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Environmental Pollution from Energy Sources in the Haditha Oil Refinery Area, Anbar, Iraq

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ABSTRACT

The environmental impact of pollution varies based on several conditions, most importantly the number of pollutants released directly into the environment. This research aims to determine the probable levels of pollution and characterize measurements outcomes with GIS techniques, shedding light on spatial correlation and comparing concentrations of heavy metals in different areas of the Haditha refinery in Iraq's Anbar Governorate. Materials and Methods: The concentrations of heavy metals (lead, cadmium, and vanadium) were measured in soil samples collected at a depth of 30 cm from different locations near the new energy refinery in Ramadi city, as well as measuring the accumulation of these elements in the *Cynodon dactylon* plant in the region. Results: The results pointed out that elemental ratios (V: 0.475, Cd: 2.625, Pb: 0.629) for soil samples and (V: 0.759, Cd: 3.65, Pb: 0.875) for *C. dactylon* with the record-breaking increase of vanadium concentration in all samples. Conclusion: Spatial analysis revealed that soil in the research area was non-contaminated with the subject elements according to the Iraqi standard as well as the world concentration scale of the heavy elements.

1. INTRODUCTION

Haditha Oil Refinery is considered one of the most important refineries of the Northern Refineries Company, affiliated with the Iraqi Ministry of Oil. Its headquarters are located in Anbar [1]. It was established in 1976 under Law No. 101. The company was managed at the time by the General Organization for Oil and Gas Refining. In 1997, the Public Sector Companies Law No. 22 was issued and became the name of the company is North Refineries Company/public company. The company produces various types of products such as unleaded gasoline, jet fuel, white oil, gas oil, black oil prepared for export, and various types of oils such as motor oil for gasoline, motor oil for diesel, oils for sewing machines, transformers, asphalt products, sulfur, fuel gas, and liquid gas as well as the main energy sources [2].

The production capacity is 16,000 barrels per day. Despite the fact that it was demolished due to the military operations against the terrorist organization ISIS, and as for the establishment of the dynamic budget workshop, it has now been completed 100%, and it is part of the work to equip the rotating plants division and increase the storage capacity in the refinery [3]. Climate in this region is one of the important natural factors that affect the characteristics of the natural environment. It affects the properties of the soil and the quality of polluting elements, their concentrations, and their variation from one season to another.

The climate of Anbar Governorate is characterized by a large change in temperature and a high percentage of humidity and rainfall compared to the rest of the governorates due to its proximity to bodies of water and its proximity to sources of the Euphrates River [2]. Their continued emission leads to an increase in their concentrations in the soil characterized by their stability and non-decomposition, and this leads to It accumulates in microorganisms, plants and aquatic organisms, which in turn is transmitted to humans through the food chain and then causes multiple health problems for humans, oil pollution emerged due to the swift technological advancements in the oil industry, resulting in heightened production and irregular utilization. However, oil refineries are considered as important sources of water pollution because the refineries used water during the process and disposed it [4].

Lead (Pb), cadmium (Cd), and vanadium (V) were selected in this study based on their environmental importance, toxicity, and close association with industrial pollution, especially in areas close to oil refineries and energy facilities. These metals are known to have negative effects on soil, plants, and human health, making them key elements to monitor in environmental studies.

1. Lead (Pb) – A long-lived environmental contaminant Lead is the most toxic and omnipresent metal within contaminated environments and is mostly generated by combustion of fuel, industrial discharges, and refining residues of petroleum products. Lead has a strong affinity to

attach itself to vegetation and soils and remain deposited there. Thus, this is transferred from plant to plant in the food chain and impacts wildlife and human health as well. Chronic lead poisoning leads to neurological and developmental problems, especially in children, as well as impacting liver and kidney function.

According to the study [5] conducted the soil around industrial areas and oil refineries contains high concentrations of lead, so monitoring is required to check the extent to which contamination has taken place.

