geostatistics software R (Reimann et al., 2008).

Geostatistical approaches are generally used for characterization of heavy metals in soil using spatial scale distribution (Jiang et al., 2017). The data was incorporated into GIS software to generate the maps. Two sites in the region of study have been selected to test out this procedure. Background site A is located arbitrarily at the junction of the three states of interest; KS, IA, and NE. Background site B is located in the Sand Hills of western NE. It has always been devoid of widespread agriculture, and it is included in this study as a background area. MAC or MCL are used for the normalization of the concentrations of the chemicals. Arc Geographic Information System (ArcGIS) was used to represent the extent and spatial variations of heavy metal distribution using interpolation technique by weighted average of the sample points. ArcGIS and Oasis Montaj geosoftwares were used to produce maps of the entire three states of this parameter (TCI) according to the following equation:

$$\text{Total chemical Influence (TCI)} = \sum_{i=1}^{n=12} C_i/L_i$$

C: concentration of each element

n: number of chemicals considered (12)

L: Limit = MAC or MCL

i: sequence of the chemicals 1:12

MAC: Maximum Allowable Concentration

MCL: Maximum Contaminant Level.

TCI: Total Chemical Influence

2.3 Description of the Study Area and Sampling Location

The area of the study is located in the mid-continent of the USA and the climate is diverse according to the geographic location (Fig. 1.1). Three states with similar topographic functional aspects, including IA, KS, and NE, were the target of study to evaluate the source of chemical loading by human input and/or natural sources. In the three states, the ecosystems are different and they have diverse plant species. The study area consists of agricultural regions and farmland covering 99% of IA and large areas in KS and NE. The agricultural grain crops in IA include corn and soy. In KS, the agricultural crops include alfalfa, corn, soy, and wheat. Agricultural activities in NE are corn, wheat, sorghum, potatoes, and sugar beets.

The annual average temperature in IA, KS, and NE is 50.85°F, 50.65°F, and 55.05°F respectively according to National Oceanic and Atmospheric Administration (NOAA, 2018). The average annual temperature in Iowa is 45° in the north and 52° in the south. The high temperature during the summer does not cause severe crop stress. IA also has seasonal variations. The rainfall can be produced through the Gulf of Mexico during the warm months, and it is significant in the growing season. In the winter and autumn, the dry Canadian airflows from the northwest, in addition to the air masses that move from the Pacific Ocean, lead to relatively dry and cold weather. However, in the summer, high temperatures are caused by hot and dry winds that come from the desert southwest.

In KS, the annual mean temperature is 58° in the south and southeast and 52° in northwest. The average low in KS is 36.6°. The wind moves from the south of the state and the wind speeds range from 10.4-12.7mph. The forceful rainfall in winter can be associated with high winds and heavy snow, and rainfall also takes place during the spring and summer (NOAA, 2018).

In NE, the Sand Hills are extensive with some lakes, valleys, and basins located in the north central and high plains in the west, and the prairies located in the east of the state formed from sandy loam or silt loam soils. Sand Hills is the biggest dune area in North America, which is take up 50.000km² (Muhs, 2017). The climate is hot and dry in the summer and temperatures may exceed 115°F, specifically in July. The rainfall is formed by warm air thunderstorms during summer and spring that may occasionally cause flooding. Geology of the area and lithological assemblages in the study area differ due to a range of factors, including geology, topography, land use, and weathering processes.

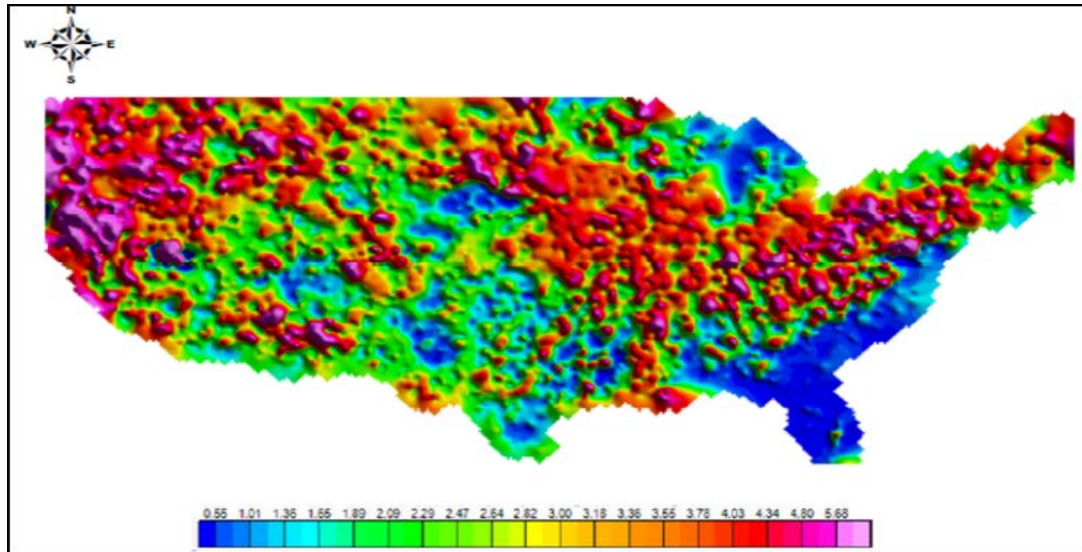
2.4 Spatial Geochemical Distribution Mapping and Interpolation of Heavy Metals Data

Moreover, geochemical maps were produced to identify and investigate the high concentrations and the values of the heavy metals in the soils. Geochemical distribution maps of TCI of heavy metals were performed using geosoftware Oasis Montaj (version 7.5.1- 4, 2012) and ArcGIS (Version 10.5.1) to identify the potential sources of heavy metals in agricultural regions and evaluate the spatial variations of heavy metals originated from potentially anthropogenic sources. The spatial interpolation maps were obtained using ordinary Kriging estimation. The spatial interpolation maps present the spatial chemical distribution of heavy metals in surface soil based on geostatistical analysis. The data were interpolated into the geosoftware after TCI calculation using gridding algorithm methods with “minimum curvature” or random gridding method (RANGRID GX) to produce grids. This method fits a minimum curvature surface to the data value points similar to the method designated by Swain (1976) and Briggs (1974). TCI data was interpolated into an equally spaced grid of cells using a coordinate system based on the North

American Datum of 1984 (NAD1984). The maps were gridded and imaged. Grid values are estimated at nodes of a coarse grid using minimum curvature. This method can evaluate the inverse distance average of the actual data within an identified search radius and the average of data points in the grid is used to fit the actual data points' nearest coarse grid nodes.

2.5 Soil Sampling Methodology

A total of 60 samples of surface soil were collected from the top surface of 0-5cm. The samples were collected in triplicates from A, B, and C sites and composited in each location, during the summer of 2016. An additional sample was collected near the sites A, B, and C to represent background metal concentration. It was therefore revealed that inside the study area there are specified high and low concentrations of heavy metals (Fig 23.1 & Fig. 23.2). The surface soil sample collection took place at the designated sites identified with high TCI values as it shown in Fig. 23.3 & Fig. 23.4. A total of 22 sampling sites were selected from agricultural fields. An approximate 1kg of each sample was collected at each site. The field features were considered, such as land cover and land use, and surface soil profiles were collected, including the nature of the fields and layer thickness, avoiding large rocks or buried vegetation. The samples were placed into containers and transported to the Act Labs for chemical analysis (actlabs, 2017).



TCI for the entire United States

Fig. 23.1:

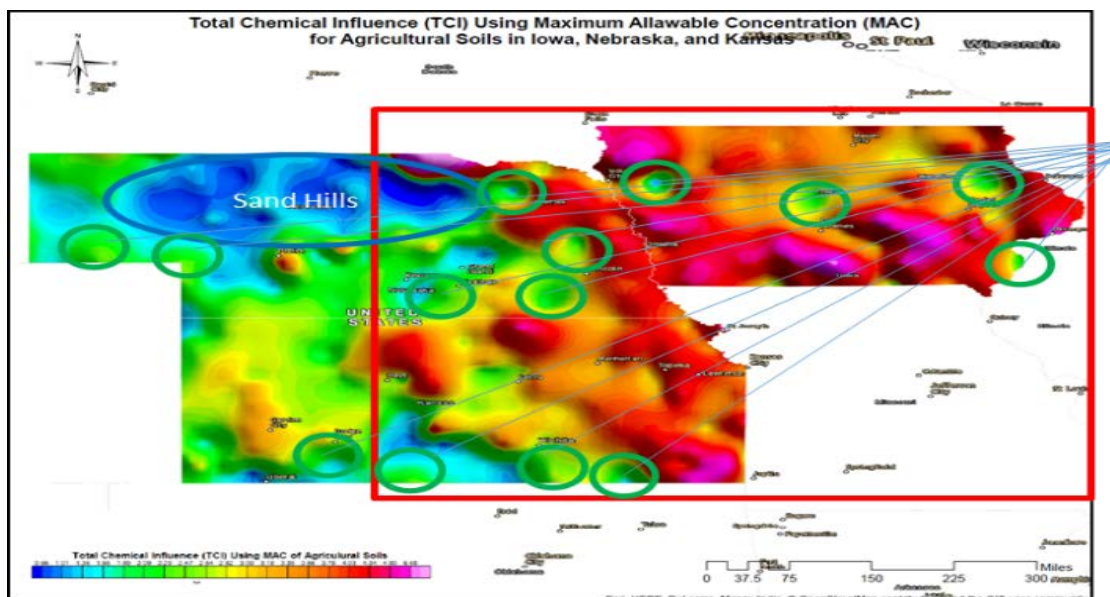


Fig. 23.2: Subset of Fig.1.1, TCI of states of interest, showing low values. Sand Hills are noticeable in northwest Nebraska

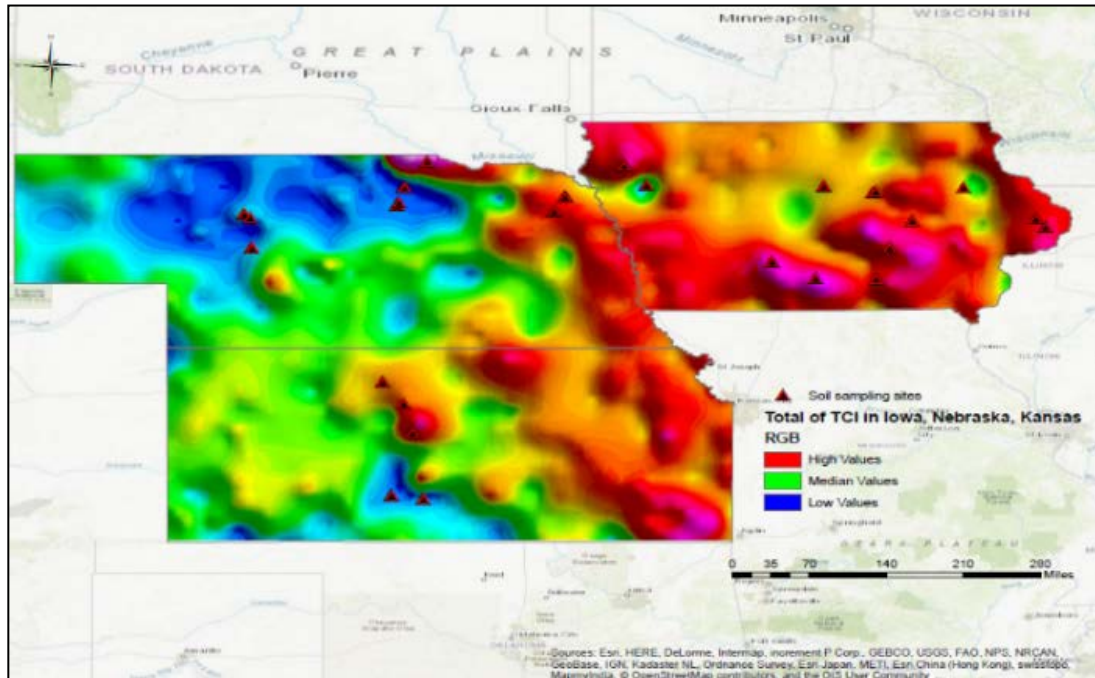


Fig. 23.3

TCI of states of interest with sample sites noted by triangles.

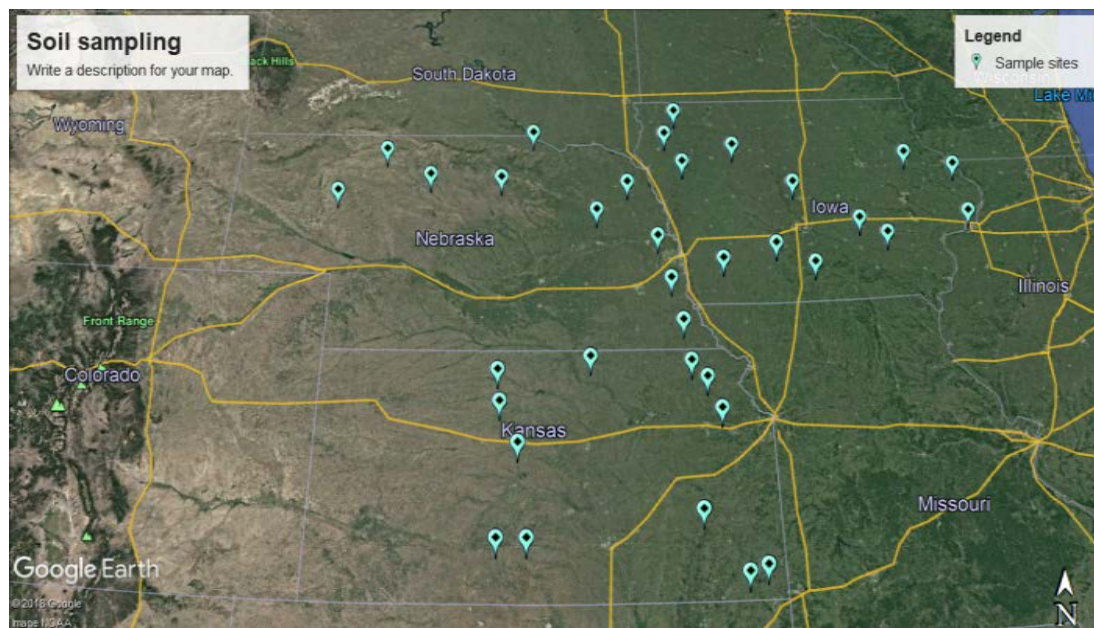


Fig. 23.4
TCI of
states of

interest with sample sites noted by triangles.

2.6 Analytical Chemical Procedures for Samples

All samples were analyzed in Act Labs (actlabs, 2017). All samples were analyzed by “trace element geochemistry and digestion specific assays” using Aqua Regia Partial extractions. These analytical methods include 1) inductively coupled plasma mass spectrometry (ICP-MS) and 2) inductively coupled plasma atomic emission spectrometry (ICP-AES), which can be also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES) to detect the concentrations of each element, as specified on the website (actlabs, 2017).

2.7 Statistical Analysis Of Data

2.7.1 Univariate Statistics and Multivariate Statistics

Data analysis included using geostatistical methods (Reimann et al., 2008). The statistical methods were produced using R Studio Version 0.98.1091. Statistical analysis of the concentrations was conducted using Univariate, Bivariate, and Multi-variate statistical analysis and Isometric Log ratio using R. Chemical levels of the surface soil were different between the states (Table 1). The soil horizon data was arranged into two groups and plotted in histograms and cumulative frequency diagrams based on the concentration of elements and mean, median, absolute deviation, and coefficient of variation were calculated for selected elements. The statistical analysis includes exploratory data analysis, uni-variate analysis, \log_{10} transformation, bivariate analysis, multivariate analysis, PCA, mahalanobis distances, and values analysis. The statistical data analysis was illustrated and presented. The data analysis showed visual variances with high and low concentrations of the heavy metals in the surface soil.

3. GENERATION OF LITHOGEOCHEMICAL MAPS (LGMS)

Some of the elements can be found naturally with low or high concentrations in certain soils. Background concentrations of the elements in the soil are associated with the mineralogy of the parent materials (bedrocks) that develop the soil through pedogenic processes. The natural forms of the trace elements are found in mineral components in the soil such as silicate and aluminosilicate minerals. The concentrations of heavy metals are dependent on the rock type as parent material to produce specific types of soil. The bedrocks of IA, KS, and NE are dominated by limestone, sandstone, and minor shale.

The anthropogenic effects may be estimated through subtracting the synthetic lithogeochemical maps from soil geochemical maps. The maximum average values of each heavy metal in the most types of bedrock in the study area, including limestone, sandstone, and shale, were used to generate lithogeochemical maps using ArcGIS software. Concentration of heavy metals As, Cd, Co, Cr, Cu, Pb, Mn, Hg, Ni, Se, V and Zn in Limestone (Ls), sandstone (Ss), and shale (Sh) is shown in Table 10 (Kabata-Pendias, 2011).

Table 10 Average concentration of heavy metals in bedrock types. Limestone (Ls), Sandstone (SS), Shale (Sh)

Rock Type	As	Cd	Co	Cr	Cu	Pb	Mn	Hg	Ni	Se	V	Zn
Ls	1.75	0.07	1.55	10.5	7.5	6.5	600	0.035	12.5	0.07	27.5	17.5
Ss	0.85	0.05	5.20	30	17.5	7.5	300	0.03	12.5	0.05	35	22.5
Sh	9	0.25	17	100	50	27	625	0.3	65	0.45	105	100

LGMs are a new type of data representation, and thus require some explanation. If soil heavy metals chemistry is controlled by bedrock type and chemistry, LGMs use this idea. Lithogeochemical maps represent an area and show the variations of one chemical element as determined by the rocks present in the subsurface. A geologic map shows the bedrock present at or near the surface of the earth. Such maps are available on the state scale from the United States Geological Survey (USGS, 2017). Different colors on the map represent areas having the presence of rocks (bedrock) of different types. Different rocks have different chemistries, thus, for a start; a geologic map can be transformed into a lithogeochemical map by representing or giving each area the chemistry of that rock which is present there. Such a map was for a specific heavy metal in the state, thus, there were many lithogeochemical maps as there are elements for which data exists for those rocks. These are synthetic, bedrock geochemical maps. They may compare best with C-horizon soil maps of the USGS. The average ranges of chemistry of rock were used. Data of chemical contents in the bedrocks were inserted with geochemical data of USGS and map plotting was carried out in ArcGIS. The objective is to make synthetic lithologic geochemical maps, which can be compared with surface and subsurface soil geochemical maps. It has been said that heavy metals geochemical soil maps are bedrock controlled. That idea can be examined through comparison of soil chemical maps with lithogeochemical maps.

4. RESIDUAL LITHOGEOCHEMICAL MAPS (RLGM) SUBTRACTED FROM GEOCHEMICAL SOIL USGS

Lithogeochemical (LGM) was created from geochemical soil data (Smith et al., 2014) to identify the source of the heavy metals in the soils. Next step was subtraction of the lithogeochemical map (LGM) from geochemical soil USGS using ArcGIS calculation tool.

Several processes have been done for creation of the maps. The first step was to convert lithogeochemical vector maps to raster maps. Add raster to mosaic dataset by transform GCS to the same data project to be able to use it for subtraction using mosaic tool. The second step was interpolating lithogeochemical raster maps using Kriging tool.

5. RESULTS AND DISCUSSION

5.1 Spatial Distribution Patterns of Elements

It was inferred that the study area may have been contaminated in some sites by anthropogenic applications. Spatial distribution of heavy metals shown on spatial interpolation maps showed homogeneity in the distribution of the heavy metals in the study area. Normality of the data was estimated by statistical analysis and visually by graphs. Geochemical data were analyzed statistically by means, histograms, and mapping geosoftwares. In KS, all the higher concentrations completely cover the northeast and northeast that extend to middle north of the state (4.80 ppm) (Fig.22.2). However, small areas have been noted in the middle and southwest with low TCI values range 0.55-2.09 ppm. Generally, the high levels of TCI were present in specific regions in geochemical maps in three states. IA was the most chemically enriched region compared to the other two states probably because it is an agriculturally active area and anthropogenic additives have been loaded into the soil. In IA, many regions have high concentrations of elements, except four small circular areas in the east, center, and west side with lower chemical values (2.09 ppm) (Fig. 22.2). In northwest and southwest of NE, there was very low chemical concentrations (0.55, 1.89 ppm respectively) compare to northeast & southeast with the higher concentrations of chemicals (5.68 ppm). This may be a signal to determine the source of chemicals from natural sources compared to anthropogenic sources. Otherwise, it has been noted that a big region located

in north & northwest of NE has had very low chemical concentrations with value 0.55 ppm where there probably are fewer agricultural applications. The areas with anomalies are located mostly in the northeast and southeast of the state. The significantly higher chemical levels in northeast and southeast of NE are correlated with agricultural and urban regions compared to the northwest and southwest regions.

5.2 Elemental Variations Between and Within Sites

The values range and nature of the data distribution are shown in the boxplots (Fig. 28, Fig.29, & Fig. 30). The first aspect that was observed is that spatial geochemical maps are dominated by high values of As, Mn, Se, V, and Zn over most farmland regions in the study area. The hotspots of the chemicals were determined using TCI maps as it shown in Fig. 24, Fig. 25, Fig. 26, & Fig. 27. The second aspect observed was the presence of three linear locations with low concentrations of TCI observed in IA, and random circular areas in KS, and NE, which cannot be elucidated as anthropogenic inputs (Fig. 23.2). The third aspect is that Sand Hills in NE is marked in all the maps with low values in the spatial geochemical map of each individual heavy metal (Fig. 24, Fig. 25, Fig. 26, & Fig. 27). It would be very interesting to discriminate whether these map patterns are subjected to natural sources or to anthropogenic inputs.

Concentrations of As in surface soils ranged from 0.02-0.13 ppm. In TCI geochemical maps, two areas show absence of As concentrations (0.02ppm) in Sand Hills located in northwest of NE and the other region is middle south of KS, surrounding areas with low levels are shown in east, middle, and east of IA, also, northwest and middle south of NE as shown in (Fig.24.1). The circular hotspots have been concentrated in northeast, southeast, north, and southeast of KS as

shown in (Fig. 24.1). Maximum Cd concentrations were observed in central, northern and southern of IA except three hot spots areas located in east, middle, and west of the state (Fig. 24.2). The northeast of NE revealed a big region of high Cd levels, and small circular areas in south of the state (Fig. 24.2). Hot spots of Cd (0.13 ppm) are present in the north and middle of KS, moreover, one hotspot region is located in northwest of KS. Cd is considered as a top priority in agricultural soils because the extensive use of Cd-containing fertilizers including organic and phosphate based fertilizers. Nevertheless, the observation of Cd was negative in northeast in IA, Sand Hills and middle south of NE, and KS. Co concentration decreased significantly in some oval regions in northeast and middle north of IA (0.12 ppm), and was completely absence in Sand Hills of NE (0.01ppm). The concentrations of Co and Se (0.74 ppm) showed a N25° W trending line located in east central NE to east central of KS. High levels were observed in northeast and southeast of NE and KS (Fig. 24.3). Some of the oval low areas of Co have been shown in northeast and middle north of IA. In NE, low levels of Co were identified in northwest and southwest. In KS, no significant levels of Co observed in northwest and southwest (0.01) (Fig. 24.3). Total Cr concentration obtained in this study was (0.02 ppm) is lower in sand hills of NE and linear region in NE, and south middle of KS. The concentration of Cr in IA was higher than NE and KS (0.35 ppm). Concentrations of Cr located in east central NE to east central of KS. It is noted that there is two circular negative regions of Cr located in east and one located in west of IA (Fig. 25.1). Significantly, high spots of Cu are shown in separated regions in IA including northeast and northwest, and there are some single hotspots regions located in south of IA (0.20 ppm). In NE, high concentrations of Cu revealed in northeast and southeast with two circular hotspots located in middle south as shown in (Fig. 25.2). One region with high concentration of Cu has been

exposed in east and southwest of KS while no significant amount identified in the south of KS. Negative Cu values were observed with few areas located in northeast, southeast, north middle, and circular hotspots located in northwest and southeast of IA (Fig. 25.2). A unique aspect was observed in most of the geochemical elemental maps in Sand Hills in NE with very low element levels (0.02 ppm). Compared to other elements, Hg concentrations were very low, almost zero, in most of the study area (0.01 ppm) except some of high concentrations observed in Middle Eastern and central southern portion of IA. In NE and KS, no Hg concentrations have been shown except few places in east of KS (Fig. 25.3). Mn levels was very high in most of IA (2.18 ppm) except three small circular regions in east, middle, and west while one area was identified in northeast of NE. However, there are high Mn levels existing in northeast and southeast of KS (Fig. 26.1). Ni concentrations show a high trending N25° W located in east central NE to east central of KS. The highest Ni levels (0.60 ppm) were identified in all IA except small circular regions in northeast southeast and northwest (Fig.26.2). However, high concentrations of Ni were located in northeast and southeast of NE (Fig. 26.2) while in KS, some high concentrations of Ni located in most of the state except in the northwest and southwest (Fig. 26.2). Two linear trends of high concentrations of Pb were located in the middle and south of IA with some high areas distributed randomly through the state. In central of KS, there is a large Pb low in a N 10°W trend, almost to the Oklahoma border, extremely negative. Interestingly, the negative trough is next to Pb high, and the Pb trough is more less north-south, and it is in the center of the state. No unusual features appeared in northwest (Sand Hills) of NE and southwest of KS. It was observed that there is a line with 4.43 ppm of Pb present in middle west of KS (Fig. 26.3). The highest Pb values in center of KS originated from anthropogenic application, which agree with USGS findings (Woodruff et al.,

2015). The possible sources of Pb are automobile exhaust fumes, and other unknown sources. Very high levels of Se (0.57 ppm) were located in almost all of IA especially middle and south except two regions located in southeast and northwest (Fig. 27.1). The concentrations of Se form a N25° W trending line located in east central NE to east central of KS. In IA, there is a wide spread region with highly elevated Se that could be agricultural activities. Interestingly, Se levels were high in the center of the Sand Hills, a provocative but unexplained result. KS map showed hotspots in the south and southeast of the state (Fig. 27.1). Levels of V were higher in KS than IA and NE (0.84 ppm) except middle south of the state, and many lines have been observed cross the state (Fig. 27.2). Higher concentrations of V in IA are located in middle, northwest, and southwest. In NE, similar to other elements, no significant V values observed in northwest, however, significant levels were identified in northeast and southeast with a line extended to the border of KS. Concentrations of Zn in IA investigated the high levels in most of the geochemical maps of elements in IA. Several lines of low concentrations trended across the IA with values of 0.39 ppm. Low concentrations are located in some small areas in east, middle, and west of IA (Fig.27.3). High concentrations of Zn were confirmed in the southeast extended to the border of IA. Most of the highest levels regions of elements were located in southeast of KS (Fig. 27.3). Conversely, there are no significant levels of Se in the north of the state. In general, As, Mn, Se, V, and Zn indicated anthropogenic point sources since the maps show smoothly decreasing values away from these points.

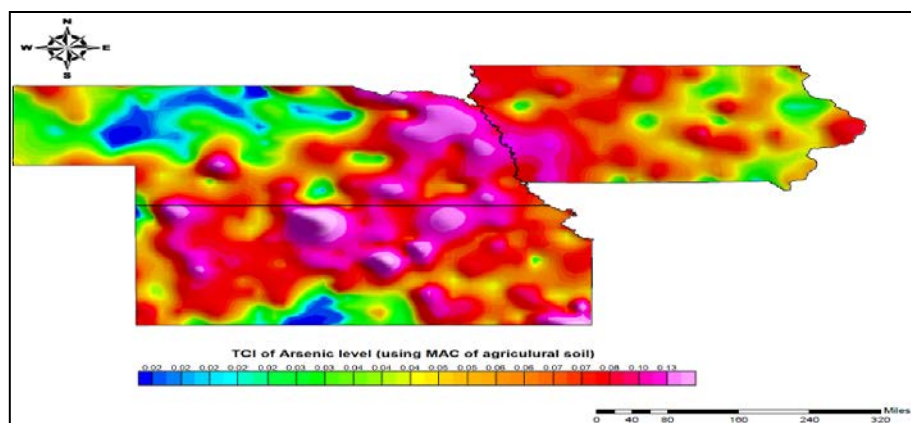


Fig.24.1

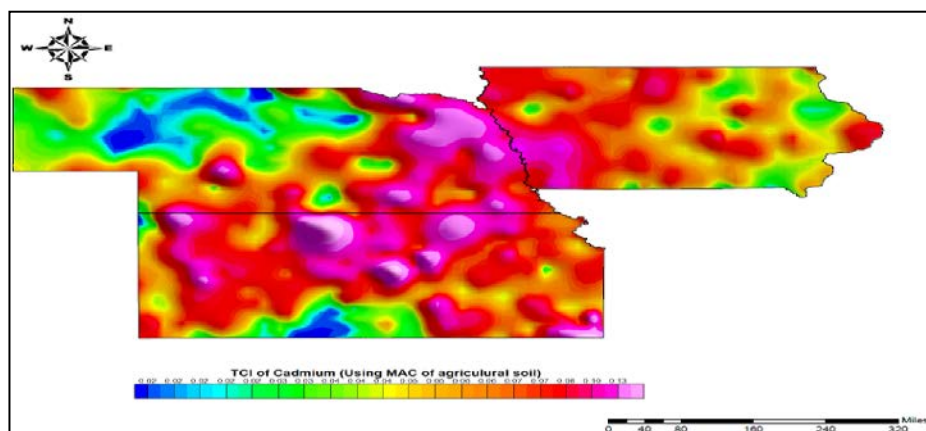


Fig.24.2

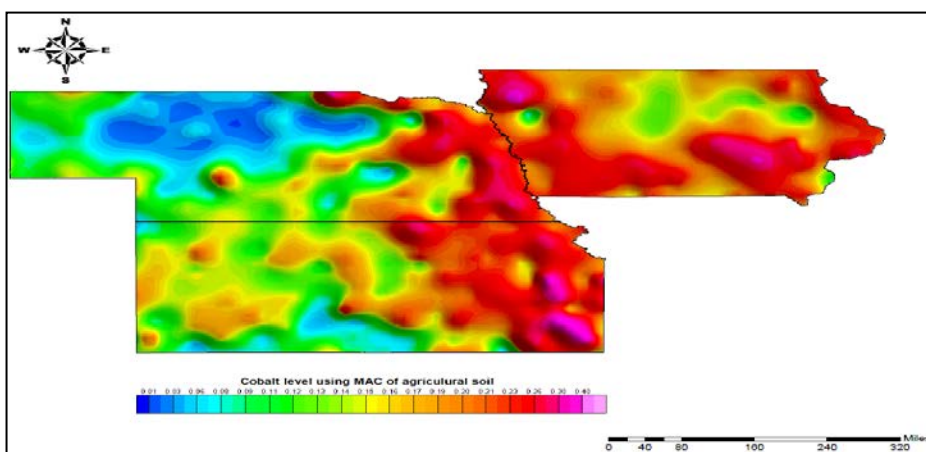


Fig.24.3

Fig. 24. 1-3 Soil geochemistry map showing total chemical concentration of As, Cd, and Co in Iowa, Kansas, and Nebraska.

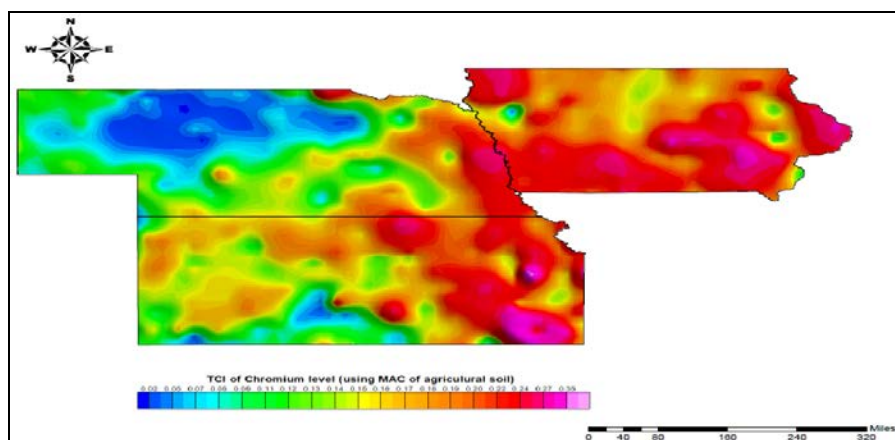


Fig. 25.1

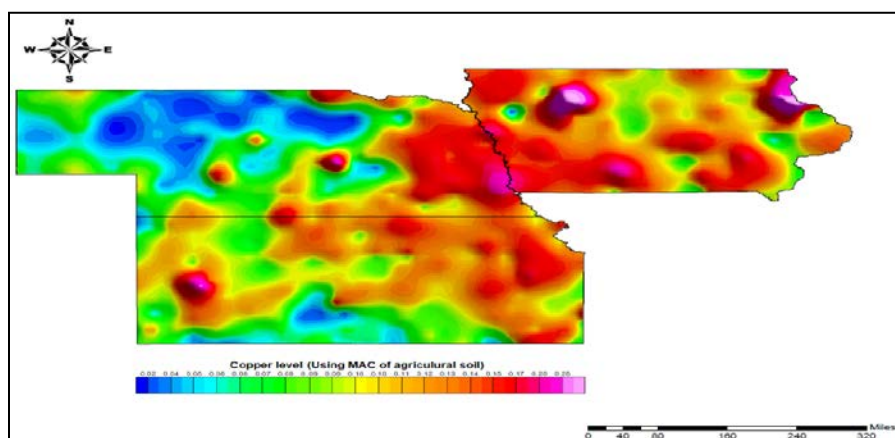


Fig. 25.2

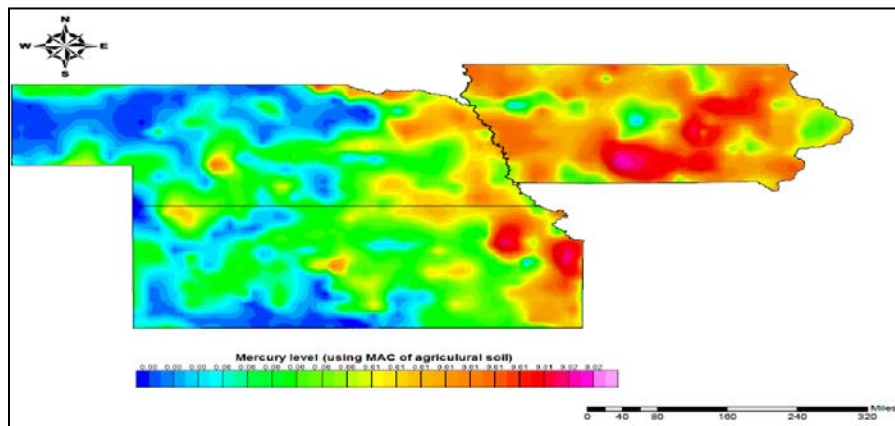


Fig. 25.3

Fig. 25: 1-3 Soil geochemistry map showing total chemical concentration of Cr, Cu, and Hg in Iowa, Kansas, and Nebraska.

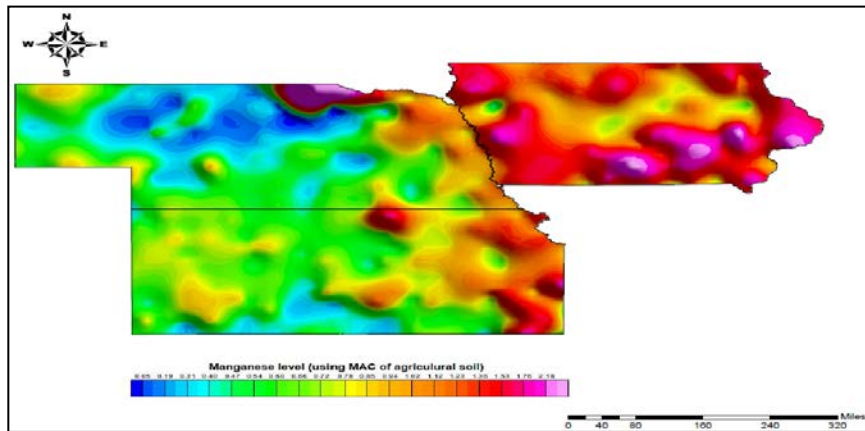


Fig. 264.1

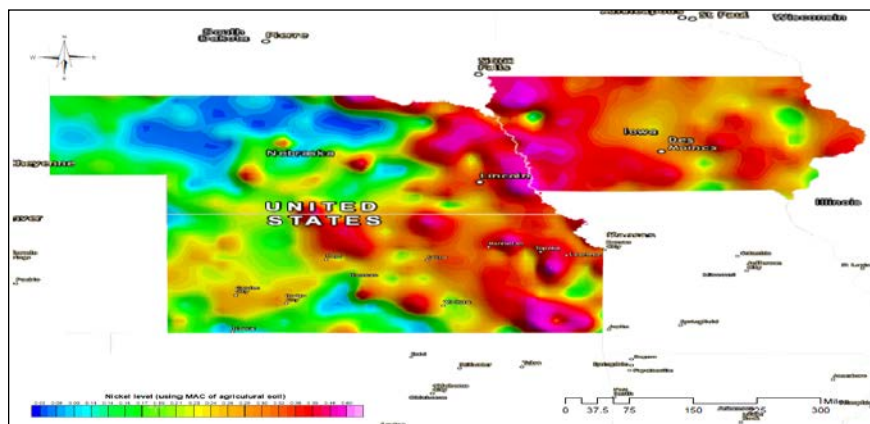


Fig. 26.2

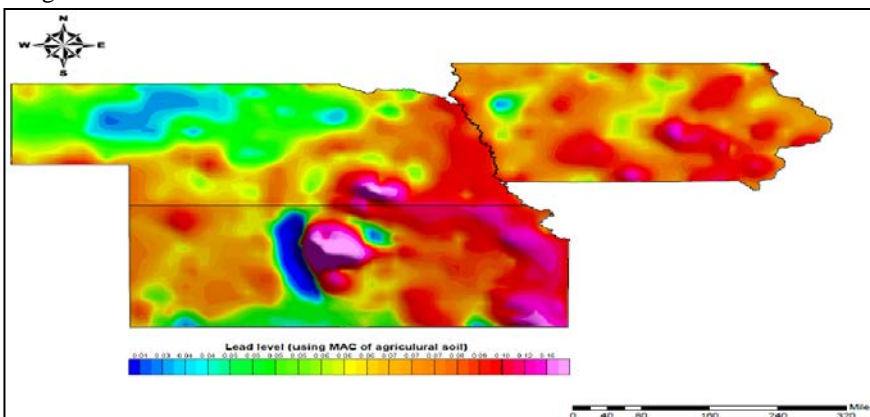


Fig. 26.3

Fig. 26: 1-3Soil geochemistry map showing total chemical concentration of Mn, Ni, and Pb in Iowa, Nebraska, and Kansas.

