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Pollution indices assessment of metal concentrations in Karabuk soil samples

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Abstract
Soil pollution refers to the contamination of soil by harmful substances that can have adverse effects on plant and animal life, it also negative affects the health-being of humans. The sources of soil pollution include industrial activities, agricultural practices, mining and transportation activities. The contaminants in soil can include heavy metals, pesticides, herbicides, fertilizers, petroleum products, and other chemicals. These contaminants can seep into the soil and accumulate over time, making the soil unsuitable for agriculture or other uses. Heavy metals are a significant concern in soil pollution due to their persistency and potential harm for living organisms. Therefore, it is essential to evaluate metal contamination in soil using ecological risk indices to protect human health. This assessment can help identify potential risks and enable effective management of contaminated sites. This study aimed to assess of the metal pollution levels, including Arsenic (As), Cobalt (Co), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), and Zinc (Zn), in soil samples from Karabuk using various ecological risk indices. These indices included the geo-accumulation index (Igeo), enrichment factor (EF), contamination factor (CF), contamination degree (Cd), pollution load index (PLI), and potential ecological risk (PERI). Furthermore, statistical techniques such as correlation and factor analysis were employed to determine the underlying sources responsible for these metals. Based on the results of the Cd, PLI, and PERI, it was found that the soil at T7 exhibited a very high degree of contamination, was moderately to highly polluted, and posed a moderate ecological risk, respectively. The results of the pollution indices suggest that the sources of pollution in the Karabuk soil samples are anthropogenic, meaning they are a result of human activities like industrial processes and improper waste disposal.
Keywords: Karabuk, Metal pollution Soil, Pollution indices, Risk management

INTRODUCTION

Environmental pollution such as soil, water and air pollution have become an important trouble for human life in the last years. Research-based studies and assessments are useful for understanding the state of environmental pollution and providing reference for further studies. Soil is crucial for human survival and societal development and its quality directly impacts food security, agricultural product quality, human health, and social progress. Unfortunately, as the economy and society continue to grow, human activities have caused a surge in soil pollution, particularly from heavy metals. This pollution disrupts the ecosystem balance and leading to decreased agricultural output and quality. Moreover, heavy metals enter the human body through the food chain and other pathways, accumulating over time and posing significant risks to human health (Zhao et al., 2022; Tian et al., 2021: Zhai et al., 2018). Metal pollution is commonly contaminants in soil ambient especially As, Co, Cr, Pb, Cu, Zn and Ni.. The founding of more than normal amounts of various metals with the rapidly development of urbanization and industrialization in the soil cause negative effects for environment and human health (Sezgin et al., 2022; Zhao et al., 2022). In recent years, there has been a growing local and global concern regarding the assessment of pollution and soil remediation techniques. This is due to the detrimental effects of long-term exposure to metals, particularly heavy metals, which can result in adverse health outcomes such as lung cancer and bone fractures. (Rai et al., 2019; Chen et al., 2016). Numerous studies used different techniques have conducted for remediating soil contaminated with heavy metals. These methods include in-situ approaches like surface capping, encapsulation, electro kinetic extraction, soil flushing, chemical immobilization, phytoremediation, and bioremediation, as well as ex-situ techniques such as landfilling, soil washing, solidification, and vitrification. The primary focus of these techniques is to reduce the concentration of heavy metals in the soil, making them less accessible or bioavailable. While these methods have shown high efficacy, they are often expensive, environmentally harmful, and time-consuming. Consequently, there is a need to implement advanced technologies for pollution assessment and remediation that can effectively and safely address heavy metal-contaminated soil (Zhao et al., 2022: Nayak et al., 2020). Assessing heavy metal pollution in soil holds great significance in combating and mitigating the escalating issue of soil pollution. The commonly employed approaches for assessing heavy metal pollution locally and globally can be broadly categorized into index methods and model methods. Index methods encompass single pollution, pollution load and cumulative indexes, and more. Model methods include the enrichment factor, potential ecological risk index and others. These assessment techniques provide valuable insights into the extent of heavy metal pollution in soil and help guide remediation efforts (Zhao et al., 2022).

In this study, pollution indexes such as enrichment factor (EF), contamination factor (CF), geo-accumulation index (Igeo), contamination degree (Cd), and pollution load index (PLI) and potential ecological risk index (PERI) were calculated for evaluating metal pollution level in soil samples of Karabuk. The amounts of the metals investigated in the Karabuk soil sample were obtained using data from an open-source report published by the Turkish Atomic Energy Authority in 2015 (Turkish: Türkiye Atom Enerjisi Kurumu – TAEK). There are many elements analyses in this report. However, As, Co, Cr, Cu, Ni, Pb, and Zn concentrations were evaluated for the pollution assessment for Karabuk soil in the study. The Fe values in the report were utilized as a reference metal.

Arsenic

Arsenic (As) is one of the naturally occurring elements in abundant quantities within the earth soil. Arsenic has existed in the air, in water and on the earth surface soil. Arsenic has two forms such as organically and inorganically forms. The latter is extremely toxic. Arsenic is a chemical element without taste or smell. In addition to its natural presence in the soil, arsenic is also released from industrial activities such as the manufacture of pesticides, dyes and in the metallurgical industry (Shrivastava et al., 2015).

Uses of Arsenic

Although As is known as a toxically element, it is used in industry. Arsenic is used in the manufacture of pesticides such as rat poison and insecticides. It is also used in the wood industry. It keeps the wood for a long time without decomposition. İt thus plays a role of wood protector. It can also be used in the glazing industry.

Arsenic in Soils

Arsenic can occur in organically and inorganically forms in soils. Generally arsenic is found as ions in soils. Arsenide(As^{+3}) is most often found in reducing environments such as waterlogged soils and arsenate(As+5) in well-drained surface soils (Roberts et al., 2010). Arsenide(As^{+3}) compounds are generally more mobile than arsenate(As^{+5}) compounds in soils. Thus arsenic through arsenites can infiltrate soil surfaces to groundwater (Shumlas et al., 2016).

Arsenic Pollution and Public Health

Arsenic present on the surface of soils can contaminate groundwater through infiltration. The consumption of contaminated water has a very serious impact on public health. According to the WHO, contaminated groundwater is the greatest threat from arsenic. Inorganic arsenic is naturally present at very high concentrations in groundwater in many countries. Drinking water, crops irrigated and food prepared with contaminated water are the sources of arsenic exposure. Arsenic and its inorganic forms have been classified as carcinogenic to humans since 1980 by IARC. Epidemiological researches have shown that chronic exposure to arsenic by inhalation is the cause of primary bronchial cancers. While chronic exposure by ingestion of contaminated water is the cause of lung, skin and bladder cancers (IARC, 2012).