2. Cadmium (Cd) – A cumulative toxic element: Cadmium is one of the most toxic heavy metals due to its high solubility in water, causing it to easily move into plants and soil. It derives mainly from oil refining operations, industrial wastes, and pesticides and is classified as a carcinogen by the Environmental Protection Agency (EPA). Cadmium accumulation in the environment results in serious health problems such as kidney disease, bone disease, and detrimental effects on the respiratory system. A study [6] found that cadmium was easily taken up by plants and hence could be used as an important biomarker in monitoring soil contamination.

3. Vanadium (V) – A metal associated with oil contamination: Vanadium is a heavy metal found in large amounts in crude oil and therefore could be utilized as a prominent indicator of plant and soil contamination near oil refineries.

It is considered to be a toxic element in large amounts as it affects the respiratory system and causes health problems when inhaled or taken through plants. It is usually found in areas near energy-producing plants and fueling stations and thus is a priority element for analysis in oil industry-contaminated sites.

Based on the research [7] vanadium can be the most prevalent element in the regions close to oil industries, which is why it should be researched as a pollution marker in the environment.

The analysis of lead, cadmium, and vanadium is critical in uncovering the extent of environmental pollution in the area around the Haditha oil refinery in Iraq, as the level of these elements portrays the extent of industrial activity influence on soil and plants. The selection of the metals therefore renders the research more credible in identifying hazard to the environment and potential health impacts.

The environmental pollution from oil refineries includes hydrocarbon leaks through accidents or discharge of untreated wastewater, which is a frequent phenomenon in refining, transportation, and storage operations. This kind of hydrocarbons would not be limited to polluting just the local environment; leakage into the aquatic environment would entail further loss regarding biodiversity and other water resources in this region besides oil pollutants, heavy metals such as nickel, lead, and cadmium have been regarded as the major environmental contaminants from refining processes; these tend to increase their concentration in soil, air, and water. These elements will be accumulated in the environment and transferred by the food chain to living organisms, including humans, producing serious health problems such as chronic poisoning, growth disorders, and respiratory diseases [5].

Understanding the sources of pollution emitted by oil refineries within the Haditha area is of prime importance, along with analyzing the environmental effects, when considering the development of effective strategies that reduce these impacts. The current study will aim to identify environmental pollution due to Haditha oil refinery in Anbar concerning water, soil, and air qualities, in an attempt to reach practical solutions that may contribute to a reduction in pollution emanating from these important industrial establishments [6]. There have been numerous earlier studies that dwelt on environmental pollution resulting from oil and refining activities in Iraq, especially in areas closely related to oil facilities like the Haditha Refinery [6].

The same in Basra, in the southern part of the country, demonstrated the contribution of heavy metal soil pollution due to the increase of elements such as nickel, lead, and cadmium in areas around oil refineries due to activities related to oil operations, refining, and transportation processes [7]. The study also explained that the highest areas of pollution were considered near the facilities of oil, especially in the western Basra area, since it is very close to fuel stations and refineries. The research touches water pollution in the central Iraq region; within this region, it considered water pollution those areas near the refineries; the results showed that the oil spills and environmental accidents were the main sources of water pollution [8].

Cynodon dactylon, or bermuda grass, was selected for research because it has unique traits that make it a good bioindicator in assessing heavy metal soil and plant contamination. *Cynodon dactylon* is very tolerant of harsh environmental conditions, including contaminated soil, which is why it was used in the investigation of environmental contamination [9].

Heavy metal accumulation potential: *Cynodon dactylon* is reported to absorb heavy metals such as lead (Pb), cadmium (Cd), and vanadium (V) from the soil and accumulate them in its tissues and therefore can be utilized as an effective bioaccumulator of environmental pollution [10].

Widely distributed and easy to grow: The plant has the ability to grow on diverse soil types, including on polluted soils, hence it can be used in multi-site ecological research [11].

High environmental pollutant tolerance: The plant has the ability to grow even in media that contain high levels of heavy metals, where the plant is applied in phytoremediation to stabilize or store these harmful elements [12].