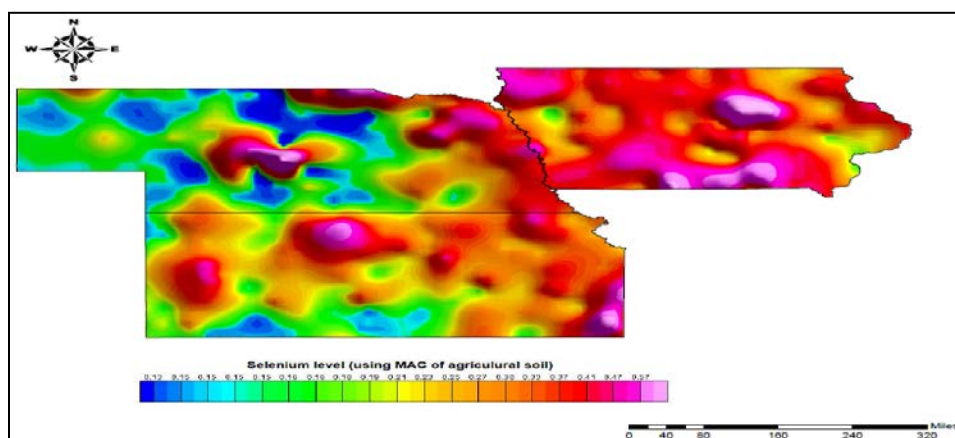


Fig. 27.1

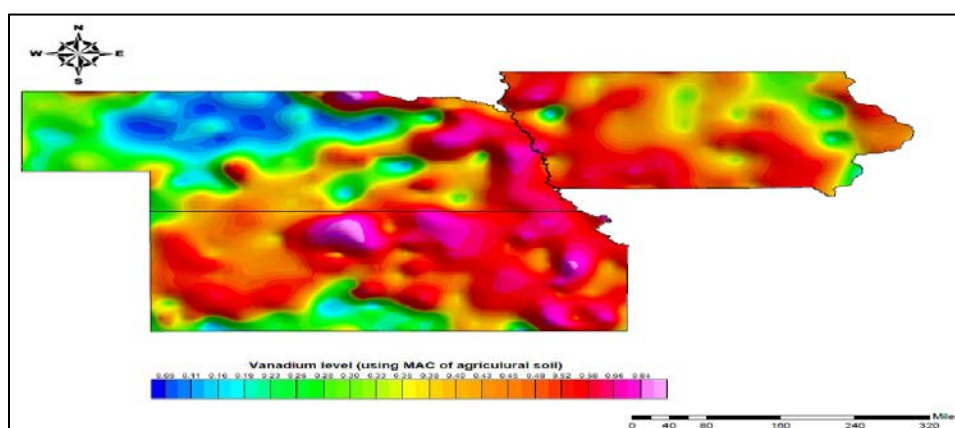


Fig. 27.2

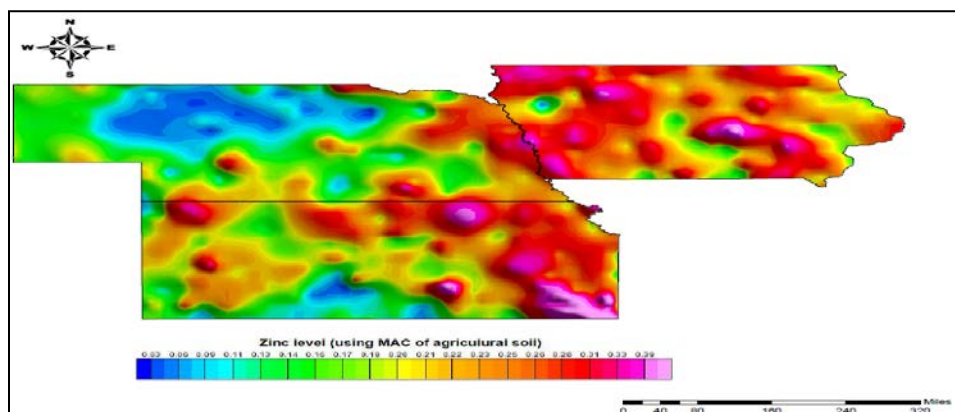


Fig. 27.3

Fig. 27: 1-3 Soil geochemistry map showing total chemical concentration of Se, V, and Zn in Iowa, Nebraska, and Kansas

5.3 Data Analysis

Concentrations of heavy metals were analyzed statistically and mapped. The basic descriptive statistical analysis is shown in Table 11. The spatial distribution of samples showed anomalies with high concentration of some of heavy metals shown with values. High element concentrations were located in different regions in east and northeast of IA, northeast and southeast of KS, and east of NE. Combinations of different graphs and histograms are required for understanding the data distribution of variables using several statistical methods include histogram combined with density trace, boxplot and one-dimensional scatterplot and Empirical Cumulative Distribution Function (ECDF) or Cumulative Probability (CP) plots (Reimann et al., 2008). The original dataset was plotted in two forms of ECDF with log-boxplot and log-transformed plot. The visualization of histograms alongside empirical cumulative distribution function (ECDF-plot) establishes very high values for some elements compared to others. Geochemical mapping was applied to identify the regions that have high values in the study area to produce the spatial distribution of mapped chemical elements.

Table 11 A summarized exploratory statistical analysis was produced showing different calculated values. The measure for central value is represented with element name (EN), the mean and median (Med). The measure for spread is represented with the standard deviation (SD), Pseudo sigma (PS). One quarter of the data fall below the first quartile (Q1), one half fall below the second quartile (Q2), three fourths fall below the third quartile (Q3).

EN	MI N	Q_0 .05	Q1	M	MEAN- LOG	MEA N	Q3	Q_0. 95	MA X	SD	MA D	PSEU DO- SIGM A	CV %	CVR %
As	0	0	3	6	5.934	5.418	8	10	15	3.407	2.965	3.706	62.89	49.42
Cd	0	0	0	0	0.9216	0.1373	0	0.7	5	0.6362	0	0	463.3	NA
Co	0	1	6	7	6.996	8	9.5	14.7	34	5.598	2.965	2.595	69.97	42.36
Cr	3	6.3	17	25	20.52	23.52	29	35	74	10.88	8.896	8.895	46.27	35.58
Cu	1	3	12	15	15.96	25.67	22	92.9	155	29.93	8.896	7.413	116.6	59.3
Hg	0	0	0	0	NA	0	0	0	0	0	0	0	NA	NA
Mn	56	91.9	345	535	452.6	548.8	753.5	964.3	1050	277.2	312.8	302.8	50.5	58.47
Ni	0	2.3	10	14	11.91	14.15	19.5	25.7	29	7.044	7.413	7.042	49.78	52.95
Pb	2	3.3	11	13	11.26	12.25	15	17	20	4.102	2.965	2.965	33.48	22.81
V	7	11	37.5	55	45.95	55.27	63.5	97.5	249	35.93	16.31	19.27	65.01	29.65
Zn	7	16.2	47	60	52.78	58.7	70	94.1	118	22.38	17.79	17.05	38.12	29.65

5.3.1 Plots of Univariate Analysis and Map Distribution

In general, the distributions of trace elements indicate the presence of stable, normal, sources of contamination. The pollution clusters of Zn/Pb/Mn, and Co/V were identified. The distribution of Cu, Co, V, and Zn supports the hypothesis that concentrations originate from two different sources (Fig. 28, Fig. 29,& Fig. 30). The positive correlation of Cu & Co, V & Co groups, concentrations of Cu, Co, V, Zn at the level of mean values (18, 6, 60, 60 mg/kg, respectively), which might be as a result of human applications specially excessive use of fertilizers (Micó et al., 2006).

The results of the statistical analysis of geochemical data involve the description of the single element and its spatial distribution. The goal of statistical and spatial analysis of geochemical data

is to examine the source of trace elements. In the chemical analysis histograms, there are different families that are interpreted with different peaks (Fig. 28, Fig. 29, & Fig. 30). Every peak is different family, but not all the families are interpreted; they can be interpreted in the figures. All the chemicals were statistically plotted except Hg and Cd because of lack of significance by the low chemical assay and no significant values have been shown in the data. An interpretation of these different family groups suggests various sources for each element. In this regard, normality or log normality of data can be evaluated visually by graphs and more rigorously by statistical tests.

The typical method of analyzing geochemical data involves the description of the single element and spatial distribution. Comparison between the chemicals can be performed graphically by plotting for each variable. These univariate non-compositional calculations were plotted using raw data then compared to log ratio plots. The distribution of significant metals was performed and plotted as a histogram and EDCF-plots for the variables presented in this research. The metal analysis is presented in two plot log scale diagrams, one dimensional scatter plot (left), and EDCF plot (right) (Fig. 28, Fig. 29, & Fig. 30). The primary observation is that for such element as Co, Cu, V, and Zn with high values that can be probably related to potential anthropogenic application. For multiple comparisons between the heavy metals, other graphs were produced to display the data distribution in pairs and groups. The values are plotted in X and Y-axes in stacked and one dimensional scatterplots, which present every single point of the data, set using logarithmic scales (Fig. 28, Fig. 29, & Fig. 30). The results present high scales of X-axis of the data set range (Reimann et al., 2008). Extreme concentrations were visible in some histograms and are present the soils are chemically impacted by human activities on a widespread scale.

The analyzed samples showed that the chemical levels in the study areas are highly varied. A comparison between raw data and log ratio transformation eliminates the possibility of values on the upper end and the lower end. Therefore, in histogram and density trace of ECDF, no high significant values of As have been identified (except one values point (15 ppm) in the plot. This value is far from the mean through limited range of the whole data set. Probably, different farmers applied different amounts of fertilizers on this point (Fig. 28.1 & Fig. 28.2). Concentrations of As are low (3-15 ppm), and few of the variables with low concentrations were observed in west and south of IA, and northeast of NE in the scale 10-15 ppm (Fig 28.2). Co concentrations show single variables at scale >14.7- 34 ppm, which may indicate to anthropogenic activities sources (Fig. 28.3). These observations are closely similar to the graph of V concentrations (Fig. 30.3 & Fig. 30.4). Comparison of the many elements shows single groups of values. There is one high break observed with two values at 6 ppm scale. Outlines and the areas of Sand Hills are clear with very low levels of the Co in these areas. There is a highest anomalous of Co in northeast side of NE. No significant concentration has been shown in KS, and there is any significant concentrations have been found in the south of the state except some slightly elevated levels identified in the northwest. However, high concentrations were recognized in the east and far west of IA (Fig. 28.4). Cr concentrations present single values at 40 and 75 ppm, which may indicate anthropogenic activities in these areas. Cr plots show a possibility of two families. An interpretation of these different family groups suggests various sources for each contaminant (family in the value 30 is considered compare to other four families with range of 0-20 and 40-45). In the Cr distribution density, element concentrations show two points in 40 and 70 ppm of values as it shown in (Fig. 28.5). In the plotted concentration maps, there are some values with concentrations in the scale 35-

74 ppm have been observed in four regions in IA, and two regions in NE (Fig. 27.5). Generally, as it shown in (Fig. 29.1), there is variance that shows possible groups at the values of 20 ppm, and 150 ppm of high concentrations of Cu in the soil. Distribution of Cu in two-plot log scale diagrams is shown in (Fig. 29.1) and presents skewed data in Cu (50-150 ppm). It is noted in the maps that most of hotspots of high Cu concentrations (> 92.9) are located in the northeast of NE, middle, and northwest of IA, in addition, areas detected in southeast of IA as shown in Fig. 28.2.

Mn is the element confirmed to have extensive anomalies with high concentrations in the study area. The ECDF plots showed that there were normal distribution >1000 ppm (Fig. 29.3). This probably suggests natural aspects of geological process. Moreover, in the produced maps, highly elevated Mn levels were identified. The important thing to note is that Mn is rich in the soil with a large amount that can come from the geological processes. The plotted maps showed just six values in IA and four values in northeast of NE between 96.4- 1050 ppm (Fig. 29.4). Ni concentrations present single values and 22-30 ppm, which may indicate anthropogenic activities sources in these areas. Ni plots show a possibility of three families. An interpretation of these different family groups suggests various sources for each contaminant family in the range 15 and 20 is considered compared to another two families with range 10-25, and 30. Ni distribution showed one peak in 30-70 ppm of values. One major peak is at 12 and two minor peaks at smaller values as it shown in (Fig. 29.5). There are three values located in west and south of IA in the range of 25.7-29 ppm, and three anomalies have been noted in northeast of NE (Fig. 29.6). In general, there is no significant observable variance observed of Pb in the soil, but there is possibly one point at the concentration of 30 ppm. Moreover, the three values are shown in the range 1-3 ppm in in the log-transformed data. The observation of Pb concentration is shown in Fig. 29.1.

One value is identified south of IA and east of NE with > 17-20 ppm (Fig. 30.2). In the range >15-17 ppm, there are two points to the east and west of IA. However, one point is identified in east of NE (Fig. 30.2). The more concentrated soils with V are located in northeast of NE and the middle and northwest of IA. No significant levels were shown in KS. The lower V concentrations were observed in middle and south of KS. Two families have been observed at the scale 0-100 with high peaks; however, the other three small peaks indicate additional values. High V concentrations have been located in the soil at 110, 180, and 250 ppm which may indicate to the contamination in this area (Fig. 30.3). The plotted maps presented high concentrations of V mostly in the southeast and far northwest of IA, moreover, in northeast of NE. There are 63.5-97.5 ppm values observed in the middle of IA and northeast of NE (Fig. 30.4). Zn concentrations present single values at 110 and 400 ppm, which may indicate to extensive anthropogenic applications sources. Zn plots show a possibility of four families. Interpretation of these different family groups suggests various sources for each contaminant family in the range 100 and 400 are considered as contaminants compare to other two families with range 0-100 ppm. Distribution of Zn showed two points with values 110 and 400 ppm. One major peak is at 150 ppm, and two minor peaks at higher values are shown in Fig. 30.5. Zn is used in agricultural fertilizers and probably is the source of these high values. In the plotted map, one high concentration has been observed on west of IA, and in east of NE with concentration 94.1-118 ppm (Fig. 29.6). In addition, there are two anomalous points in middle and west of IA and northeast of NE (Fig. 30.6).

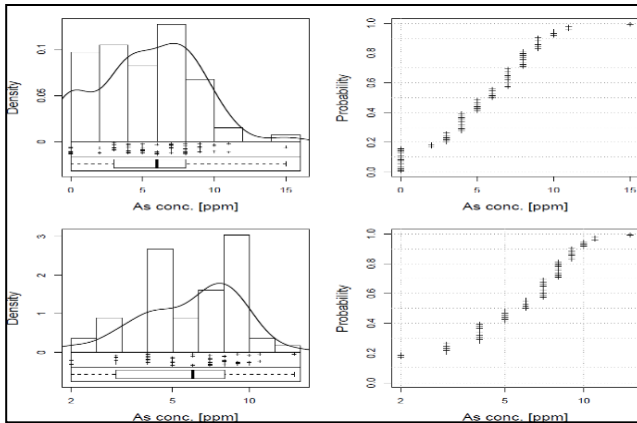


Fig. 28.1

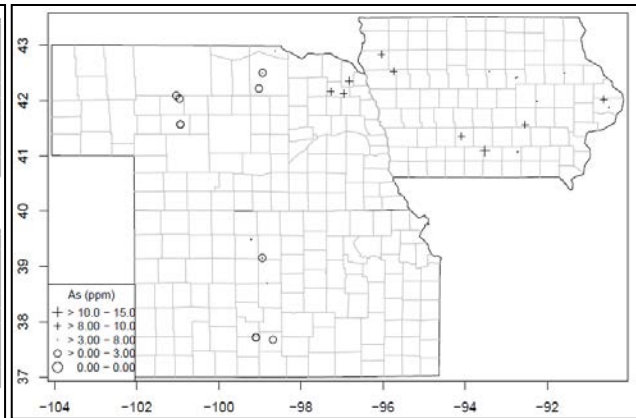


Fig. 28.2

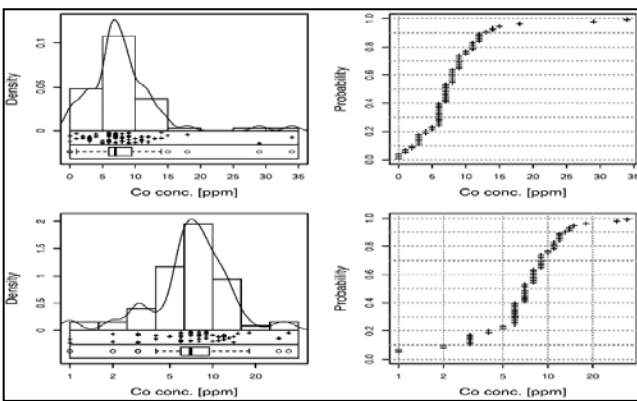


Fig. 28.3

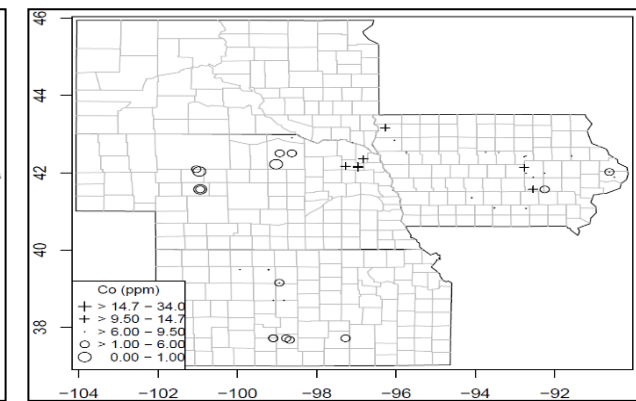


Fig. 28.4

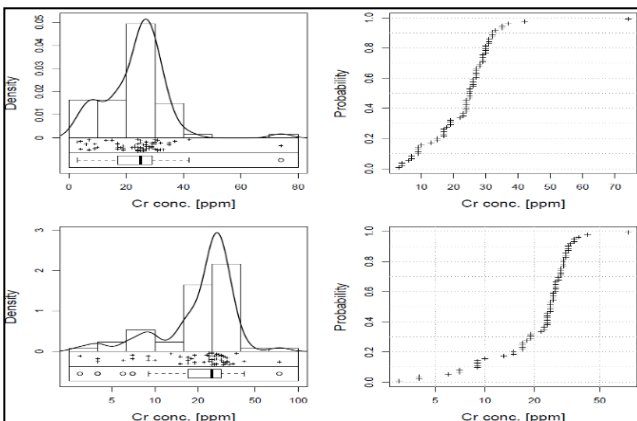


Fig. 28.5

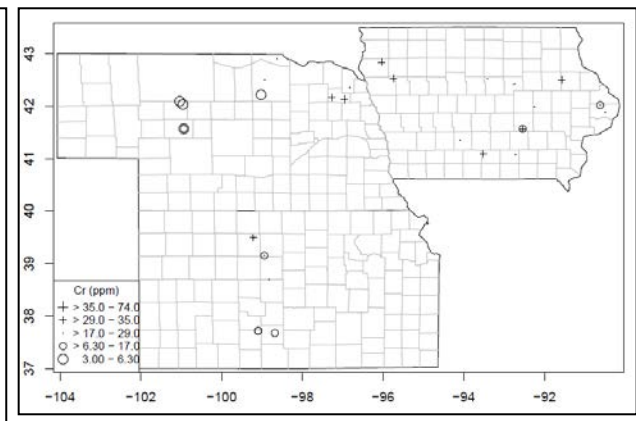


Fig. 28.6

Fig.28: 1-6 Histogram, density trace, one-dimensional scatterplot, and Tukey boxplot, combined with the ECDF- plot. Upper diagrams: original data, lower diagrams: log-transformed data. Boxplot class based map showing average element concentration and distribution of values.

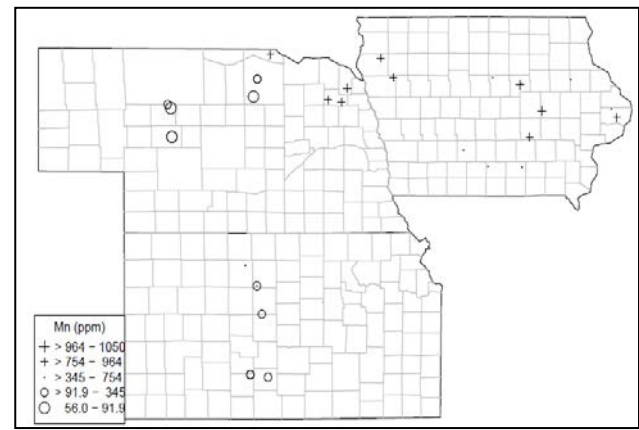
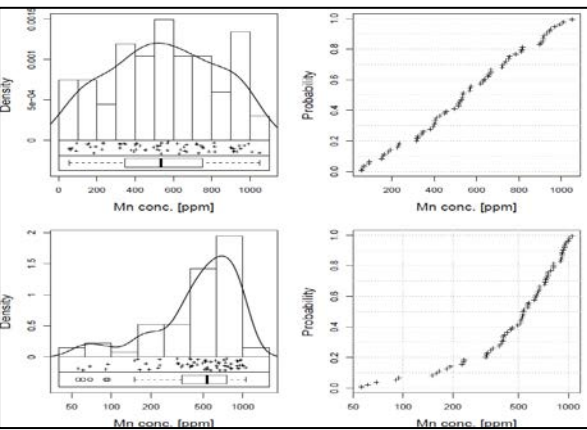
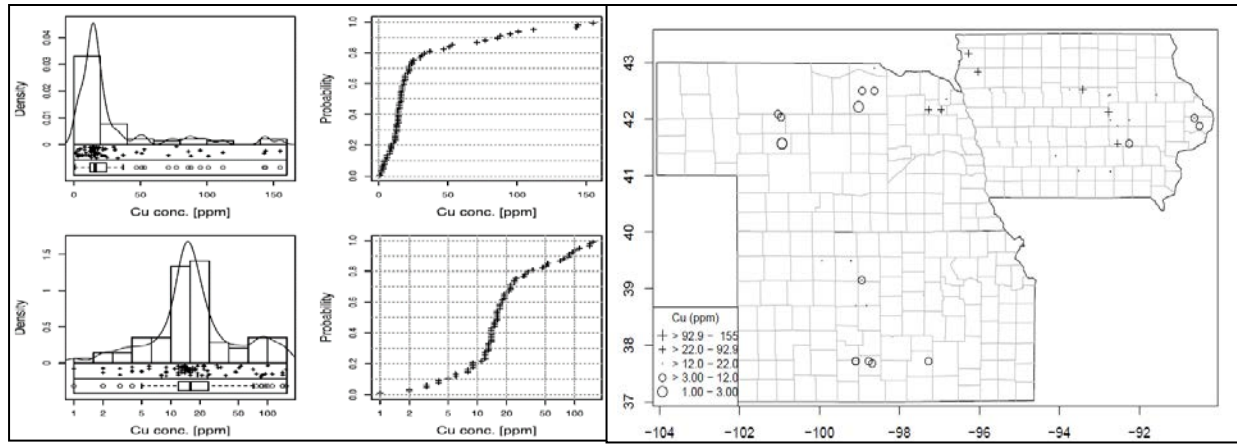


Fig. 29.1

Fig. 29.2

Fig. 29.3

Fig. 29.4

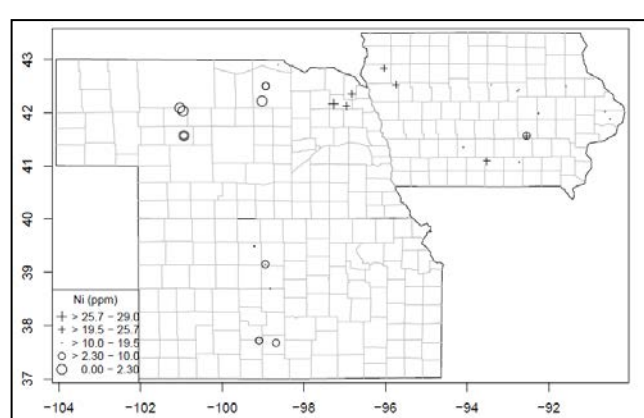
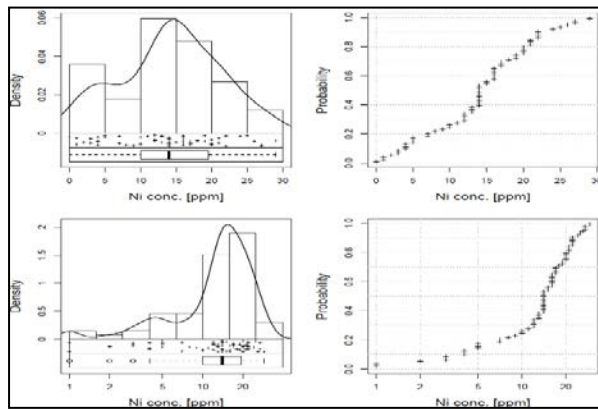


Fig. 29.5

Fig. 29.6

Fig. 29: 1-6 Histogram, density trace, one-dimensional scatterplot, and Tukey boxplot, combined with the ECDF- plot. Upper diagrams: original data, lower diagrams: log-transformed data. Boxplot class based map showing average element concentration and distribution of values.

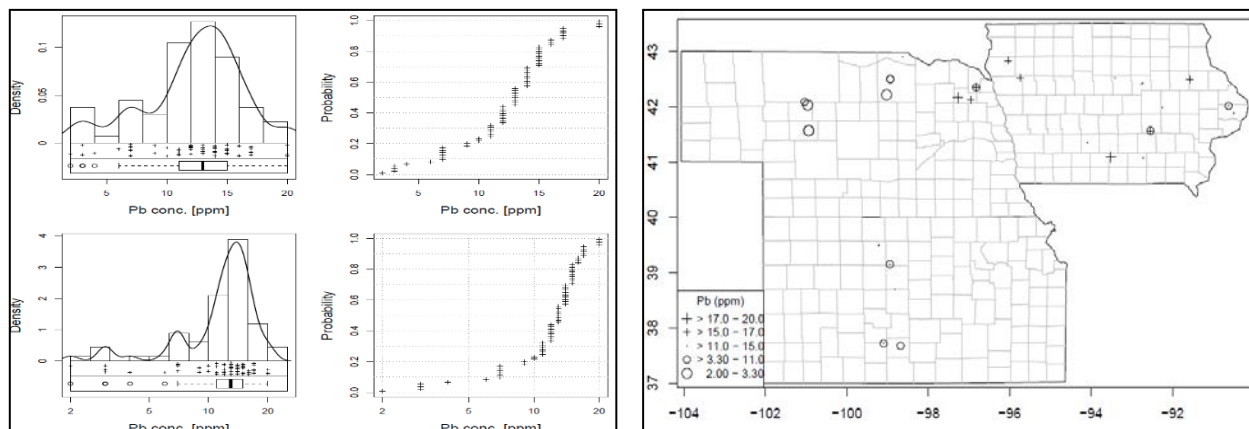


Fig. 30.1

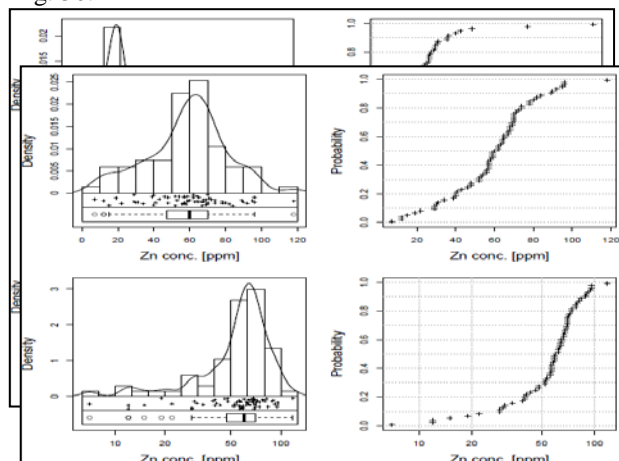


Fig. 30.3

Fig. 30.5

Fig. 30.2

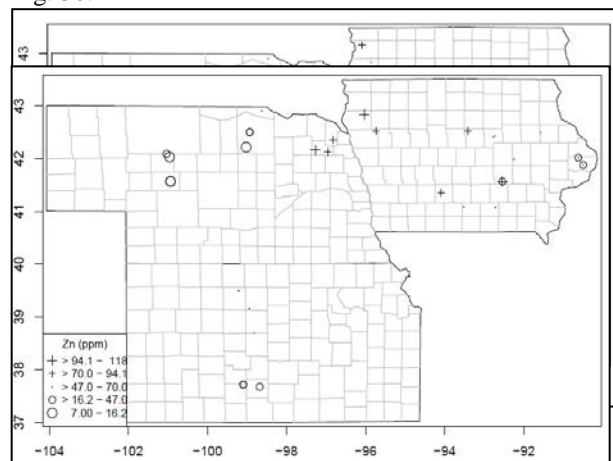


Fig. 30.4

Fig. 30.6

Fig. 30: 1-6 Histogram, density trace, one-dimensional scatterplot, and Tukey boxplot, combined with the ECDF- plot. Upper diagrams: original data, lower diagrams: log-transformed data. Boxplot class based map showing average element concentration and distribution of values.

5.3.2 Multivariate and Bivariate Analysis Results

Patterns of the correlation between multiple heavy metals were investigated. The correlated distinctive relationships between the chemicals have been studied are shown in Table 12, Fig. 31.1. Multivariate data analysis was performed using principle component analysis (PCA) and bivariate pairwise analysis to identify points of correlations of the relationships and covariance between the heavy metals. Statistically, PCA showed correlation between the trace elements as in Fig. 31.1. The closer values are to 1 the more positive correlations are identified between the elements. Significantly, all levels of heavy metals show a positive correlation as it shown in Table 12. A strong correlation is identified between Cd (0.37) and Cu (0.58) in the soil of agriculture in three states. Elements Mn (0.58) and Ni (0.74) are strongly correlated with each other compare to other elements. It is clear that there is chemically strong correlation between the elements: As (0.67) Co (0.87), Cr (0.82), Pb (0.80), V (0.85), and Zn (0.80) because they are very closely correlated in the regions. The correlated distinctive relationships between the chemicals have been investigated as is shown in Fig.31.1; representing PC1 of the multivariate analysis with values (67.5%) contrasted with PC2 and with a value (18.4%). The correlated distinctive relationships between the chemicals have been investigated as is shown in Fig.31.1. The chemical analysis demonstrated significant spatial variability between the chemical elements (Fig. 31.2). Some variables indicate trends related to each other as correlated groups. The parallel linear directions that include Co and V are demonstrating strong correlations between these chemical pairs. However, the chemical family including As, Ni and Mn is significantly correlated. The associations between pairs Pb and Zn are also correlated.

Table 12 Pairwise analysis identifying correlation of the trace elements

Elements	Cd	Cu	Mn	Ni	Pb	Zn	As	Co	Cr	V
Cd	1	0.379239	0.233503	0.145218	0.440267	0.42568	0.259454	0.281934	0.196339	0.330762
Cu	0.379239	1	0.585979	0.609282	0.637414	0.696293	0.734216	0.852125	0.692595	0.833252
Mn	0.233503	0.585979	1	0.748932	0.729183	0.772642	0.76177	0.703489	0.630079	0.57762
Ni	0.145218	0.609282	0.748932	1	0.776251	0.686791	0.851731	0.753262	0.882914	0.687322
Pb	0.440267	0.637414	0.729183	0.776251	1	0.807625	0.734313	0.688151	0.755059	0.64991
Zn	0.42568	0.696293	0.772642	0.686791	0.807625	1	0.677045	0.664089	0.628506	0.612984
As	0.259454	0.734216	0.76177	0.851731	0.734313	0.677045	1	0.874726	0.840903	0.809591
Co	0.281934	0.852125	0.703489	0.753262	0.688151	0.664089	0.874726	1	0.825736	0.930443
Cr	0.196339	0.692595	0.630079	0.882914	0.755059	0.628506	0.840903	0.825736	1	0.85124
V	0.330762	0.833252	0.57762	0.687322	0.64991	0.612984	0.809591	0.930443	0.85124	1

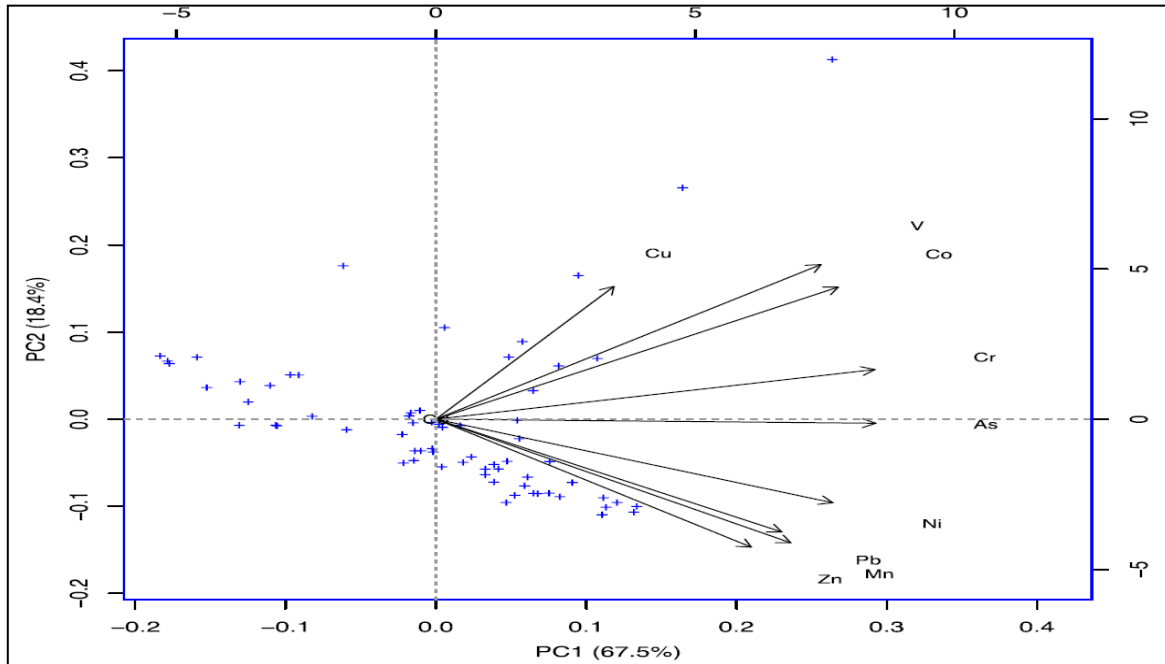


Fig. 31.1 Biplot of PC1 (67.5%) versus to PC2 (18.4%) for robust PCA.