Cobalt

Cobalt (Co) is a chemical element discovered in 1735 by Georg Bandt. It is a naturally occurring hard gray heavy metal with atomic number 27. Cobalt is a significant element in the metabolism and grow up for animal and vegetable cells. İt is generally found in inorganic compounds in several forms. Its most abundant forms are its 2+ ions and 3+ ions (Mahey et al., 2020). It also exists in a radioactive form of cobalt. This latter form of cobalt comes from nuclear waste and nuclear accidents. Generally, the presence of cobalt in the environment results from the burning of coal and mining of cobalt-containing ores. The production and use of cobalt-based chemicals are also sources of cobalt in the environment. Cement industries and carbide tool grinding plants are also responsible for cobalt leaching. Cobalt is also found in the fumes of thermal power plants or incinerators and in the exhaust of combustion engine vehicles (INERIS, 2006; Abraham and Hunt, 1995).

Uses of Cobalt

Cobalt is a heavy metal that is widely used in industry. Many industrial applications use cobalt. It is used in metal form or as a compound with oxides, sulfate, sulfide and chloride. It is used, among other things, in the composition of resistant alloys used in the electrical, aeronautical and automotive industries, permanent magnets, cutting tools, surgical alloys (prostheses), agricultural fertilizers and animal feed additives. Cobalt salts are used as pigments (glass, ceramics, paints, varnishes) (INERIS, 2006). Cobalt is also used in the manufacture of batteries. It also knows a pharmaceutical use as veterinary products, and feed additives for cattle. At low doses, cobalt is also an essential trace element, constituent of vitamin B12 (found in meat and dairy products) (URL-1).

Cobalt in Soils

Cobalt is a heavy metal naturally present in soils. It is also present in water and rocks. Cobalt can be found in surface water through rainwater runoff. In soils, cobalt can react with other compounds or adsorb to soil particles. It may also adsorb to sediments in water. Soils near mining and smelting operations are very rich in cobalt (URL-1).

Cobalt Pollution and Human Health

Cobalt has been classified by the IARC since 1991 and revised in 2006 as a metal that may be carcinogenic to humans if exposed by inhalation. With the conclusions of the IARC, the European Union has classified cobalt sulphate in group 1B; that is to say, as a substance that should be regarded as carcinogenic to humans through inhalation exposure (IARC, 2012).

Chromium

Chromium (Cr) is one of the most abundant elements in the earth surface soil and exists in the environment as Cr (III) or Cr (VI). Other intermediate valence state of Cr also exist in the natural environment, but they are mainly not stable. Pure chromium has a silver white color and is obtained by reaction of aluminum and chromium oxides. This reaction is done by electrolysis or from chromium iodide (Cary, 1982).

Uses of Chromium

Chromium is widely used in industry for the manufacture of rust resistant surfaces. Hard chrome plating is a very hard and slippery compound used in anti-wear coatings. It is less expensive and allows a better protection of new parts at acceptable prices. It is an electrolytic coating that is applied to metals such as steel, copper, bronze and aluminum alloys. It can be found in almost all sectors of activity such as the automotive, steel, mechanical, food, aeronautical, hydraulic, printing, glass, foundry, metallurgy, recycling of industrial waste, paper, tires, textiles, plastics, tooling and medical (Ashley et al., 2003).

Chromium in Soils

The manner in which chromium behaves in soil is significantly impacted by its speciation, which is determined by the soil's pH and redox potential. Typically, chromium is predominantly found as a chromium(III) among of their forms in mostly soil. This form is comparatively insoluble, unreactive, and poses a low risk of toxicity to living organisms (Ashley et al., 2003; Barnhart, 1997). However, certain conditions can result in the presence of chromium(VI) in the soil, such as oxidizing conditions, which can give rise to highly soluble, mobile, and toxic forms of chromium such as CrO_4^{-2} and $HCrO_4$ (James et al., 1997). Under anaerobic conditions where oxygen is limited, chromium(VI) can be reduced to chromium(III) through the presence of S^{-2} and Fe^{+2} in the soil. Such reduction can also take place in soils that have adequate organic matter and a low pH. In contrast, the oxidation of chromium(III) to chromium(VI) in soil can take place in the presence of organic matter, oxygen, manganese dioxide, moisture, and high temperatures, as seen during brush fires (EPA 1990b; Salem et al., 1989; Calder, 1988; Cary, 1982).

Chromium Pollution and Public Health

Chromium especially Chromium (IV) is a heavy metal toxic to humans. It has several forms that each have a different degree of toxicity. Among others, we have the nanoparticle, oxide and valence forms. The nanoparticle form can have adversely effect on the respiratory system following inhalation in high concentrations. In addition to the presence of Chromium in water and soils, it is also found in some organisms such as food plants. It can therefore through the food chain cause impairment of human health. Excess inhaled Chromium (IV) can cause nosebleeds or even nasal irritation. However, it is also important to mention that Chromium (III) is necessary for humans, whose deficiency can have cardiac consequences or even on diabetes (Cary, 1982).

Copper

Copper(Cu) is a reddish metal. The earth's crust contains an average of 50 mg/kg. It is corrosion resistant and has excellent thermal and electrical conductivity. It is an essential element for living organisms. Copper has 29 isotopes, two of which are natural and stable: ^{63}Cu and ^{65}Cu. The others are radioactive and artificially produced. Copper is a non-renewable resource, but it is fully recyclable and can be re-smelted and reused. In 2008, 2.5 million tonnes of copper were recycled in Europe, which is almost 45% of total copper consumption. The main producing countries are Chile, China, Peru and the USA. Global reserves are estimated at 630 million tonnes, while global production was 18.1 million tonnes in 2013 (URL-3).

Uses of Copper

Copper is used in the electrical, electronic and telecommunications industries, for power cables, computer chips, television cables and batteries. It is used in construction for plumbing, fittings and valves. In architecture, its compounds give roofs a characteristic green color. Copper is also used in transport, machinery, marine and armaments. Finally, copper's antibacterial, fungicidal and algicidal properties make it a product used in hospitals and for aquaculture. Some of its isotopes also have medical applications (URL-3; Catherine, 2016).

Copper in Soils

Copper mining and refining activities are the main sources of copper in soils. Other sources of copper contamination in soils include landfill sites, domestic sewage, fossil fuel combustion, pulp and paper, use of organic and chemical fertilizers and forest fires. Copper alone remains immobile in soils. It gains mobility when transferred to water or the atmosphere. It is adsorbed by clays, organically matters, carbonates and iron and manganese oxides and hydroxides (Yarlagadda et al., 1995). Copper can also react with carbonates.

Copper Pollution and Public Health

Excess copper is toxic to aquatic organisms, vascular plants and farm animals. In humans, drinking water with excessive copper can cause nausea, vomiting, cramps and diarrhea. Chronic ingestion of excessive amounts of copper can cause irreversible liver and kidney damage, even death (Catherine, 2016). Excessive ingestion of copper in humans can result in severe mucosal corrosion, extensive capillary damage, liver and kidney damage and central nervous system irritation followed by depression (Singh and Kalamdhad, 2011).

Nickel

Nickel(Ni) is a chemical element found almost everywhere in the environment. İt is a bright white and hard metal. Its average concentration on the earth's crust is about 20mg kg^{-1}. İt can be present in air, and in airborne particles. Nickel originates from the incineration of household waste, the burning of coal and wood.

