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Calculating pollution indices of heavy metals in surface soil at Baiji refinery

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Abstract: Baiji refinery produces many pollutants from fuel combustion, which can cause the soil to become contaminated with heavy metals. This research examines the contamination variables in the soil next to the refinery. Four soil samples were taken from various locations to evaluate five heavy metals (Ni, Zn, Co, Cr, and Pb). The results found that the percentage of the metal (Ni) at site No. 1 was the highest, 149.945524 ppm, due to its presence near the oil flame and in the direction of the wind. Two indices were applied to detect pollution levels: Pollutant Load Indicator (PLI) and Toxicity Factor (CF). The Co, Cr, Zn, and Pb showed class 1 relative values, indicating that the sites were only slightly polluted, while the Ni showed class 2 relative values, indicating moderate ranges of pollution. While the contamination factor for Ni was classified as class 2, indicating moderate contamination, the contamination factors for Co, Cr, Pb, and Zn were all rated as class 1, which indicates low contamination values. PLI levels in all investigated sites categorized as class 1 indicate slight contamination as a result of the gases released by the predominant wind impacting the metal percentage distribution pattern.
Keywords: *Baiji refinery, Heavy metals, PLI, Toxicity Factor.*

1. Introduction

Soil pollution occurs when hazardous substances, chemicals, salts, radioactive materials, or pathogenic agents build up in the soil, harming plant growth and animal health [1].

Exploration and production activities can have severe negative consequences in oil field locations [2]. Sediment chemistry data is an important part of sediment assessment processes for determining the effects of hazardous and bioaccumulative compounds [3].

Contaminants in soil can come from a variety of sources, some of which are human (primarily fertilizers and petroleum removal wastes), while others are natural [4].

The metal concentration charts, in general, show variations in heavy metal concentrations that can be linked to human activity [5-8].

The most frequent methods for assessing soil enrichment with metals are the pollutant load index (PLI). This index determines if anthropogenic contaminants have been deposited on surface soil and how heavily they have been present [9]. A composite statistic called the pollution load index (PLI) measures the overall toxicity of heavy metals in a sample by determining how frequently the amount of heavy metals in the sediment exceeds the baseline value [10]. Using environmental pollution indicators, the current study is to investigate the concentration of specific heavy metal contamination in the soil of the Baiji refinery region and its effects on the surrounding areas.

Although heavy metals are found in the environment naturally and are necessary for life, they can become harmful when they build up in living things.

The following heavy metals are frequently found in the environment: lead, nickel, copper, chromium, arsenic, mercury, and cadmium. The atmosphere is exposed to cadmium emissions due to

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both organic and anthropogenic processes, resulting in varied exposure levels for humans as well as animals. Cadmium contamination in aquatic ecosystems transpires via surface runoff, industrial effluents, and absorption into soils and sediments. Cadmium poisoning can occur when people eat tainted food, breathe in contaminated air, or drink water that has high concentrations of the metal. Cadmium has no characteristics that benefit plant development and metabolic functions [11].

Limited amounts of the non-biodegradable mineral lead are found in nature. Human endeavors such as mining, manufacturing, and the combustion of fossil fuels are causing atmospheric lead concentrations to continuously rise. Lead is detrimental to human health when exposure exceeds optimal levels. Children face an elevated risk of lead poisoning; exposure to dust contaminated with ambient lead exacerbates the severity of poisoning [12].

The element chromium is toxic and carcinogenic. In the environment, it may be found in two stable oxidation states: chromium (III) and chromium (VI). Chromium (III) is a less dangerous version of chromium (VI). They can mutually transform throughout industrial processes. The conversion of chromium (VI) to chromium (III) is less detrimental to the environment because of the latter's decreased toxicity. Numerous enterprises that employ chromium endanger local climates.

Ferrochrome industrial emissions surpass environmental chromium emissions that occur naturally. Figure 1 shows the emission of heavy metals from industries, cities, and agriculture and their leaching into water and soil [13, 14].