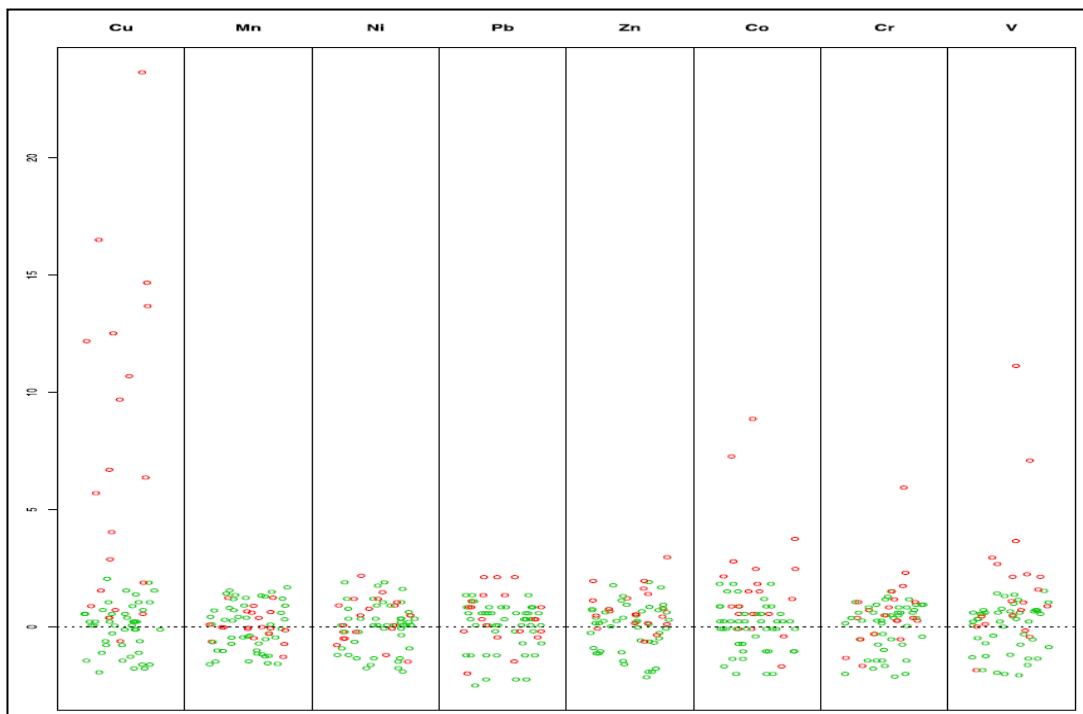


Fig. 31. 2 Univariate scatterplots analysis shows single element plot for values identification (red color $^{\circ}$ = values and green color $^{\circ}$ = non- values)

Additional data exploration methods were applied to the same variables in univariate display as identified in multivariate analysis, with the distribution of univariate scatterplots (Filzmoser, 2005). This particular plot (Fig.31.1) offers a visual detection for apparent values for easy identification for elemental data exploration. Variables are presented as a series of vertically scaled parallel bars (Filzmoser, 2005). The values occur over the complete univariate ranges including the extreme ranges. Besides multi-statistical and uni-variate analysis, Fig. 31.2 presents univariate scatterplots analysis that displays detected values of the trace elements such as Cu, Co, Cr, and V. However, other elements present lesser data values including Mn, Ni, Pb, and Zn. The variability of the elements is showed by parallel bars. The red circles show the values for each

element in the columns. These distribution maps showed previously established an important difference suggesting the principal role of chemical loading as a serious anthropogenic source of these elements.

6. RELATIONSHIP OF HEAVY METAL COMPOSITION OF SOIL WITH MINERALOGY AND OTHER SITE PROPERTIES

Some heavy metals have naturally and/or anthropogenic additions with high concentrations. The rock type is different in various regions, therefore, properties of soil is dependent on the type and chemical concentrations of the rock (Lollar et al., 2004). It is investigated that Mn has the most abundance in limestone, sandstone, and shale rocks compared to the other heavy metals.

6.1 Synthetic Bed Rock, As Lithogeochemical Maps (LGMS)

Regional geochemical mapping (RGM) is a standard worldwide accepted scientific methodology. It comprises several subsidiary routines including several of those carried out in these chapters. However, a new routine is developed and presented here. This is trace element lithogeochemical or bedrock geochemical maps. These are invented here and consist of “average rock chemistry” as determine by numerous scientists (Lollar et al., 2004 & Kabata-Pendias, 2011) combined with geologic maps. Primary, original, data of this type, “average rock geochemistry”, in the states under consideration (IA, KS, and NE) would necessitate the drilling of thousands of holes to deep bedrock and the chemical analysis of the bottom hole samples, which would cost large amounts. In the meantime, the trace element lithogeochemical maps (LGM) invented here will suffice.

The study of regional geochemical maps is essential at different scales because the distribution of the rocks and thus chemicals are heterogeneous on the surface of the earth (Vila & Martinez-Llado, 2015). Initially, elemental concentrations are documented and these may be smoothed, contoured, and colored. One of the main aims of the generation of lithogeochemical maps is to visualize the geochemical data structure in relation to natural bedrock. In the present study, the geologic map shows the presence and distribution of different rocks, and the lithogeochemical maps show the maximum of the average range of the chemistry of those different rocks. In another way, the specific value for each heavy metal shown on the map is the maximum of the range of values or concentrations of this specific metal in the rock found in that area. The choice of the maximum of the range is a bias; a more conservative choice could have been made. These are the generated lithogeochemical maps as is shown in Fig. 32, Fig. 33, Fig. 34, & Fig. 35). Background concentrations of the metals are associated to the mineralogy of the parent materials (bedrocks) that develop the soil through pedogenic processes. The natural forms of the heavy metals are found in mineral components in the soil such as silicate or aluminosilicate minerals. Concentrations of heavy metals are dependent on the rock type of the parent material to produce specific types of soil. Basalt and black shales have elevated natural concentrations. However, these rocks are nonexistent on the geologic maps of the study area. Surprisingly, results of generated lithogeochemical maps showed different aspects of soil chemistry.

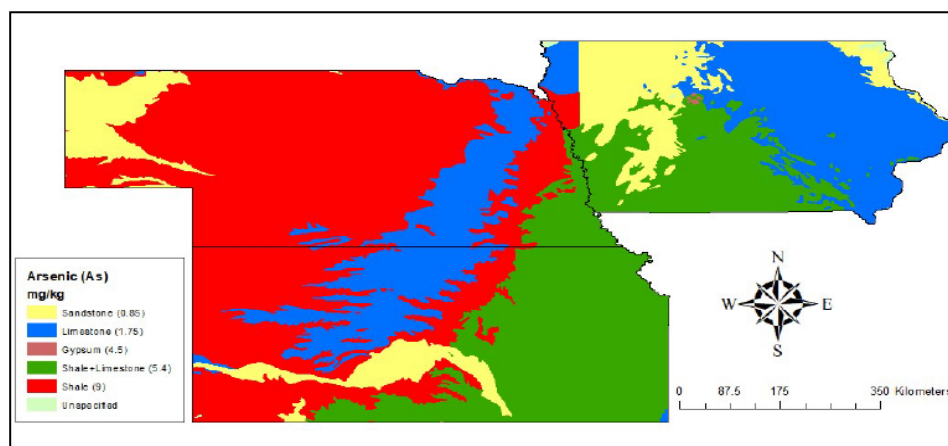


Fig. 32.1

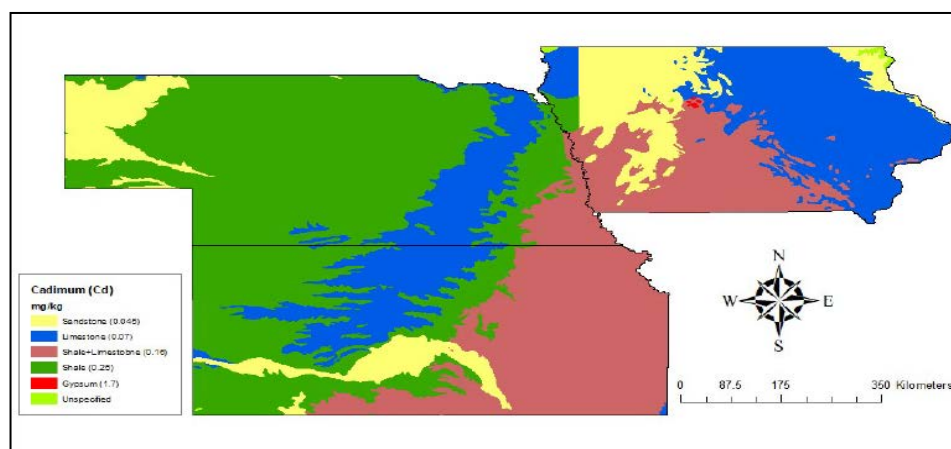


Fig. 32.2

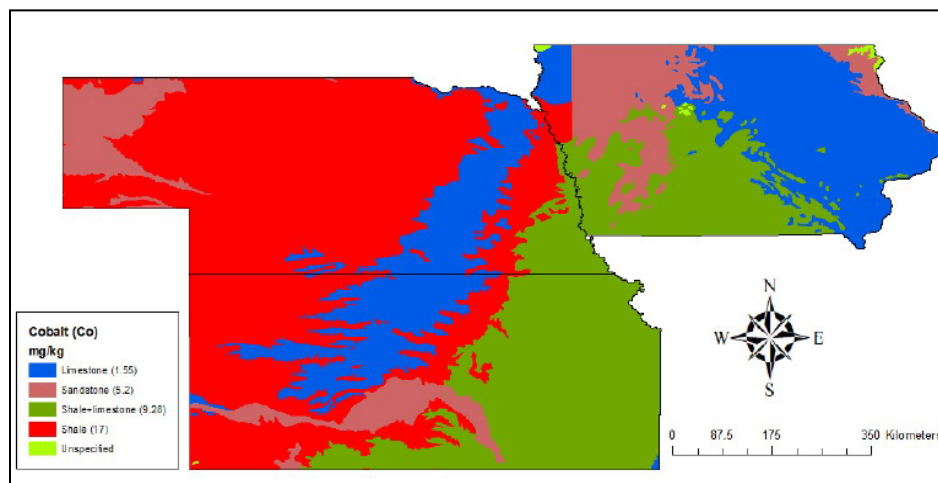


Fig. 32.3

Fig.32: 1-3 Lithochemical maps of As, Cd, Co in IA, KS, and NE.

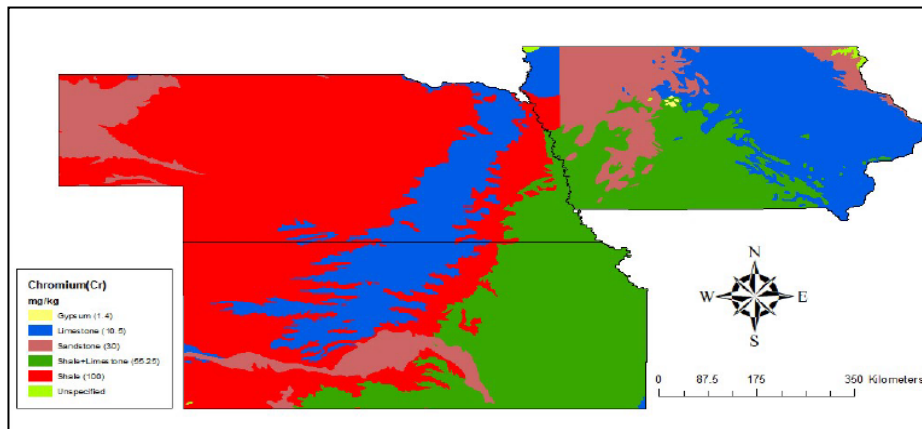


Fig. 33.1

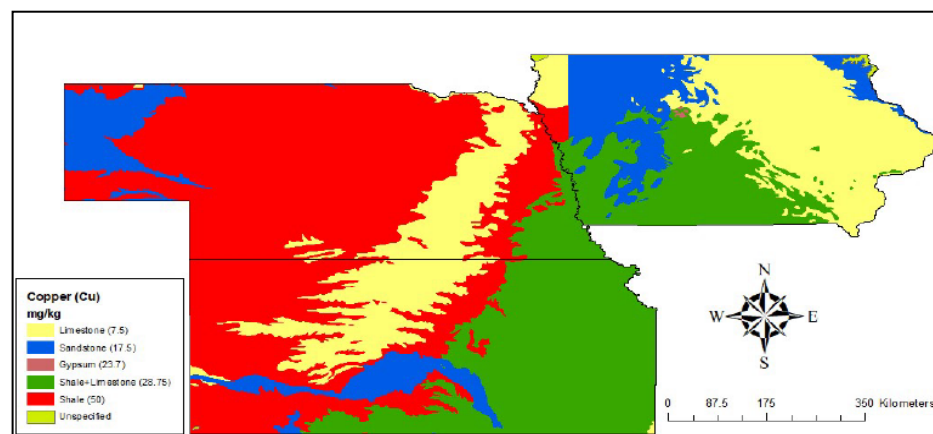


Fig. 33.2

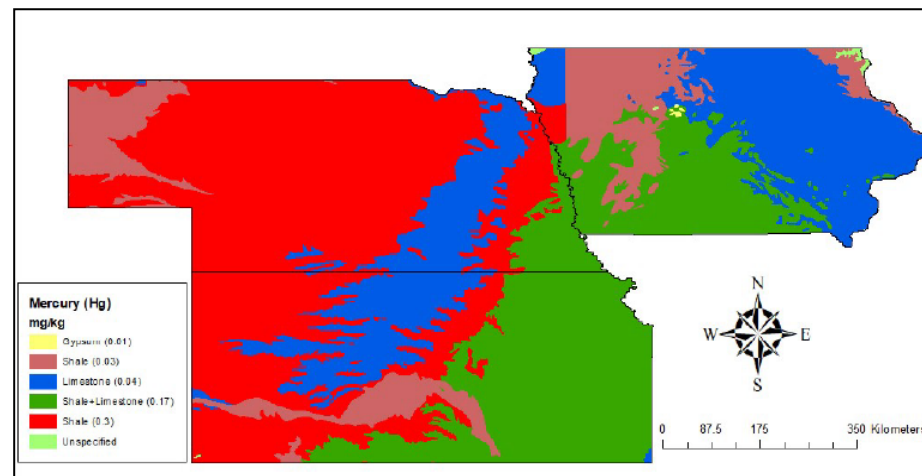


Fig. 33.1

Fig. 33: 1-3 Lithochemical maps of Cr, Cu, and Hg in IA, KS, and NE.

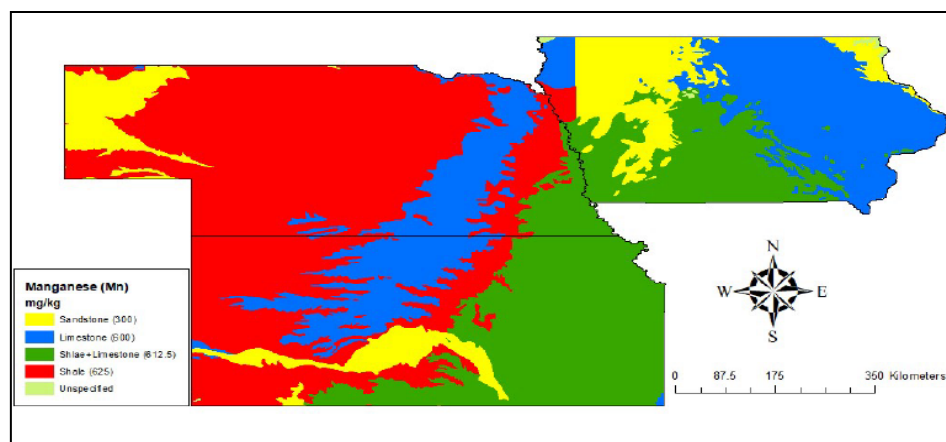


Fig. 34.1

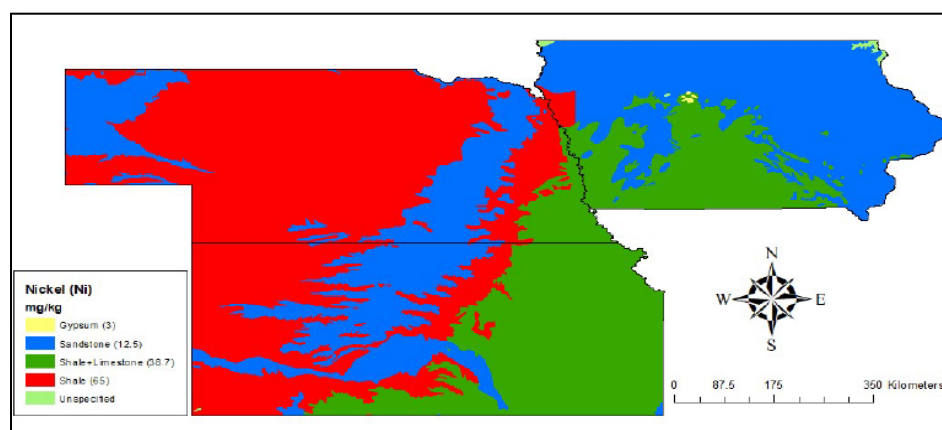


Fig. 34.2

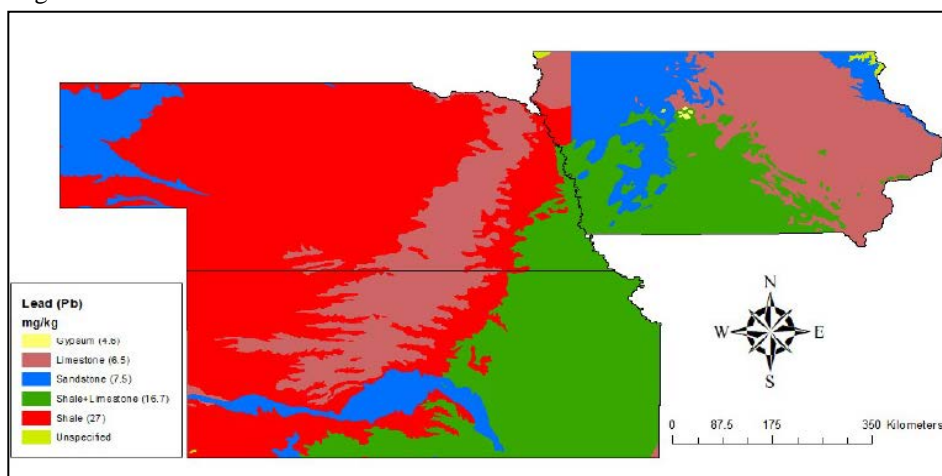


Fig. 34.3

Fig. 34: 1-3 Lithochemical maps of Mn, Ni, and Pb in IA, KS, and NE.

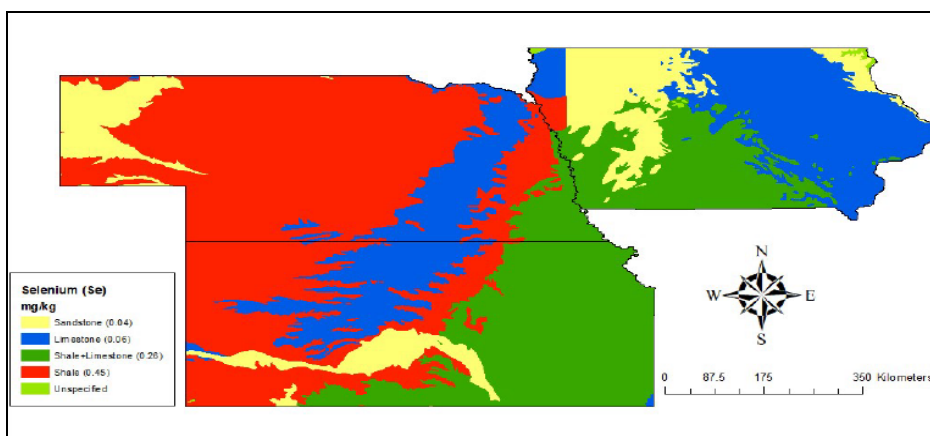


Fig. 35.1

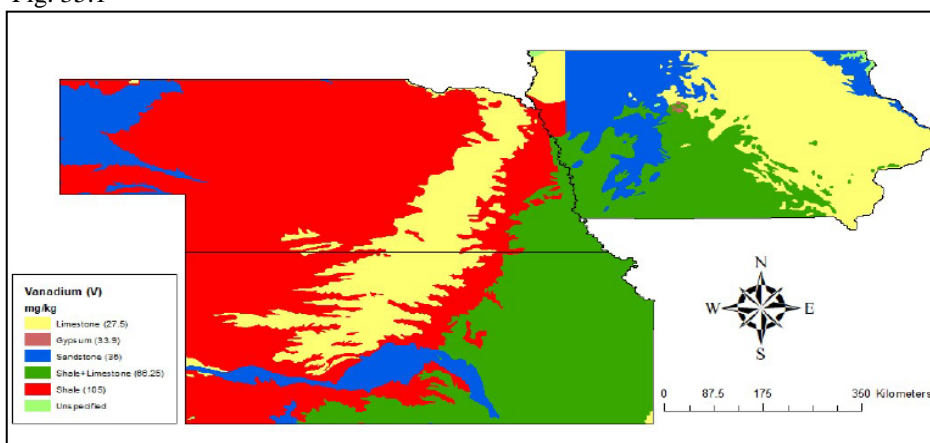


Fig. 35.2

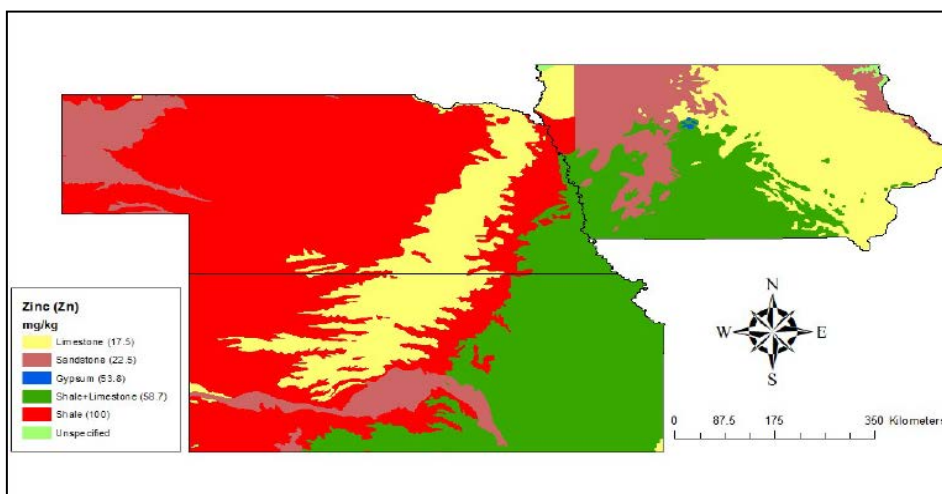


Fig. 35.3

Fig. 35: 1-3 Lithochemical maps of Se V, and Zn in IA, KS, and NE.

6.2 Residual Lithogeochemical Maps (RLGM)

Lithogeochemical maps were subtracted from the USGS soil data of the C horizon to produce residual lithogeochemical maps (RLGM). The results indicate the difference between the metal concentrations of these two data types. The negative values shown in the map scale are permissible in the element maps. Negative values may indicate leaching. Furthermore, as a conservative methodology, the maximum of the range of element concentrations in the rocks were the numbers used. Selection of the number of classifications in the legend can be used to focus on values. Experiments have been run with different numbers of classifications and it was decided that five classes would be used. Observation of an As residual lithogeochemical map shows that there are anomalies in the range 4.18-8.18 mg/kg trending from the northwest extend to south west of NE, and few of the anomalous points are present in the south of KS (Fig. 36.2). Cd maps showed that there are anomalies present in the east of IA and further to the west of NE, and one region located in the north of KS, southwest across NE and into KS, except for some regions or minor additional locations (Fig. 36.2). The anomaly in southeastern KS is due to mining in the Tri State Lead Zinc District (Fig. 38.3 & Fig. 38.3). Another anomaly is present in the northeastern corner of IA. It is suggested that this anomaly may be along the Mississippi River (Fig. 37, Fig.38, & Fig.39). Investigation of the Pb map shows a strong anomaly in eastern NE within the area of several additional anomalies as will be mentioned below (Fig. 38.3). This anomaly is repeated so many times below that is given the name eastern NE. The second anomaly appears in central KS. The Mn map is presented in Fig. 38.1 and shows that the most abundant anomalies are located in western and southern IA, and in NE the anomalies are present in the east and the north along the Missouri river. The Ni map has a very small high anomaly in far eastern part at the border of

Missouri, and a small high anomaly in northern central KS, but not at the same location as lead anomaly mentioned above (Fig. 38.2). The V map shows a large and strong anomaly in eastern NE. The reason of the point source anomaly is not known and EPA website should be consulted (Fig. 39.2).

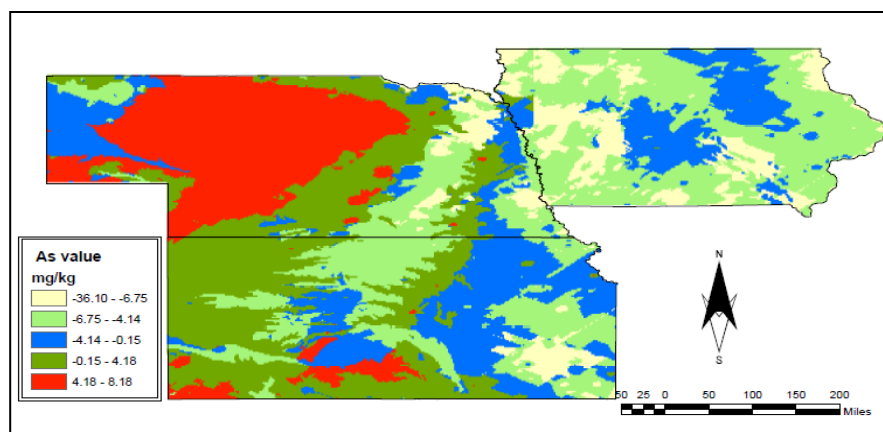


Fig. 36.1

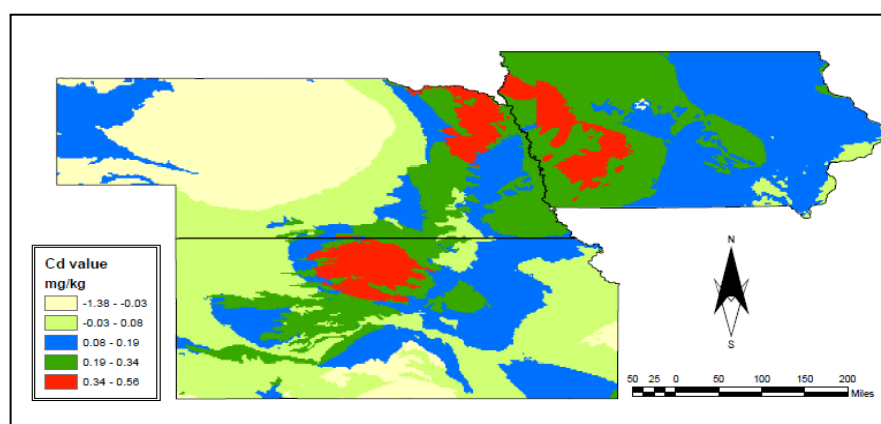


Fig. 36.2

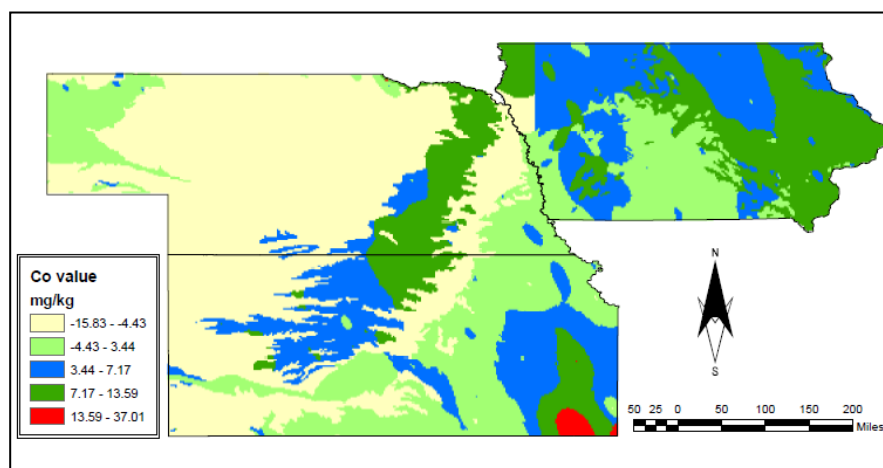


Fig. 36.3

Fig. 36: 1-3 Residual lithochemical maps of As, Cd, Co in IA, KS, and NE

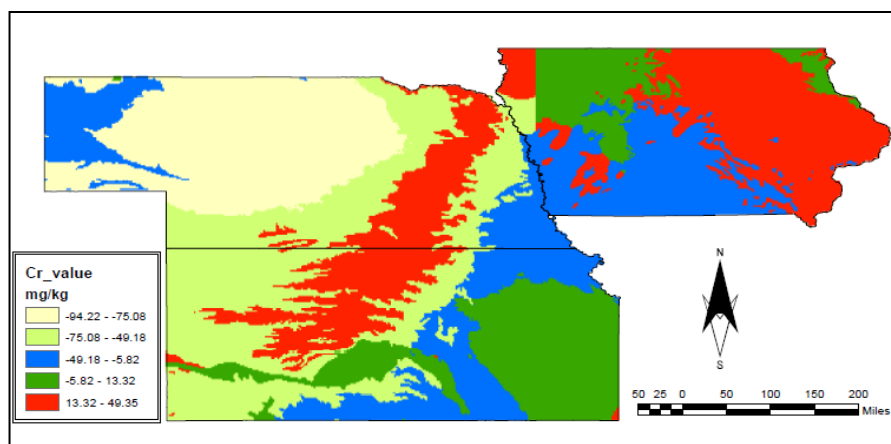


Fig. 37.1

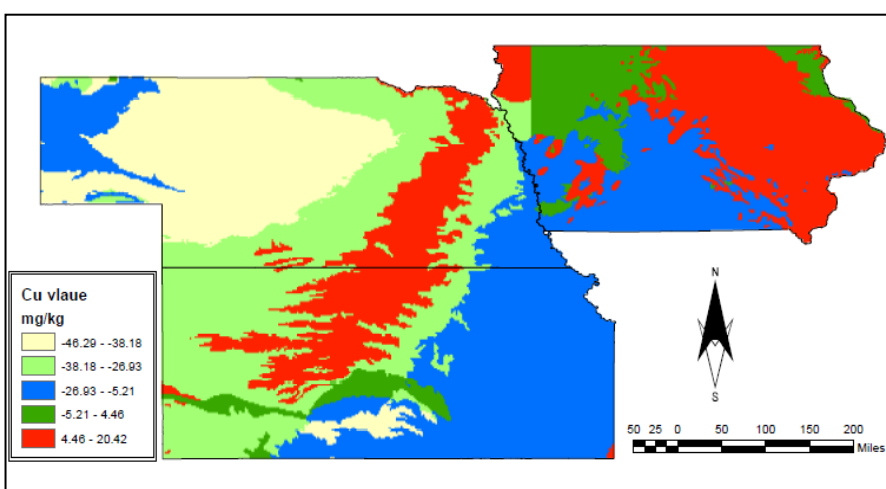


Fig. 37.2

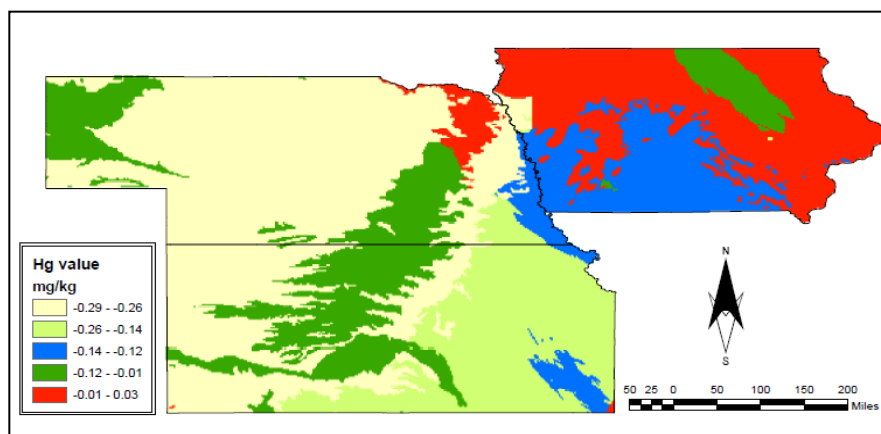


Fig. 37.3

Fig. 37: 1-3 Residual lithochemical maps of Cr, Cu, and Hg in IA, KS, and NE

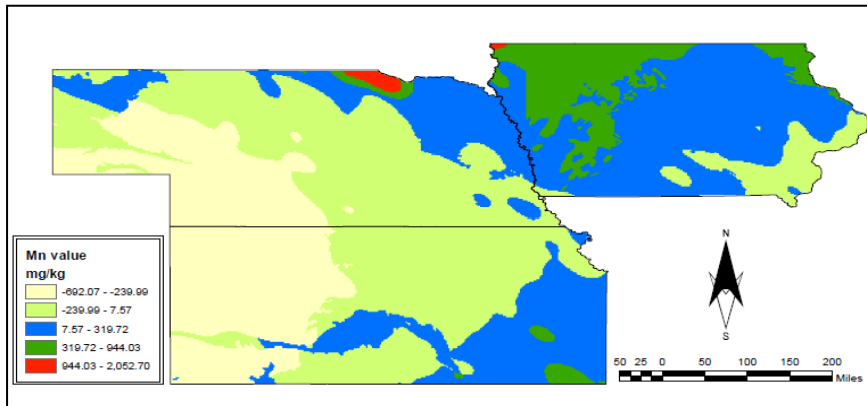


Fig. 38.1

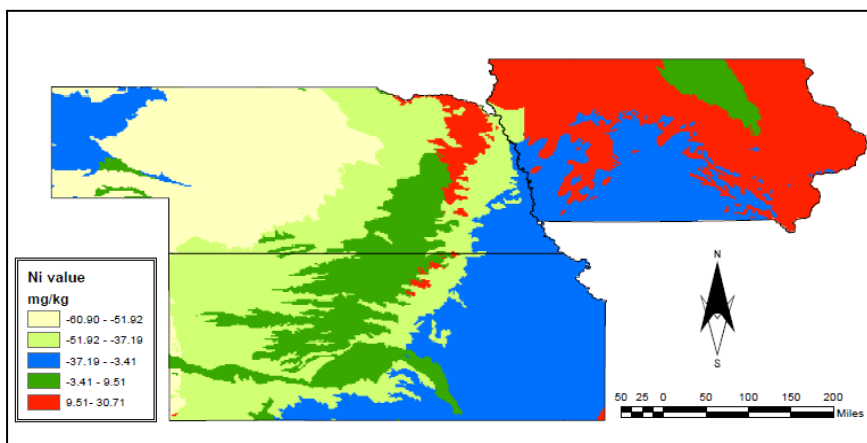


Fig. 38.2

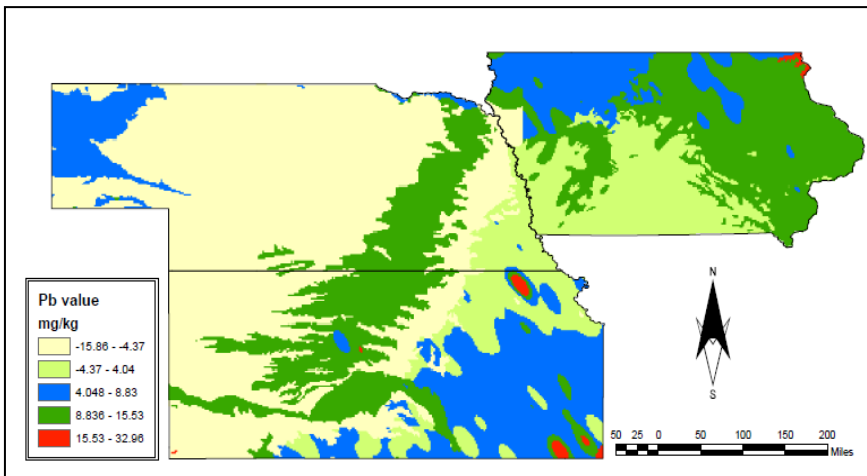


Fig. 38.3

Fig. 38: 1-3 Residual lithochemical maps of Mn, Ni, and Pb in IA, KS, and NE.