1.1 Role in environment and application

Apart from its environmental use as a bioindicator, *Cynodon dactylon* has other environmental uses such as soil stabilization and minimizing soil erosion, adding to its utility in green sustainability planning [13].

Its importance as a bioindicator in pollution studies: *Cynodon dactylon* has been proven to be utilized as a bioindicator by a number of studies, given that it has been shown by studies that it can accumulate and concentrate heavy metals from the ground, thereby serving as an adequate model for the study of oil refinery and industrial soil pollution [14]. In addition, research into the concentration of these metals in vegetation can also provide accurate information on the level of pollution in a specific area, and thus might be useful in environmental risk assessment [15].

This study aims to assess potential pollution levels and present the findings using Geographic Information Systems (GIS) technology, highlighting spatial relationships and comparing heavy metal concentrations across various areas of the Haditha Oil Refinery in Anbar, Iraq.

2. MATERIALS AND METHODS

2.1 Study area and sample collection

The study was conducted near Haditha oil refinery in Al Anbar Governorate, Iraq, that is located in the extreme west of Iraq and surrounded by the cities of Al-Qaim and Al-Rutba, between longitudes (coordinates: 34°4'13" N 42°19'11" E) [1], which was highly affected by the previous military operations. The authors have used the image of the Landsat satellite for the year 2019 and 2020 in this study, for carrying out a spatial analysis of the area, test temporal change in element ratios within the geographic information system environment (ArcGIS software). Three main sites within the refinery were randomly selected to collect samples. In each site, three holes were dug to collect samples from a depth of 30 cm surrounded by *Cynodon dactylon* plants. The samples were wrapped in strong plastic bags with site data, site name, and sample number along with the date of sample collection [9].

The depth of 30 cm was chosen because it represents the layer most affected by industrial activities and environmental pollution, as heavy metals are concentrated in this layer due to atmospheric deposition, oil spills, and the interaction of pollutants with the soil. This depth is commonly used in environmental studies because it reflects the extent of soil pollution before metals move to greater depths and the availability of metals to plants such as *Cynodon dactylon*, which absorb heavy elements from this layer [10].

2.2 Sample transportation and laboratory analysis

According to the study [10], all samples were transported to the laboratories of the Department and Quality Control, Iraqi Ministry of Trade. Thereafter, the digestion process was begun as the first step of a two-stage analytical procedure

Digestion: 1g of the dried sample was weighed into heat-resistant tubes, then added to a mixture of HNO_3 and HCl in 1:1 ratios (3 ml of each acid).

The samples were positioned on the hot plate at a temperature of 80°C until the sample reached a semi-dry stage. Against the sample, 2 ml of perchloric acid ($HClO_4$) and 2 ml of hydrofluoric acid (HF) were added in 1:1 ratio. The samples were prepared on the hot plate until almost dry. After removing, drops of hydrochloric acid (0.5 M) were added to dilute the samples to the required volume for measurement.

3. RESULTS AND DISCUSSION

The tables below show the standard concentrations of international standards for elements and results obtained for soil and plant samples in the study area

Based on the data in the Table 1, concentrations in *C. dactylon* samples are higher than those in soil, especially for cadmium (3.65) and vanadium (0.759), while lead is also present in higher amounts (0.875).

Table 1. Mean of three elements concentration according to our study for different locations in study area

Type Samples	Pb	Cd	V	P Value
Soil Samples	0.629	2.625	0.475	0.005
C. dactylon	0.875	3..65	0.759	0.001

P value less than 0.05 (in this case 0.005 for soil samples and 0.001 for *C. dactylon* samples indicates that the differences in metal concentrations between soil samples *and C. dactylon* are statistically significant. Low P values also indicate that the differences observed in Pb, Cd and V concentrations between soil and *C. dactylon* are not due to chance, and that there is a real and noticeable effect of the presence of these metals in the environment or their uptake by plants.

As for the comparison between metal concentrations, it was for lead (Pb): the concentration of Pb in *C. dactylon* (0.875) is higher than its concentration in soil (0.629), but the difference is not very large. However, this indicates the ability of the plant to absorb lead.