Uses of Nickel

Nickel is an important element in the manufacture of stainless steel, non-ferrous alloys such as coins and in the manufacture of Ni-Cd batteries. Nickel is also used as a catalyst in organic chemistry (Pichard et al., 2006).

Nickel in Soils

In nature, nickel can be found in different oxidation states (+II, +III and +IV) but is mostly found in its +II state. Its solubility in water varies greatly depending on its chemical form. Nickel compounds such as acetate, chloride, nitrate and sulfate are highly soluble, followed by carbonates and hydroxides, sulfides and disulfides, while the oxides are practically insoluble (WHO, 2021). the location of nickel in the soil is linked to its origin. Thus, geogenous nickel is adsorbed preferably on iron and manganese oxides, whereas nickel of anthropogenic origin tends to remain exchangeable and to bind to organic matter and carbonates (Baize, 1997). Like other metals, the mobility of nickel increases with the acidity of the environment.

Nickel Pollution and Public Health

Nickel compounds are mainly absorbed by humans via the respiratory route and can cause chronic bronchitis and asthma. Intoxication via skin absorption is not to be neglected. Indeed, some costume jewelry contains traces of nickel and causes numerous skin reactions, a phenomenon regularly seen in young girls. Nickel also has a chronic toxicity since the International Agency for Research on Cancer (IARC) classifies nickel compounds as carcinogenic to humans and metallic nickel as a possible human carcinogen (Pichard et al., 2006).

Lead

Lead (Pb) is an element present in several natural minerals such as sulphites, sulphates, carbonates, oxides, hydroxides and phosphates. The main mineral sources of lead are galena (PbS), cerussite ($PbCO_3$) and anglesite ($PbSO_4$). We most often encounter lead compounds associated with minerals composed of zinc, cadmium, silver and copper (Catherine, 2016; Laperche et al., 2004, Pichard, 2003).

Uses of Lead

The contamination caused by the use of lead in paint makes him infamous. Indeed, cerussite and anglesite (a lead carbonate and sulphate, respectively) providing a white color pigment were used for water pipes, gasoline additives, cable sheaths and in agricultural pesticides. In recent years these uses have greatly diminished due to pollution caused by lead. (Laperche et al., 2004; Mercier, 2000; Bonnard et al., 2006). Many scientific works spread the concerns around its use. In addition, it has been widely used in printing, metallurgy and the manufacture of accumulators, capable of providing much more energy than an ordinary battery (Bonnard et al., 2006, Laperche et al., 2004). Today, lead is used in the composition of electric batteries, automobile radiators, ammunition and alloys (Pichard, 2003). Finally, recent technological advances have favored the emergence of the use of lead. For example, lead sheet provides effective protection against radiation used in medical imaging and radiotherapy (Catherine, 2016). The fields of use of lead and its various compounds are given in the Table 1.

Lead in Soil

Since lead is not very mobile, it attaches itself to the upper surface of soils. Lead is mainly adsorbed on clays, oxides and hydroxides, carbonates and organic matter (Basta et al., 2005). The lead-organic complexes formed are stable. An alkaline pH results in the precipitation of lead in the form of carbonates or phosphates; its complexation with organic matter makes it more soluble. According to Yarlagadda et al. (1995), lead can be found in all particle size fractions of contaminated soils.

Lead Pollution and Public Health

Humans absorb lead by three main routes; (1) inhalation of dust or fumes of lead or lead oxides, (2) ingestion of food, dust, soil or paint containing lead, (3) cutaneous absorption, for example, organic and fat-soluble lead used in the composition of creams and cosmetics (Laperche et al., 2004; Lyn, 2006; Miquel, 2001). Thus in children from 0 to 5 years old, lead poisoning mainly takes place by ingestion of dust or contaminated soil. The harmful effects of lead on the health of young children, and in particular on the development of the nervous system, are all the more recognized as they often result from an unfavorable socio-economic situation (unsanitary housing or located near industrial areas) (Catherine, 2016). Lead is physiologically and neurologically toxic to humans. Acute lead poisoning can lead to dysfunction of the kidneys, reproductive system, liver and brain. Lead can be harmful even in very low concentrations.

Lead toxicity can lead to a range of harmful effects on the body, including teratogenicity, inhibition of hemoglobin synthesis, and damage to the central and peripheral nervous systems. Other chronic symptoms such as anemia, gastrointestinal problems, and anoxia may also arise. Pregnant women may experience difficulties, and individuals may develop high blood pressure and joint/muscle pain. In summary, lead poisoning can result in an overwhelming sense of exhaustion and fatigue. It is also capable of causing damage to the gastrointestinal system and urinary tract thus causing bloody urine (Singh and Kalamdhad, 2011).

Table 1. Common uses of lead and its compounds (Catherine, 2016)

Application domain	Chemical formula
Cotton printing	$Pb(CH_3COO)_2$
Wood conservation	$PbC_{14}H_{30}O_2$
Cosmetics and disinfectant	$Pb(CH_3COO)_2$
Enamel, glaze	PbS
Semiconductor	PbS, PbSe, PbTe
Catalyst for polyurethane polymerization	$PhPb(OAc)_3$
Ceramic	$PbSi_2O_5$
Putty and matches	PbO, PbO_2 , Pb_3O_4
Makeup	PbS
Textile dyeing	$Pb(NO_3)_2$
Oxidizer in fireworks	PbO_2

Zinc

Zinc(Zn) is a blue-gray metal, moderately reactive in water, oxygen and CO_2. It has the property of releasing hydrogen in the presence of weak acids. The earth's crust contains a mean of 70 mg kg^{-1}. This makes it the 24th most abundant element. It is an essential trace element involved in cell development in particular and present in nearly 200 enzymes (Abarnou et al., 2000).

Uses of Zinc

Zinc is mainly used for the galvanization of iron and the production of alloys. It is used in the manufacture of conductive agents for electrical and electronic equipment. It is also used in construction, in the automotive industry and for railways. Its compounds are used to make plastics, pigments, lubricants, pesticides and fungicides. Zinc is used in the pharmaceutical industry as a dietary supplement for the treatment of deficiencies and dermatoses. It is involved in the human body in the maintenance of immune function, blood clotting, wound healing, thyroid function and spermatogenesis (URL-2).

Zinc in Soils

Industrial and mining activities, agricultural sludge spreading, road transport and waste incineration are the commonly resources of zinc in the environment and soils. Zinc is most often found in the oxidation state, as ZnS, and in different ionic forms in soils. Although mobile, it is most often found at the soil surface. The half-life of zinc in soil is estimated to be about 80 years (Catherine, 2016).