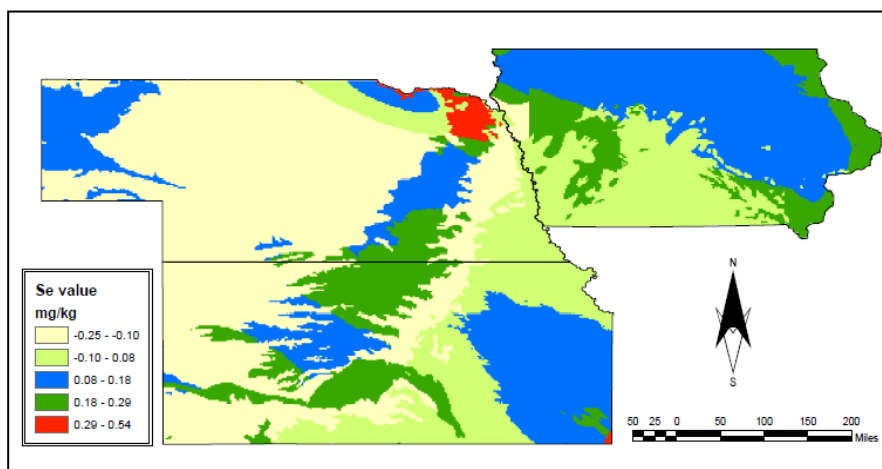


Fig. 39.1

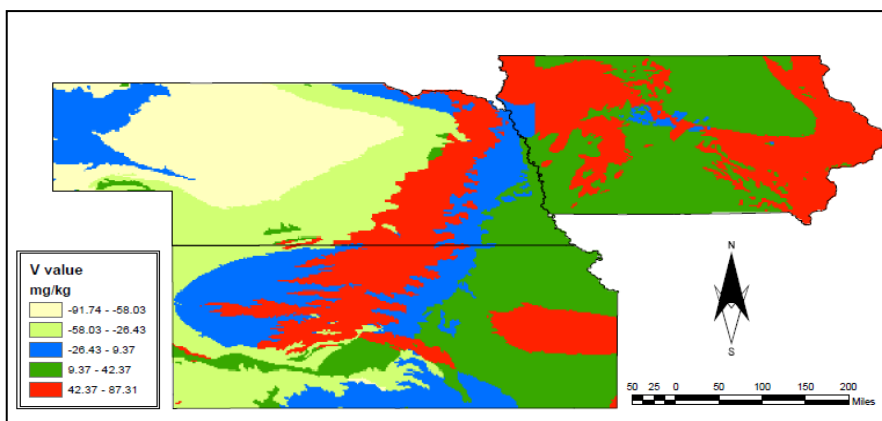


Fig. 39.2

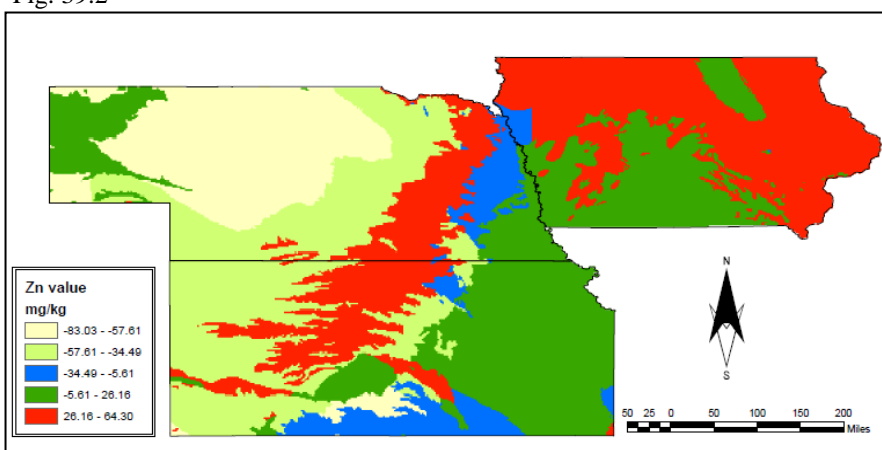


Fig. 39.3

Fig. 39: 1-3 Residual lithochemical maps of Se, V, and Zn in IA, KS, and NE.

7. CONTRIBUTION OF GLACIAL AND LOESS SOILS IN SAMPLE GEOCHEMISTRY

Geochemistry of the loess can provide much information about the terrestrial records of interglacial and glacial cycles, tectonic process, climate conditions such as temperature and moisture, and atmospheric processes (Ruhe, 1983 & Muhs, 2013). Loess is distinctive sediment and accumulated with different thicknesses over landforms (Muhs, 2017). In addition, loess deposits are the uppermost glacial sediments in North America.

The loess in North America includes areas in the Mississippi river valley and Great Plains. The loess distribution in North America with respect to this study exists in the Great Plains region (Mason, 2001 & Muhs, 2017). It is distributed from northwestern KS to the northeast across NE. Loess in the Great Plains comes from different sources; one important source of loess is Tertiary siltstone of the White River Group that is found extensively in NE, which is controlled by volcanoclastic source and silt particles. Another source of loess in this region is fluvial that includes the Platte River system (Muhs, 2017). Loess was deposited during soil formation in middle Pleistocene (Muhs, 2017). The younger loess is thicker than the older loess, and two of the youngest loess in the mid-continent of USA are the Loveland loess and Peoria Loess (Muhs, 2017).

Another body of loess appears in western IA, which is Peoria loess of last glacial age. The loess has accumulated according to the time of the deposition to different thicknesses up to approximately 40 meters (Muhs et al., 2013), and non-glaciogenic Peoria Loess in central of NE equal to 45 meters (Muhs et al., 2008).

This distribution of losses showed repeatedly in the following diagrams in brown (Fig. 40, Fig. 41, Fig. 42, & Fig. 43) as an example of maps generated to show loess distribution. There is a wide distribution of the loess in USA and its deposits date to post glacial periods.

Moreover, glacial and non-glacial materials could be the source of the silts, which form the bulk of the loess. Southeast of the Sand Hills there is a southwest trending narrow belt which correlates with loess distribution, with repeated chemicals. This is the thickest loess, and the background is low, which makes it visible. Elsewhere loess bodies are overlaid on regional high chemical values, and they do not show up. According to the overlay geochemical maps, there is very little influence on soil chemistry by loess.

Glaciers moved from the north to the south several times in the region of interest. The glaciated area is mainly in IA as a large loop located in the northwest, extending to the south at least half way across the state, presented on the figure as a dashed pattern, which is used to indicate the presence of glacial activity. Surprisingly, the east part of lobe has lower chemical values than western part (Fig. 40, Fig. 41, Fig. 42, & Fig. 43).

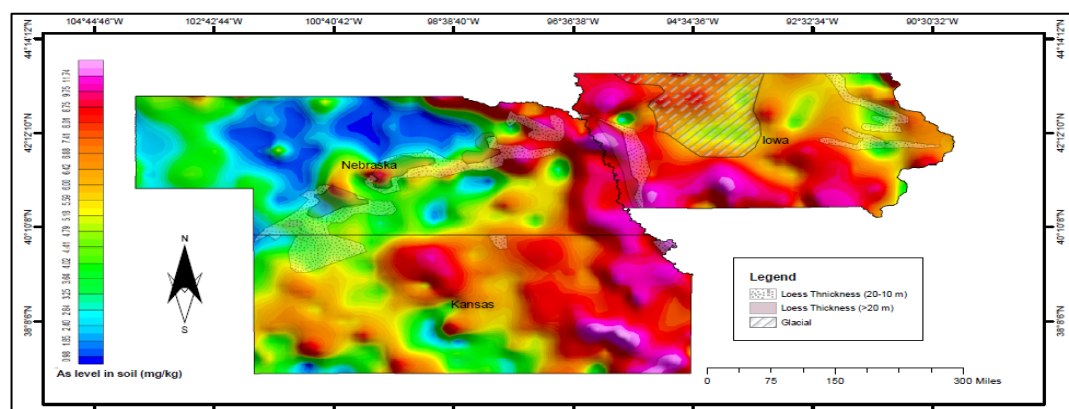


Fig. 40.1

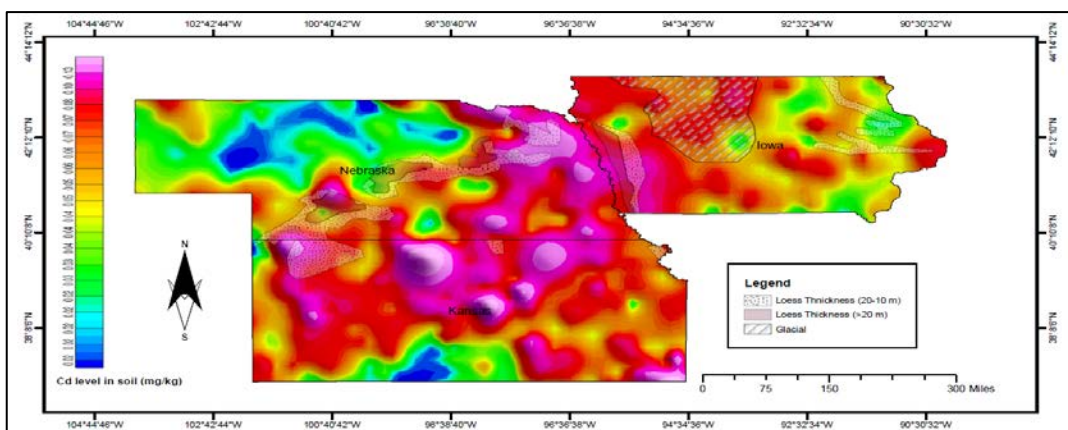


Fig. 40.2

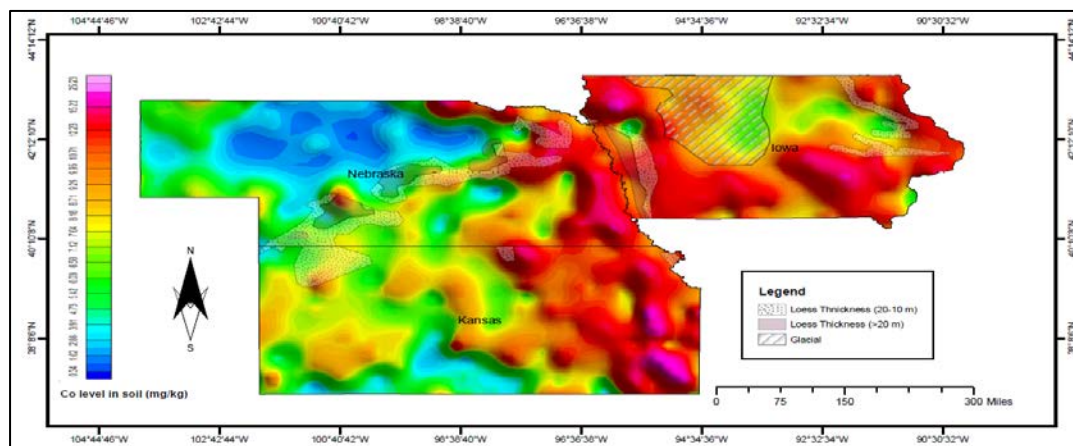


Fig. 40.3

Fig. 40: 1-3 Glacial sediment and loess distributions overlay on geochemical data maps (Smith et al., 2014)

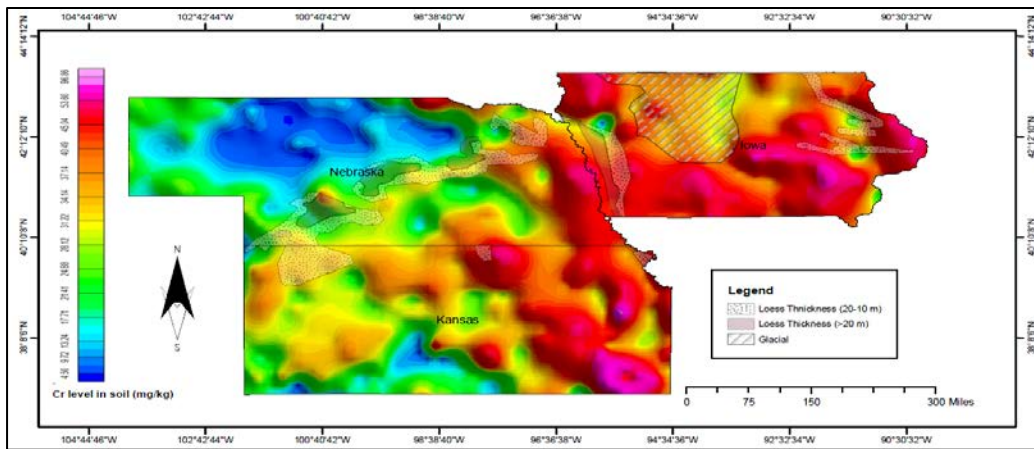


Fig. 41.1

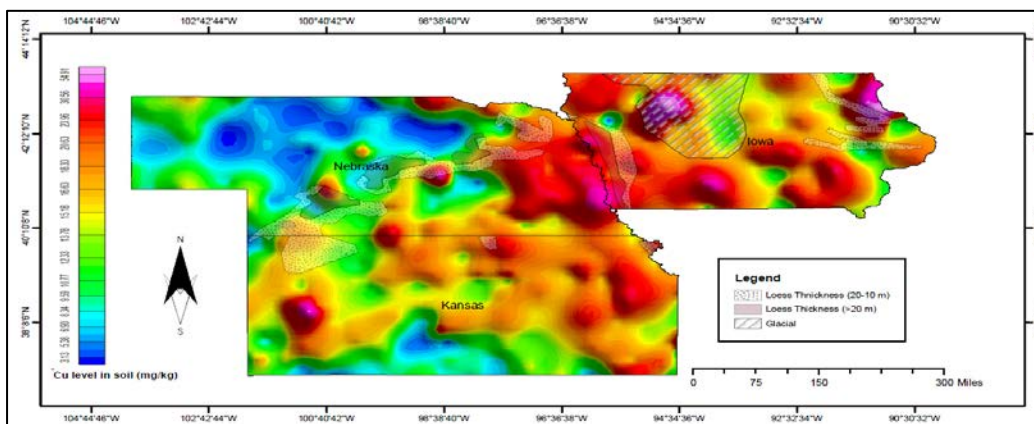


Fig. 41.2

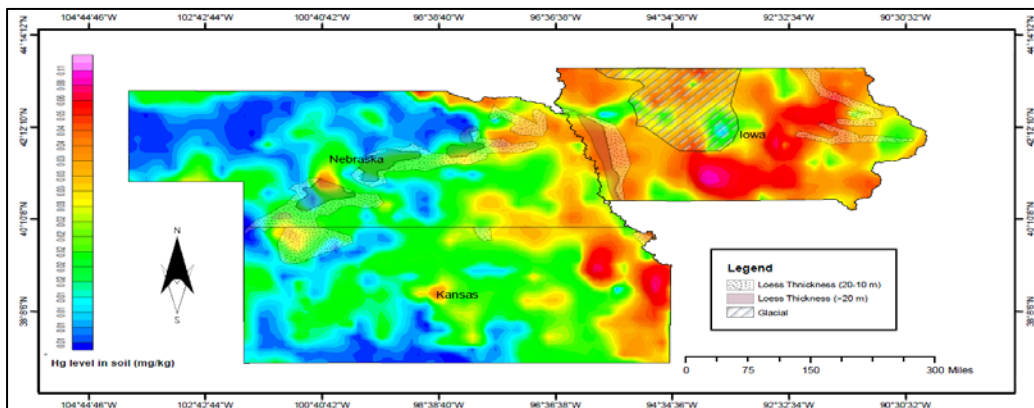


Fig. 41.3

Fig. 41: 1-3 Glacial sediment and loess distributions overlay on geochemical data maps (Smith et al., 2014)

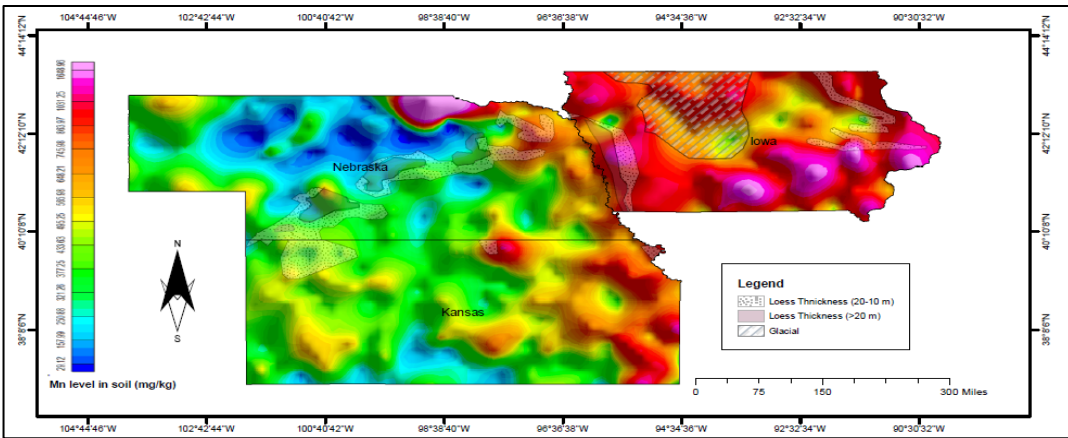


Fig. 42.1

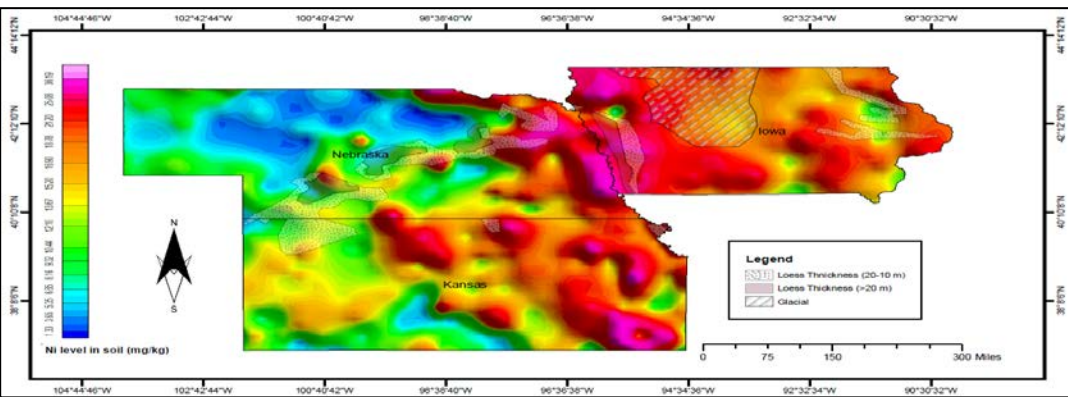


Fig. 42.2

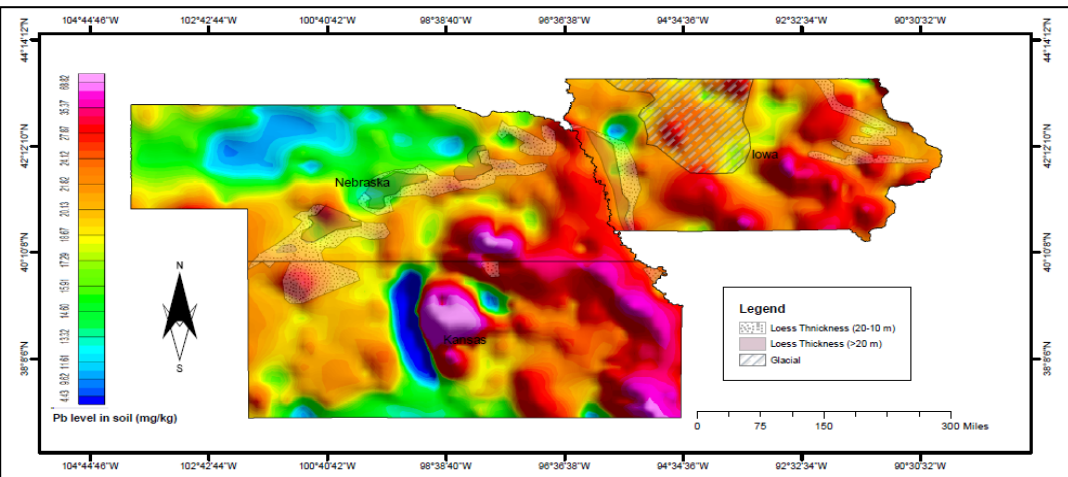


Fig. 42.3

Fig. 42: 1-3 Glacial sediment and loess distributions overlay on geochemical data maps (Smith et al., 2014)

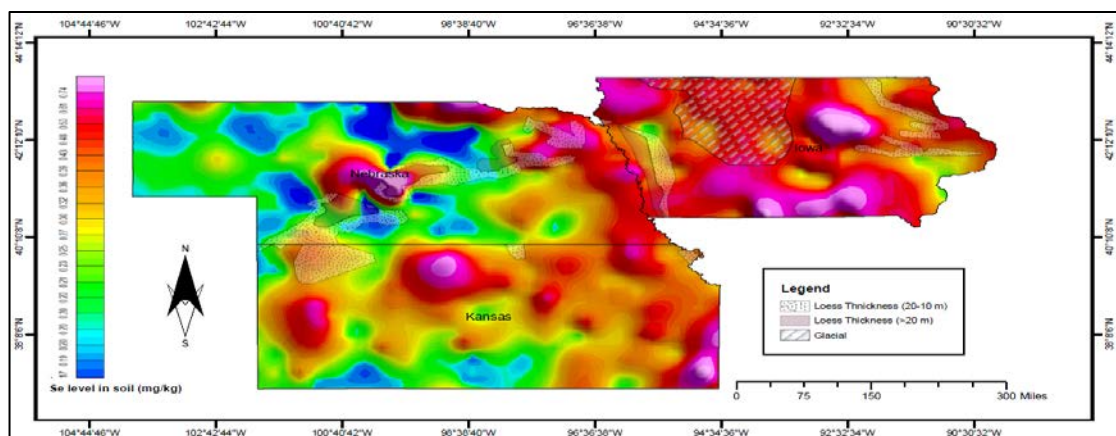


Fig. 43.1

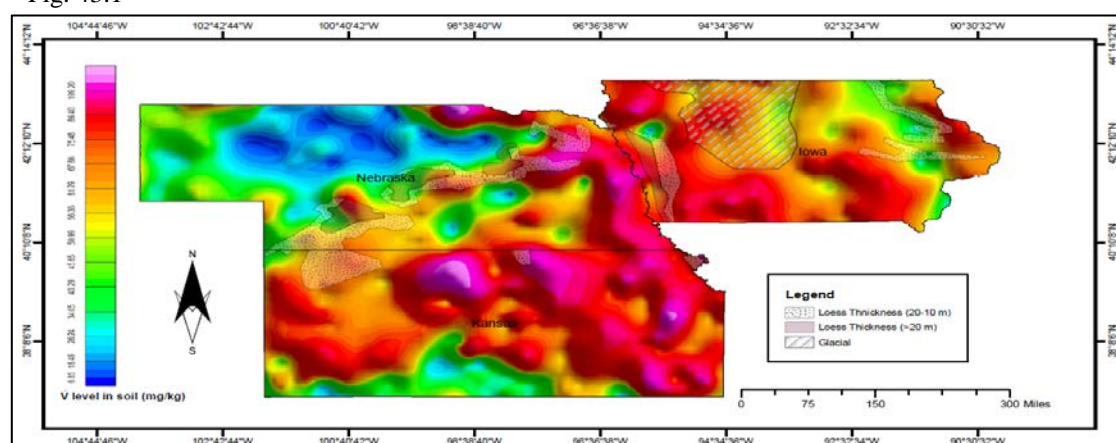


Fig. 43.2

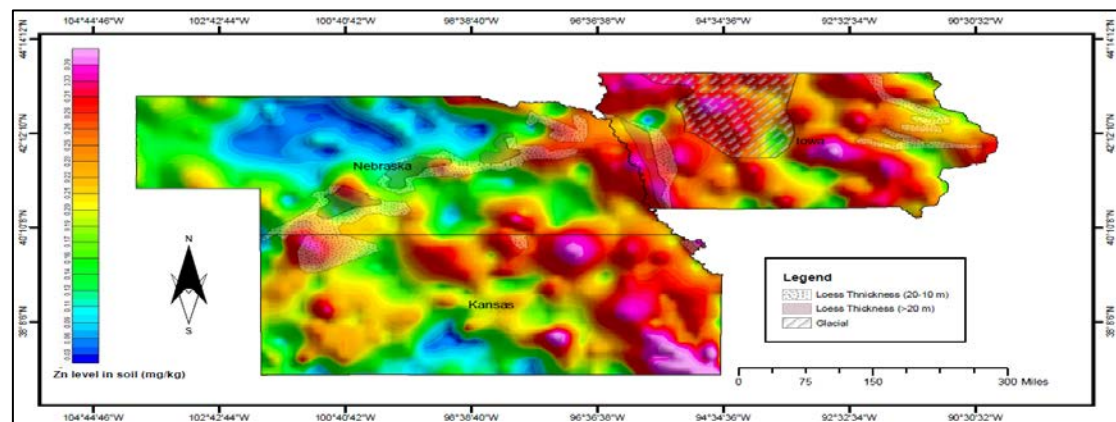


Fig. 43.3

Fig. 43: 1-3 Glacial sediment and loess distributions overlay on geochemical data maps (Smith et al., 2014)

8. DISCUSSION

Heavy metal enrichment in the soils was observed, and indexes calculated to differentiate and estimate the natural and anthropogenic impacts were useful. The chemical structure of soils is formed originally from the weathering of rocks and minerals. Every geographic region/ location has different minerals and rocks, which can determine the nature and the source of trace elements in that soil type. Some of the heavy metals naturally occur in the environment; there are other elements can come from human activities and can be accumulated in soils from different sources such as chemical additives, fertilizers, bio solids and manure, metal mining applications (only southeastern KS), air borne sources (Wuana and Okieimen, 2011). The air borne emissions have been tested by the present study of toxic release inventories (see Chapter.1).

United States Department of Agriculture (USDA) divides IA into 23 soil regions that include generally soils of southern, eastern, and western IA which is loess-derived, however, soils of northern and central Iowa are till-derived. Almost of the IA regions have soils extremely appropriate for agriculture, which make this state to be one of the most productive farming areas in the world.

Kraepiel et al. (2015) discussed the elemental behavior in the surface soils of Al, Fe, V, Co, Cr, which showed little to no enrichment in the surface soils, and their levels were determined mostly by soil production fluxes with little effect of atmospheric inputs or biological activity. The elements that were sensitive to the variations in the atmospheric deposition fluxes include Cu, Zn and Cd while Mo and Mn indicated strong enrichment in the surface soils, which may reflect past anthropogenic fluxes (Kraepiel et al., 2015). Mn has long residence time in the soil because it can

be returned to the surface soils by biological activities (Kraepiel et al., 2015). There was no dealing here with pesticides because they are organic molecules.

Heavy chemicals in the soil have been considered and found with low concentrations in rocks and soil (Wilson et al., 2008). Some of these elements such as As and Se occur as anions, and others such as Cd, Cr, Cu, Hg, Ni, Pb, and Zn occur as cations (Wilson et al., 2008). Understanding the differences between the natural concentrations, sources and anthropogenic impacts of trace elements is required to determine the quality and the health of the soil through the determination of the bioavailability of these trace elements in the soil (Wilson et al., 2008). Cu and Zn are used for feed additives for enhanced growth and treatment of diseases of animals; therefore, it is expected to be with high values in agricultural lands (Sun et al., 2013).

To begin an accurate interpretation of the results produced, abundance and relative variability must be pointed out. General interpretations (Kraepiel et al., 2015) of these variables are assumed but were not studied extensively. Use of commercial chemicals such as fertilizers, pesticides, and fungicides can affect the soil substantially by increase metals loading in soils (Sun et al., 2013). Due to the nature of the ongoing changes of land use and lack of historical documentation for this area in an agricultural sense, interpretations of these plots and data cannot be made here, but could be investigated with future studies.

Univariate data (section 5.3.1) for all contaminants show that every element has at least a bimodal distribution. This could be an interpretation for various sources of these elements. It can be suggested that the lower concentrations of the elements resemble geologic sources due to low abundance and higher concentrations from anthropogenic sources. This is the suggested interpretation when looking at the data. In addition, log ratio transformation shows possibility of

various families as well as a better defined normal distribution. Analyses of the trace elements plots show the possibility of additional families that supports the hypothesis of indicating several sources of varying concentrations. Bivariate data allows us to correlate relationships between contaminants. In USGS data, high correlation coefficients between Cu and Zn show a direct relationship. This is expected from the distribution of fertilizers since the concentrations of Cu and Zn are relative to each other and constant.

The positive correlation of Cu & Co, V & Co groups, concentrations of Cu, Co, V, and Zn as mean values (18, 6, 60, 60 ppm, respectively) indicates significant impacts of agronomic or industrial activities on the soil. The spatial distribution of samples showed anomalies with high concentration of some of the elements analyzed in this study. The greatest levels are mainly located in the east and northeast of IA, East of NE, and northeast and southeast of KS. Thus, the histograms for the variables show correlation between the potential trace elements and the additive sources. A series of histograms were plotted to present the variables. The primary observations in such elements show high concentration values of Co, Cu, V, and Zn with that the values suggested a potential contamination. For multiple comparisons between the elements, other graphs were produced to display the data distribution in pairs and groups. The values are plotted as X and Y cross plots in stacked and one dimensional scatter plots that present every single point of the data set using logarithmic scales.

The results of spatial distribution maps of Cd and Zn show no contamination in most of the cultivated soil. The most useful data used to derive conclusions were spatial maps with a log ratio transformation. These maps show that there are homogenous high concentrations of contaminants in Iowa and in eastern KS. In general, the plotted maps in IA, NE, and KS show an obvious spatial

pattern in the values distribution. These anthropogenic sources suggest some possibilities such as type of fertilizer used in agricultural areas, different fertilizers for each type of crop planted. Relative variability needs to be considered in greater depth in order to conduct more investigations.

Bedrock is one of the potential contributors of trace elements in agricultural soils, but not all these elements can come from geological processes. Many researchers have studied these elements regularly in USA (Reimann, et al, 2008 & Jennings, 2013). Almost all of these elements are necessary for plant growth, animal, and human foods such as Zn, Cu, and Mn. However, other elements are not required for plant growth, but important for animals and humans and include Cr and Co. The most toxic and contaminated elements considered in agricultural soils in USA are As, Pb, Cd, and Hg even in very low concentrations (USEPA). None of these elements are biodegradable and suffer transformation into water insoluble and soluble organometallic compounds. The long term problem is in increasing of the agricultural applications for a long time, which affects the ecological systems and public health (Kabata-Pendias, 2011). IA farms have been cultivating different crops in different seasons. Farms are more than 100 years old and farmers conduct expensive farming using various types of chemical fertilizers to maintain the crop yield, in addition to other chemical products such as pesticides and insecticides, which can contribute to the increase the concentrations of trace elements in agricultural soils over the years. The background concentrations of the trace elements in soil dependent on the bedrock type source. Lollar et al. (2004) gives chemistry for a variety of rock types. The most abundant bedrocks in the Midwest USA are limestone and sandstones (Adriano, 1992, Alloway, 1995, & Lollar, et al., 2004).

Based on Lollar's data (2004), the rocks with the highest concentrations of the elements from this study are black shales and basalts, for which data are presented. These rocks are present under less than 1% of the areas of the states IA, NE, KS targeted in the present study. The concentrations of trace elements in soil are small, however, the concentrations continuing increasing and accumulation overtime that cause soil pollution (Pierzynski et al., 2005). In the global environment, there is contamination of soil due to the accumulated of toxic chemicals in agricultural soils.

The metal enrichment in surface soils usually comes from agricultural sources rather than atmospheric deposition. In addition to trace elements that are naturally occurring in the environment, there are other elements that can come from human activates such as mining, industrial activities, and agricultural applications. Element levels were determined mostly by soil production fluxes with little effect of atmospheric inputs or biological activity, however, Pb, Cu, Zn and Cd were moderately enriched in top soil layers because of atmospheric deposition and biological aspects (Kraepiel et al., 2015). The plot that contained high Pb contents were located in towns suggesting that industrial fume, coal burning exhausts, and wastes charges may contributing to the Pb contamination in soil.

Intensive agricultural applications may lead to accumulation of heavy metals due to excessive agrochemicals in the agricultural areas. United States Department of Agriculture (USDA) divides IA into 23 soil regions that include generally soils of southern, eastern, and western IA which is loess-derived, however, soils of northern and central IA are till-derived. Most of the IA regions have soils extremely appropriate for agriculture, which make this state to be one of the most productive farming areas in over the world.

9. CONCLUSION

The outcomes of total chemical influence (TCI) revealed that the heavy metals are ordered $Mn > Zn > V > Cu > Cr > Ni > Pb > Co > As$ with the average concentrations $548.8 > 58.7 > 55.27 > 25.67 > 23.52 > 14.15 > 12.25 > 8 > 5.418$ ppm respectively. However, no significant high values were confirmed for Cd and Hg in the study area. These values were higher than their natural background values. These elements were accumulated in agricultural soils. Significantly, principal component analysis (PCA) and Pearson's correlation analysis showed a strong positive correlation between Mn and Ni, and in addition, As, Co, Cr, Pb, V, and Zn are very strongly correlated. Another correlation was observed between Cd and Cu representing PC1 with values (67.5%) contrasted with PC2 and with values (18.4%). investigated that heavy metals may be sourced from anthropogenic activities. Cu is an anthropogenic component especially from agricultural applications.

Geochemical maps of TCI showed a significant spatial variability between the chemical elements. Soils have been chemically impacted on a widespread scale because heavy metals were accumulated in soil. Geochemical distribution maps of As, Cd, Co, Cr, Cu, Ni, Se, V, and Zn present significant human inputs with anomalies regions. Hg presents no anomalous values, which means there were no human inputs. Mn is found in elevated values widespread among the states. The most interesting point that there are unusual Pb anomalies in center of KS and a broad trough of low values contrasted against high peaks was noted. The similar aspects between the elements presented duplicate potential sources contribute to the soils. In general, there are no relationship between air and land emissions and anomalies of soil, air emission are very low in most of the states, and there is no proof those emissions are causing the soil anomalies. These observations in

the enriched soil profiles are assumed to result from human inputs, and one important source is believed agricultural additives such as fertilizers.

CHAPTER 3

ASSESSMENT AND MONITORING THE QUALITY OF AGRICULTURAL SOILS USING GEOACCUMULATION INDEX AND DIGITAL SOIL MAPPING IN MID-CONTINENTAL USA

1. INTRODUCTION

The soil can act as a sink for a wide variety of heavy metal emissions, released from different sources. One such source can be natural rock weathering. However, other sources can be anthropogenic (Essington, 2004; Barbieri et al., 2016). In addition, if the soil is subjected to agricultural applications, other possible sources, such as chemical fertilizers, must be considered. Heavy metals may potentially be accumulated overtime and can cause soil contamination, therefore affecting the organisms (Xue et al., 2000). Some of the metals can also be leached from the soil through groundwater flows and surface erosion (Blaser et al., 2000).

The geo-accumulation index (I_{geo}) has been used to determine soil contamination since the 1970s and it has been applied to heavy metal studies to evaluate the soil and sediment contamination (Odat, 2015; Muller, 1969 & Huang, et al., 2016). Calculations of the I_{geo} are dependent on a comparison of current and pre-anthropogenic activities, to estimate the pollution level. Desaules (2012) stated that the heavy metal values obtained from “on-site” surfaces, as compared to the deep soil layer concentrations, are more effective and accurate in estimating soil contamination in the same soil profile. Using the concentration of the element in the topsoil and comparing it at the depth, at the same site, can minimize the natural special variation (biogeochemical and localized lithogenic processes). The important point that should be considered is that some types of organic fertilizers have high concentrations of heavy metals, such

as As, Cd, and Pb. It was investigated that As concentration range for organic fertilizers is 0.50–24.4 mg/BG, while for Cd and Pb it was 0.10–11.4 and 1.13–126 mg/BG, correspondingly. High concentrations of Cr, V, and Zn were reported, with more than 3475mg/BG-1 of P, 288 mg/BG-1 of P (Molina et al., 2009).

The primary idea is that any change in the concentration of the chemical at the soil surface is due to additional sources (such as human input) and the ratio is around 1 in case of the absence of an external source. The enrichment factor (EF) and I_{geo} are environmental indices used to evaluate the soil contamination (Edwin et al., 2013). In the previous portion of this research, an EF has been calculated to test the environmental contamination. The general goal of this strategy is to test different pollution indices to see which is more effective, and can be applied to examine the soil quality and health with respect to the sustainability criteria or land management strategies.

Within this area of study are the intensive farming activities in IA, east KS, and NE. Air and land emissions indicate that they are mostly not associated with the geochemical maps. However, a few of these emissions can be correlated to anomalies. Research on the quantification of heavy metal concentrations in cultivated soil, to determine their sources, has been rare in midcontinent USA. The objective of this study is to test the environmental contamination index, I_{geo} , to estimate long-term contamination. In addition, the objective of this study is to identify the origin of heavy metals in the soil and generate chemo-spatial distribution maps of the following heavy metals: As, Cd, Co, Cr, Cu, Pb, Mn, Ni, Pb, V, Se, and Zn in the soils of IA, KS, and NE.

2. MATERIALS AND METHODS

2.1 Study Area and Site Description

The area of the study is in mid-continental USA. The states of IA, KS, and NE (Fig. 44.1 & Fig.44.2) were the target of this study, to evaluate the chemical loading by human inputs from varying sources. The study area is an agricultural farmland, covering 99% of IA and large areas in KS and NE. The agricultural grain crops in IA include corn and soy. In KS, the agricultural crops include alfalfa, sunflowers, and wheat. Agricultural activities in NE include the cultivation of wheat, sorghum, potatoes, and sugar beets. The western half of NE contains the famous Sand Hills, and the western half of KS is mainly grassland. Geologically, bedrock consists mainly of limestone and sandstone. Shale is present in lesser amounts.

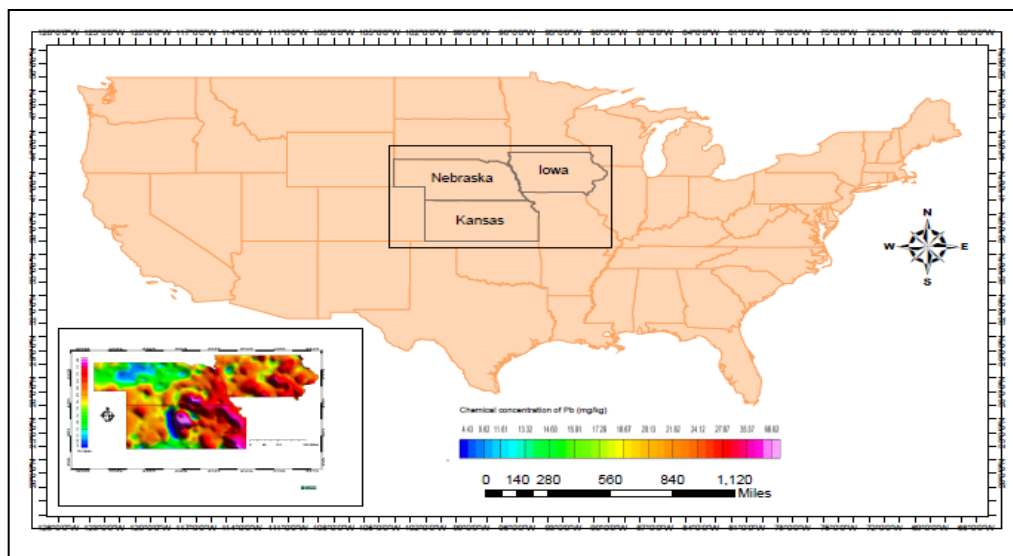


Fig.44.1
Map

shows the area of study and soil geochemistry and spatial distribution of chemical concentrations of As, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, Se, V, and Zn, in the United States (Smith et al., 2014).