Cadmium (Cd): The concentration of cadmium in *C. dactylon* (3.65) is much higher than that in the soil (2.625), suggesting that the plant may be better able to absorb cadmium from the soil.

Vanadium (V): The concentration of vanadium is higher in *C. dactylon* (0.759) than in the soil (0.475), suggesting that the plant has some ability to absorb this metal, although the difference is less pronounced than for cadmium.

The analysis indicates that *C. dactylon* tends to accumulate higher concentrations of lead, cadmium and vanadium than the soil, with statistical significance confirmed by low P values (0.005 for soil and 0.001 for *C. dactylon*). This suggests that *C. dactylon* may be a useful bioindicator for the presence of these metals in the environment, especially in polluted areas. The ability of plants to absorb cadmium and vanadium suggests their potential for use in phytoremediation applications to remediate metal pollution agree with Kabata-Pendias [12].

The results were compared with a table of international percentages and with local studies, due to it being an area that witnesses, there is a less movement of transportation and automobile movement, as lead is used in the manufacture of car tires and as a result of the combustion of gasoline, which leads to deposition of lead in the soil. The results of these analyzes indicate that the soil and plants in the studied areas is not contaminated with lead, meaning that it did not exceed the natural limit or the standard limit.

The results of our current study were compared with a local study of Basra Governorate [13]. It was found that the percentage of Cadmium was (33.41) in the Karma area, as it attracts large traffic of means of transportation and human and medical pollutants, and in the Abu Al-Khasib area (40.90). Through making a comparison, it was found that the percentage Cd did not witness a high increase in the studied areas. It was found that the total concentration of partial and residual Vanadium during the study period was high compared to some studies in global soils [14].

The results of the statistical analysis showed that there were no statistically significant differences between the study categories, with a significant positive relationship between lead and vanadium, from the soil and plant were also recorded. Given that oil extraction affects the topography and geology of the region and the social conditions and climatic conditions are in their nature, the exploration process and their extraction often leave significant effects that may cause significant damage to it, or may cause permanent or temporary change in it, and it also leaves clear effects on the natural resources and environmental components on the surface of the earth. High concentrations of these two elements were recorded, exceeding the permissible limits internationally and in the Arab world, according to what was mentioned in the study [15], that's show in Figure 1.

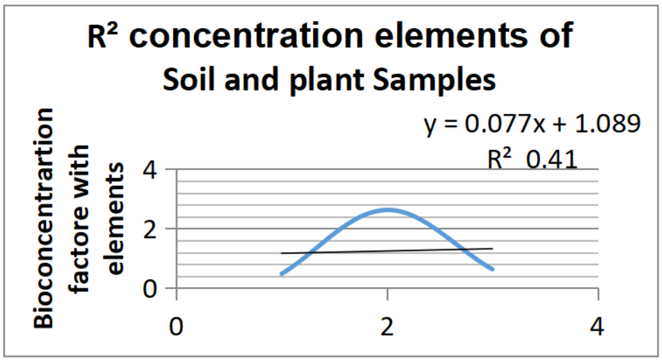

Figure 1. Concentration elements in plant and soil in study area

When our results are compared with the standard concentrations of international standards for average elements according to Table 2, it is observed that lead concentrations in the studied area are much lower than the levels specified in most international studies such as Kabata-Pendies and USEPA but still higher than some standards such as Do and Ren. where the value of cadmium is found to be higher compared to most international studies, putting into consideration Kabata-Pendias and USEPA values.