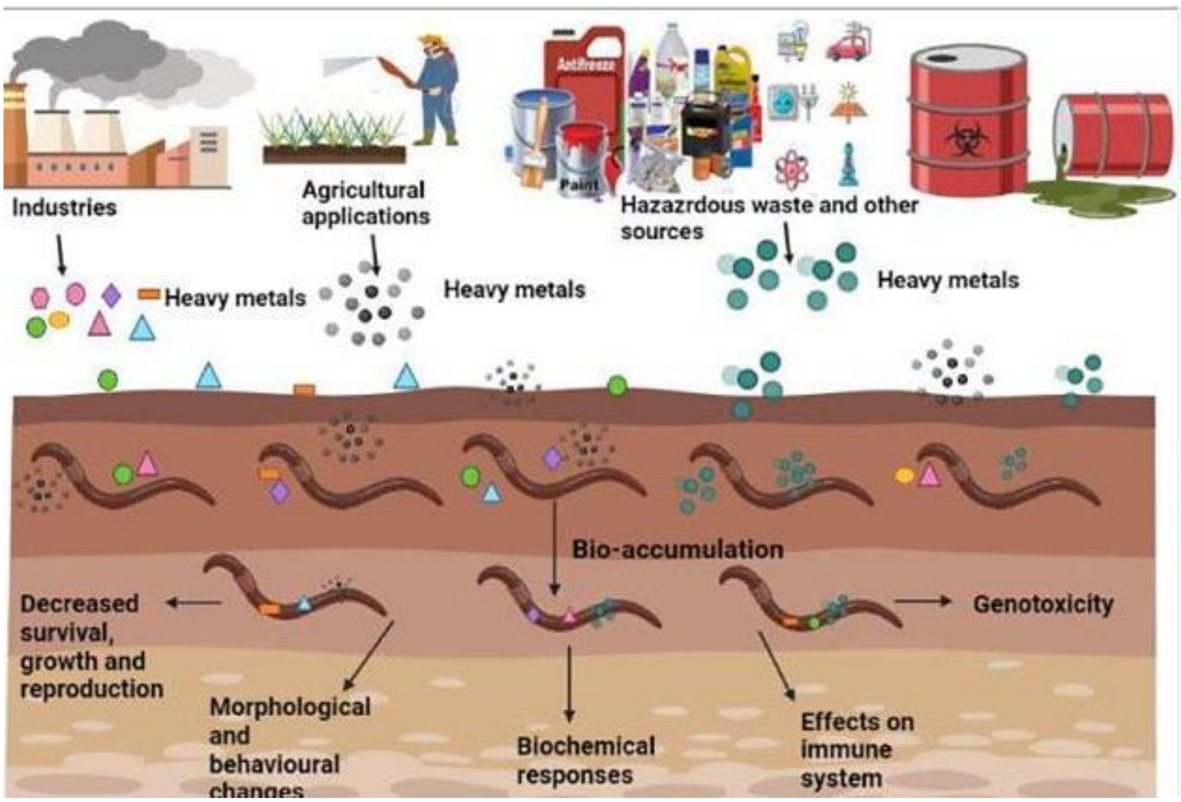

Figure 1.
Emission of heavy metals from industries cities and agriculture.
Source: Das, et al. [13].

Cobalt is prevalent in several environmental mediums, including flora, is used in the synthesis of alloys, and is found in soils, rocks, and water. Despite its modest discharge rate, it poses a significant hazard to people. Cobalt influences the human body in both advantageous and detrimental ways.

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Minimal quantities of cobalt often pose no adverse effects; nevertheless, substantial releases into the environment might result in fatalities.

An element that is abundant in nature is nickel, which possesses several industrial applications. Both natural and man-made sources emit it into the atmosphere. It has several detrimental effects on people, such as respiratory and cardiovascular disorders, allergies, and lung and nasal cancer. disorders due to the intake of polluted air [15].

It is recognized that copper is a necessary micronutrient for living things. It contributes to the routine physiological functions of plants, encompassing chlorophyll synthesis, photosynthesis, and the metabolism of carbohydrates and proteins.

Copper deficiency alters important metabolic processes, and elevated exposure causes toxicity [16]. One essential and ubiquitous metal is zinc. It functions as a cofactor and is linked to several enzyme processes. The kind and extent of exposure determine zinc toxicity. The two main sources of zinc are mining and smelting. The processes of mineral processing release a significant quantity of zinc into the environment, which impacts both living things and ecosystems [17].