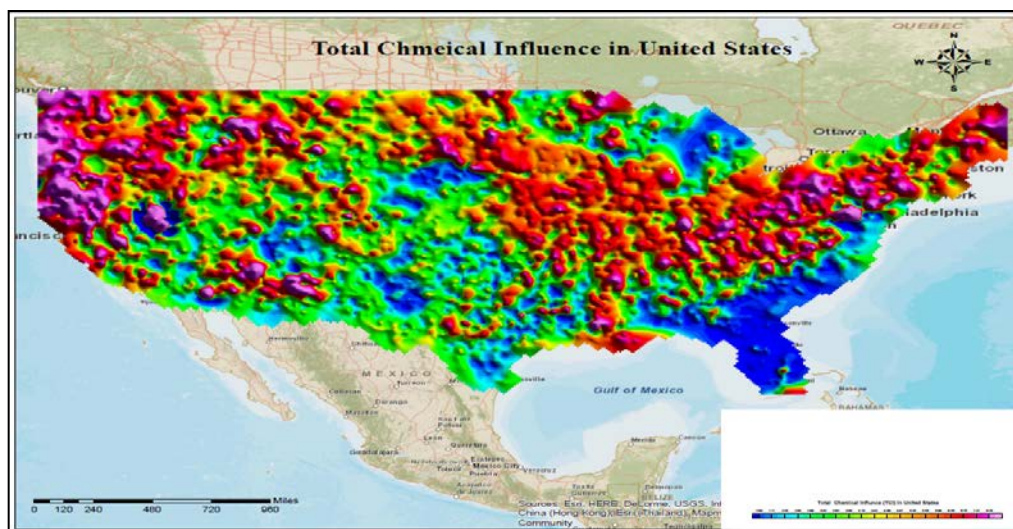


Fig.44.2 Map shows the area of study and soil geochemistry and spatial distribution of chemical concentrations of As, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, Se, V, and Zn, in the United States (Smith et al., 2014).

2.2. Climate of the Area

The annual average temperature in IA, KS, and NE is 50.85°F, 50.65°F, and 55.05°F, respectively. The average annual temperature in IA is 45° in the north and 52° in the south according to National Oceanic and Atmospheric Administration (NOAA, 2018). The high temperature during the summer does not cause severe crop stress. IA also has seasonal variations, rainfall comes in through the Gulf of Mexico during the warm months, and it is significant during the growing season. In the winter and autumn, the dry Canadian air flows from the northwest, in addition to the air masses that move in from the Pacific Ocean, leading to relatively dry and cold weather. However, in summer, the high temperatures are caused by hot and dry winds that come from the desert southwest. In spring and summer, gusts of high wind flow in for short periods of time, at an excess of 50 mph. In KS, the annual mean temperature is 58° in the south and southeast, and 52° in the northwest. The average low temperature is 36.6°. The forceful rainfall in winter can

be associated with high winds and heavy snow, and it also occurs during spring and summer (Natural Centers for Environmental Information (NOAA, 2018). In NE, the Sand Hills are extensive with some lakes, valleys, basins, located in the north central and high plains in the west, with the prairies located in the east of the state, forming sandy loam or silt loam soils (Fig. 45). Sand Hills is the biggest dune area in North America, located in NE spread over 50.000km² (Muhs, 2017). The climate is hot and dry in the summer and temperatures may exceed 115°F, especially in July. The rainfall is formed by warm air thunderstorms during summer and spring that may occasionally cause flooding. The geology of the area and the lithological assemblages in the study area differ due to a range of factors, including geology, topography, land use, and weathering processes.



Fig. 45 Location of Sand Hills in Nebraska modified from (NOAA, 2018)

2.3 Sample Collection and Chemical Procedures

The data used in this study was obtained from the USGS (Smith et al., 2014). The analyzed published data and chemical methods of analysis of several heavy metals are available in the link (Smith et al., 2014). The samples were collected from the surface soil (0–5 cm) while the C-horizon samples were collected from a depth 18–167cm in IA, from 10–100cm in KS, and 10–153cm in NE (Smith et al.,2014). 91 samples were collected from IA, 132 from KS, 130 from NE (Smith et al., 2014). These 353 samples were extracted from the database for use in this study.

2.4. Data Analysis

The statistical analysis of the data was performed on a spatial scale and to test the correlation between the heavy metals. The probability and statistical data analyses of the study were carried out using the SPSS 24 software. Descriptive statistics and the ANOVA multivariate was determined using the Tukey post-hoc test at the 5% level to estimate the variance between the means of the analyzed geo-accumulation (I_{geo}) indices. The Duncan's multiple range test (DMRT) was carried out to test the differences between the means (significance level < 0.05). The means and the standard deviations (SD) were determined. A Pearson's correlation matrix (PCM) was employed to identify the relationship between the variables. Thus, the differences between the values at significance level were $P < 0.05$, which indicates a statistically significant difference between the means of the soil heavy elements among the states and within the states. A spatial distribution analysis was performed to graphically display the distribution of the heavy metals. The I_{geo} distribution maps were created using an Oasis Montaj software.

2.5. Assessment of Soil Chemical Loading Based on Geoaccumulation (I_{geo}) Index

The anthropogenic activities on the topsoil can be evaluated using the I_{geo} index (Sucharova et al., 2012 & Zahra et al., 2014). It is used for contamination assessment in the research area. In general, the data is normalized to conservative reference elements (Titanium) on-site because the topsoil and deep soil layers are not comparable 1:1, which means that the metal concentrations in surface soil are different from that of the deep soil (Desaules, 2012). In off-site references, the mean element content in the parent earth crust for I_{geo} calculations cannot provide the accurate background values for I_{geo} evaluation (Reimann & De Caritat, 2000). Values of the deep soil layer (C-horizon) are the most suitable for on-site references of the same soil profile (Bourennane et al., 2010). For on-site references, the soil samples collected from the topsoil are developed from the same parent materials as the deepest horizons at the same site.

2.5.1 Geo-accumulation Index (I_{geo})

I_{geo} is a geological assessment that is widely used to measure the magnitude of heavy metal loading within studied soils. Soil contamination can be quantified using I_{geo} , as defined and suggested by Muller (1969). It is also used to measure the extent of heavy metals or for the indication of human input in the soil by analyzing the natural fluctuations of metals in the soil. Many researchers have applied the I_{geo} index to assess different heavy metal contaminations, such as Abraham and Parker (2008), Varol (2011), Zhiyuan et al., 2011, Nowrouzi et al., 2014, Barbieri et al., 2015, Nweke and Ukpai (2016), Izah et al. (2017), Muzerengi (2017), Huang et al. (2017), & Mehr et al. (2017).

Several researchers have also used the average shale values or the average crustal abundance data as a reference baseline (B_n), using the equation below. Taking B_n as the average global crustal abundance that has no relationship to the location of the samples in the study. Since the contamination levels differ among soil types, according to the place and time, it is more accurate to evaluate soil pollution using the regional background values (Yaqin et al., 2008). The point of this consideration is that the heavy metal contents in each regional natural background are different (Anderson and Kravitz, 2010).

The calculation of I_{geo} is based on exchangeable fractions that present the actual bioavailable fraction (Barbieri, 2016). The values of the I_{geo} index was determined by calculating the base 2 logarithm of the total metal concentration, over the average (crustal) concentration of the element in the shale as background (Odat, 2015). To quantify the degree of heavy metals contamination, the mathematical equation proposed by Muller (1969) was formulated as follows:

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

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 the given metal in the crust or reference value of the metal “ n ”). The factor 1.5 is the background matrix factor (correction factor), for minimizing the impact of possible variations in the standard values. It is used because of the possible impact of the variations in background values/lithogenic for a given metal in the environment, as well as for tiny anthropogenic impacts that may be attributed to lithologic variations or impacts in the soils. Yaqin et al. (2008) indicated

that the parameter of geochemical background values were differently determined and used by several researchers. Loska et al. (2003) & Naveedullah et al., 2013) used the Earth's crust as a background, while Silva et al. (2017) and Rubio et al. (2000) used the world average shale. However, it is suggested that geological components vary according to the geographic location. Therefore, using the Earth's crust average or the average shale are not as useful as the local C-horizon concentrations.

Muller (1969) categorized the I_{geo} index into seven class indicators used to define the degree of metal contamination. According to the criteria, $I_{geo} \leq 0$ indicates uncontaminated soil. Values 0–1 indicate un-polluted to moderately polluted soil, while values of 1-2 indicate moderately polluted soil. Values of 2-3 indicate moderately or strongly polluted soil, 3-4 indicate strongly polluted soil, 4-5 are a sign of strongly to extremely contaminated soil, and values > 5 show extremely polluted soils. The classification of I_{geo} indices are demonstrated in Table. 13.

Table 13 The degree of soil contamination in terms of five geo-accumulation (I_{geo}) classes suggested by Muller (1969).

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

3. RESULTS AND DISCUSSION

The I_{geo} was calculated to compare each specific element with a standard background value. Factor 1.5 is the constant used in I_{geo} calculations to account for the natural fluctuations of the target metal due to minor human inputs in the environment (Izah et al., 2017). The I_{geo} value of the evaluated metals includes the log function and the variation factor of 1.5 (Aiman et al., 2016). It was suggested that minimum I_{geo} values might be due to the lithological value of 1.5 in the equation (Izah et al., 2017). These values were estimated by Hasan et al. (2013) and it was found that Co, Cu, Mn, Cd, Cr, and Zn were recorded with high concentrations in some stations of the sediment samples of Sitakund Upazill, Chittagong, India, which reflected a slight to strong contamination from industrial sources, according to the I_{geo} grades.

Significant I_{geo} mean values (values 0–2) were observed in IA, ranging from -0.33–1.20, for KS it ranged from -0.37–0.20, and in NE from -0.20–0.34 (Table 14). These values show a lack of soil contamination in terms of Cd in the three states (Fig. 46). In addition, uncontaminated soil I_{geo} values of Co were investigated in IA and NE and were reported to be moderately contaminated, with mean values 0.03, and 0.25, and 0.08, respectively, but KS was uncontaminated, with a mean value -0.25 (Fig. 46). The I_{geo} class for Cr indicating at moderately contaminated soils, with estimated values alongside mean the value at 0.36 and 0.00, in IA and NE, respectively, while the mean value in KS is -0.15, indicating at uncontaminated soil (Fig. 46, 47, and 48). This observation indicates that the Cr is probably derived from anthropogenic activities in IA and NE. According to the I_{geo} indicators, the values of Cu being ≥ 0 indicate that this individual metal's source is natural rather than anthropogenic activities (0.05, -0.11, and -0.01). The level of Cu may indicate depletion, possibly due to leaching. The I_{geo} values of Hg are more than zero as calculated 0.12, 0.24, and 0.10 in IA, KS, and NE, respectively. Dependent on the I_{geo} index, the Hg levels are classified as moderately contaminated. Mn sources are considered anthropogenic deposits with the assessed positive values of 0.32, 0.07, and 0.14 (Fig 46).

One of the smallest I_{geo} values is for Ni that can be explained through negative human inputs of Ni in the soil. The calculation for Ni shows low values, -0.33, -0.37, and -0.14 in IA, KS, and NE, respectively. For Pb, it shows moderate pollution in IA, KS, and NE, with the mean values 0.46, 0.19, and 0.21, respectively (Fig. 46). Se has the highest I_{geo} mean values of heavy metals studied in IA, with a mean value 1.20, as compared to Se concentrations in KS and NE with mean values 0.20, and 0.34, respectively (Fig. 47). The values suggests a non-anthropogenic influence on V concentrations in the soil with negative values at -0.14, -0.18, and -0.01, in IA, KS, and NE,

correspondingly. The I_{geo} calculation of Zn in IA, KS, and NE were 0.36, 0.18, and 0.19, respectively, indicating moderately contaminated soils, if we consider calculating I_{geo} using on-site data. There are significant differences in I_{geo} concentrations for heavy metals ($P < 0.05$); therefore, this finding can establish the most likely anthropogenic metal source.

Table 14 Descriptive statistics of geo-accumulation (I_{geo}) for data set of IA, KS, and NE, mean and standard deviation (std) values of heavy metals.

Element	State ID	Mean	Std. Deviation	Element	State ID	Mean	Std. Deviation
Igeo_As	IA	0.02	0.60	Igeo_Mn	IA	0.32	0.71
	KS	-0.27	0.44		KS	0.07	0.52
	NE	-0.02	0.68		NE	0.14	0.68
Igeo_Cd	IA	0.18	0.77	Igeo_Ni	IA	-0.33	0.54
	KS	0.36	0.72		KS	-0.37	0.52
	NE	0.29	0.65		NE	-0.14	0.69
Igeo_Co	IA	0.03	0.45	Igeo_Pb	IA	0.46	0.39
	KS	-0.25	0.45		KS	0.19	0.51
	NE	0.08	0.61		NE	0.21	0.24
Igeo_Cr	IA	0.36	0.61	Igeo_Se	IA	1.20	0.60
	KS	-0.15	0.49		KS	0.20	0.59
	NE	0.00	0.71		NE	0.34	0.67
Igeo_Cu	IA	0.05	0.62	Igeo_V	IA	-0.14	0.52
	KS	-0.11	0.42		KS	-0.18	0.46
	NE	-0.01	0.66		NE	-0.01	0.58
Igeo_Hg	IA	0.12	0.70	Igeo_Zn	IA	0.36	0.61
	KS	0.24	0.66		KS	0.18	0.51
	NE	0.10	0.57		NE	0.19	0.64

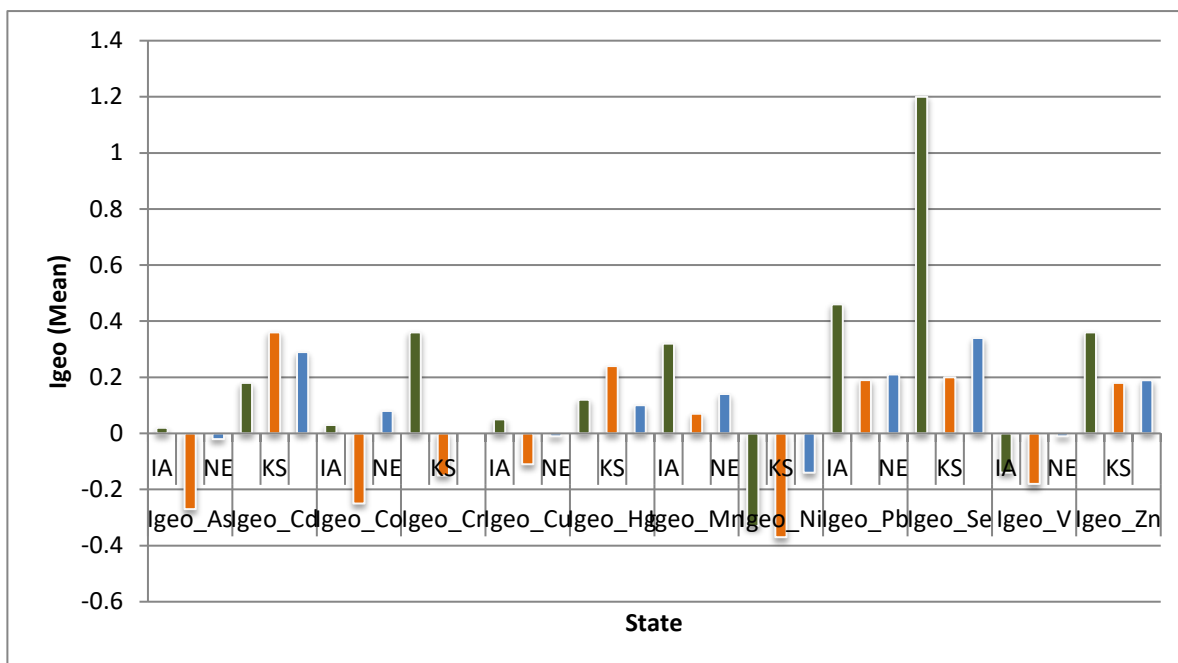


Fig. 46 Geo-accumulation (I_{geo}) values of heavy metals in the surface soils of IA, KS, and NE

The results of the I_{geo} as a soil pollution indicator showed little variation between the elements in IA (Table. 15). High values were recorded for all the metals, except Ni and V (-0.33 and -0.14), and the mean values of the I_{geo} ranged from 0.02 to 1.20. However, the surface soils were polluted with heavy metals, except Ni and V (Fig. 46). The results of the I_{geo} are, As (0.02 ± 0.60), Cd (0.18 ± 0.77), Co (0.03 ± 0.45), Cr (0.36 ± 0.61), Cu (0.05 ± 0.61), Hg (0.12 ± 0.70), Mn (0.32 ± 0.71), Pb (0.46 ± 0.39), Se (1.20 ± 0.60), and Zn (0.36 ± 0.61) (Fig. 46). The outliers have been presented in the geochemical map in Fig. 49.

Table 15 Descriptive statistics of geo-accumulation (I_{geo}) for the IA data set showing element name (EN), maximum (max), minimum (min), mean, and standard deviation (std) values of heavy metals in IA soil.

EN	Igeo_ As	Igeo_ Cd	Igeo_ Co	Igeo_ Cr	Igeo_ Cu	Igeo_ Hg	Igeo_ Mn	Igeo_ Ni	Igeo_ Pb	Igeo_ Se	Igeo_ V	Igeo_ Zn
Mean	0.02	0.18	0.03	0.36	0.05	0.12	0.32	-0.33	0.46	1.20	-0.14	0.36
N	91	91	91	91	91	91	91	91	91	91	91	91
Std	0.60	0.77	0.45	0.61	0.62	0.70	0.71	0.54	0.39	0.60	0.52	0.61
Median	-0.01	0.00	0.00	0.20	-0.03	0.00	0.22	-0.38	0.40	1.32	-0.23	0.30
Std. Error	0.06	0.08	0.05	0.06	0.06	0.07	0.07	0.06	0.04	0.06	0.05	0.06
Sum	2.10	16.74	2.90	32.38	4.73	10.63	29.53	-30.21	41.48	109.57	-12.98	33.13
Min	-1.54	-1.32	-1.08	-1.06	-1.65	-1.81	-1.26	-1.83	-0.34	-1.00	-1.31	-0.93
Max	2.24	2.58	1.76	2.84	2.55	2.81	2.39	2.04	1.76	2.81	2.26	2.79
Variance	0.36	0.59	0.20	0.37	0.38	0.49	0.50	0.29	0.15	0.37	0.27	0.38
Kurtosis	3.35	-0.12	3.59	3.81	3.85	2.29	0.81	4.11	1.05	1.42	5.65	2.29
Skewness	0.93	0.33	1.14	1.52	1.12	0.91	0.73	0.82	0.98	-0.52	1.60	0.96

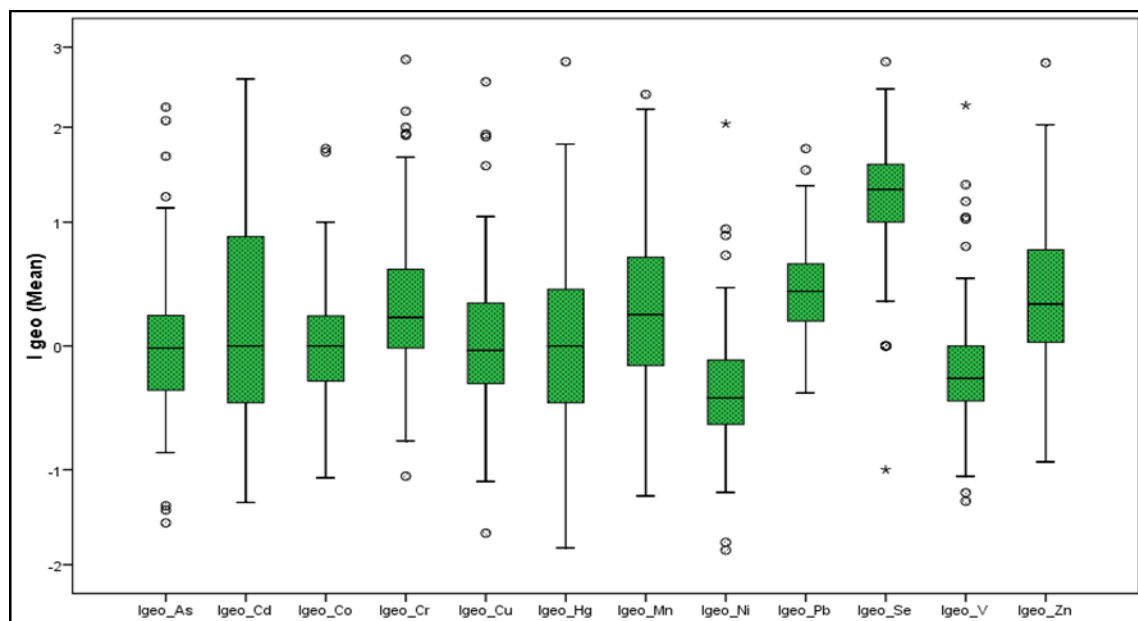


Fig.

47 Boxplot showing geo-accumulation (I_{geo}) values of individual heavy metals in the surface soil of IA.

The summary of the Pearson correlation coefficients (PCC) of the soil samples are provided in Table 16. The values in the PCC table show a significant correlation ($p < 0.01$) among the metals studied in the surface soil. A significant relationship between As and some metals including Cr ($r = 0.63$), Cu ($r = 0.70$), Ni ($r = 0.61$), V ($r = 0.74$), and Zn ($r = 0.65$) is seen. Moreover, Cd is related to Mn ($r = 0.65$), Co is correlated significantly with Cr ($r = 0.67$), Ni ($r = 0.79$), and V ($r = 0.72$), and Cr with As ($r = 0.63$), Co ($r = 0.67$), Cu ($r = 0.84$), Ni ($r = 0.70$), V ($r = 0.88$), and Zn ($r = 0.76$). Cu has a strong correlation relationship with As ($r = 0.70$), Cr ($r = 0.84$), Hg ($r = 0.60$), Ni ($r = 0.69$), V ($r = 0.84$), and Zn ($r = 0.87$). Hg is correlated with Cu ($r = 0.60$), and Mn with Cd ($r = 0.65$). A relationship also was observed among Ni and As ($r = 0.61$), Co ($r =$

0.79), Cr ($r = 0.70$), Cu ($r = 0.69$), V ($r = 0.82$), and Zn ($r = 0.60$). Significantly, Pb is correlated with Zn ($r = 0.72$) and V is significantly correlated with As ($r = 0.74$), Co ($r = 0.72$), Cr ($r = 0.88$), Cu ($r = 0.84$), Ni ($r = 0.82$), Zn ($r = 0.75$), indicating that human inputs may be the source of these elements. Zn's association was also recorded with As ($r = 0.65$), Cr ($r = 0.76$), Cu ($r = 0.87$), Ni ($r = 0.60$), and V ($r = 0.75$).

Table 16 Pearson correlation Matrixes of geo-accumulation (I_{geo}) for heavy metals in IA
(**Correlation is significant at the 0.01 level.*Correlation is significant at the 0.05 level).

As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
As	1										
Cd	0.193	1									
Co	.523**	.400**	1								
Cr	.632**	0.205	.677**	1							
Cu	.709**	.244*	.596**	.843**	1						
Hg	.481**	.386**	.461**	.533**	.600**	1					
Mn	0.196	.652**	.555**	0.202	0.136	.340**	1				
Ni	.610**	.359**	.794**	.701**	.694**	.505**	.404**	1			
Pb	.445**	.426**	.485**	.583**	.597**	.560**	.295**	.370**	1		
Se	0.194	-0.052	0.135	.326**	.337**	0.091	0.026	0.195	0.201	1	
V	.744**	.207*	.723**	.884**	.849**	.569**	.213*	.825**	.537**	.337**	1
Zn	.652**	.371**	.553**	.762**	.879**	.586**	.235*	.601**	.724**	.234*	.757**

The statistical analyses of heavy metals in KS show that they accumulate in the surface soil except, As, Co, Cr, Cu, Ni, and V. The mean accumulation rates measured are for Cd (0.36 ± 0.72), Hg (0.24 ± 0.66), Mn (0.07 ± 0.52), Pb (0.19 ± 0.51), Se (0.20 ± 0.59), and Zn (0.18 ± 0.51) (Table 17 & Fig. 48). It is observed that the highest I_{geo} values are ordered as follows: Cd > Hg > Se > Pb > Zn > Mn, while I_{geo} values of As, Co, Cr, Cu, Ni, and V are less than 0. The estimated I_{geo} values of the six previous heavy metals are within the corresponding class 0, indicating to moderately contaminated soils in the study area. However, the elements with negative I_{geo} values were less than the minimum class of I_{geo} standards and may be associated with depleted metals or natural depletion (Table 17). The outliers of I_{geo} values are presented in Fig. 48 & Fig. 49. This finding suggests that the soils under study have been contaminated through human applications.

Table 17 Descriptive statistics of geo-accumulation (I_{geo}) for the KS data set. Element name (EN), minimum (Min), maximum (Max), standard deviation (std).

EN	Igeo_ As	Igeo_ Cd	Igeo_ Co	Igeo_ Cr	Igeo_ Cu	Igeo_ Hg	Igeo_ Mn	Igeo_ Ni	Igeo_ Pb	Igeo_ Se	Igeo_ V	Igeo_ Zn
Mean	-0.27	0.36	-0.25	-0.15	-0.11	0.24	0.07	-0.37	0.19	0.20	-0.18	0.18
N	127	127	127	127	127	127	127	127	127	127	127	127
Std	0.44	0.72	0.45	0.49	0.42	0.66	0.52	0.52	0.51	0.59	0.46	0.51
Median	-0.24	0.42	-0.24	-0.20	-0.14	0.00	0.08	-0.38	0.14	0.00	-0.21	0.14
Std. Error	0.04	0.06	0.04	0.04	0.04	0.06	0.05	0.05	0.05	0.05	0.04	0.05
Sum	-33.98	45.81	-32.20	-19.66	-13.61	30.16	9.05	-47.16	24.51	25.40	-22.35	22.24
Min	-1.53	-1.00	-2.32	-2.56	-1.34	-1.42	-2.17	-2.77	-0.89	-1.58	-1.38	-0.99
Max	1.20	3.00	1.54	1.85	1.52	2.32	1.67	1.43	4.25	2.32	2.19	2.21
Range	2.73	4.00	3.87	4.41	2.85	3.74	3.84	4.20	5.15	3.91	3.57	3.19
Variance	0.19	0.52	0.21	0.24	0.18	0.44	0.27	0.27	0.26	0.35	0.21	0.26
Kurtosis	1.05	1.35	5.38	7.30	4.00	0.80	3.21	4.87	33.22	0.90	10.18	3.75
Skewness	-0.04	0.85	-0.43	-0.18	0.98	0.49	-0.48	-0.14	4.43	0.11	2.08	1.23

The level of statistical correlation ($p < 0.01$) of the heavy metals of KS soils is recorded in Table 18. A significant correlation is present amongst As and Ni ($r = 0.60$) and V ($r = 0.66$). Co was correlated to Cr ($r = 0.63$), Mn ($r = 0.74$), Ni ($r = 0.76$), and V ($r = 0.70$), while Cr was correlated with Ni ($r = 0.65$) and V ($r = 0.66$). The three metals that are associated with Cu include Ni ($r = 0.60$), V ($r = 0.65$), and Zn ($r = 0.68$), and Ni is correlated with V ($r = 0.75$). These observations suggest that the metals may have originated from the same source, notwithstanding it being natural or anthropogenic.

Table 18 Pearson's correlation matrix of geo-accumulation (I_{geo}) for heavy metals in KS soil.
(**Correlation is significant at the 0.01 level.*Correlation is significant at the 0.05 level).

As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
As	1										
Cd	0.131	1									
Co	.514**	.274**	1								
Cr	.404**	.164*	.638**	1							
Cu	.521**	.342**	.589**	.519**	1						
Hg	0.092	.166*	0.037	0.119	.197*	1					
Mn	.177*	.255**	.740**	.446**	.328**	0.016	1				
Ni	.609**	.206*	.767**	.657**	.606**	0.093	.500**	1			
Pb	.148*	.286**	.337**	.231**	.297**	.178*	.330**	0.146	1		
Se	.193*	.247**	.170*	.214**	.208**	0.102	0.133	.240**	0.035	1	
V	.669**	.285**	.701**	.669**	.656**	0.024	.376**	.757**	.164*	.298**	1
Zn	.540**	.486**	.375**	.459**	.680**	.237**	.195*	.497**	.369**	.171*	.589**

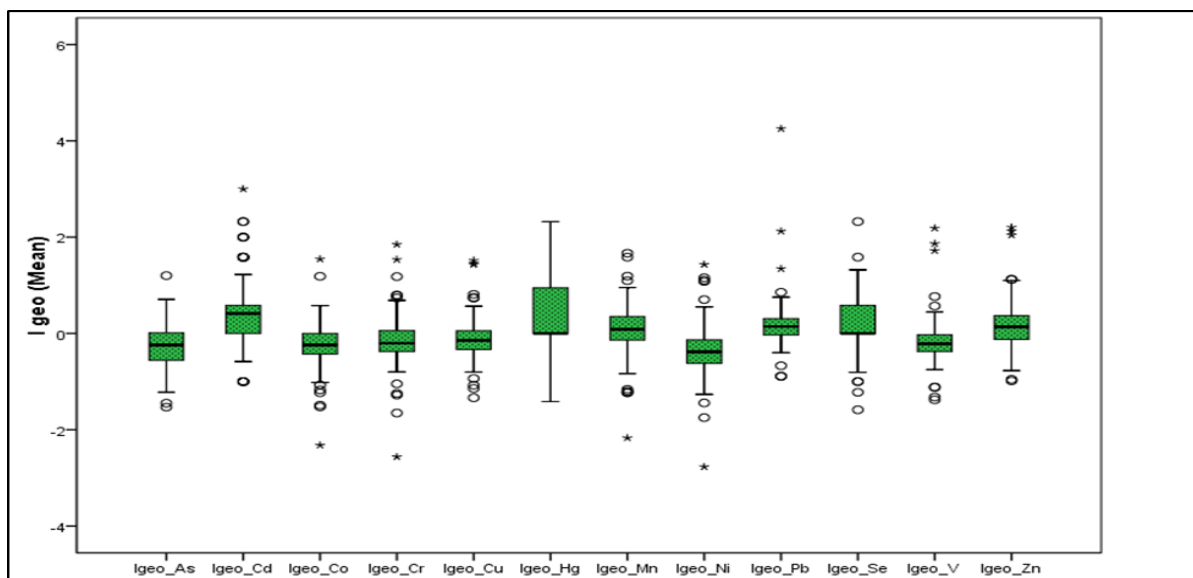


Fig. 48 Boxplot showing geo-accumulation (I_{geo}) values of individual heavy metals in the surface soil of KS

All I_{geo} values of heavy metals in NE were negative, less than 0, which are classified according to the I_{geo} criteria with the minimum class being translated to mean un-contaminated soils. The mean accumulation rates measured are for Cd (0.29 ± 0.65), Co (0.08 ± 0.61), Hg (0.10 ± 0.57), Mn (0.14 ± 0.68), Pb (0.21 ± 0.24), Se (0.34 ± 0.67), and Zn (0.19 ± 0.64) (Fig. 49). The highest I_{geo} values are as ordered, Se > Cd > Pb > Zn > Mn > Hg > Co (Fig. 49). The observation of the I_{geo} values of As, Cr, Cu, Ni, and V are probably related to depletion or the leaching of metals from the soil area under study (Table 19). The outliers of the I_{geo} values are presented in Fig. 49.

Table 19 Descriptive statistics of geo-accumulation (I_{geo}) for the NE data set. Element name (EN), minimum (Min), maximum (Max), standard deviation (std).

EN	Igeo_ As	Igeo_ Cd	Igeo_ Co	Igeo_ Cr	Igeo_ Cu	Igeo_ Hg	Igeo_ Mn	Igeo_ Ni	Igeo_ Pb	Igeo_ Se	Igeo_ V	Igeo_ Zn
Mean	-0.02	0.29	0.08	0.00	-0.01	0.10	0.14	-0.14	0.21	0.34	-0.01	0.19
N	130	130	130	130	130	130	130	130	130	130	130	130
Std	0.68	0.65	0.61	0.71	0.66	0.57	0.68	0.69	0.24	0.67	0.58	0.64
Median	-0.09	0.00	-0.01	-0.01	-0.12	0.00	0.09	-0.26	0.18	0.00	-0.09	0.08
Std. Error	0.06	0.06	0.05	0.06	0.06	0.05	0.06	0.06	0.02	0.06	0.05	0.06
Sum	-2.79	37.94	10.65	-0.56	-1.07	12.97	18.11	-17.65	27.10	43.63	-1.54	25.26
Min	-2.51	-3.00	-1.72	-2.36	-2.19	-2.00	-1.92	-2.12	-0.61	-2.70	-2.00	-1.43
Max	2.69	1.81	2.65	2.42	2.20	1.58	3.25	2.42	1.53	3.75	2.21	2.54
Variance	0.47	0.42	0.37	0.51	0.43	0.32	0.46	0.48	0.06	0.45	0.34	0.41
Kurtosis	3.31	6.21	3.64	3.42	1.93	1.31	4.38	2.42	7.91	7.22	3.58	2.44
Skewness	0.73	-1.17	1.32	0.95	0.74	0.00	0.83	1.08	1.44	0.73	0.84	1.10

The correlation matrix analysis ($p < 0.01$) for NE showed significant associations of As with Co ($r = 0.71$), Cr ($r = 0.60$), Cu ($r = 0.68$), Mn ($r = 0.64$), Ni ($r = 0.66$), V ($r = 0.80$), and Zn ($r = 0.70$). Moreover, Co is also significantly correlated with Cr ($r = 0.75$), Cu ($r = 0.73$), Mn ($r = 0.78$), Ni ($r = 0.82$), V ($r = 0.88$), and Zn ($r = 0.76$). A significant correlation was also recorded for Cr with Cu ($r = 0.69$), Mn ($r = 0.60$), Ni ($r = 0.69$), V ($r = 0.72$), and Zn ($r = 0.64$). The heavy metals that were correlated with Cu included Hg ($r = 0.27$), Mn ($r = 0.69$), Ni ($r = 0.78$), V ($r = 0.76$), and Zn ($r = 0.79$). Mn has a significant correlation with Ni ($r = 0.71$), V ($r = 0.80$), Zn ($r = 0.77$) and Ni has it with V ($r = 0.81$) and Zn ($r = 0.68$). V is correlated only with Zn ($r = 0.83$) (Table. 20). Therefore, these observations may be interpreted to mean that most of these

elements have the same origin. Disassociation of Cd, Hg, Pb, Se, and Zn with other metals may be due to their reduction by leaching.

Table 20 The Pearson correlation matrixes of geo-accumulation (I_{geo}) for heavy metals in NE Element name(EN). (**Correlation is significant at the 0.01 level.*Correlation is significant at the 0.05 level).