Table 2. Standard concentrations of international standards for Mean elements ppm

Universal Studies	Lead Pb	Cadmium Cd	Vanadium V
Kabata-Pendies (2001) [12]. Trace elements in the soil and Plants. 3rd CRD Press. 413	550	230	190
Do and Ren (2019) [13]	55	1.6	3.5
USEPA (2007) [14]	300	20	50

Similarly, vanadium is also more concentrated in this current study than that compared in some studies such as by Do and Ren [13] but higher than many such as Kabata-Pendies [12], Brian G. Bearden. This analysis indicates that the Haditha Oil Refinery area is highly polluted with heavy metals, especially cadmium and vanadium, in comparison to their levels as reported by some international studies. Some of this pollution exceeded international environmental standards, and therefore this area deserves more attention to impose measures for pollution reduction and to conduct more environmental studies according to the study [16].

Figure 2 shows the percentage of accumulation of elements (lead, cadmium, vanadium) in the soil and surrounding plants. This indicates that the soil and plants were within a positive relationship for biological treatment to get rid of contaminated materials in the soil. It is highly efficient in reducing pollution of soils that are contaminated with elements as a result of internal combustion. For fuel, as well as domestic and industrial waste that is disposed of in varying quantities in different regions. However, the soil is considered not contaminated with elements if it is compared to the international standard for element concentration, which is twice the concentration [16].

It was nearly twice the global standard for vanadium concentration that the soil of this region is not significantly polluted with this element due to the effectiveness of the soil in absorbing polluted materials and the lack of sources of pollution. Through the evaluation matrix of pollution levels based on the subgroups of toxicity, stability, flammability, viscosity and element accumulations, it is considered a less level. Taking the characteristics to illustrate the level of the process, which R 0.41%, which is the result of a comprehensive assessment of the degree of pollution resulting from less oil spills on the surface this is agree with Ajmi [17].

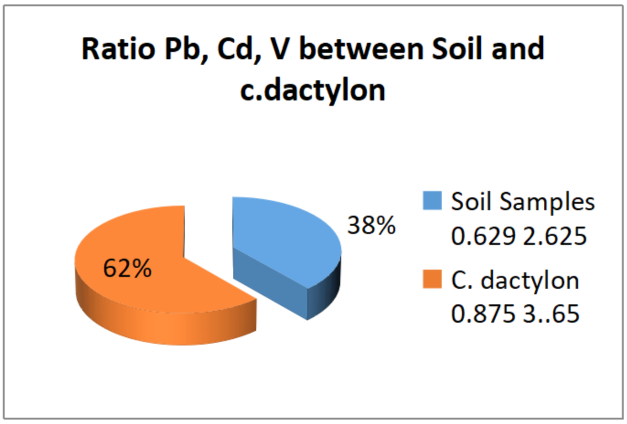

Figure 2. Percentage of accumulation of elements (lead, cadmium, vanadium) in the soil and surrounding *C. dactylon* plant in study area

Calculating the Bioconcentration Factor (BCF). By comparing the BCF values of certain metals (lead Pb, cadmium Cd, and vanadium V) in *C. dactylon* with that in soil, certain conclusions can be drawn about the plant's capacity to concentrate these metals in its tissues.

1. Lead (Pb): BCF = 1.39

This result indicates that *C. dactylon* is able to concentrate lead 1.39 times more than in the soil. This indicates that the plant has an average ability to concentrate lead compared to other metals, and this may indicate the ability of the plant to uptake the metal from the soil. This ratio is, however, not very high to guarantee that the plant is a good "filter" for the substance in the polluted environment.

2. Cadmium (Cd): BCF = 1.39

Similar to lead, C. dactylon can also adsorb cadmium to the same extent, 1.39. This result reflects that the plant has a similar response for cadmium similar to lead, it adsorbs this metal to a moderate degree from soil. With high toxicity of the plant and soil for cadmium, this may imply that the plant would also serve as an environmental marker of the availability of the metal in the surrounding environment.

3. Vanadium (V): BCF = 1.60

This result is an indicator that *C. dactylon* has higher accumulation of vanadium to a larger extent than the accumulation of lead and cadmium to the value of 1.60. This is a sign that the plant has more effective uptake of vanadium than any of the metals being researched. Vanadium is relatively rare metal element found in the environment, yet this quantity may be an indicator that the plant possesses a better mechanism of metal uptake compared to other metals.