Zinc Pollution and Public Health

Zinc is a trace element necessary for the proper functioning of the human body. It is essential for proper development of the human body, animals and plants. A deficiency of zinc can lead to malfunctions such as dermatitis, growth retardation and poor tissue healing. Conversely, excess zinc is also toxic to living beings. In humans, the routes of exposure are ingestion (through food), inhalation (workplace fumes) and skin contact (cosmetics). Zinc chloride ($ZnCl_2$), zinc oxide (ZnO), zinc sulphide (ZnS) and zinc sulphate ($ZnSO_4$) are the most widely studied compounds in zinc toxicity. Effects of excessive zinc exposure include gastrointestinal discomfort, lung irritation (alveolar fibrosis and bronchopneumonia), anemia, liver and kidney damage, endocrine and neurological disturbances, miscarriage, and cancers (prostate and gonads) (URL-2; Naert, 2017; Catherine, 2016).

MATERIALS AND METHODS

Karabuk province is located in the Western Black Sea region of Turkey, between the latitudes of 40°57′ and 41°34′ North and the longitudes of 32°04′ and 33°06′ East. The province has a surface area of 4,145 square of kilometer and a population of 252.058 according to 2022 estimates. The economy of Karabuk has developed based on the iron and steel industry. KARDEMIR (Karabuk Iron and Steel Works), one of Turkey's important industrial facilities, has been active in the province since 1939. In addition, the rolling mills and foundries established in the city are other institutions related to the iron and steel industry. Iron trading, transportation, and forestry are also important economic activities in the city. In recent years, the provincial economy has begun to diversify, with the establishment of textile, marble, forestry, and cement industries. The economy of the central district is mainly based on manufacturing. Additionally, Safranbolu district, with its rich historical past, is an important tourism center among the districts (URL-4). In the report, pollution indexes were evaluated for selected metals at only 37 specific locations out of the total sample points. One particular sample point, labeled as 78T008 in the report, was chosen as a reference soil sample. This specific sample point was distinct from the other 37 points evaluated and was selected due to its significantly lower metal content compared to the rest. The graphical representation of all the investigated sample points can be found in Figure 1. Collecting and analysis of Karabuk soil samples in the TAEK report, 2015 are defined as below:

Soil samples were taken from areas 20 cm in diameter and 10 cm deep from the surface. While selecting the sampling sites, care was taken to ensure that the sample place was flat, uncultivated and not accumulated by erosion. In addition, samples were taken after cleaning the stone, grass, grass and garbage from the soil surface to be sampled. Each soil sample was obtained after mixing several samples from an area of approximately 400-500 m^2 and the samples were placed in nylon bags and numbered. After, all collected samples were dried at the room temperature for 1 week in the laboratory. After drying all samples were powdered and sieved using a 200 mesh diameter stainless sieve for trace elements analysis. Trace element analyzes have been performed using the Wavelength Dispersive X-ray Fluorescence (WDXRF) method. For XRF analysis, 12 g powder soil samples have mixed with 3 g cellulose in the agate mortar for 5 minutes. Then, to pellet the samples, they were pressed for 3 minutes using a 25-ton hydraulic press with 40 mm diameter steel pellet containers. Finally, prepared pellets have been analyzed by WDXRF spectrometry to determine trace elements.

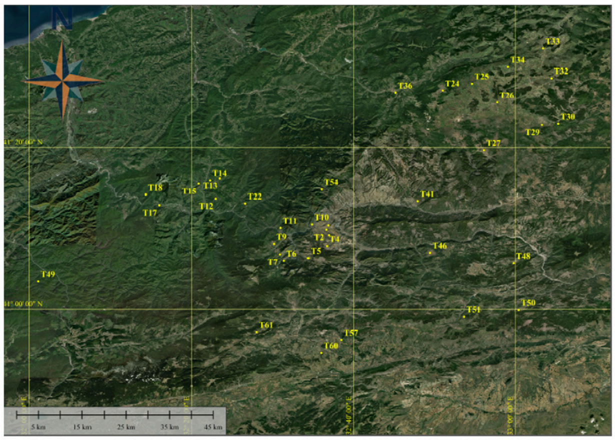

Figure 1. Soil sampling locations in Karabuk

The relationships between metal components are valuable for understanding the sources of metal resources (Lu et al., 2010). Pearson's Correlation Coefficients and Principal Component Analysis (PCA) are statistical analyses commonly utilized to explore these relationships in many previously studies. Pearson's correlation coefficient, employed in this study using IBM SPSS 21.0, measures the strength and direction of the linear correlation between pairs of pollutants present in the analyzed samples. By assessing the correlation matrix, we can identify positive correlations, indicating that metal components originate from similar sources, whether natural or anthropogenic, or are co-contaminants. Conversely, negative correlations suggest that metal pairs come from different sources in this statistical analysis (Chandrasekaran et al., 2015). PCA, another statistical technique employed in this study, is used to reduce the number of variables and derive a smaller set of latent factors or principal components (PCs) (Chen et al., 2014). These components provide insight into the relationships between observed variables. PCA facilitates the identification of metal resources, distinguishing between natural and anthropogenic origins (Saedi et al., 2012; Tokalioğlu and Kartal, 2006). In summary, Pearson's Correlation Coefficient and PCA are employed to assess the relationships between metals and their potential sources. Pearson's correlation coefficient measures the strength of linear correlation between pollutants, while PCA reduces variables and identifies latent factors or principal components, aiding in the analysis of relationships between observed variables and identification of metal resources. These statistical analyses are commonly used in environmental studies on soil samples (Sezgin et al., 2022).

Pollution indexes and Factors

In this study, pollution indexes and factors such as Igeo, EF, CF, Cd, PLI, and PERI were used to the assessment of pollution in Karabuk soil samples. Equations of all pollution indexes and factors are given in Table 2 and their classification/categorizations are shown in Table 3.

Table 2. Pollution indexes and factors equations

Pollution indexes/Factors	Equations	Explanations
Igeo (geo-accumulation index),	$Igeo = log_2\left(\frac{C_s}{1.5C_r}\right)$	Cs:The measured concentration of the elements in the soil samples, Cr:The geochemical reference value. The constant 1.5 given in the equation is used to consider the potential differences in the reference values since they are influenced by natural fluctuations and anthropogenic influence (Sezgin et al., 2022).
EF (Enrichment Factor)	$EF = \frac{\left(\frac{C_x}{C_{ref}}\right)_{sample}}{\left(\frac{C_x}{C_{ref}}\right)_{background}}$	Cx is the concentration of the investigating metal in the sample and background (reference) soil sample, Cref is the concentration of reference metals in the sample and background (reference) soil sample (Christoforidis and Stamatis, 2009).
Contamination Factor (CF)	$CF = \frac{C_s}{C_r}$	According to the pollution factor proposed by Hakanson (1980), Cs represents the metal concentration in the sediment sample, while Cr represents the metal concentration in the reference sample (Keshavarzi et al., 2015; Sezgin et al., 2019).
Contamination Degree (Cd)	$C_d = \sum_{n=1}^{n} CFs$	(Keshavarzi et al., 2015; Sezgin et al., 2019).
Pollution Load Index (PLI)	$PLI = \sqrt[n]{CF_1 x CF_2 x \ldots\ldots CF_n}$	(Hołtra and Zamorska-Wojdyła, 2020).
Ecological Risk (Er)	$Er = Tr.CF$	The contamination factor (CF) is calculated using the equation provided earlier. Tr represents the coefficients defined as "toxic-response factor" by Hakanson (1980) (Sezgin et al., 2019; Hołtra and Zamorska-Wojdyła, 2020).
Potential Ecological Risk (PERI)	$PERI = \sum_{n=1}^{n} Er$	(Hołtra and Zamorska-Wojdyła, 2020).