EN	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
As	1											
Cd	.304**	1										
Co	.718**	.311**	1									
Cr	.607**	.292**	.755**	1								
Cu	.687**	.308**	.734**	.693**	1							
Hg	.297**	.292**	.270**	.247**	.273**	1						
Mn	.642**	.338**	.783**	.608**	.690**	.249**	1					
Ni	.669**	.254**	.826**	.694**	.783**	.225*	.712**	1				
Pb	.430**	.412**	.541**	.448**	.546**	.290**	.491**	.419**	1			
Se	0.172	0.156	.201*	.195*	0.101	.257**	.214*	0.05	.324**	1		
V	.807**	.316**	.885**	.722**	.768**	.317**	.806**	.817**	.504**	0.138	1	
Zn	.706**	.329**	.764**	.648**	.793**	.224*	.771**	.684**	.565**	0.121	.834**	1

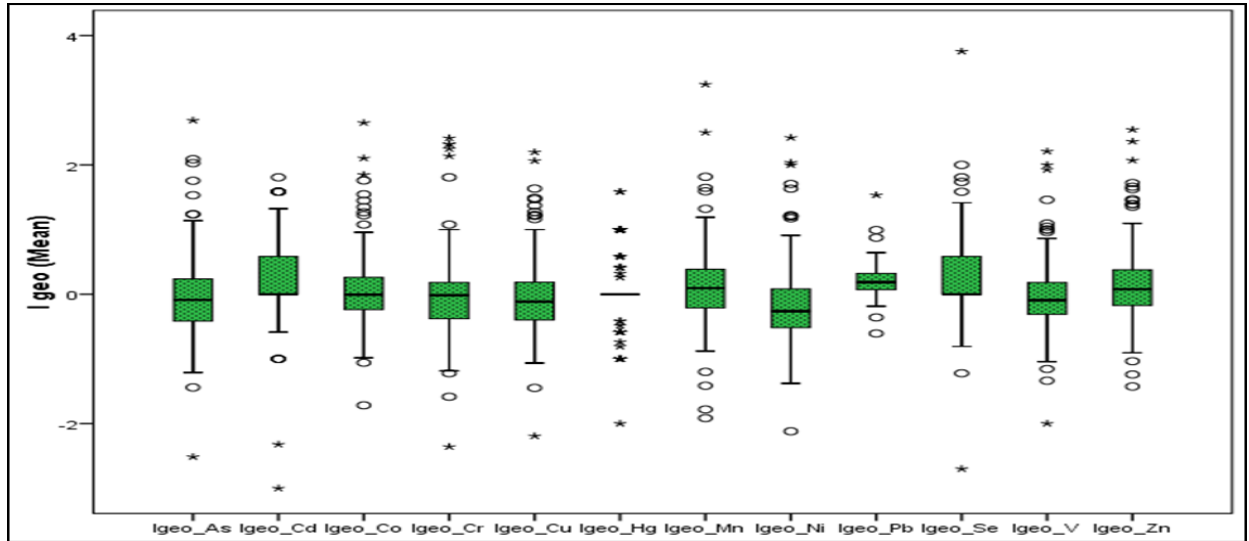


Fig. 49 Boxplot showing geo-accumulation (I_{geo}) values of individual heavy metals in the surface soil of NE.

The summary of descriptive statistics for I_{geo} values in the soil are presented in Table 2. Generally, the results indicate that there is a difference between the heavy metals in the study area and most of the I_{geo} values of heavy metals are 0–1, indicating moderately contaminated soils. The statistical analysis of the metals showed that the I_{geo} values vary from one element to other within the state. The elements with values less than 0 have been reported as depleted or uncontaminated. An anthropogenic I_{geo} , significant for heavy metals, can be considered because there are significant points of chemo-agricultural additions or anthropogenic inputs in the crop land, observed with respect to air and land emissions superimposed on geochemical maps presented elsewhere. In general, the observations of I_{geo} results indicate that the soils under study are moderately contaminated with heavy metals because most of the mean values are between 0–1 of the I_{geo} index.

The minimum and maximum values with high or low levels of the metals are presented in the I_{geo} geochemical maps.

4. SPATIAL ANALYSIS OF GEO-ACCUMULATION (I_{geo}) OF THE HEAVY METALS MAPS

Geochemical distribution maps of I_{geo} of heavy metals were performed using the geo-software Oasis Montaj, version 7.5.1-4, (2012). The spatial interpolation maps are obtained using ordinary kriging estimation. These maps present the spatial chemical distribution of heavy metals in the surface soil, based on geostatistical analysis. The results of the mapping analysis of the point sources show extensively different patterns. The soils under the study regions are potentially affected by various sources of anthropogenic applications of heavy metals. According to I_{geo} , agricultural soils in IA, KS, and NE are chemically loaded with Cd (1.12), Cu (1.18), Hg (1.63), Mn (1.62), and Pb (1.06), as illustrated in the I_{geo} distributed maps (Fig. 50.1). Similar investigations of geochemical maps detected Mn, Ni, Se with maximum values of $0.16 < 0.87 < 1.62$ (Fig. 50.1, 50.2, and 50.4). The heavy metals include Cd, Pb, V, and Zn, with maximum values $0.02 < 0.88 < 1.06 < 1.12$ and have similar features on the geochemical maps (Fig. 50, Fig. 51). There is an association between the I_{geo} distribution maps of As, Cr, Co, at $0.31 < 0.52 < 0.74$ (Fig. 50.1, 50.3, and 50.4). The distributions of I_{geo} for the analyzed heavy metals indicate high spots in specific regions, as compared to other regions within each state. Homogeneous hot spots have been observed in IA, KS, and NE. The range of I_{geo} values of As is 1.92–0.52 (Fig. 50.1). The maximum value of I_{geo} indicates uncontaminated soils, according to Muller's (1969) criteria. The minimum negative values have been observed in some regions of the study area. The

maximum geochemical value of I_{geo} of Cd is 1.12 in the study area, indicating moderate contamination in the three states. According to I_{geo} spatial maps, the most polluted regions are in the west of IA, extending to the east of NE, and the north of KS (Fig. 50.2). Two extended hot spot domains are located in the west of IA and east NE (in border connected regions) that indicates high Cd concentration, attributed to human activities, potentially from the agricultural activities in these regions. It is noticed that similar geochemical distribution maps were observed of the I_{geo} calculated for As and Co. The maximum I_{geo} value of As is 0.52, while it is 0.31 for Co (Fig.50.1, Fig. 50.3), which indicates that I_{geo} values range from 0–1, referring to uncontaminated to moderately contaminated soils. The I_{geo} of Cr showed no significant values and the spatial variations range from minimum to maximum values 1.85–0.74 in IA, KS, and NE. Homogeneous geochemical distribution has been detected in IA, KS, and NE, the 0.74 value spots were randomly distributed (Fig. 50.4). In the east of KS, significant concentrations of Cr have been recorded, which can be explained probably by the presence of anthropogenic applications as well as a lack of the rock types that contain Cr in their chemical structures. I_{geo} values indicate that this soil is more contaminated with Cu than other locations. Significantly enriched I_{geo} values of Cu were detected at 1.18 that fall in the range of I_{geo} signs 1–2 (class 2). Three hotspots of Cu were observed in the east of IA (one spot), and in the west of NE (two spots) (Fig. 50.5). The class 2 I_{geo} values of the indicators are interpreted as unpolluted to moderately polluted soils. The spatial pattern of the anthropogenic I_{geo} 's values of Hg in the agricultural soil fall within the range of 1–2 in class 2 of Muller's geo standards. Two areas located in IA and KS were influenced by anthropogenic Hg inputs. The high concentration spots were detected, with one hotspot located in the east of IA and the other in the east of KS (Fig. 50.6). Negative anthropogenic points were observed in

most of the study areas. The I_{geo} values were detected to be greater than the minimum indicator of I_{geo} in IA, more than KS and NE. The locations that have high concentrations of Mn are sited in the east and west of IA and were calculated at 1.62. The high I_{geo} value of Mn is in the range of 1–2 (class 2), indicating to moderately contaminated soil. One big hotspot was noted in the north of NE and three, close to each other, in the southeast of IA (Fig. 51.1). Most of the IA regions have been affected by moderately contaminated soils (Fig. 51.1). Ni is one of the heavy metals that presented negative I_{geo} with a lower value range of -2.24 - 0.16. Class 0 in I_{geo} refers to uncontaminated soil in IA, KS, and NE (Fig. 51.2). This observation determines that the sources of the small Ni amounts are mostly non-natural. The values of I_{geo} of Pb lie within class 2, with a maximum value of 1.06. Extended areas were observed that present anthropogenic contribution to the contamination load with small hotspots located in the south of IA and KS. In addition, two large domains were observed in the east and middle of KS (Fig. 51.3). The huge domain located in the southeast of KS suggests human activity rather than natural geological processes; Pb mines existed in this region. The geochemical distributed maps of Se in the agricultural soils of IA, KS, and NE showed a big hotspot located in the southeast of KS, in addition to two very small areas in the north of NE and KS (Fig. 51.3). The values were calculated to be less than 1, which is classified as uncontaminated to moderately contaminated soil (Muller, 1969). The distribution frequency of I_{geo} values of soil Se revealed non-anthropogenic regions in all the study areas (Fig. 51.4). The I_{geo} values of V were between 0–1, the maximum value was 0.02 (Fig. 51.5). I_{geo} of Zn was lower than its corresponding average C-horizon value (background). They were in the < 1 range, indicating no significant pollution or chemical loading. Most of the regions in IA, KS, and NE presented low concentration values of Zn, as shown in Fig. 51.6.

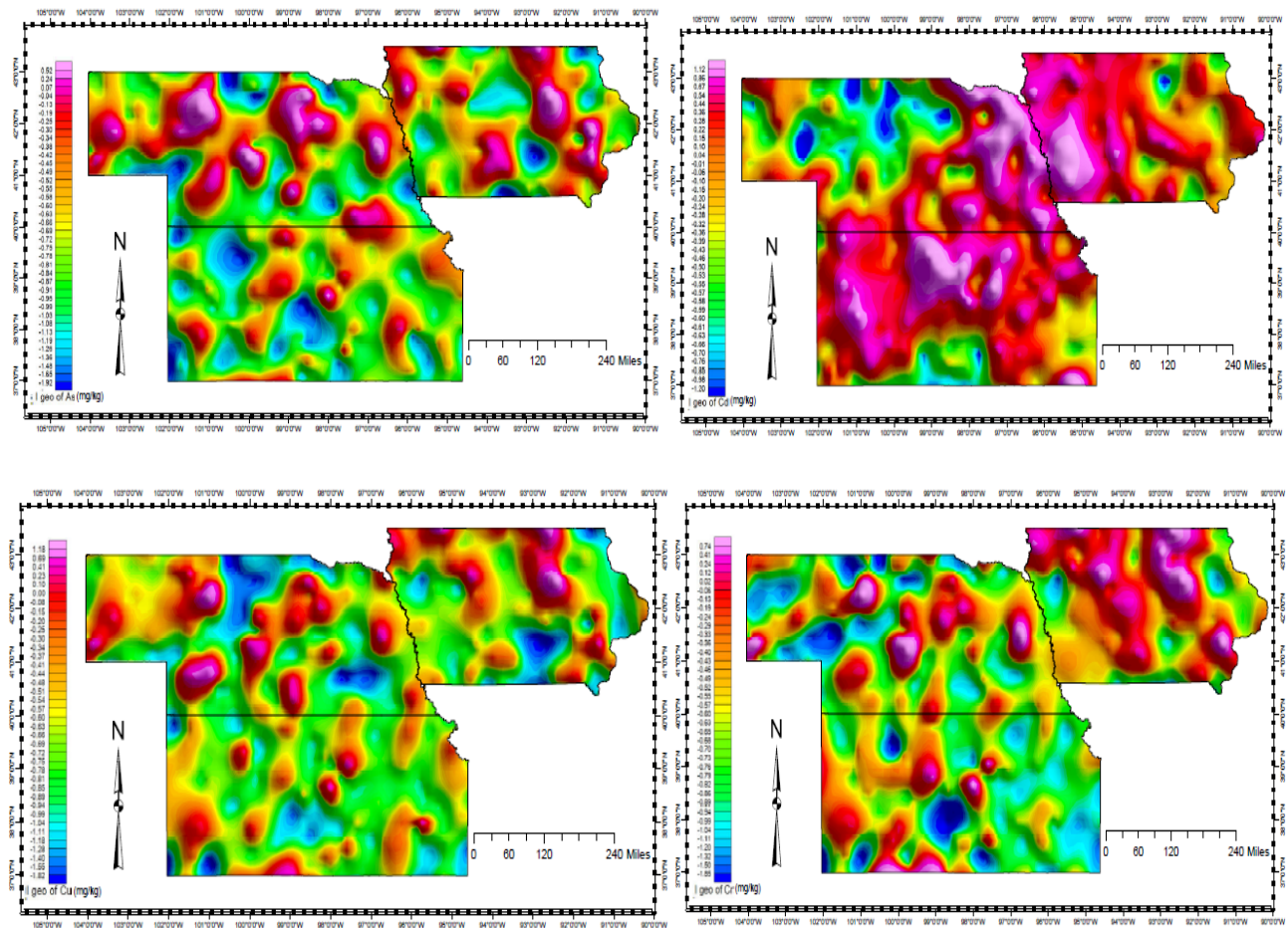


Fig. 50.1
Fig. 50.3

Fig. 50.2
Fig. 50.4

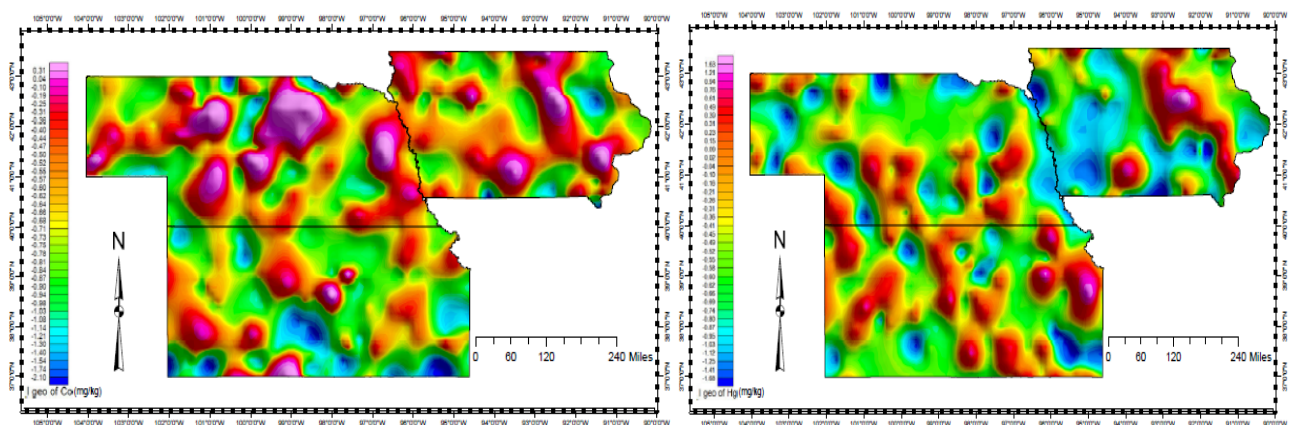


Fig. 50.5

Fig. 50.6

Fig. 50. 1-6 (As, Cd, Co, Cr, Cu, Hg) Distribution maps show geo-accumulation (I_{geo}) values of various heavy metals in the surface soil in the study area.

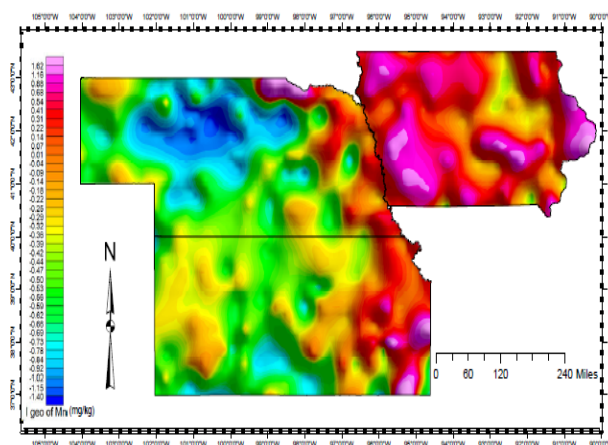
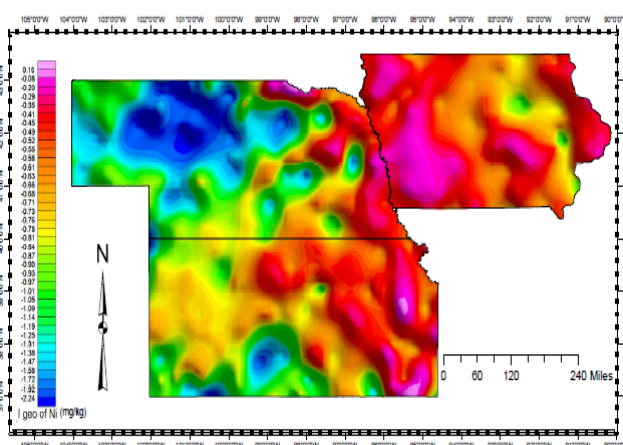


Fig. 51.1



51.2

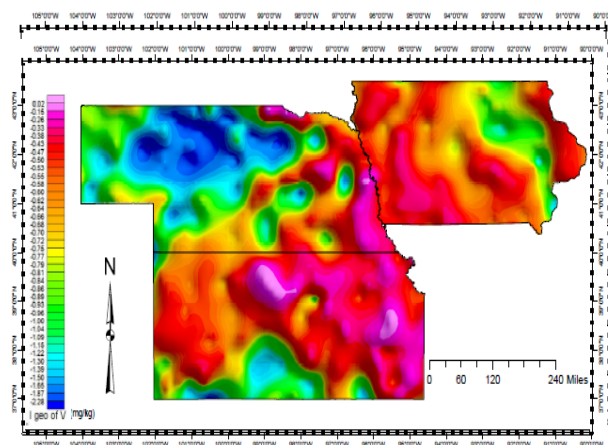


Fig. 51.3

Fig. 51.5

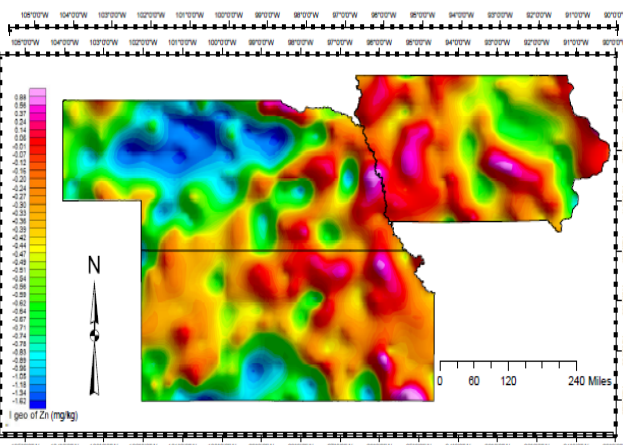


Fig. 51.4

Fig. 51.6

Fig. 51. 1-6 (Mn, Ni, Pb, Se, V, Zn) Distribution maps showing geo-accumulation (I_{geo}) values of various heavy metals in the surface soil in the study area.

5. DISCUSSION

Identifying the chemical element sources is significant for the evaluation of the elemental contributions of humans. The best quantification of I_{geo} is using the -ite values of the surface soil data, subtracted from the C-horizon data variable and locally natural conditions (Desaules, 2012).

It is noteworthy that most of the high levels of chemical elements were recorded in the majority of IA and in the east of KS and NE. There is significant, intensive farming application in IA, therefore, the results of the current study indicate a significant enrichment in most of agricultural areas in regional soil background maps. The areas located in the southeast of KS, showing high values of Zn and Pb, are located within the areas of mining sites, pointing to the source of those elements anthropogenic mining activities. The results of the I_{geo} is probably a weak tool to measure the degree of soil contamination, with respect to the geologic background values (shale average), which is not the most dominant bedrock type in the areas of interest. All the I_{geo} values were negative ($I_{geo} < 1$), except for Se in IA, probably due to leaching associated with low pH.

The drainage water from mining has high concentrations of the chemical elements and can be released into agricultural regions through irrigation, which can cause soil contamination. Some of the areas that have high geochemical backgrounds are cities that have released a lot of chemicals into the air, land, and/or as wastewater. Other sources can also contribute to element inputs in the soil, such as natural weathering processes or the area being hypoxic “dead zone” one of the most important issues of 2018. This is observed in the Gulf of Mexico where the oxygen depleted water is increasingly moving towards the Gulf surface, indicating that nutrients and nitrogen flow down the Mississippi river (Hurst, 2018; Maher, 2018).

6. CONCLUSION

Geochemical maps reflect various potential influences of heavy metals in agricultural soils within the study area, across mid-west USA. The highest recorded I_{geo} values of heavy elements were in IA are As, Cd, Co, Cu, Cr, Hg, Mn, Pb, Se, and Zn. However, similar I_{geo} results of heavy

metals have been observed in KS and NE. I_{geo} values in KS are for Cd, Hg, Mn, Pb, Se, and Zn, while in NE they are for Cd, Co, Hg, Mn, Pb, Se, and Zn. According to the calculated I_{geo} grades, the values of these heavy metals in the soil are influenced by anthropogenic activities or chemical overloading. However, there are significant differences in the I_{geo} concentrations of the heavy metals ($P < 0.05$).

The findings revealed that there is a difference between the I_{geo} distribution maps of the states, in terms of the heavy metal content. These maps illustrate the point sources, inferred as anthropogenic inputs, when the chemical source is known. However, chemical hotspots that are located in some agricultural regions could have resulted from agricultural inputs because most of these areas are unindustrialized.

CHAPTER 4

EVALUATION OF NUTRIENTS MICROBIAL ACTIVITY AND THE CONFLICTING IMPACTS OF AGRICULTURAL APPLICATIONS ON SOILS IN MID-CONTINENTAL USA

1. INTRODUCTION

Soil is a fundamental part of the ecosystem that provides nutrients and water for plant growth. It plays a significant role in all aspects of life and acts as a network interacting with the atmosphere, biosphere, and lithosphere (Woodruff et al., 2015). The nutrient cycling is a very important factor for crop production. The most abundant communities in the soil are bacteria and fungi, which contribute to nutrient cycling. It is estimated that one gram of soil contains up to a billion bacteria (Trevors, 2010). Moreover, soil microbial communities play a significant role in nutrient cycling of elements such as carbon (C), nitrogen (N), and phosphorous (P) breaking down organic matter, and thus helping in the sustainability of agricultural regions. Heterotrophic microorganisms depend on the plant's C input and productivity. Soil microorganisms, such as bacteria and fungi, can be used to estimate the exhaustive agricultural applications because they respond rapidly to the changes in the environment, like fertilization. Agricultural applications involving chemical additives that farmers use, can affect the chemical and physical characterization of soil, and therefore, the sustainability of microbial biomass communities. The environmental factors such as soil particles, pH, cation exchange capacity, organic components, and temperature also impacts microbial communities.

The total organic carbon (TOC) in the soil is expressed as a percentage of weight (g/100 g or g/BG of the fine earth fraction). Compared to other soils overlying the horizons, the C horizon

is comprised of slight organic matter and carbon. The amount of soil organic carbon (SOC) affects the availability of important nutrients for plants, such as N, that are required in relatively large concentrations for their growth. Organic matter can be used to determine soil fertility and physical conditions. Plant nutrient sources are released in assimilated forms during microbial degradation. SOM contains 5% nitrogen (N), 0.5% phosphorous (P), and 0.5% sulfur (S), thereby having a ratio of 10:1. Organic matter in the soil is estimated by the amount of C present, as this element represents an average of 52–58 % of the organic matter, and the C:N ratio is 10:15. Soil microbes comprise approximately 2% of the total organic matter.

The overall goal of this study was to identify the lithogenic and/ or anthropogenic sources that contribute to NO_3^- , NH_4^+ , and PO_4^{3-} content in soils of extensive farming applications in the west mid-continent of the USA including IA, KS, and NE by employment of an ANOVA test. The present work is developed from the research project data of USGS (Smith et al., 2014), which aims to investigate nutrients over loading into agricultural soils for refining the soil sustainability and keep protection of intensive farming applications.

The goal of measuring nutrients and microbial activity is to characterize the soil nutrients, soil fertility and carbon sequestration across different land management regimes in IA, KS, and NE. It is important to identify the properties of individual soil sites in order to find the natural and/or anthropogenic input sources of nutrients in cropped lands. Additionally, a goal was to examine the soil sustainability and health through measurement of microbial activity using LI-COR Gas Analyzer (CO_2) to measure the soil respiration rate (SRR). Nutrient availability and SRR can reflect overall soil health. Regular monitoring of soil quality for numerous years can determine if soil quality is improving or degrading.

2. BACKGROUND OF SOIL MICROBIOLOGY

Soil health is defined as the sustainability of its productivity as a vital living system to preserve plant, animal, and human health (Doran & Zeiss, 2000). Soil microorganisms are comprised of bacteria, protozoa, nematodes, springtails, beetles, plants, and fungi. Anthropogenic activations can increase the soil organic matter, which releases more carbon dioxide (CO₂) into the atmosphere (Singh et al., 2011). Microorganisms play a critical role in terrestrial ecosystems through the turnover of organic matter in the soil. They can live if there is a source of carbon available, which they require to produce energy. Soil microorganisms are the key factor in all soil processes and applications. Thus, their activities are affected by physiochemical and geological interactions. Sometimes the smaller biomass in the soil is bacteria because of their microscopic sizes. However, the fungus community cannot tolerate the changes or disturbances in the soil conditions, in comparison to bacteria and protozoa.

The microbial communities and invertebrate species are necessary for food chains and ecosystem structures (Singh et al., 2011). In addition, their responses to land use and climate change are extremely variable and dependent on many biological factors, such as the life cycle of the organism, its reproductive rate, nutrition source, distribution properties, and adaptation ability (El-Bestawy et al., 2014). It is important to note that soils involve the genetic diversity of the earth. The estimation of the density of prokaryotic organisms in the soil is approximately 10^{13} cells per cubic meter in the soil, while the prokaryotic density in the ocean is 10^8 organisms per cubic meter (Whitman et al., 1998). The prokaryotes and the total amount of carbon cells on earth is approximately $4\text{--}6 \times 10^{30}$ cells and 350–550 Pg of C (1 Pg = 10^{15} g), and the prokaryotes comprise 85–130 Pg of N and 9–14 Pg of P (Whitman et al., 1998).

In fertilized soils, the biota may have biomass exceeding 20t. ha⁻¹ tonne (t) equals 10³ BG and one ha = 10⁴ m²), with life forms ranging from microscopic bacteria to larger organisms such as earthworms (Doncova & Kaloyanova, 2008). The significant concentrations of different highly biologically active chemical elements existing in the soil affect the vital system, the functioning of the soil, soil fertility, and human health (Doncova & Kaloyanova, 2008 and Singh et al., 2011). Some microorganisms can be active destructors of organic pollutants, but not heavy metals or other chemicals. This can generally lead to a change in the resistance of the soil ecosystem (Doncova & Kaloyanova, 2008). In most terrestrial ecosystems, the soil contains the highest diversity of organisms, as compared to other environments. Over the past years, there has been an increased interest in studying soil microbiology and ecology, using molecular techniques that target the functional role of microorganisms in natural environments and specific soil processes (Enriqueta et al., 2005 & Rastogi & Sani, 2011).

The essential functions of soil organisms are the degradation of plant and animal matter for the release of nutrients and trace elements from the organic soil fraction (Schinner, et al., 1996). It is of interest that the estimation of anthropogenic soil effects can be condensed into just the composition, size, and activity of the microbial community (Doncova & Kaloyanova, 2008). Many bioindicators are used to monitor the changes in the microbial communities, due to soil pollution. For instance, cultures of microorganisms are sensitive to the determination of specific types of soil additives, the number and ratio of taxonomic and ecologic trophic groups of microorganisms, bacterial community tolerance, and the intensity of microbiological processes, soil respiration, nitrogen fixation, and cellulose decay (Doncova & Kaloyanova, 2008).

The recent development of molecular bio techniques to study phylogeny or the evolutionary history of taxonomic groups has enabled the characterization of naturally occurring microbial biota without cultivation, allowing for the accurate assessment of how microorganisms are represented in their Biosystems (Rincon et al., 2013). Thus, changes in the microbial equilibrium can serve as an early warning for negative alterations in the soil conditions, before they become irreversible.

Microbial biodiversity is required for healthy soils and it can serve as a strong indicator for monitoring the changes in soil quality. The definition of microbial biomass is the living portion of organic matter that supports of flows C and N from plants and other organisms to the mineral forms of CO_2 , NH_4^+ , or NO_3^- ions in soil. The biological activities of microbial communities plays a significant role in the regulation and transportation of the nutrients, plant health, and soil quality as well as several chemicals vital to soils, such as C, N, P, and potassium (K) (Fatima et al, 2014). In recent years, the physiochemical properties and soil health is being determined by using enzymatic, molecular, and organism-based procedures (Rincon et al., 2013). The bio techniques of testing microbial molecular biomass are an advanced practice to determine the abundance of soil microorganisms (Bouzaiane et al., 2007). For instance, the total microbial biomass can be determined, which is an early indicator of soil threats such as contamination and changes in agricultural applications (Ranjard et al., 2006). Understanding the biological activity in the soil is dependent upon the estimation of the microbial biomass. The microbial biomass can be defined as the living portion of the soil organic matter except in soil, for plant roots and animals it is higher than $5 \times 10^{-3} \text{ um}^3$ (Ley et al, 2001). Microorganisms in the soil play an important role in the fertility, the synthesis, and the mineralization of organic compounds (Setia et al., 2012). It is important to

note that microbial biomass involves approximately 2% of the total organic C (Ley et al., 2001), and 5% of the organic matter (Setia et al., 2012).

The nutrients can be recycled from animals, vegetable composites, and biological cycling from nitrogen fixation and mycorrhizae. The soil microbial biomass is the primary controlling center of biological activity and plays an important role in the soil as a source sinking the nutrients, including C, N, P and S. Determining the source or flow of C and N in the soil of plant and/or minerals forms, such as NH_4^+ , CO_2 , and N, it is required to investigate the soil health. Biological organisms play an important role in soil processes that include regulation, nutrient storage, and transformations that determine the soil quality through the analysis of the quantity of microbial biomass (Ranjard et al., 2006).

C is a critical element for all the living organisms in soil, which include microorganisms, plants, animals, and insects. Thus, the soil organic matter (SOM) is the most important source for providing living organisms with the required nutrients and energy to survive. In addition, soil organisms can transform plant materials to humus, and plant and animal residues can deposit organic matter in the soil (United States Department of Agriculture & Xiao, 2015).

For agricultural soils, microbiological populations are related directly and indirectly to crop production. There is a relationship between the diversity of microbes, soil and plant quality, and sustainability of the ecosystems (Kennedy & Smith, 1994 & Doran et al., 2000). It is necessary to monitor the changes in size, composition, and activity of the microbial population in anthropogenically polluted soils. More research should be conducted in order to better study the structure, activity, and diversity, and biomass of the soil microbes, and to study the relationship

between soil contaminations that might affect the microbial communities in the surface soil (Rincon et al., 2013).

With an increasing demand for agricultural production globally, is also the use of many variations of artificial fertilizers. Agricultural applications, such as commercial phosphate and nitrogen fertilizations, can change the soil's physical, chemical, and biological properties, thus, biologically affecting the soil microbial community. Soil microbes are the major agent and a critical indicator for controlling biological activity as they act as a transformer of the SOM.

3. STUDY AREA DESCRIPTION AND SAMPLES COLLECTION

The area of the study is in the mid-continental USA. The states of IA, KS, and NE (Fig. 52.1) were the target of this study to evaluate the chemical loading by human inputs from different sources. The study area is an agricultural region and farmland covers 99% of IA, and large areas in KS and NE. The agricultural grain crops in IA include corn and soy. In KS, the agricultural crops include alfalfa, sunflowers, and wheat. Agricultural activities in NE are the cultivation of corn, wheat, sorghum, potatoes, and sugar beets.

A total of 60 samples of the surface soil were collected from the top surface of 0–5cm. The samples were collected in triplicates from A, B, C, 44 sites, and composited in each location during the summer of 2016. Additional samples were collected from near the three sites to represent the background metal concentration. The collection of surface soil samples took place at the designated sites identified with high TCI values, as shown in Fig. 52.2. It was therefore revealed that among the study area there are specific high and low concentrations of heavy metals (Fig 52.2). A total of 22 sampling sites were selected from agricultural fields. An approximate 1kg of each sample was collected. During the samples collection, foreign materials were removed immediately. The field features were noted, such as land cover and land use, and the surface soil profiles were noted, including the nature of the forest and layer thickness, in order to avoid big rocks or buried wood. The sampling process included the collection of samples from sites that were considered as control, and from other sites as a background. The background soils were located in nearby, non-agricultural regions, usually a hundred feet away. These background samples sometimes are a little further away on a road side, but close to the field and were collected

from a distance of approximately 150 meters to the field. Furthermore, some of these samples were samples from the deeper soil layer (C-horizon).

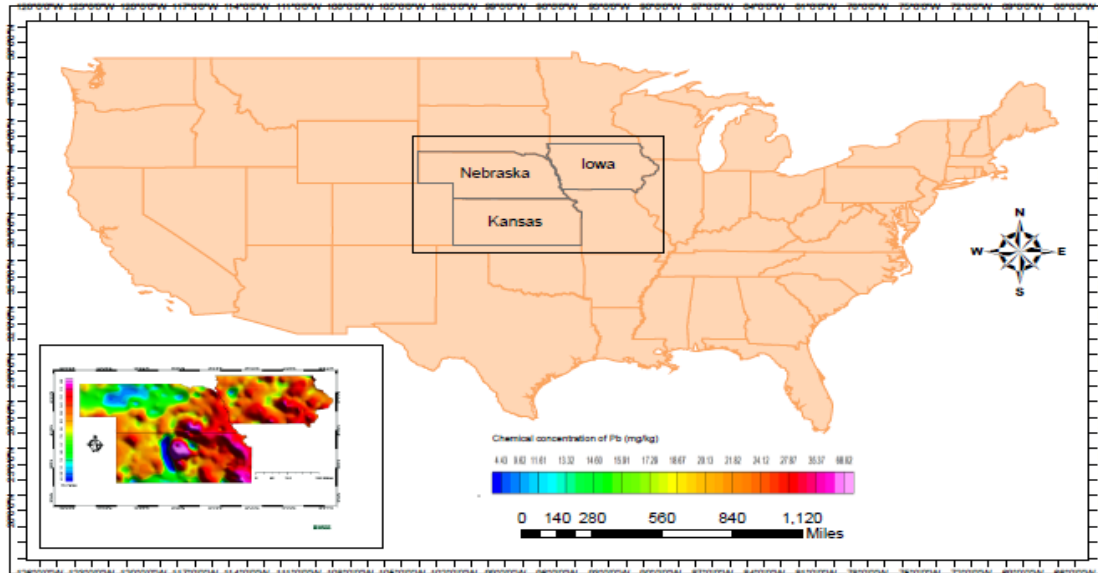


Fig.52.1 Map shows area of study and soil geochemistry and spatial distribution of chemical concentrations of As, Cd, Cr , Co, Cu, Pb, Mn, Hg, Ni, Se, V, and Zn, in the United States (Smith et al., 2014).

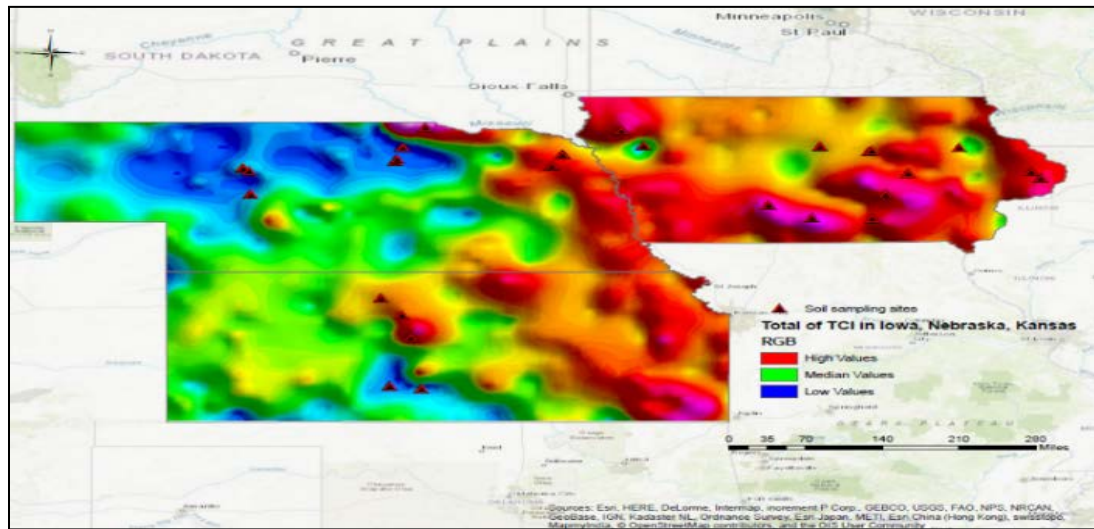


Fig.52.2 TCI of states of interest with sample sites noted with triangles (Smith et al., 2014)

4. CLIMATE OF THE AREA

The area of the state of IA is 56,288 m², located in the middle latitudes between the Mississippi and Missouri rivers. The rainfall in the area, during the warm months, comes from the Gulf of Mexico. In the winter and autumn, the dry Canadian air flows in from the northwest, beside the air masses that move in from the Pacific Ocean. The annual average temperature in IA, KS, and NE is 50.85°F, 50.65°F, and 55.05°F, respectively (NOAA, 2018). The average annual temperature in IA is 45° in the north and 52° in the south. The high temperature during the summer does not cause severe crop stress (NOAA, 2018). IA also has seasonal variations. Furthermore, the average low temperature in KS is 36.6° (NOAA, 2018). The elevation in the southeast ranges from < 900 feet above sea level to 1,200 feet in the northeast. The Sand Hills contains some lakes, valleys, and basins in the north-central and high plains in the west, and the prairie is located in eastern part of the state, formed from sandy loam or silt loam soils (Fig. 53). There are fluctuations in the seasonal temperatures. In NE, temperatures rise to above 100°F, especially June through September. The rainfall is formed by warm air thunderstorms during summer and spring that may occasionally cause flooding. (NOAA, 2018).