C. dactylon possesses intermediate capacity for the uptake of lead and cadmium and may prove to be a good bioindicator for the presence of these metals in the environment. It possesses stronger capacity for the concentration of vanadium, which may be an expression of the variation in the capability of the plant to absorb various metals.

These observations make *C. dactylon* a potential candidate to be employed for the purpose of the study of heavy metal pollution because it can act as an indicator of the potential concentration of such heavy metals in the soil of the surrounding environment.

3.1 Spatial analysis of elements

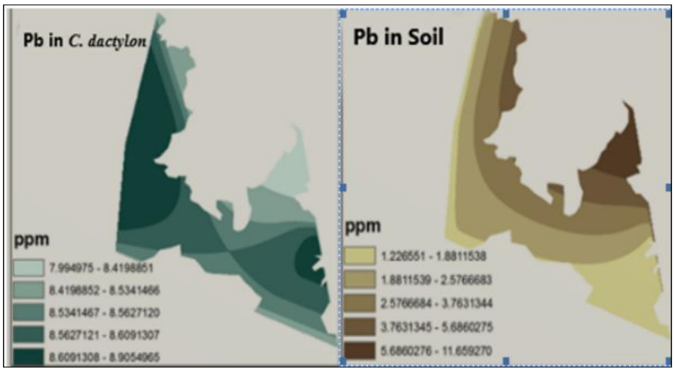

Figure 3. Spatial analysis of Pb concentration in soil and *C. dactylon* plant in study area

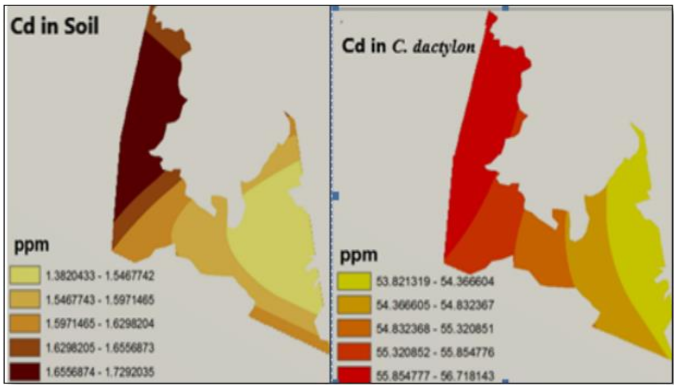

Figure 4. Spatial analysis of Cd concentration in soil and *C. dactylon* plant in study area

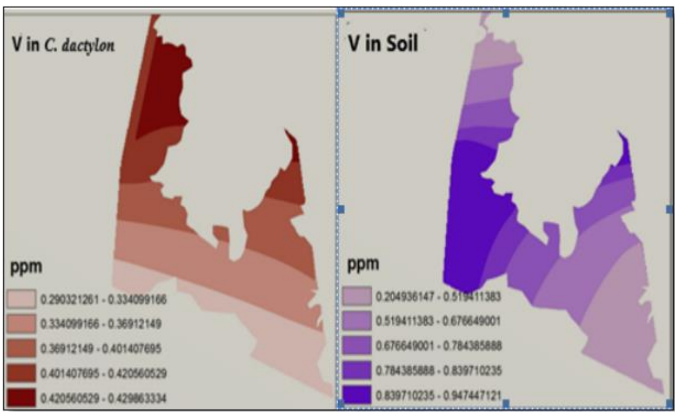

Figure 5. Spatial analysis of V concentration in soil and *C. dactylon* plant in study area

The data was displayed on satellite visuals for the elements (Lead, Cadmium, Vanadium) by linking them to a spatial relationship in order to clarify the way the elements are distributed and to show which areas contain a high concentration. The following figures show the spread of the elements in different locations of the current study and shows that the percentage of Vanadium was high concentration areas, by displaying the results on the visual satellite using the method.

Interpolation Spatial analysis of the element lead showed that the soil of this region was not contaminated when the percentages were compared with local studies of the region, meaning that it did not exceed the standard rate [18]. The Figures 3-5 below show the distribution of elements concentration.