Igeo, which is recommended by Muller, is successfully used to pollution assessment in soil and implements a logarithmic operation to the results of sample analysis. 1.5 is uses as a constant in Igeo calculation and its allows to the eliminate of likely differentiations in the contents of the investigated elements in soil due to the likely variation in the background (Bn) and a small influences of anthropogenic activity (Sezgin et al., 2022). This index presents an opportunity of comparing with now and before concentrations (or non-industrial conditions) (Hołtra and Zamorska-Wojdyła, 2020). Table 3 presents Muller's classification for the assessment of the contamination level of Igeo (Sezgin, 2019). Enrichment factor (EF) is generally used to determine metals sources which arise from naturally or anthropogenic resources. (Sezgin et al., 2022; Wei et al., 2010; Meza-Figueroa et al., 2007). This parameter is calculated to depend on normalization of an investigated elements versus a reference element. The elements such as Al, Fe, Sc and Sr are often selected as a reference element because of they have low occurrence variabilities (Klos et al., 2011; Han et al., 2006; Turner and Simmonds, 2006). Fe was determined as a reference element among of these elements in this study. Equation of EF and classification criteria were given in Table 2 and Table 3. Contamination factor (CF), which defines a rational approach of the metal concentrations in the investigation soil samples to individual metal concentrations in reference soil

Table 3. The pollution indexes/Factors and Soil classifications/Categories

Igeo classification		
Igeo Value	**Class**	**Soil Quality**
Igeo≤ 0	0	Unpolluted
0 < Igeo ≤ 1	1	Unpolluted to moderately polluted
1 < Igeo ≤ 2	2	Moderately polluted
2 < Igeo ≤ 3	3	Moderately polluted to severely polluted
3 < Igeo ≤ 4	4	Severely polluted
4 < Igeo ≤ 5	5	Severely polluted to extremely polluted
5 < Igeo	6	Extremely polluted
Enrichment categories of EF values		
EF value	**Enrichment category**	
EF ≤ 2	Minimal enrichment	
2 < EF ≤ 5	Moderate enrichment	
5 < EF ≤ 20	Significant enrichment	
20 < EF ≤ 40	Very high enrichment	
40 < EF	Extremely high enrichment	
CF	**Cd**	**Contamination category**
CF < 1	Cd<8	Low degree of contamination
1 ≤ CF < 3	8 ≤ Cd<16	Moderate degree of contamination
3 ≤ CF < 6	16≤ Cd <32	Considerable degree of contamination
6 ≤ CF	32 ≤Cd	Very high degree of contamination
CF < 1	Cd<8	Low degree of contamination
PLI value	**Soil quality**	
0 < PLI < 1	Unpolluted	
1 < PLI < 2	Moderately polluted to unpolluted	
2 < PLI < 3	Moderately polluted	
3 < PLI < 4	Moderately to highly polluted	
4 < PLI < 5	Highly polluted	
5 < PLI	Very highly polluted	
PERI values	**Ecological risk category**	
PERI < 150	Low ecological risk	
150 ≤ PERI < 300	Moderate ecological risk	
300 ≤ PERI < 600	Considerable ecological risk	
600 < PERI	Very high ecological risk	

samples that is used as a preindustrial concentration, and contamination degree (Cd), which is defined as a total of contamination factors all investigated elements, is proposed by Hakanson (1980) to explain of the pollution of toxic substance in soil (Sezgin et al, 2022). On the other hand, one of the pollution indexes is PLI which is the geometric average of the contamination factors. This parameter determines the contribution of all metals in a sample point and it allows to assess the level of environmental pollution with a view to undertake monitoring or repair activities aimed at improving soil quality (Holtra and Zamorska-Wojdyła, 2020; Tomlinson et al. 1980;). CF, Cd and PLI equations and classification of pollution were given Table x and Table Y respectively. The CF is also used the another indexes calculation that are called ecological risk (Er) index for each elements and potential ecological risk index (PERI), which are introduced by Hakanson (1980), in the soil samples. In these equations Tr is defined as a "toxic-response factor" for a given substance and demonstrated this value for As, Co, Cr, Cu, Ni, Pb, and Zn to be 10, 5, 2, 5, 5, 5 and 1 respectively (Sezgin et al., 2019).

RESULTS AND DISCUSSION

Descriptive statistics of metal concentrations

Descriptive statics of investigated metal concentrations in this study and background (reference) soil values were given in Table 4. As seen Table 4, the means of As, Co, Cr, Cu, Ni, Pb, Zn and Fe were determined as 8.28, 15.69, 88.27, 39.89, 50.50, 17.05, 92.39 and 35329.22 mg kg^{-1}. The mean concentrations of these metals were shown severely higher than background (reference) soil concentrations (except Fe) in Table 4. According to

Table 4. Descriptive statistic of metal concentrations in Karabuk soil samples (mg kg^{-1})

	As	Co	Cr	Cu	Ni	Pb	Zn	Fe
Minimum	3,13	5,88	38,39	18,00	12,00	5,44	35,00	17889,00
Maximum	17,06	46,49	236,14	58,00	175,00	72,60	243,00	57827,15
Range	13,93	40,61	197,75	40,00	163,00	67,16	208,00	39938,15
Mean	8,28	15,69	88,27	39,89	50,50	17,05	92,39	35329,22
Std. Deviation	2,90	7,49	40,49	9,53	31,46	11,37	37,07	9014,65
Skewness	1,01	1,96	1,80	-0,28	2,34	3,54	2,06	0,30
Kurtosis	1,29	6,60	3,84	-0,09	6,68	15,70	6,86	0,02
Background Soil	6.31	5.88	38.39	18.00	12.00	7.05	35.00	22173.64

these results, it is may said that the investigated metals are come from anthropogenic sources. Skewness values of investigated metals in Karabuk soil samples were calculated positively (except Cu). If skewness value is positive that it presents the average concentration of metals are lower than their median value. On the other hand, negative skewness value is means the mean metal concentration is higher than their median value. The maximum value of skewness is Pb (3.54) among all investigated elements.

Assessment of Pollution Indexes and Factors Results

To assess the pollution levels and soil classification/ categories, as well as the potential anthropogenic effects on soil samples from Karabuk, this study was calculated Igeo, EF, CF, Cd, PLI and PERI values. The results of these pollution indexes and factors were presented in Figures 2-6. As shown in Figure 2, the Igeo results indicated that the soil quality of Karabuk is severely polluted for Ni at T7 sample point. The soil is also moderately to severely polluted for Co at the T3, for Cr at the T7, for Ni at the T2, 5, 6, 24, and 61, and for Pb and Zn at T46. Moreover, the soil quality of other sample points is determined to be unpolluted, unpolluted to moderately polluted, or moderately polluted based on the Igeo results in this study.