2. Bio Accumulation of Heavy Metals in Biological Systems

Overabundance of essential or non-essential trace elements can cause genetic disorders or anomalies in morphology or physiology alterations, including growth inhibition or cessation, as well as mutations. [18]. Food crops are a fundamental aspect of human nutrition and may include various important and hazardous metals, contingent upon the characteristics of the utilized growth medium. The predominant source of human exposure to heavy metals is the consumption of vegetables, which constitutes 90% of total intake. The residual 10% is attributable to dermal contact and inhalation of contaminated dust [19]. The increasing demand for food in recent decades has made food safety a significant public health issue. This scenario aims to encourage scientists and researchers to investigate the health dangers associated with the use of pesticides, heavy metals, and food tainted with toxins.

The food chain is constantly refilled with vital and unnecessary elements as a result of the overuse of untreated sewage, industrial effluents, municipal wastewater, and agrochemicals for irrigation [20]. In the toxicity classification system of the Agency for Toxic Substances and Disease Registry, heavy metals and metalloids such as arsenic, lead, and cadmium are rated as 1, 2, and 7 on a scale of 1 to 7. Mineral resources and elements, including copper, chromium, iron, manganese, and zinc, are vital for both humans and animals due to their roles in various metabolic processes, enzyme activity, receptor sites, hormonal functions, and protein transport at certain concentrations. A distinct category of elements, comprising arsenic, cadmium, lead, and mercury, is non-essential and has no advantageous role in plants, animals, or humans. They have little nutritional value as they are highly toxic.

Establishing quality standards and identifying dangers to food and human health safety necessitates a description of the sources and concentrations of heavy metals in soil. Pollution from heavy metals is enduring, insidious, and chronic. Due to their non-biodegradable nature and extended half-life, metals cannot be decomposed by biological organisms, leading to their accumulation in bodily tissues and the environment, hence presenting health hazards.

Because heavy metals may move from polluted soil and water into the food chain, their bioaccumulation in vegetables poses a health danger [21]. Soil qualities are essential for the production of food, and the pollution of this essential resource by heavy metals, together There are serious health and environmental problems associated with their subsequent absorption and bioaccumulation in food crops, especially in developing countries. Concentrations of heavy metals are affected by soil type, plant genotype, and their interactions. Mineral fertilizers, in contrast to organic manure, possess elevated concentrations of heavy metals; hence, their application results in heightened levels of heavy metal contamination in soil [22].

The health risks associated with hazardous metals depend on exposure time and concentrations in certain media. Health problems may arise from long-term, chronic exposure to even trace levels of hazardous metals. Heavy metal toxicity constitutes a primary abiotic stressor for plants, rooted in the physiochemical properties of heavy metals [23].

3. Location of Study Area

Baiji Refinery Figure 2 is one of Iraq's largest refineries, located approximately 210 km north of Baghdad in Salah al-Din Province. It consists of three main units: the northern location, Salah Al-Din 1, and Salah Al-Din 2. The refinery processes approximately 58,000 barrels of crude oil per day and plays a crucial role in Iraq's energy sector. It is connected to the North Oil Company in Kirkuk as its primary crude oil source and is linked via pipelines to major cities like Baghdad, Mosul, and Kirkuk. These pipelines transport oil products and crude to meet regional energy demands. However, the refinery faces challenges, including frequent oil leaks during extraction, transportation, and processing, which lead to soil contamination and environmental hazards. Heavy metal soil contamination in Baiji Refinery is a serious environmental problem facing many areas of Baiji Refinery and surrounding areas.

Lead, mercury, cadmium, zinc, and copper are examples of heavy metals that can accumulate in the surface soil as a result of various factors such as mining industries, solid waste, and air pollution.

Figure 2.
Baiji Refinery.

4. Methodology

Soil samples were collected from the Baiji refinery area to study the effects of petroleum contamination. The sampling focused on several strategic locations:

Pipeline Areas (Salah Al-Din Stations 1 and 2): Samples were obtained near damaged pipelines (as shown in fig. 3) that caused crude oil spills.

The crude oil, primarily heavy and medium fractions, leaked due to pipe deterioration, contaminating the surrounding soil with heavy metal.

Four sample locations were chosen. The soil samples were obtained by scraping the surface layer at a depth of 5 cm using a clean plastic scoop and thereafter kept in polyethylene bags . The amounts of heavy metals were measured at the University of Tikrit using an atomic absorption spectrometer.