Fig. 53 Location of Sand Hills in Nebraska (NOAA, 2018)

5. NUTRIENT AVAILABILITY

5.1 Analysis of Nitrate (NO_3^-), Ammonium (NH_4^+), and Phosphate (PO_4^{3-})

Plant nutrients become available for uptake in soil solutions through several processes, including soil-mineral weathering (soils sometimes are depleted, but not always in elements, relative to the parent mineral), decomposition of organic matter, ion exchange processes, applications of soil amendments, and deposition (Malcolm et al., 1993). The analysis of nutrients was used as criteria for the evaluation of the chemical contents in the soil, and to study if there was any association between the anomalous regions in the geochemical analysis and the nutrient levels in agricultural soils in the study area.

Despite the increased use of fertilizers, more macronutrients are substantially being removed annually from the soil than is being applied to it (Bajgiran, 2013). The sources of plant nutrients can be natural, synthetic, biological inoculants (bio fertilizers), and recycled wastes. Those in straw and farmyard manure replace some of the nutrients removed, but on average, the nutrient balance is likely to remain negative. This applies especially to less developed parts of the world. The analysis of the soil was performed based on the estimate of the nutrient status of the agricultural soils.

Macronutrients in the soil include N, magnesium (Mg), P, calcium (Ca), and S in quite small quantities. The micronutrients include iron (Fe), manganese (Mn), boron (B), molybdenum (Mo), copper (Cu), zinc (Zn), chlorine (Cl), cobalt (Co), and nickel (Ni). These routine analyses can provide input regarding whether the agricultural applications meet the recommended, determined concentrations as a basis for using fertilizers for crop production. It is hypothesized that the use of extensive fertilizers in the surface soils of the cultivated cropland of IA, and the east

of KS and NE, contribute to high amounts of nutrients in soils that might cause long-term soil contamination. Moreover, the higher the concentrations of these nutrients, the more likely it is fertilizers or manures, which include a high amount of the nutrients. As stated by Woodruff et al. (2015), P concentrations were naturally high (27,400 mg/bg) in the C-horizon in Kentucky, but P concentrations in the A-horizon across the American Midwest shows possible chemical overloading of P in the surface soil.

5.2 MATERIAL AND METHODS

Most of the study areas are active agricultural regions that are rich in organic matter. A total of 104 surface soil samples were analyzed in this study. This was done using colorimetric (NO_3^- and NH_4^+ , and PO_4^{3-}) microplate assays. Availability is determined as low, medium, high, or excess, by the colorimetric analysis. The NH_4^+ was determined using a modified Berlet hot reaction (Rhine et al., 1998), NO_3^- using a modified Griess reaction (Doane & Horwath, 2003), and inorganic PO_4^{3-} using the Malachite Green method (D'Angelo et al., 2001).

Frozen samples (5g) were extracted with potassium sulfate (K_2SO_4), by shaking them for three hours on a rotary shaker at 50–60 rpm. Filtration using a vacuum was performed using 1cm pore-size, glass fiber filter paper with compressed air to remove residual C from chloroform. The extracts then were frozen at -20°C until analysis. Microbiological analyses can be performed to determine the concentrations of available nutrients, including NH_4^+ and NO_3^- . The average selected soil nutrient values, in IA, KS, and NE were for the surface of agricultural soils.

6. RESULTS AND DATA ANALYSIS

The concentrations of NH_4^+ , NO_3^- , and PO_4^{3-} were variable from one state to another, depending on their origins, soil properties, geographic location, and crop types.

6.1 Nitrate (NO_3^-)

The concentrations at individual sampling sites were determined from the surface soil. Concentrations of NO_3^- in IA showed several variations between the sites within the state, as shown in Table.21 and Fig. 54. The concentrations of NO_3^- are different from the control samples, as compared to the background samples. The average values in seven agricultural sites 1, 2, 3, 8, 9, 10, 11, 12, and 14 (9.75, 11.38, 13.34, 8.30, 2.55, 5.00, 15.64, 10.33, 10.72, respectively) were the higher concentrated NO_3^- soil, as compared to the average of the background soil as it shown in Table 1, which have similar or the same average values (4.28, 4.10, 4.31, 4.29, 2.55, 5.00, 5.68, respectively) (Table.21 & Fig. 54). It is suggested that sites of higher concentrations of NO_3^- indicate that chemo-agricultural additives were probably deposited into the surface soil. The sites that had the same, or nearly equal to average concentrations, might indicate to the same point origin it might be a natural source rather than an anthropogenic one.

Table 21 Univariate analysis of (NO₃⁻ in Iowa (IA) shows mean, replicated number of analyzed samples (N), standard deviation (Std, Deviation).

Sample location	Mean	Std. Deviation	Median	Sum	Minimum	Maximum
I-1	9.7533	7.43674	12.0350	58.52	0.54	16.84
I-1BG	9.5950	9.72272	9.5950	19.19	2.72	16.47
I-2	11.3767	2.94909	11.0300	68.26	8.16	15.22
I-2BG	14.9100	0.62225	14.9100	29.82	14.47	15.35
I-3	13.3417	6.93556	14.8100	80.05	3.03	19.90
I-3BG	0.9450	0.13435	0.9450	1.89	0.85	1.04
I-4	4.2783	0.36537	4.4450	25.67	3.79	4.60
I-5	4.0983	0.68397	4.0650	24.59	3.35	5.10
I-6	4.3067	1.13859	4.4700	25.84	2.85	5.85
I-7	4.2867	3.55880	2.0700	25.72	1.91	8.91
I-8	8.3033	0.85848	8.0650	49.82	7.34	9.66
I-8BG	2.8800	1.18794	2.8800	5.76	2.04	3.72
I-9	2.5567	0.36615	2.6600	15.34	2.10	2.91
I-9BG	2.0100	0.04243	2.0100	4.02	1.98	2.04
I-10	5.0017	0.89852	4.6250	30.01	4.10	6.22
I-10BG	3.8200	2.51730	3.8200	7.64	2.04	5.60
I-11	15.6450	1.35212	15.1550	93.87	14.28	17.34
I-11BG	2.6000	0.00000	2.6000	5.20	2.60	2.60
I-12	10.3267	8.98826	5.4750	61.96	3.29	21.97
I-12BG	4.3500	0.00000	4.3500	8.70	4.35	4.35
I-13	5.6817	0.66868	5.4400	34.09	5.10	6.79
I-13BG	9.5050	0.21920	9.5050	19.01	9.35	9.66
I-14	10.7200	5.75893	8.3750	64.32	5.72	18.22
I-14 BG	2.5950	0.09192	2.5950	5.19	2.53	2.66

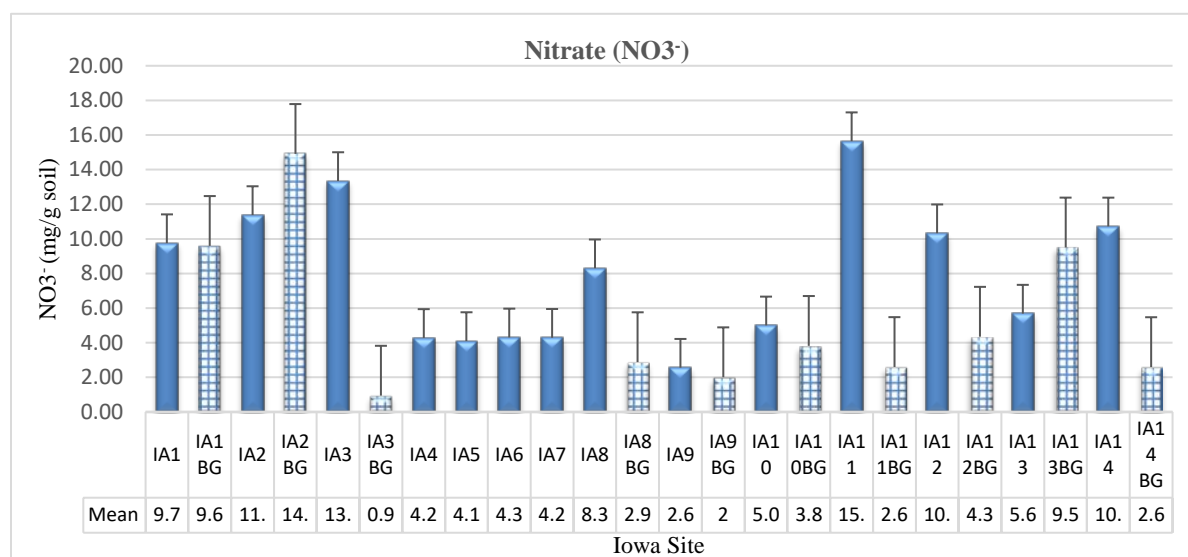


Fig. 54 Nitrate (NO_3^-) Concentrations in top soil 0-5 cm of soil in control and background (BG) sites in Iowa (IA).

A summary of statistics of KS is presented in Table 22. The observation showed that the average of the surface soil samples were higher than the average of the soil samples from C-horizon in sites 5 (2.97) and 6 (7.07). In addition, the surface soils of site 5 more than site 4, with average values of 9.78 and 2.63 respectively. However, an interesting point is that four sites with lower average values of 3.11, 1.06, 2.18, and 2.63, were the approximate average values (Fig. 55). The similarity between soil sites 1, 2, 3, and 4 with low values suggest that NO_3^- concentrations are originating from the natural nutrient cycling in the soil, and they are not results of anthropogenic inputs.

Table 22 Univariate analysis of NO_3^- in Kansas (KS) shows mean. Horizon (CH), standard deviation (Std, Deviation).

Sample location	Mean	Std. Deviation
KS1	3.10867	.381929
KS2	1.05717	.215204
KS3	2.18200	1.293656
KS4	2.62967	.630657
KS4(CH)	5.50400	.043841
KS5	9.78367	2.256812
KS5(CH)	2.97350	.088388
KS6	9.45033	4.742760
KS6(CH)	7.06600	.309713

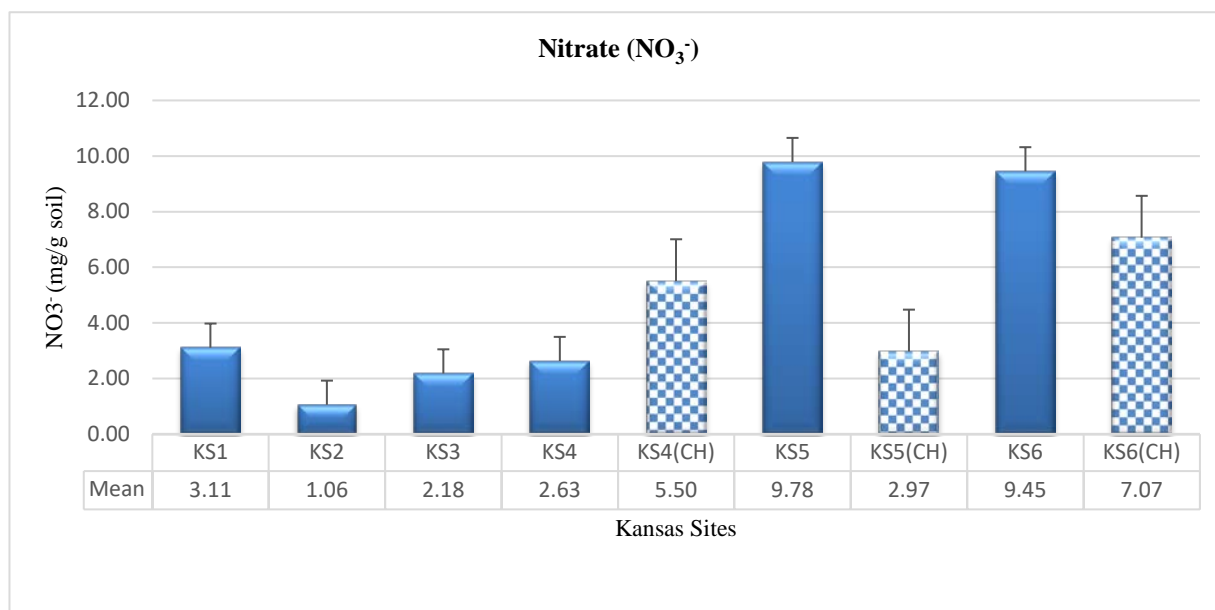


Fig. 55 Nitrate (NO_3^-) concentration in top soil 0–5 cm of soil compared to the deeper C-horizon (CH) in Kansas (KS)

According to the statistical analysis of the soil samples collected from eastern NE, the average concentrations of NO_3^- in site 5 was 13.56, which is higher than those from the other 6 sites 1, 2, 3, 4, 6, 7 (1.84, 0.85, 0.92, 1.51, 6.47, 4.54, respectively). NO_3^- concentration in site 5 was almost 9 to 11 times greater than its equivalent concentration in the other sites. It is noted that most of east NE has low concentrations of NO_3^- , as shown in Table 23 & Fig. 56.

Table 23 Univariate analysis of NO_3^- in Nebraska (NE) shows mean, standard deviation (Std, Deviation).

Sample location	Mean	Std. Deviation
NE1	1.8383	.37392
NE1(CH)	1.0700	.04243
NE2	.8483	.11071
NE3	.9233	.20877
NE4	1.5133	.81919
NE5	13.5633	8.03857
NE5(CH)	1.9100	.08485
NE6	6.4717	1.11661
NE7	4.5350	2.22485
NE7 BG	6.3150	.13435

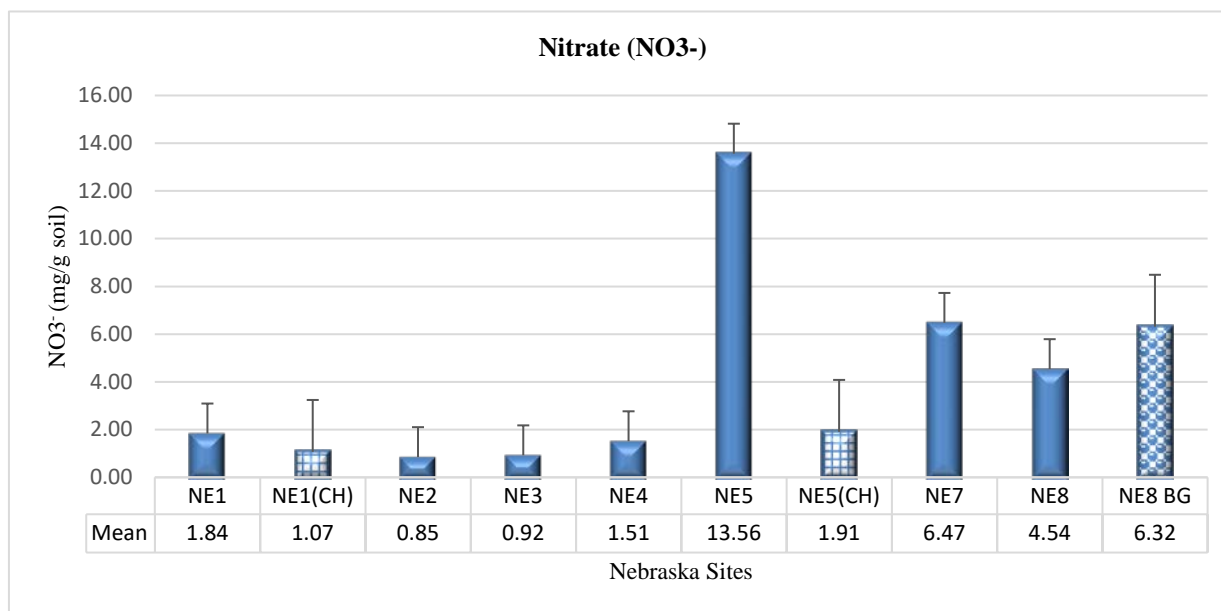


Fig 56 Nitrate (NO₃⁻) concentration in top soil 0-5 cm in sampling sites in control, background (BG) sites, and deeper C. Horizon (CH) in Nebraska (NE)

In general, the concentrations of NO₃⁻ were higher in IA soil, as compared to other states (Fig. 54, Fig. 55, & Fig. 56). This observation may be explained that agricultural activities are more in IA, as compared to KS and NE. This aspect has been of distinct interest. The comparison of the average concentrations of soils in KS and NE, between the surface soils to the deeper soils, C-horizon, showed an increase in the concentration of NO₃⁻ in the surface soils as compared to the C-horizon, except site 4 in KS, as shown in Fig. 57

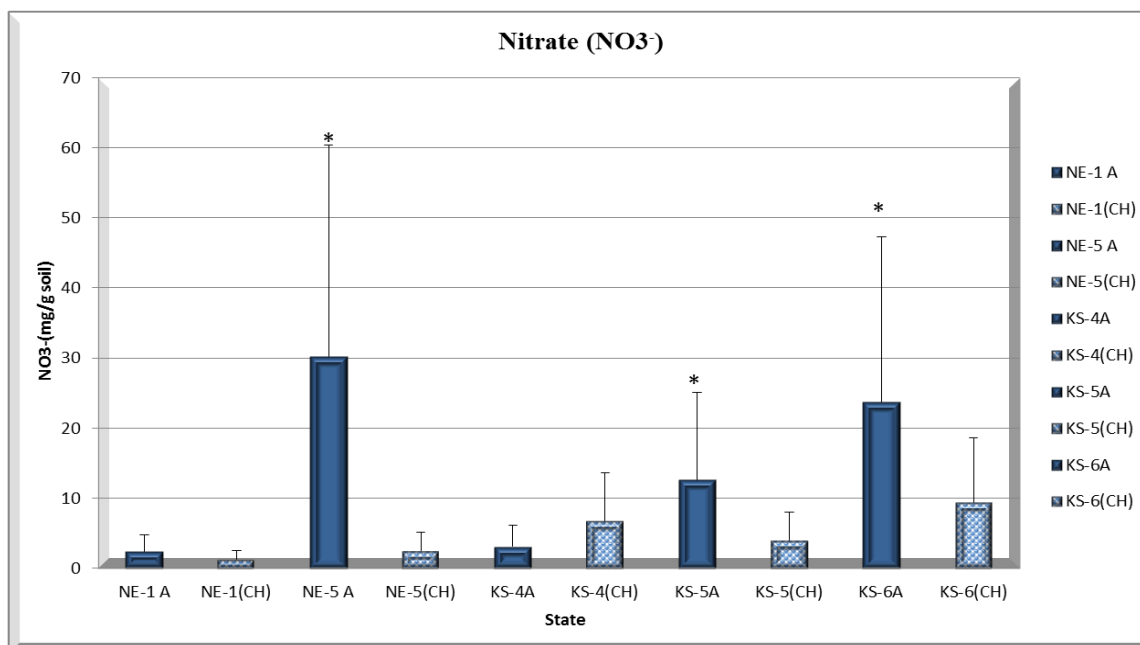


Fig. 57 Nitrate (NO_3^-) concentration in the top soil as compared to C-horizon (CH) soils in Nebraska (NE) and Kansas (KS)

6.2 Ammonium (NH_4^+)

NH_4 analysis of soils in IA showed that there are significant differences between the sites (Table. 24 & Fig. 58). In IA, low concentrations of NH_4 were observed in most of the sites and the highest average concentration was observed in site 5 (17.81). However, a high concentration was observed in control soil site 1 (7.28), versus the average background value (3.19). Likewise, the average value control site (6.02) was greater than the background in site 13 (3.58) (Fig. 58)

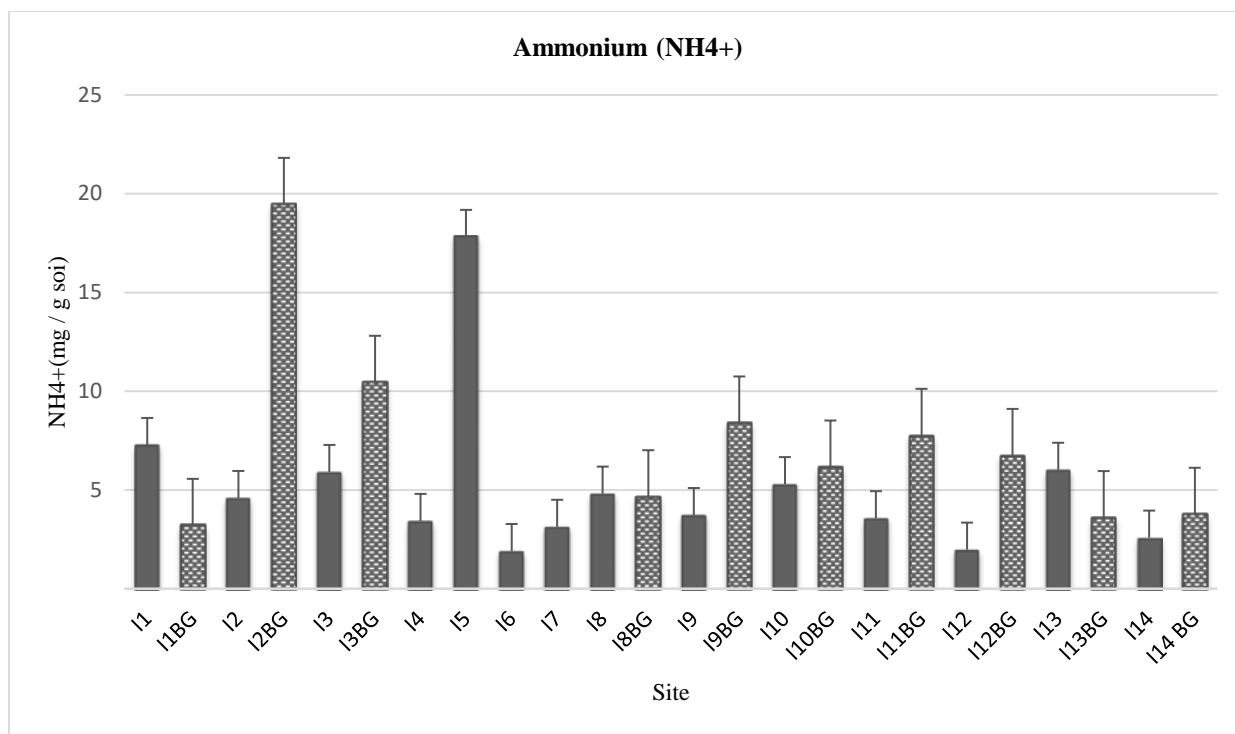


Fig. 58 Ammonium (NH₄⁺) concentrations in the surface soil as compared to background sites (BG) in Iowa (IA)

Table 24 Univariate analysis of NH_4^+ in Iowa (IA) shows mean, C. Horizon (CH), standard deviation (Std, Deviation), percentage (%).

Sample location	Mean	Std. Deviation	Median	Sum	Minimum	Maximum	% of Total Sum
I1	7.28	5.10	5.58	43.65	2.00	13.64	0.08
I1BG	3.19	1.93	3.19	6.37	1.82	4.55	0.01
I2	4.59	1.30	4.75	27.55	3.03	6.00	0.05
I2BG	19.44	1.65	19.44	38.88	18.27	20.60	0.07
I3	5.91	2.85	5.61	35.45	1.72	10.30	0.06
I3BG	10.43	0.08	10.43	20.86	10.38	10.48	0.04
I4	3.43	0.45	3.38	20.58	2.82	3.98	0.04
I5	17.81	10.98	19.22	106.86	4.49	29.47	0.18
I6	1.91	0.38	1.85	11.44	1.43	2.45	0.02
I7	3.13	1.52	2.74	18.79	1.61	5.08	0.03
I8	4.81	2.01	4.60	28.87	2.71	7.50	0.05
I8BG	4.64	3.41	4.64	9.27	2.22	7.05	0.02
I9	3.73	0.44	3.62	22.36	3.26	4.36	0.04
I9BG	8.37	5.54	8.37	16.74	4.45	12.29	0.03
I10	5.29	1.37	5.45	31.75	3.30	6.98	0.05
I10BG	6.14	1.51	6.14	12.28	5.07	7.21	0.02
I11	3.57	0.40	3.36	21.40	3.26	4.22	0.04
I11BG	7.75	0.17	7.75	15.49	7.62	7.87	0.03
I12	1.98	0.15	1.93	11.85	1.82	2.26	0.02
I12BG	6.73	0.05	6.73	13.46	6.69	6.76	0.02
I13	6.02	2.22	5.50	36.12	3.50	8.78	0.06
I13BG	3.58	0.12	3.58	7.16	3.49	3.66	0.01
I14	2.58	0.46	2.70	15.51	1.98	3.23	0.03
I14 BG	3.75	0.33	3.75	7.50	3.52	3.98	0.01
Total	5.58	5.06	3.98	580.21	1.43	29.47	1.00

The statistical analysis of NH_4^+ in KS is presented in Table 25. Analytic results of NH_4^+ showed higher average concentrations of NH_4^+ in soil samples from sites 2 and 3 (7.46, 5.90, respectively). On the other hand, lower average values have been observed in sites 1, 4, 5, 6 with average concentrations of 3.5113, 2.8325, 1.9717, and 2.3817, respectively, present similarity or approximate values (Fig. 59). The average concentrations of NH_4^+ in the surface soil, as compared to the deeper soil (C-horizon), were almost equal values to the surface soil (1.97) and deeper soil (2.29) of site 5 and also of site 6 (2.38, 2.54, respectively). However, the exception was observed in site 4 that showed elevated concentrations of NH_4^+ in the surface soil, as compared to the deeper soil, with values 2.83, 2.05, respectively (Fig. 59).

Table 25 Univariate analysis of NH_4^+ in Kansas (KS) shows mean, C-horizon (CH), standard deviation (Std, Deviation), percentage (%).

Sample location	Mean	Std. Deviation	Median	Minimum	Maximum	% of Total Sum
K1	3.5113	2.32624	2.3950	1.92	7.39	18.9%
K2	7.4600	.44490	7.5200	6.96	7.84	20.1%
K3	5.9083	3.70375	5.7300	1.82	10.62	23.8%
K4	2.8325	.27825	2.9550	2.42	3.00	7.6%
K4CH	2.0550	.48790	2.0550	1.71	2.40	2.8%
K5	1.9717	.53229	1.7950	1.48	2.71	8.0%
K5CH	2.2900	.04243	2.2900	2.26	2.32	3.1%
K6	2.3817	.34914	2.3650	1.96	2.79	9.6%
K6CH	2.5400	.04243	2.5400	2.51	2.57	3.4%

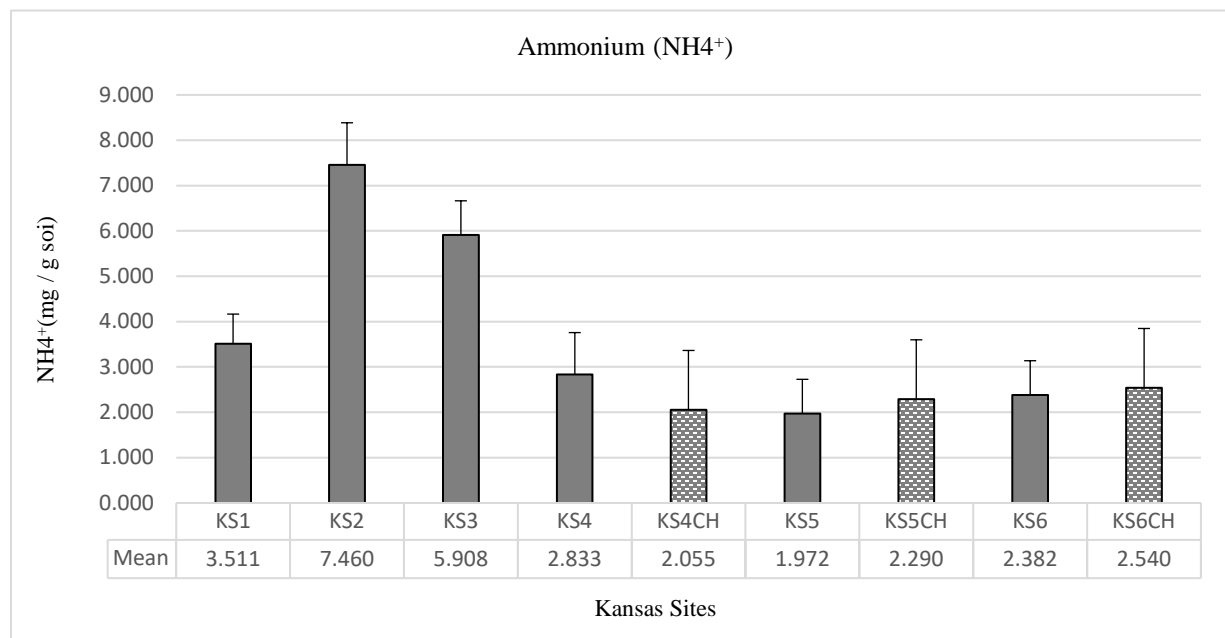


Fig. 59 Ammonium (NH₄⁺) concentrations in the surface soil compared to deeper soil, C-horizon (CH) in Kansas (KS)

In NE, the average concentrations of NH₄⁺ generally is lower in sites 1, 2, 3, 4, and 7 than in sites 5 and 6 (Table 26 & Fig. 60). Site 6 had the highest content of NH₄⁺ in the surface soil, with an average concentration of 26.52, followed by site 5 with an average of 13.55 (Table 26 & Fig. 60). There are other features of the NH₄⁺ average values which were detected in the deeper soils of site 1 and site 5 that are small, relative to the increased values in the surface soil (surface = 5.14, C-horizon = 1.77) in site 1, (surface = 13.55, C-horizon= 3.42), as shown in Fig. 60.

Table 26 Univariate analysis of NH_4^+ in Nebraska (NE) shows mean, replicated number of analyzed samples (N), standard deviation (Std, Deviation), percentage (%).

Sample location	Mean	Std. Deviation	Median	Sum	Minimum	Maximum	% of Total Sum
N1	5.1417	1.64665	4.7350	30.85	3.52	7.24	8.8%
N1CH	1.7750	.12021	1.7750	3.55	1.69	1.86	1.0%
N2	2.4950	.28205	2.4650	14.97	2.15	2.90	4.3%
N3	1.9633	.44791	1.9350	11.78	1.48	2.63	3.4%
N4	1.5100	.98821	.9950	9.06	.76	2.89	2.6%
N5	13.5550	5.33299	11.2200	81.33	9.10	20.50	23.2%
N5CH	3.4200	.11314	3.4200	6.84	3.34	3.50	1.9%
N6	26.5167	28.30502	12.8050	159.10	3.72	62.87	45.4%
N7	4.9250	1.32723	5.2800	29.55	3.09	6.35	8.4%
N7BG	1.8800	.08485	1.8800	3.76	1.82	1.94	1.1%
Total	7.3081	12.50485	3.4200	350.79	.76	62.87	100.0%

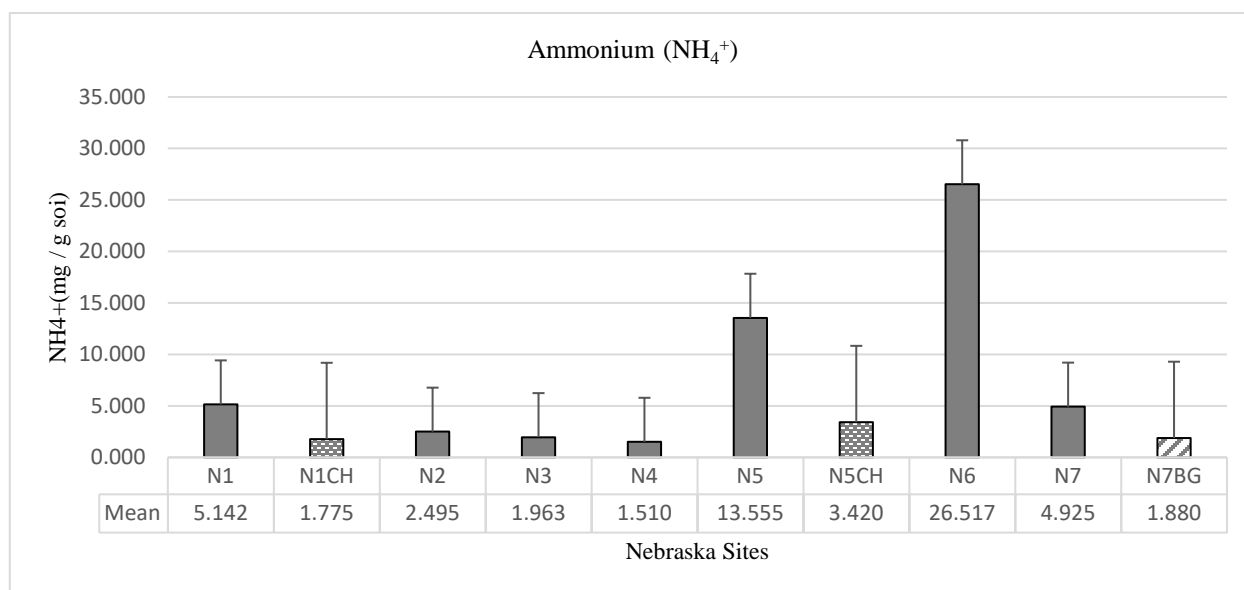


Fig. 60 Ammonium (NH_4^+) concentrations in the surface soil, compared to deeper soil, C-horizon (CH), and background (BG) in Nebraska (NE)

6.3 Phosphate (PO_4^{3-})

P is a significant molecular component in all living cells and especially in plant cells. It plays an important role in the process of photosynthesis as it helps capture the energy from the sun (Mullins, 2009). The plant vegetation is then capable of responding to the addition of nutrients applications. P is relatively immobile in the soil. Increasing P levels in the top soil can damage the aquatic ecosystems and lead to excessive vegetation growth (Horneck et al., 2011). The concentration of PO_4^{3-} in IA varied widely. It is noted that PO_4^{3-} differs from one site to other but the concentrations were greater in IA, in comparison to NE and KS (Fig. 61). PO_4^{3-} analysis indicates that there are larger concentrations in the IA, in sites 1, 2, 4, 6, 8, 10 and 14 (94.36, 117.76, 163.10, 137.72, 167.25, 105.40, 36.08, respectively), as compared to the other sites. A

high PO_4^{3-} in IA may result from the extensive application of P fertilizers to agricultural soils (Table 27 & Fig. 61). In IA, there were significant differences between the control and background sites (67.74, 39.04; 117.76, 5.23; 167.25, 97.18; 105.40, 67.06, respectively), as shown in Fig. 61, which supports the hypothesis that the extensive application of P fertilizers is more common in IA than in KS and NE. The average concentration of PO_4^{3-} in three background sites in IA site 3 (64.34, 112.04), site 11 (12.47, 100.28), and site 14 (36.08, 77.11) were higher than the average concentration of soils from agricultural sample sites. Concentrations of PO_4^{3-} are higher in agricultural sample sites than the background for site 9, 26.00, 25.96 (Fig.61).

Table 27 Univariate analysis of PO_4^{3-} in Iowa (IA) shows mean, standard deviation (Std, Deviation), percentage (%).

Sample location	Mean	Std. Deviation	Median	Sum	Minimum	Maximum	%Total Sum
I1	94.36	67.74	52.30	566.18	49.06	186.48	0.07
I1BG	28.90	39.04	28.90	57.79	1.29	56.50	0.01
I2	117.764	21.05	114.78	706.58	90.52	154.22	0.09
I2BG	5.230	0.11	5.23	10.46	5.15	5.31	0.00
I3	64.34	37.77	64.89	386.04	1.46	104.83	0.05
I3BG	112.04	15.33	112.04	224.09	101.20	122.89	0.03
I4	163.10	17.38	156.07	978.61	143.52	189.33	0.13
I5	82.76	29.03	81.75	496.56	40.80	117.50	0.07
I6	137.72	10.78	139.69	826.35	118.12	147.58	0.11
I7	66.28	8.37	64.83	397.67	57.19	77.42	0.05
I8	167.25	30.92	177.68	1003.51	121.56	198.87	0.13
I8BG	97.18	11.49	97.18	194.37	89.06	105.31	0.03
I9	26.00	15.15	27.63	156.00	8.27	45.46	0.02
I9BG	25.96	0.29	25.96	51.93	25.76	26.17	0.01
I10	105.40	50.66	86.97	632.38	43.78	177.00	0.08
I10BG	67.06	0.42	67.06	134.12	66.77	67.36	0.02
I11	12.47	2.27	13.06	74.85	9.57	15.22	0.01
I11BG	100.28	6.40	100.28	200.56	95.76	104.81	0.03
I12	13.74	8.46	18.25	82.44	2.54	20.90	0.01
I12BG	4.04	0.66	4.04	8.07	3.57	4.50	0.00
I13	5.36	1.32	5.62	32.18	2.78	6.34	0.00
I13BG	3.82	2.26	3.82	7.63	2.22	5.41	0.00
I14	36.08	22.58	46.24	216.45	2.31	54.55	0.03
I14 BG	77.11	5.98	77.11	154.23	72.88	81.34	0.02
Total	73.07	58.00	63.46	7599.08	1.29	198.87	1.00

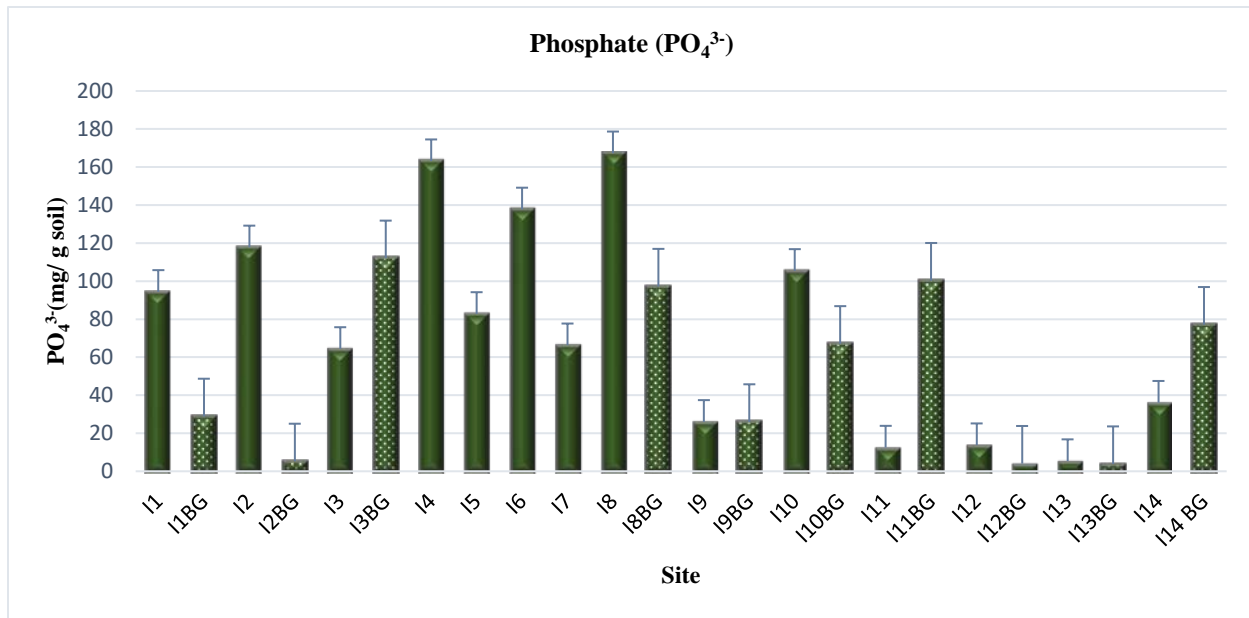


Fig 61 Phosphate (PO₄³⁻) level at the surface soil in the control and background (BG) sites in Iowa (IA)

The estimated average concentration in KS shows two sites presenting high concentrations of PO₄³⁻, sites 1 and 4, with average values of 18.58 and 20.04, respectively, while sites 3, 5, and 6 have lower concentrations of the nutrients (1.25, 3.83, and 0.79, respectively) (Fig. 62). Comparison of the surface soil and the C-horizon is shown in Fig. 61, with very low or zero PO₄³⁻ in the C-horizon, for sites 4, 5, and 6 of average values 20.04, 3.83, 0.79 (surface soil) and 10.80, 0.30, 0.00 (deeper soil) (Table 28). These observations support the opinion that PO₄³⁻ is significantly more concentrated in the surface soil than the C-horizon, if there are long-term accumulations of fertilizers in the agricultural soil.