Figure 3 displays the results for the enrichment factor (EF) assessment for Karabuk soil samples. The EF values for Ni at T5, T6, and T7 sampling points were found to be within the range of 5 to 20, indicating a significant enrichment of Ni concentrations. In contrast, moderate levels of enrichment were observed for Co (T3, 7, 14, 15, 25, 26, 32, 49, and 51), Cr (T5 and 7), Cu (T5, 29, 48 and 54), Ni (T2-4, 18, 24-27, 29, 30, 32, 33, 36, 41, 48-51, 57, 60, and 61), Pb (T14, 18, 30, 34, 41, and 46), and Zn (T18, 26, 29, 30, 34, 41, 46, and 48) at their respective sampling points. On the other hand, minimal enrichment was also

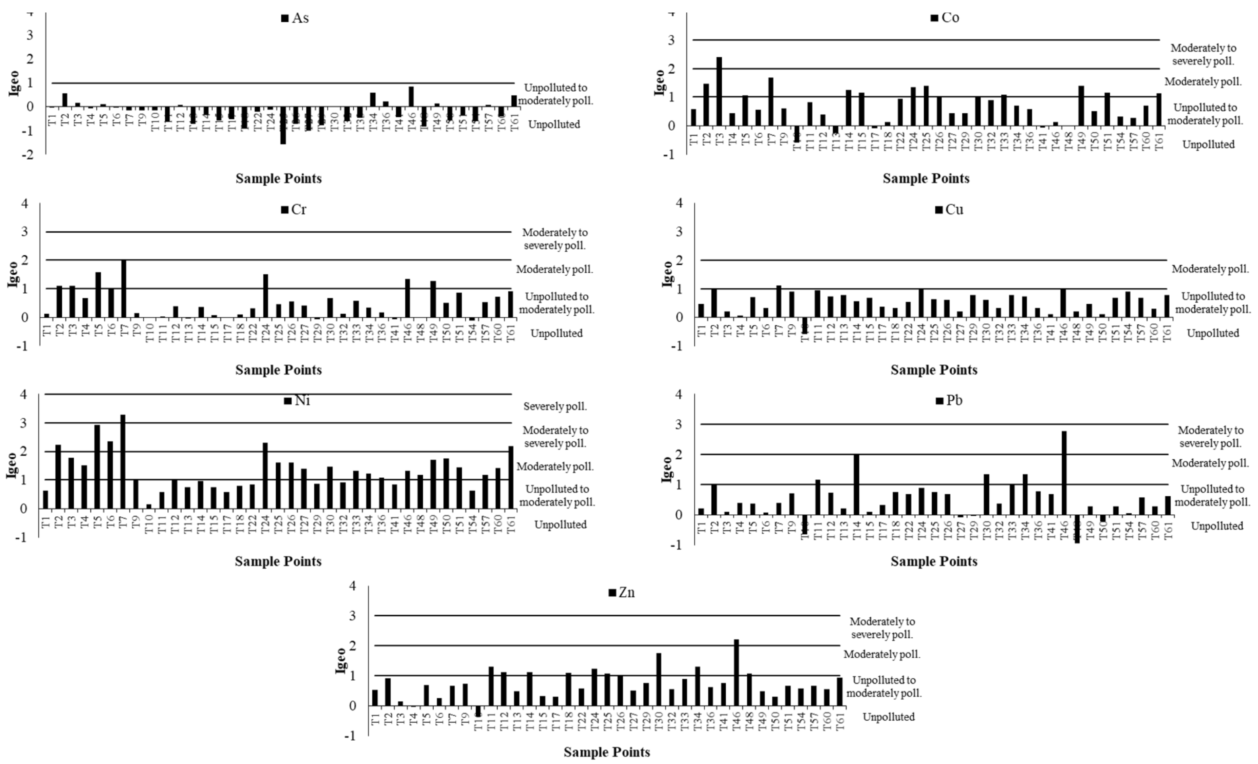

Figure 2. The Igeo values of Karabuk soil samples and soil quality

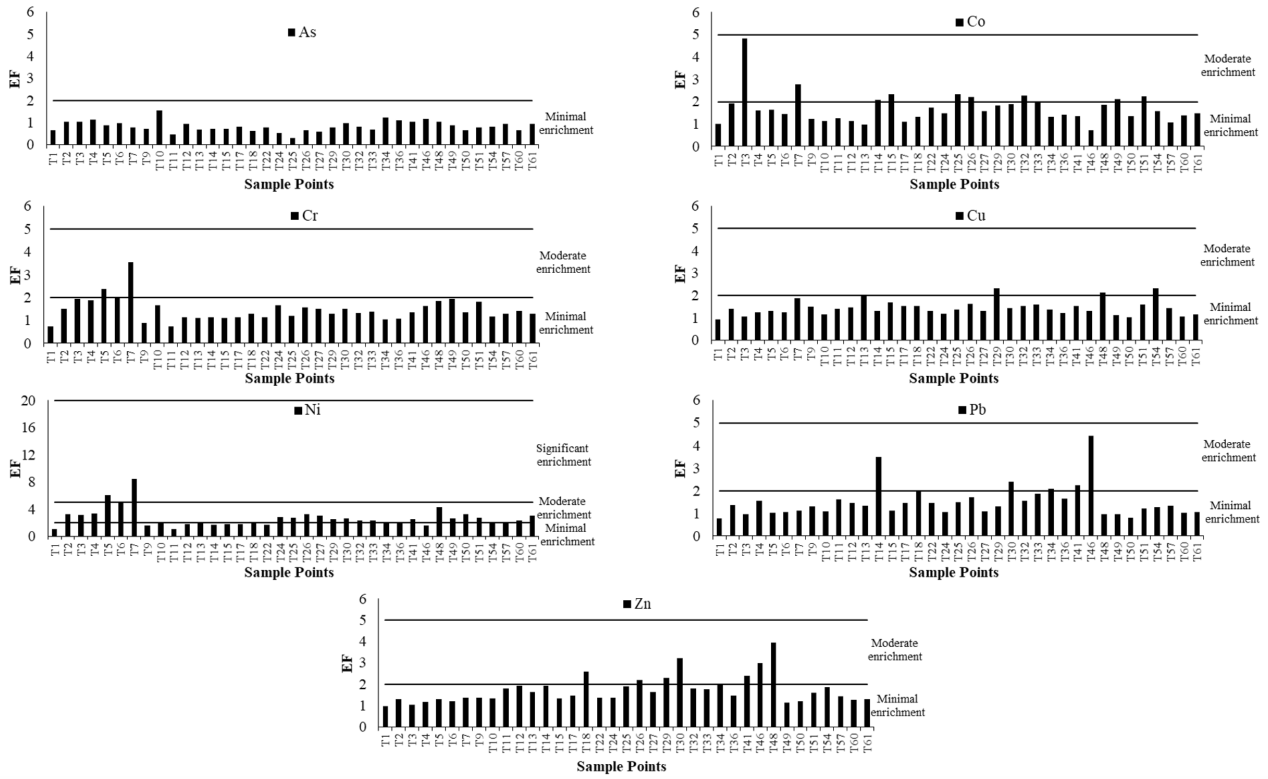

Figure 3. The EF values of Karabuk soil samples and enrichment levels

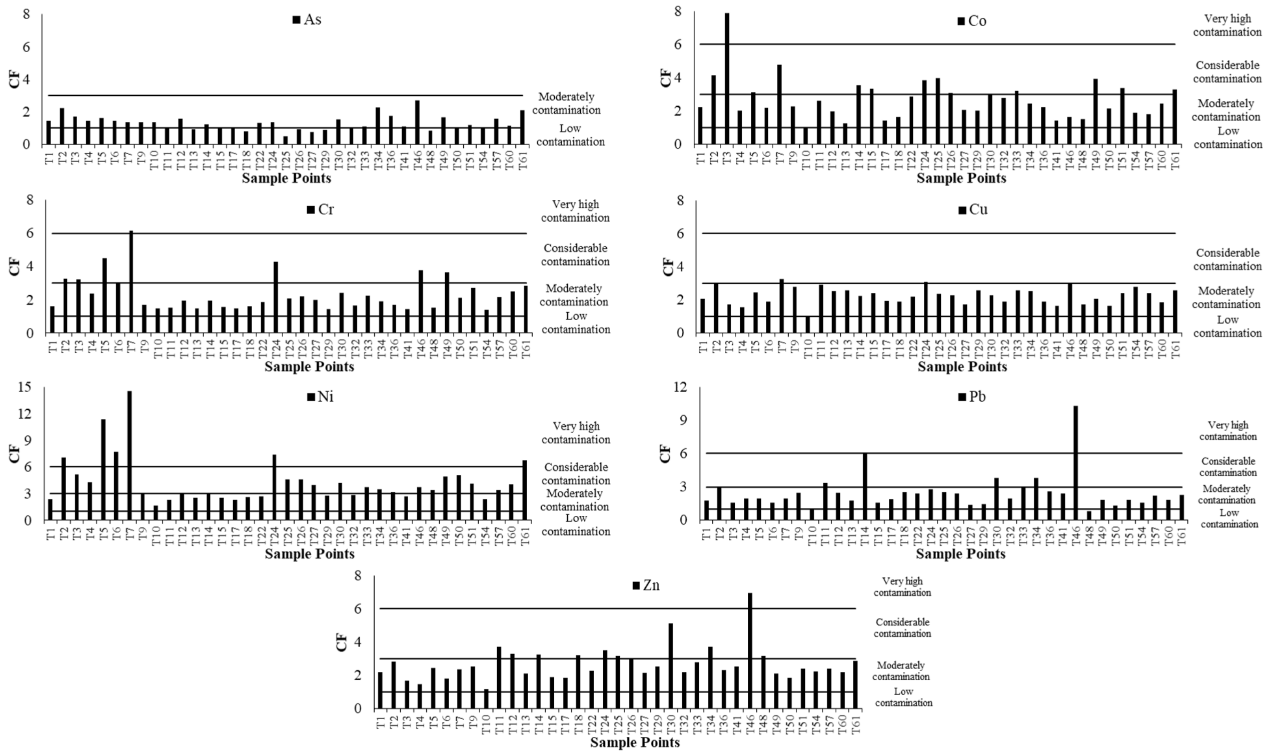

Figure 4. The CF values of Karabuk soil samples and soil contamination categories

determined at other sampling points in Karabuk soil.