Table 3. Predictions of heavy metal concentrations (Pb, Cd, V) at new sites based on spatial analysis

Location	Predicted Pb	Predicted Cd	Predicted V
Site 1	0.700	2.900	0.560
Site 2	0.750	3.400	0.640
Site 3	0.680	2.850	0.600

According Table 3 to calculate the prediction using spatial analysis based on the data of metal concentrations in the samples (soil and plants), the spatial analysis techniques Kriging or Inverse Distance Weighting (IDW) were used. Kriging uses the spatial interaction between points to generate a prediction map. It can be determined whether there is a spatial pattern in the data as accumulation around a pollution source to estimate the metal values at the missing sites [19].

IDW: A higher weight was assigned to points closer to the target point. Pb, Cd, and V were the variables estimated in the contour maps and to determine the range of influence (the distance at which points affect each other), the prediction map provided the expected future concentrations of the elements at the studied and unstudied sites based on the spatial relationship between the points [20].

It is indicated that the values at the different sites show a small difference in metal concentration between Site 1 and Site 3, with Site 2 being more concentrated in cadmium and vanadium. This may be showing differences in environmental conditions such as soil type or source of pollution around each site. As *C. dactylon* exhibit higher lead, cadmium, and vanadium uptake, the prediction is that new sites can be more susceptible to bioaccumulation of these elements. Such information could prove useful in environmental monitoring studies or in environmental research using plants as pollution bioindicators [21, 22]. Spatial analysis (IDW or Kriging) helped identify locations with elevated contamination or potentially under higher rates of heavy metal buildup, helping make environmental decisions on where to monitor or what needs remedial action.

Based on predictions, Site 2 should be monitored in particular because of its cadmium and vanadium levels. Whether the sites have plants such as *C. dactylon*, the capability of these plants to adsorb more metals should be investigated. Based on heavy metal level predictions (Pb, Cd, V) at new sites based on spatial analysis are in agreement with studies [23, 24].

4. CONCLUSIONS

Results obtained from the study of heavy metal concentration in *Cynodon dactylon* (sesbania) and soil surrounding it showed that the crop possesses an excellent ability to uptake and accumulate certain mineral elements from the environment. Lead (Pb), cadmium (Cd), and vanadium (V) levels in plant material were higher than in soil where plants were grown. This disparity suggests a physiological process in the plant that is effective and helps it absorb these elements from the ground and accumulate them in its tissue so that it may be a suitable option for use as a bioindicator for heavy metal pollution.

On statistical examination of data, the variance test result revealed that P-values for all parts were less than 0.05, confirming statistically significant variation in metal content in the plant and soil and eliminating chance as a factor. This, in turn, represents an actual effect of metal enrichment in plants through the virtue of exposure to polluted soil. Comparison of the results with global environmental standards indicated that the lead content in the plant was within the safety limits permitted by certain global agencies.

This notwithstanding, the levels of cadmium and vanadium exceeded the limits in certain zones, which creates the possibility of real-life environmental contamination that requires intervention and monitoring on an ongoing basis. These results confirm that the air surrounding and within the oil refinery is contaminated with vanadium and cadmium, which reflects the impact of industrial activities on the ground and vegetation surrounding it. Applying spatial analysis techniques, the patterns of distribution of heavy metal deposits between the various sites that were investigated were seen to be obviously different. This serves to emphasize the importance of using GIS for tracking the extent of pollution and mapping high-risk zones. This variation indicates that the source of pollution is not uniformly distributed, but rather is influenced by a large number of spatial factors such as proximity to emission points, wind directions, and gradient of the terrain.

From this, the study recommends that observation of regions which have shown high concentrations of cadmium and vanadium continues, and also the use of *Cynodon dactylon* as a better bioresearcher in environmental monitoring. It recommends that application of spatial analysis be extended to better predict areas that are contaminated so that it will contribute to making proper environmental decisions for planning future treatment or containment policies.

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