Table 28 Univariate analysis of PO_4^{3-} in Kansas (KS) shows mean, standard deviation (Std, Deviation), percentage (%).

Sample location	Mean	Std. Deviation	Median	Sum	Minimum	Maximum	% of Total Sum
K1	18.58	13.45	16.92	111.47	1.03	42.62	0.34
K2	6.00	7.31	2.63	36.02	0.00	16.21	0.11
K3	1.25	1.00	1.47	7.48	0.00	2.33	0.02
K4	20.04	21.83	18.73	120.22	0.00	45.35	0.37
K4CH	10.80	0.19	10.80	21.60	10.66	10.94	0.07
K5	3.83	5.93	0.00	22.96	0.00	11.75	0.07
K5CH	0.30	0.21	0.30	0.61	0.16	0.45	0.00
K6	0.79	1.23	0.00	4.74	0.00	2.51	0.01
K6CH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	7.74	12.35	1.47	325.10	0.00	45.35	1.00

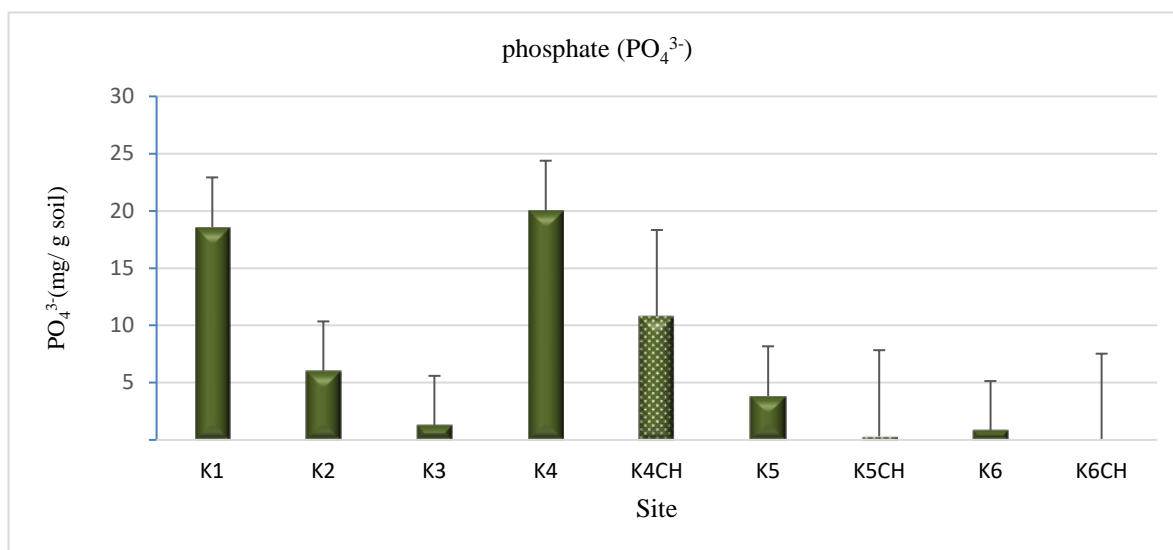


Fig 62 Phosphate (PO_4^{3-}) level at the surface soil in control and C-horizon (CH) sites in Kansas (KS)

The overall observation of PO_4^{3-} in NE point out the negative anthropogenic input of fertilizers or other chemical additives in the soil. The values were very low or zero in sites 1, 2, 3, 4, 5 6 (11.19, 6.87, 5.23, 1.35, 0.34, 0.52, respectively) (Table 29 & Fig. 63). Two unique average values of PO_4^{3-} have been observed in sites 7 and 8 (20.15, 50.07, respectively) (Fig. 63).

Table 29 Univariate analysis of PO_4^{3-} in Nebraska (NE) shows mean, standard deviation (Std, Deviation), percentage (%).

Sample location	Mean	Std. Deviation	Median	Sum	Minimum	Maximum	% of Total Sum
N1	11.19	6.23	11.36	67.12	4.28	18.90	0.08
N1CH	8.33	0.17	8.33	16.66	8.21	8.45	0.02
N2	6.87	3.34	6.84	41.22	3.36	10.43	0.05
N3	5.23	0.86	5.34	31.37	3.72	6.04	0.04
N4	1.35	1.47	0.75	8.07	0.49	4.28	0.01
N5	0.34	0.47	0.22	2.07	0.00	1.27	0.00
N5CH	0.40	0.18	0.40	0.81	0.28	0.53	0.00
N6	0.52	0.27	0.59	3.13	0.06	0.77	0.00
N7	20.15	29.87	1.07	120.89	0.50	58.74	0.14
N8	50.07	49.90	34.60	300.43	3.48	115.25	0.35
N8 BG	133.88	0.49	133.88	267.76	133.53	134.23	0.31

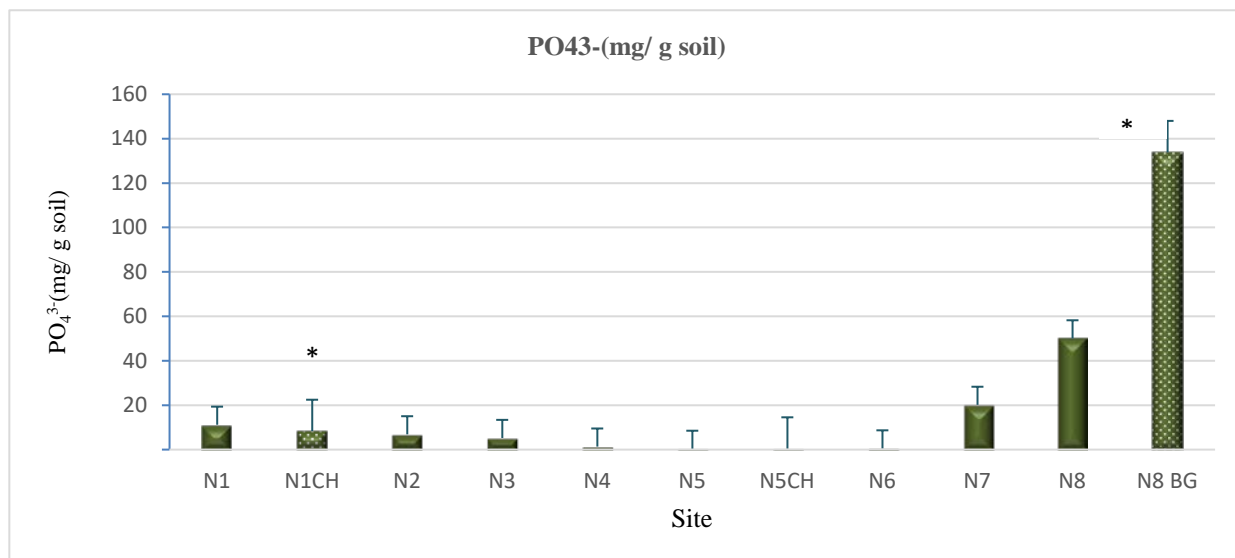


Fig. 63 Phosphate (PO_4^{3-}) level at the surface soil in control, C-horizon (CH), and background (BG) sites in Nebraska (NE)

7. MEASURING MICROBIAL ACTIVITY

7.1 Introduction

Measuring the microbiological community activity in the soil can determine directly the abundance and activity of microbial life. Thus, the measurement of CO_2 from soil respiration has been used as an indicator for the quality and fertility of different kinds of soil as well as for the quantification of influences of input practices on soil microbial activity, and it might provide critical insight into the efficiency of these biological processes (Haney et al., 2008).

Soil respiration means the measurement of the total CO_2 produced from the breakdown of SOM from different living organisms, including soil microbial decomposition, respiration process by plants roots, and animals (Lajtha et al., 2017). Several techniques have been developed for measuring CO_2 with various detectors, such as a gas chromatograph, the titration method, and an

infrared gas analyzer (IRGA). Haney et al. (2008) established that titration and IRGA methods are correlated with a significance of $r^2=0.95$.

In this research, a similar basis is applied for the evaluation of soil microbial respiration through jar incubation using IRGA. This method provides a quick measure of the soil respiration rate through a potential system of mechanization because of the electronic output. Bowling et al. (2001) obtained high CO₂ mixing ratios using bellows to extract the compressed air into an IRGA system for analysis with a high accuracy.

7.2 Measurements of Soil Respiration Rate (SRR), Called (CO₂ Measurements) Using LI-COR Gas Analyzer

This system describes a method for the determination of CO₂. Basal respiration was measured using a CO₂-H₂O analyzer to indicate overall soil microbial activity. The CO₂-H₂O analyzer is stable and highly selective to measuring gas. CO₂ consists of dissimilar atoms that absorb infrared radiation (IR). The IR sensor can measure water and other gases. The samples must be fresh or stored in the freezer (-20) before measuring CO₂. The procedure was modified following Dr Darrouzet Nardi (personal communication) to quantify CO₂. It was conducted for all 99 samples in the lab.

First, set up the instrument to measure soil respiration (CO₂ production). Second, test the instrument by injecting some air sample in the syringe and connect it to the computer program to make sure that all the parts of it work perfectly, without the loss of gas during the experiment for accurate measurements. Third, fill the gas standard bag with CO₂ from the supply tank filled at

known concentration for test the instrument to provide accurate measurements before measuring the CO₂ in the soil.

7.2.1 Set Up For Measurement of Carbon Dioxide (CO₂)

The core of the measurement system is the LI-COR 840 detector that achieves the detection of CO₂. The system is connected to the LI-840A instrument, set up on an optical bench. The apparatus of the analyzer includes several parts, and each one is applied for a specific job in the system to gain absolute CO₂ measures. The instrument set has a pump and is fitted with an air drying system and flow controllers for the reference and sample gases. The airflow is controlled using pump air that is connected to line tubing at a flow rate of ~100 mL/min. The system is powered by a pump/voltage 12 VDC and has a cable for data output.

7.2.2 CO₂ Detector System (LI-COR-840A)

LI-COR-840A is a high performance, stable and non-dispersive infrared gas analyzer, used for measuring CO₂ flux. It can measure CO₂ at a range of 0–20.000 ppm (parts per million, or μmol/mol), and H₂O at a range of 0–80 ppt (parts per thousand, or mmol/mol), which means 1 ppt = 1 mmol/mol. The airflow system was assembled by connecting several parts to allow airflow through the system. It involves internal chemical scrubbers for the observation of absorbing gases out of internal places that are a part of the optical path. Bare wire leads are connected to the terminal strip in the instrument at positions 1 and 2. The serial cable on the LI-840A is connected to the other end to a serial port on the computer. There are three applications to construct the LI-840A, zero calibration, span calibrations, and set up the parameters for recording

experimental data. The analyzer should be calibrated with ZERO-CO₂ before use for accurate measurements. The instrument tubing was set up in the circulation system, the pump was turned on with the switch the valves, simultaneously, to allow the air to be pulled from the atmosphere to a soda lime and flush of CO₂ lines. Then the CO₂ comes in from the injected samples and is captured by LI-CORE after the water is absorbed. The system consists of an air pump model TD-4N35 Brushless DC Diaphragm pump. The power supply is kept ~ 100cc/min, a Bogen 12VDC 300mA is used to pump the air gas into the analyzer and the data output is collected in the computer. There are two suitable CO₂ scrubbers containing soda lime and Ascarite II. They are used to track the mass of CO₂ molecules during the respiration of living organisms. The cell volume (ml) and the flow rate (ml/s) can be used to determine the system time constant (T) and measure of how quickly the system responds, as follows:

$$T = \text{Cell volume/Flow rate}$$

An air flow system was built to move the sample air streams through the analyzer. A short piece of tubing was connected, fitting the LI-480A, and then the air flowed in. Clear polyurethane ether-based tubing was connected to the scrubbers. An external air filter was installed into the sample air stream for before it enters the flow in port. A high accuracy flow meter (rotameter) model was used to maintain airflow of 2.5 LPM into the closed system. A one liter Tedlar bag, designed for vapor sampling at atmospheric pressure, is filled by CO₂ from the gas tank, disposable syringes with blunt needles was used to inject the CO₂ sample into the port. Jars with lids are required for withdrawing the air samples. The cap is screwed on and lid placed. Each lid has a rubber stopper (septum) in the lid. The system is connected to a laptop with a built-in serial port.

The Swagelok T-splitter is used for calibration with connects at both ends. The CO₂ sample was flowed to the standard gas bag and the pressure was registered on the gauge.

7.2.3 System Operation

The overall principle for CO₂ measurements is extracting the gas from the soil samples. CO₂ concentrations were monitored with the LI-COR 840A IR gas analysis (LI COR). The atmospheric air is pulled, respectively, in the connected tubes. Then, the air passes through the soda lime scrubber, past the pump, the flow meter, the port of injection, past the desiccant, then the filter, and into the IRGA. The system is open flow, but some of the continuing tubes can make the flow frequent, by adding extra tubing bits. Data can be grabbed using the R program for statistical analysis through grapping the peaks from the recorded measurements

The LI-840A is calibrated and followed by the span calibration. For the span process, this step can be conducted by connecting a span gas (non-zero calibration gas) with a known CO₂ concentration, as a primary standard to the input air stream. For the sample preparation and for obtaining the values for soil CO₂, the IRGA analysis was performed by digging samples from the surface soil to a depth of 0–15 cm. The soil samples were stored after collection in the freezer at -20°C until the CO₂ measurement. Fifty grams of moist soil samples were weighed and placed into 100 ml mason glass jars. The jars were sealed with one valve and incubated, undisturbed for 30 minutes. Subsequently, the soil CO₂ was measured. Each jar was connected to an IRGA system and the computer. During the operation, the pump pulls the ambient air to prevent dust from entering the system. Then, the air passes through a vertical column filled with soda lime scrubber for absorbing the atmospheric CO₂, removing all of it for a clean air stream. The air stream passes

the pump that is employed to draw atmospheric air through the open side of the valve. Therefore, the LI-CORE 840A can remain unattached to the vent capturing CO₂, using the soda lime, by turning the valve position, connecting it to the atmosphere. This air stream is regulated by the flow meter to a velocity 100 cc/min to ensure that all the CO₂ is removed and to get the reliable measurements. After calibration, the instrument air sample was injected by inserting the syringe into the jar-lid septum, drawing 5 ml from the jar into the syringe to put into the air stream, through the injection port, and then it passes through the desiccant (filled with the drying agent). Drierite can absorb water from the injected air sample to get absolute CO₂ measurements. Then, the air sample passes into the filter, finally into the IRGA, outputting the voltage. CO₂ produced from the microbial respiration is measured. The system is calibrated each time the sample is run. The reference gas sample, with known CO₂ concentration (449, 49 ppm CO₂), was used as the standard. The voltage output from the IRGA is measured by a data logger in ppm. The peak of each reading was recorded and stored by the IRGA software data logger and graphically presented in the program. The data logger in LI-CORE 840A was used to capture the CO₂ data measurements every second. After the data was collected, it was analyzed using an ANOVA-T. Test to determine the differences between the CO₂ concentrations in the soil.

8. RESULTS

Biological soil quality and fertility was examined by measuring the CO₂ in the soil using LI COR, designed and applied in this study. Monitoring of CO₂, using a simple and quick quantifying test is a good tool for examining soil fertility and for improving landform

administration. Concentrations of CO₂ in the soil were calculated according to the following equation:

$$\text{Soil respiration} = \text{MAX} \left(\frac{(\text{Sample ppm} - \text{Ambient})}{\text{Standard}} * 1000 * \left(\frac{1}{22.4} \right) * 0.237 \right) / \text{Dry weight} / \left((\text{Sample time} - \text{Start time}) * 24 \right), 0).$$

Table 30 illustrates the descriptive statistics of CO₂ measurements with umol CO₂ s⁻¹ in IA. The microbial activity was significantly higher/lower in the agricultural soils as compared to the background. The basal respiration mean was higher in the agricultural control regions, compared to the background sites of 2, 8, 9, 10, 11, and 14 (0.22, 2.47; 0.40, 0.58; 0.24, 0.56; 0.58, 0.72; 0.53, 1.31; 0.15, 1.02, respectively,) as shown in Fig. 64. This may indicate towards active microbial biomass. However, the sites 1, 3, 8, 12, and 13 showed lower CO₂ releases from the soils in the control sites, compared to the soils from background sites (0.70, 0.22; 0.48, 0.23; 0.40, 0.58; 0.47, 0.27; 0.62, 0.45, respectively) (Table 30, Fig. 64).

Table 30 Summary ANOVA statistics of CO₂ Concentrations in Iowa (I) and background (BG), standard deviation (std, deviation).

Site	Mean	Std. Deviation	Median	Sum	Minimum	Maximum	Variance	% of Total Sum
I1	0.70	0.94	0.10	6.30	0.00	2.34	0.89	0.08
I1BG	0.22	0.07	0.22	0.66	0.15	0.30	0.01	0.01
I2	0.22	0.14	0.23	1.99	0.00	0.48	0.02	0.02
I2BG	2.47	0.10	2.53	7.42	2.36	2.54	0.01	0.09
I3	0.48	0.18	0.44	4.31	0.27	0.82	0.03	0.05
I3BG	0.23	0.13	0.20	0.70	0.12	0.37	0.02	0.01
I4	0.43	0.20	0.46	3.89	0.06	0.67	0.04	0.05
I5	0.29	0.13	0.25	2.65	0.17	0.56	0.02	0.03
I6	0.28	0.21	0.28	2.55	0.00	0.56	0.04	0.03
I7	1.21	0.52	0.88	10.92	0.85	1.96	0.27	0.13
I8	0.40	0.20	0.46	3.64	0.14	0.68	0.04	0.04
I8BG	0.58	0.31	0.71	1.74	0.23	0.80	0.09	0.02
I9	0.24	0.09	0.26	2.20	0.11	0.36	0.01	0.03
I9BG	0.56	0.04	0.58	1.68	0.52	0.58	0.00	0.02
I10	0.58	0.10	0.57	5.20	0.45	0.70	0.01	0.06
I10BG	0.72	0.01	0.72	2.15	0.71	0.73	0.00	0.03
I11	0.53	0.14	0.56	4.78	0.25	0.70	0.02	0.06
I11BG	1.31	0.09	1.30	3.94	1.22	1.41	0.01	0.05
I12	0.47	0.14	0.46	4.25	0.34	0.79	0.02	0.05
I12BG	0.27	0.09	0.22	0.80	0.20	0.37	0.01	0.01
I13	0.62	0.13	0.62	5.55	0.33	0.82	0.02	0.07
I13BG	0.45	0.20	0.54	1.35	0.22	0.58	0.04	0.02
I14	0.15	0.12	0.15	1.35	0.00	0.42	0.02	0.02
I14BG	1.02	0.14	0.98	3.06	0.90	1.18	0.02	0.04

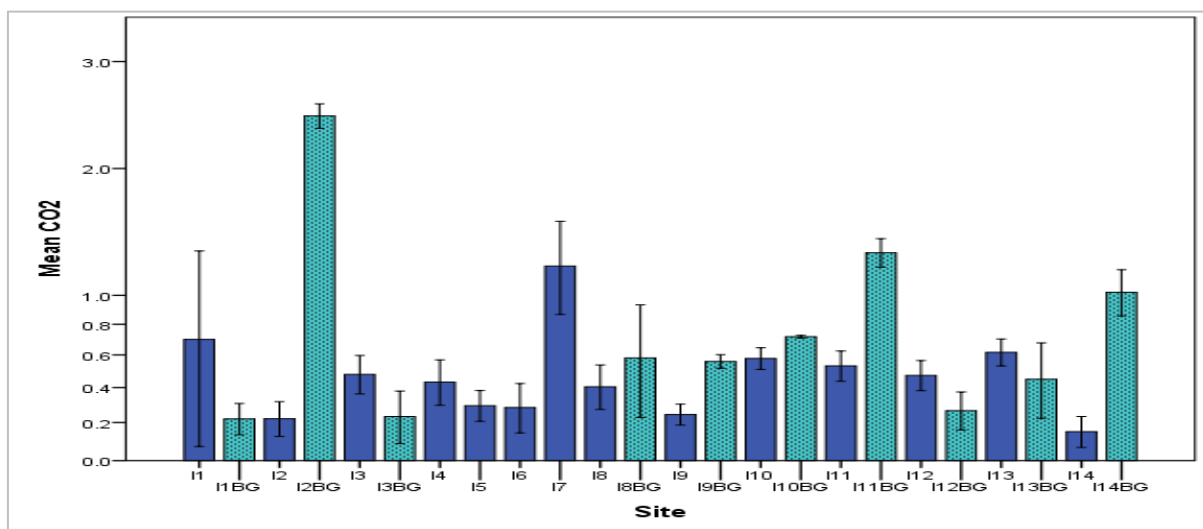


Fig. 64 CO₂ levels released in the surface soil in control sites, compared to background (BG) sites in Iowa (IA)

Table 31 shows the variations that have been observed between the sites, in KS, in the surface soil. The highest mean concentration was recorded in site 2, with a value 0.41; this might indicate negative anthropogenic application and that the CO₂ is naturally released from the living microbial biomass (Fig.65). However, another observation is the surface soils from sites 4 (0.50, 0.47) and 5 (0.39, 0.36) that show an increase in the released amount of CO₂ in the deeper soil at the same site (Fig. 65). Additionally, on the other hand, a very small amount was released from site 1 (Fig. 65). Based on these results, it is assumed that the soil in site 1 had a hard chemical-loading affecting the microbial activity.

Table 31 Summary ANOVA statistics of CO₂ Concentrations in Kansas (KS) and background (BG), standard deviation (std, deviation).

Site	Mean	Std. Deviation	Median	Sum	Minimum	Maximum	% of Total Sum
K1	0.04	0.06	0.01	0.41	0.00	0.19	0.02
K2	1.03	0.41	1.08	9.27	0.23	1.72	0.35
K3	0.18	0.20	0.09	1.66	0.00	0.52	0.06
K4	0.50	0.01	0.50	4.52	0.48	0.52	0.17
K4CH	0.47	0.01	0.47	1.40	0.46	0.47	0.05
K5	0.39	0.04	0.39	7.08	0.34	0.45	0.27
K5CH	0.36	0.03	0.36	2.16	0.33	0.40	0.08
Total	0.41	0.34	0.39	26.51	0.00	1.72	1.00

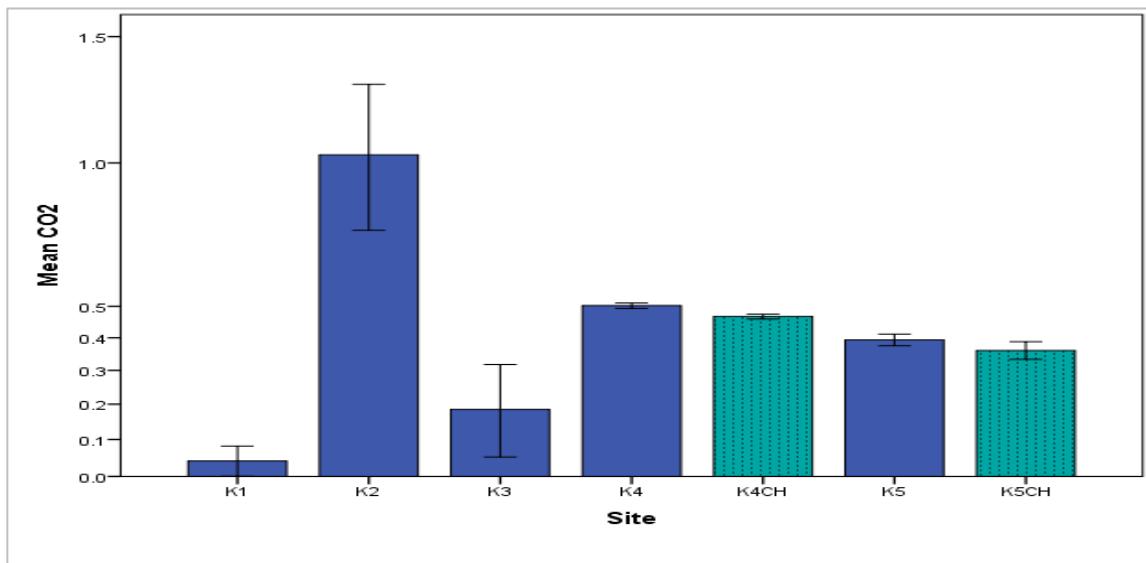


Fig. 65 CO₂ levels released in the surface soil in control sites compared to C-horizon (CH) sites in Kansas (KS)

There are significant differences among the control and BG sites. Generally, in the soil CO₂ respiration rate in NE, high soil respiration rates were noted in sites 2 (0.15), 3 (0.12), and 7 (0.12). Thus, the rate of CO₂ increasing probably is associated with high available C or greater microbial activity. However, Site 4 has low CO₂ respiration rate. Sites 1, 5, and 8 were nearly comparable (0.07, 0.06, and 0.07, respectively) (Table 32 & Fig. 66). Because the data presented in this study indicates that anthropogenic applications may potentially influence the microbial activities in the soil, if not, much more carbon will be available in the soil.

Table 32 Summary ANOVA statistics of CO₂ Concentrations in Nebraska (NE), C. Horizon (CH), and background (BG), standard deviation (Std. Deviation).

Site	Mean	Std. Deviation	Sum	Minimum	Maximum	% of Total Sum
N1	0.07	0.12	0.74	0.00	0.40	0.13
N1CH	0.06	0.01	0.18	0.05	0.06	0.03
N2	0.15	0.14	1.32	0.00	0.32	0.23
N3	0.12	0.09	1.09	0.02	0.23	0.19
N4	0.03	0.04	0.24	0.00	0.11	0.04
N5	0.06	0.06	0.57	0.00	0.15	0.10
N5CH	0.00	0.00	0.00	0.00	0.00	0.00
N6	0.17	0.11	0.67	0.00	0.26	0.11
N7	0.08	0.11	0.40	0.00	0.20	0.07
N8	0.07	0.06	0.64	0.00	0.17	0.11
N8BG	0.00	0.00	0.00	0.00	0.00	0.00
Total	0.08	0.10	5.83	0.00	0.40	1.00

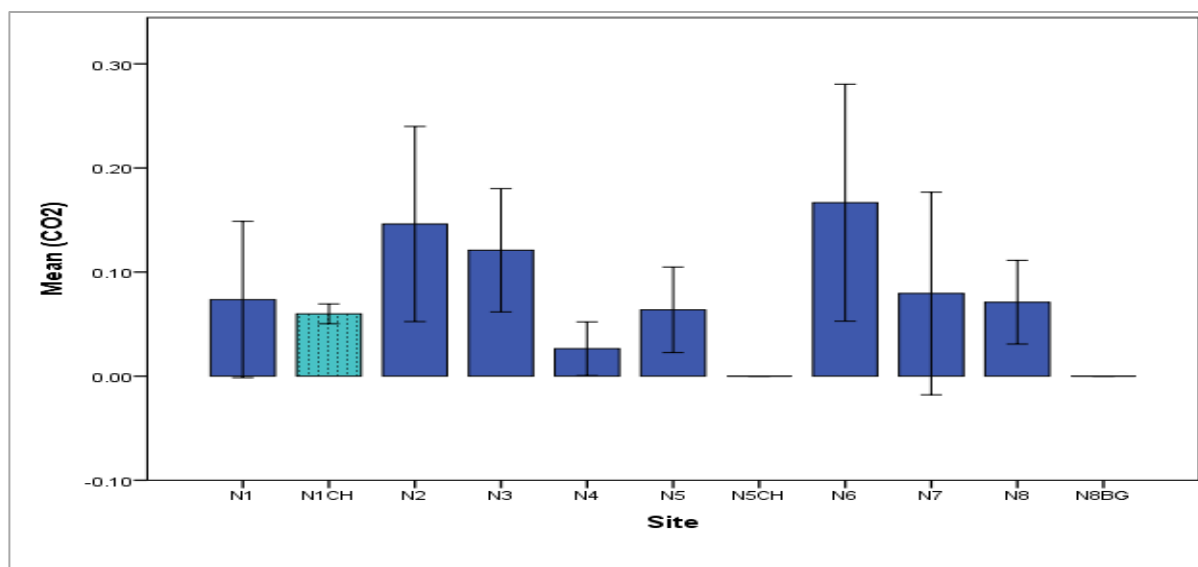


Fig. 66 CO₂ levels released in the surface soil in control sites compared to C. Horizon (CH), background (BG) sites in Nebraska (NE)

9. DISCUSSION

Soil health is intricately associated with sustainability, is dependent on nutrient retention capacities and soil reactions. The increasing use of chemical additives, such as fertilizers, pesticides, insecticides, and herbicides are resulting in nutrients being removed from the soil, more than is applied to it annually; therefore, the average of the nutrient balance is mostly negative (Sillanpaa, 1982). Agricultural applications management may have an excessive influence on the soil microbial communities for their importance in crop rotation and soil sustainability (Palm et al., 2001).

Environmental regulations such as United States Environmental Protection Agency (USEPA) have published guidelines for the maximum concentration (MCL) for fertilizers in the

USA (USEPA, 1999, California code of regulations, 2001, & USEPA, 2002). Even though there are permit guidelines from maximum allowable concentration (MAC), for chemical additives such as fertilizers, more regular and yearly tests must be conducted to minimize its utilization. On the other side, the chemical inputs, such as P fertilizers in agricultural soils, might be higher than the outputs through leaching and plant uptake (Molina et al., 2009).

The application of fertilizers is one of the primary factors responsible for a dramatic increase in productivity in the farming sector (Kabata-Pendias, 2011). Due to the increasing demand for food demand, fertilizers are widely used to increase the crop production in mid-continental USA. A most significant concern is that if they exceed their critical concentration threshold, they can cause environmental toxicological risks, and affect human health and other organisms. These states, located in the nation's corn belt, are three out of the top nine states responsible for approximately 50% of the nation's fertilizer use. NH_4^+ , NO_3^- and PO_4^{3-} have been frequently used for plant growth. Heavy metals were included in zinc micronutrient fertilizers (Mortvedt, 1985). Therefore, the expensive use of agrochemicals in farms might be the source of these chemicals.

In 1996, consumption of nitrogen fertilizers, such as nitrates, ammonium salts, and liquid ammonium, in the United States, was estimated to be 23, 412,475 tons. The largest amount of nitrogen fertilizers was consumed in the West North-Central region, at 7,547,376 tons, and in the East North-Central region, at 4,568,739 tons. It was investigated that IA is one of two states that consumes the largest amount of nitrogen fertilizers in USA (US Environmental Protection Agency, 1999).

Anthropogenic genesis in this research refers to extensive fertilizer applications, in some regions, for agricultural purposes. In this study, it is noted that IA was most abundant with nutrients than KS and NE, since most of IA is agriculturally fertilized. The concentrations of the nutrients in the soil increased or decreased according to many factors soil properties, chemical additives, fertilization, microbial activity interactions.

Generally, the PO_4^{3-} was highly enriched in the surface soil, as compared to NO_3 , NH_4 . Concentrations of nutrients (NO_3^- , NH_4^+ , and PO_4^{3-}) varied between soil sites in IA, NE, and KS, and the nutrient availability showed significant difference between the control, background, and C-horizon sites. The highest concentrations of As, Cd, Cu, Cr, Ni, V, and Zn were investigated in the component of phosphorus fertilizers (Molina et al., 2009).

Possible human applications can contribute high concentrations of P and Pb in the surface soil, across conterminous United States (Woodruff et al., 2017). Though the source of elements might come from lithology or natural processes, it is excepted that the anthropogenic inputs increase the elemental concentrations in the surface soil, when compared to the concentrations in the deep soil that are determined naturally (Woodruff et al., 2015).

Long term applications of P fertilizers inputs in agricultural regions might result increasing and accumulating of heavy metals specially, As and Cd, in the surface soils, which exceed the output rates consumed or absorbed through leaching and planting (Molina et al., 2009). If the chemical concentration in surface soil is higher than the concentration in the deeper soil layer (C-horizon), this may support the hypothesis that long-term fertilization is one of the sources of these accumulated nutrients. It is suggested that high P concentrations in the surface soil (A-horizon) in midcontinent regions is caused by human P-loading over time (Woodruff et al., 2015). The results

of PO_4^{3-} observed in this study support the idea that extensive agricultural activities, using phosphate fertilizers or manure, in IA, is probably causing the increase in P concentrations in the surface soil, as compared to the deeper soil (Fig. 61, 62, & 63) (Woodruff et al., 2015). The minimal contributions of these chemicals from natural geological process in the study area reflect the idea that the chemicals are loaded into the soil from agricultural activities. This may affect negatively on the microbial activity in the soil.

It is important to understand if the microbial communities have adaptive mechanisms to adjust or react to the long term chemical additions, when the chemical concentrations exceed their tolerance levels in the agroecosystems. Fertility of the soil can be determined through the measurement CO_2 respiration from different soils because it indicates to living organisms in the soil (microbial activity) of the bio ecosystem, and is associated directly with other non-living features of the soil, such as organic matter content, and nutrient availability (Singh et al., 2011).

CO_2 respiration is used to measure the effects of human inputs on microbial activity in the soil (Haney et al., 2008). The data obtained from this study suggest that the higher amount of CO_2 released likely refers to healthy soils and less anthropogenic influence, as shown in the study area. Besides, the microbial cells need organic carbon for respiration, increased CO_2 rate in these soils, is almost related to the high abundance of C in the surface soil, which reflects the active microbial biomass. Increased CO_2 released from the surface soil is expected, since oxygen is available in the surface soil. These findings, through the mentoring of CO_2 flux, shows that there is a potential association between soil fertility and soil microbial respiration.

Land management practices affect the soil C component and may increase C outputs from the soil more than the inputs (Singh et al., 2011). Study of multi factor analysis of soil respiration

is very limited (Singh et al., 2011). More attention should be focused on the measurements, overtime, of the multifactor study of CO₂ enrichment in the soil.

10. CONCLUSION

Although understanding all four variables is crucial to fully grasp the interactions needed to develop an unbiased conclusion, wide ranges of human activities, using fertilizers, can cause serious environmental problems. Many researchers have studied the overloading of agricultural additives in different regions in the USA that may cause impressions on the natural soil sustainability, but there are rare or no study or research focusing on the source of those chemicals and the influence of anthropogenic activities on the soil in the Midwest regions of USA, which are almost predominantly agriculture-based states. Extensive future research is recommended in order to investigate the reliability of the conclusions of this study. Moreover, controlling and validating fertilization practices in the agricultural soil, the study of past cropping patterns or land management, fertilization processes, local environmental factors, and plant conditions are required for better land management and healthy agricultural soil sustainability.

The possibility of having other sources than simply geologic and anthropogenic (fertilizers and pesticides) is ones must not be overlooked and cannot be rejected. Collecting and analyzing data of the major elements found in fertilizers and pesticides is also an important subject for future research. By understanding the source of contaminations, a plan of action can be derived in order to prevent further environmental risk to the biosphere.

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