Based on the results of the CF analysis presented in Figure 4, it was observed that the sample points had a high level of contamination for several metals. Specifically, the metals Co (T3), Cr (T7), Ni (T2, 5-7, 24, and 61), as well as Pb, and Zn (T46) were found to have very high contamination at the sample points that are given in the parenthesis. Furthermore, the CF analysis revealed

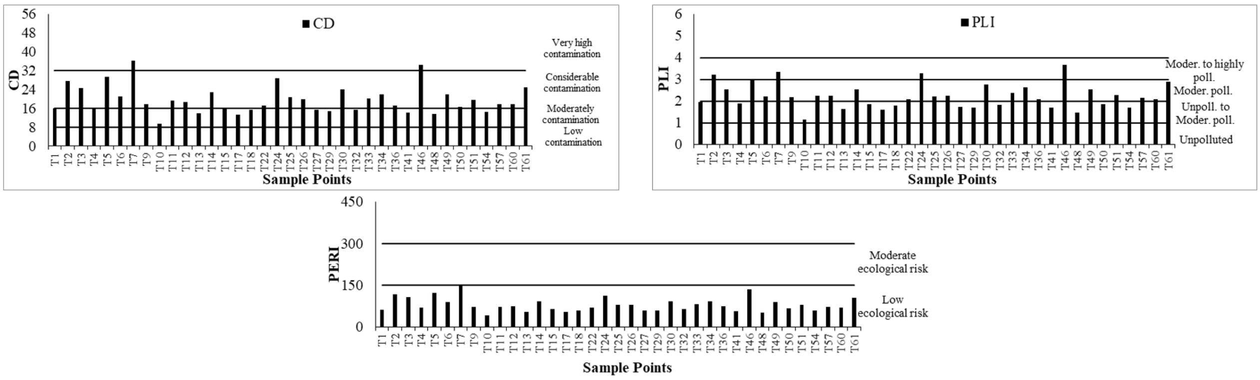

Figure 5. The CD, PLI and PERI values of Karabuk soil samples and soil categories

Table 5. Pearson's correlation matrix among the metals in Karabuk Soil Samples

	As	Co	Cr	Cu	Ni	Pb	Zn	Fe
As	1							
Co	0,190	1						
Cr	0,446**	0,564**	1					
Cu	0,300	0,293	0,464**	1				
Ni	0,275	0,500**	0,909**	0,405*	1			
Pb	0,544**	0,019	0,217	0,426**	-0,024	1		
Zn	0,412*	0,003	0,215	0,542**	0,039	0,839**	1	
Fe	0,587**	0,413**	0,549**	0,644**	0,396*	0,485**	0,464**	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

that moderate to considerable levels of contamination were present for the investigated metals in many sample points of the Karabuk soil samples. The very high degree and considerable degree contamination level of CF values observed in the Karabuk soil indicate a high level of contamination and suggest a higher risk of exposure to the corresponding metals. These findings suggest that the anthropogenic sources of these metals are a cause for concern.