Two indices were utilized for contamination assessment to detect pollution levels: the contamination factor (CF) and the pollutant load index (PLI). The laboratory work includes the following steps:

1- Dry the model, then place it in a ceramic mortar and homogenize the components of the model.

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2- 20 grams of a particle size in the range (75 µm- 250 µm) was used. The heavy metals were then separated using a bromofµorm solution, and thin slices were made of the heavy fraction that settled in the entire sample for the purpose of identifying heavy metals.
3- One gram of a particle size of the clay, fine sand, and silt fraction less than 75µm, in which trace elements are concentrated, was taken for the purpose of conducting a trace element test.

Figure 3.
Pipeline Spills.

4.1. Contamination Factor (CF)

CF: is employed to categorize the extent of metal contamination in soil samples as shown in table 1 [24]:

$$CF = C\ metal\ /\ C\ background\ value \quad (1)$$

Where:
Metal C is the average substance content of at least 4 sample sites.
Background C is the pre-industrial reference level of the material.

4.2. Pollution load index (PLI)

The pollution load index represents the degree of pollution of all heavy metals in a sample site (as shown in table 2) and is composed of contamination from certain heavy metals [7]. The pollution load index (PLI), developed by Gideon [8] is progressively determined as follows:

Table 1.
Classified grades of CF.

CF	Class	Classification
CF<1	Class1	Very little contamination
1≤CF<3	Class2	Moderate levels of pollution
3≤CF<6	Class3	Significant contamination
CF>6	Class4	Extremely high levels of pollution

$$PLI = n\sqrt{(CF1 * CF2 * CF3 * \ldots CFn)} \quad (2)$$

Where:
CF: is the single contamination index factor

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n: is the heavy metals count of the species.

Table 2.
Classified grades of PLI

PLI	Class	Classification
PLI<1	Class 0	Perfection
PLI=1	Class 1	Baseline level
PLI>1	Class 2	Deterioration on-site quality

5. Result and Discussion

Tables 3 and 4 indicate the results of laboratory tests of soil samples for the four sites. Table 3 shows the results of metal concentrations in the soil for the four sites and the element concentrations in the Earth's crust, while Table 4 shows the calculations of the pollution values resulting from the metal concentration in the soil for the four sites, as shown below.

Table 3.
Results of metal concentrations in the soil.

Samples	Zn PPm	Ni PPm	Pb PPm	Co PPm	Cr PPm
S1	51.174756	149.945524	43.689782	25.546531	95.173632
S2	72.46464	82.34545	27.486774	19.783769	105.391926
S3	70.74572	107.03777	56.632832	17.258212	132.919262
S4	55.279571	142.70364	31.115377	26.686128	124.161495
Element concentrations in the Earth's crust	70	20	14	10	100

Table 4.
Pollution Indices of Soil Samples.

Sample NO.	Co	Ni	Cr	Zn	Pb	PLI
S1	0.2475	0.279	0.0130	0.042	0.045	0.07
S2	0.0696	1.730	0.022	0.931	0.0386	0.15
S3	0.0928	3.768	0.0579	0.971	0.0474	0.24
S4	0.154	0.226	0.0149	0.080	0.0077	0.049

To know the percentages of metal contamination in the Baiji refinery within the four sampling sites, these concentrations were compared after calculating the values and the pollution index with the natural limits for the presence of metals in the soil, which are shown below in Table 5.

Table 5.
Pollution Range and Rate of Soil Samples.

component	Range	Rate	Category
Zn	(0.042-0.97)	0.5	Low pollution
Ni	(0.27-3.7)	1.49	Moderate pollution
Pb	(0.0077-0.047)	0.03	Low pollution
Co	(0.069-0.247)	0.14	Low pollution
Cr	(0.0130-0.0579)	0.027	Low pollution

The PLI Co, Zn, Cr, and Pb were rated as low pollution with no complete contamination at all sites studied. While the concentration or pollution index of Ni was medium pollution, A variety of sources produce heavy metals, and soils are thought to be their final sink [9] Human health and agricultural products are seriously in danger from heavy metal poisoning in the soil. So determining the spread of heavy metal pollution is critical [25].

Furthermore, this heavy metal enters the environment and interacts with soil or water, potentially harming plants and animals [26]. Figure 4 shows the percentage of soil-borne heavy metals in different sites.

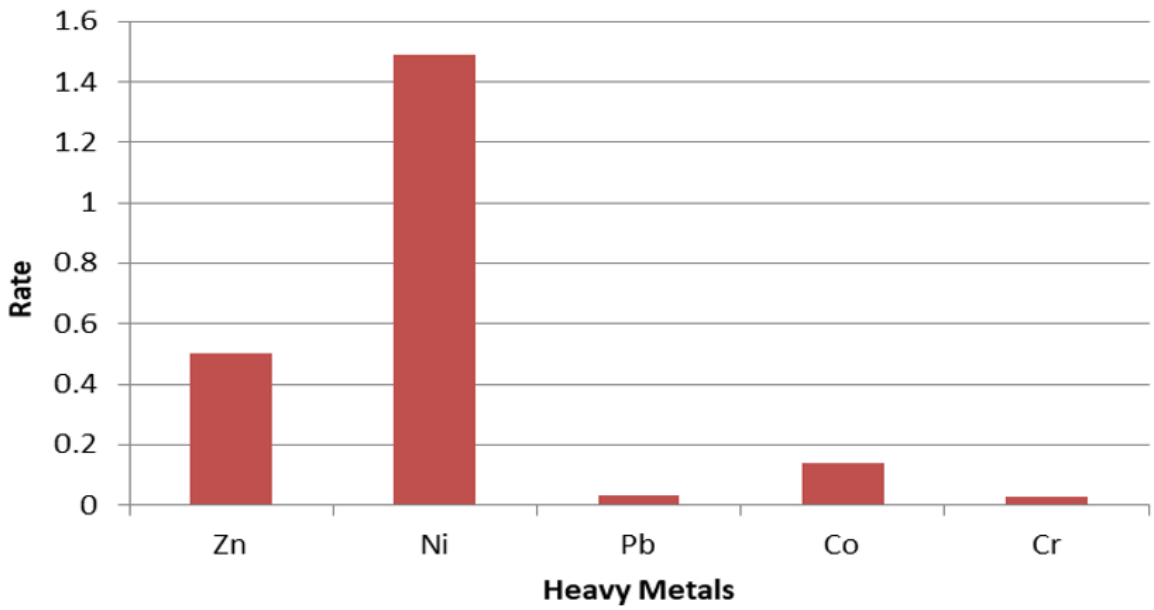

Figure 4.
Percentage of heavy metals in soil in deferent sits.

Heavy metal contamination may be disseminated in soils by mechanisms such as wind, hydrodynamics, and plant absorption. Table 4 shows the concentrations of certain heavy metals in the soil samples.

The average amounts of Ni were determined to be 1.49 ppm. The rise in nickel (Ni) is attributed to combustion products, leading to elevated concentrations of Ni in the atmosphere, which then accumulates in the soil [27] influenced by oil installations in proximity to the research region [28] (Figure 3).

The average concentration of Zn was 0.50 ppm. The rise in Zn content in soil is attributable to industrial operations that elevate Zn levels in the atmosphere, subsequently affecting the soil [29]. The elevated levels of Zn in certain samples have been ascribed to the oil spills. The mean concentration of CO in the current study was 0.14 ppm. The levels of CO_2 in soils are mainly increasing due to fuel combustion [30] and due to anthropogenic sources [31]. The mean concentrations of Pb and Cr, on the other hand, were found to be 0.03 and 0.027 ppm, respectively, because of the products of fuel combustion.

6. Conclusions

In the soil of the Baiji refinery, the concentrations of Co, Ni, Cu, Zn, and Pb in soil samples were determined and employed as indicators for pollution. The findings from the comparison between this study and the studies of Coetzee, et al. [12] and Das, et al. [13] show that the concentrations of heavy metals are very low, based on CF and PLI. It was found that CF for Co and Zn showed relative amounts of class 1, indicating low contamination, and CF for Cr and Pb in the analyzed locations showed relative values of class 1, which indicated some pollution [14-17]. Co, Zn, Pb, Cr, and Ni have class 1 contamination factors, representing low contamination. PLI results in all investigated locations were categorized as class 1, indicating class 1, meaning no pollution. The direction of the wind and the gases released impacted the metal percentages' dispersion pattern [30, 31].

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Transparency:
The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.

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