According to the Cd values calculated by summing the CFs in Figure 5, it was found that high and considerable levels of contamination were present at all sample points except for 12 sample points (T1, 10, 13, 15,17, 18, 27, 29, 32, 41, 48, and 54). This indicates that the majority of the sample points were heavily polluted with anthropogenic sources. In addition, very high pollution was found at T7 and 46 sample points due to Cd results in Figure 5. The sample points of T2,7, 24 and 46 were found moderately polluted to highly polluted soil according to PLI results that was given in Figure 5. The other sample points were determined moderately polluted and moderately polluted to unpolluted soil for PLI results. Lastly in Figure 5, it was seen moderate ecological risk due to PERI results for T7 sample point. On the other hand, the low moderate ecological risk was determined at the other sample points for PERI results in this study.

Statistical Analysis

Multivariate statistical techniques, such as Pearson correlation and Principal Component Analysis (PCA), were used to explore the potential sources of heavy metals in sediment samples. Correlation analysis examines the relationships between quantitative variables by calculating the Pearson correlation coefficient. Table 5 displays Pearson's correlation coefficients of the elements investigated in the Karabuk soil samples. The results revealed significant positive correlations between certain pairs of elements, such as Cr-Ni and Pb-Zn. Moderate positive correlations were also observed between As-Pb, As-Fe, Co-Cr, Co-Ni, Cr-Fe, Cu-Zn, and Cu-Fe.On the other hand, the positive correlations were relatively lower between As-Co, As-Cr, As-Cu, As-Ni, As-Zn, Co-Cu, Co-Fe, Cr-Cu, Cr-Pb, Cr-Zn, Cu-Ni, Cu-Pb, Ni-Fe, Pb-Fe, and Zn-Fe.The Pearson's correlation coefficients results suggest that there is a significant positive correlation between Cr, Ni, Pb, and Zn, which is likely due to their common anthropogenic sources. However, the relatively lower positive correlations observed among the other pairs of elements suggest that their sources may be more diverse, including both natural and anthropogenic sources. Overall, the use of Pearson's correlation coefficients proved to be a useful tool in identifying the sources of the metals found in the soil samples. The results obtained help to shed light on the possible origins of the contaminants and aid in the development of strategies for mitigating their impact on the environment and human health.

PCA was conducted on the metal concentrations in the sediments to better understand the grouping of metals in Karabuk soil samples originating from the same source.

The validity of PCA was assessed using the Kaiser-Meyer-Olkin test and Bartlett's test. Principal components (PCs) with eigenvalues greater than one were deemed relevant (Vasiliu et al., 2020; Yang et al., 2014). To determine the contribution of elements to a specific group, components with factor loadings > 0.6, 0.4–0.6, and 0.3–0.4 were classified as highly, moderately, or weakly associated with elements in that group, respectively. Similar classification approaches have been employed in related studies focused on identifying sources of heavy metals in soil samples (Vasiliu et al., 2020; Maina et al., 2019; Javed et al., 2018). The results of the analysis, conducted using IBM SPSS 21.0, were presented in Table 6 and include eigenvalues and commonalities. Two eigenvalues were found to be higher than 1, with the two factors accounting for 72.043% of the total variance. In each factor column, values exceeding 0.6 were identified and highlighted in bold. The first factor, which explains 44.084% of the total variance, is heavily loaded with As, Cu, Pb, Zn, and Fe, suggesting that these metals share common sources. Co, Cr, and Ni, on the other hand, were appeared in the second factor, and indicated that they come from the same originate, with second factor explaining 23.960% of the total variance.

Table 6. The rotated component matrix for data Karabuk soil

Elements	Component		Communalities
	1	2	
As	0.650	0.301	0.513
Co	0.021	0.756	0.572
Cr	0.262	0.899	0.877
Cu	0.621	0.433	0.572
Ni	0.039	0.914	0.837
Pb	0.923	-0.086	0.859
Zn	0.906	-0.063	0.825
Fe	0.664	0.517	0.708
Eigenvalue	3.847	1.917	
% of variance	48.084	23.960	
% of cumulative	48.084	72.043	

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization. Rotation converged in 6 iterations.

CONCLUSIONS

In this study, an assessment of metal pollution (including As, Co, Cr, Cu, Ni, Pb, and Zn) in soil samples from Karabuk was presented using various pollution indices and factors such as Igeo, EF, CF, Cd, and PERI. The concentration of Fe was used as a reference metal for calculating the pollution indices. All the metal concentrations in the Karabuk soil samples were obtained from an open-source report by the Turkish Atomic Energy Authority (Türkiye Atom Enerjisi Kurumu – TAEK) in 2015. Thirty-seven sample points were used for the assessment of pollution indices and factors in this study.

The results of EF, CF, and Cd showed that there was moderate to high pollution at many sample points in Karabuk soil. Nickel (Ni) enrichment in soil was significant level at several sample points according to EF analysis. CF results showed very high contamination for Co, Cr, Ni, as well as Pb and Zn at the similar investigated sample points. Additionally, based on Cd values, high and considerable levels of contamination were present at all sample points except for 12 sample points. Moreover, the PLI results indicated moderate to highly polluted conditions at T2, T7, T24, and T46, and moderately potential ecological risk at T7 according to PERI results. The pollution near industrial facilities, such as iron and steel factories, and steel production works, particularly at T2-7, was likely due to anthropogenic activities. Pollution at other sample points may have been caused by atmospheric transportation. These findings highlight concerns regarding anthropogenic sources of metals in the Karabuk soil, especially near industrial facilities. Statistical analysis, including Pearson's correlation coefficients and principal component analysis (PCA), was employed to determine the sources of metals in Karabuk soil samples. Metals were classified into anthropogenic and natural categories. The study identified a significant positive correlation between Cr, Ni, Pb, and Zn, suggesting their anthropogenic origin. PCA revealed two factors explaining 72.043% of the total variance. Factor 1 included As, Cu, Pb, Zn, and Fe, while Factor 2 comprised Co, Cr, and Ni, commonly associated with anthropogenic sources. Overall, statistical analysis effectively determined that certain metals, particularly those linked to industrial activities, originated from anthropogenic sources. PCA provided additional insights into the contamination sources in the soil samples. According to the results obtained in this study, it was observed that there is pollution in Karabuk soil due to anthropogenic activities. However, due to limited available data on atmospheric transport, a detailed analysis could not be conducted within the scope of this study. Long-term monitoring studies are recommended to observe the seasonal variations of the pollution caused by the identified elements that pose risks to the environment and human health. Furthermore, it is advisable to develop sector-specific recommendations for reducing pollution at its source. These suggestions can guide future studies and efforts aimed at monitoring pollution and implementing measures to mitigate its effects.

COMPLIANCE WITH ETHICAL STANDARDS

Conflict of interest

The authors declared that for this research article, they have no actual, potential or perceived conflict of interest.

Author contribution

The contribution of the authors to the present study is equal.

All the authors read and approved the final manuscript. All the authors verify that the Text, Figures, and Tables are original and that they have not been published before.

Ethical approval

Ethics committee approval is not required.

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Data availability

Not applicable.

Consent for publication

Not applicable.

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