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Kamal Kant Joshi
Department of Environmental Science, Graphic Era Hill University, Dehradun, Uttarakhand, India

Correspondence
Kamal Kant Joshi
Department of Environmental Science, Graphic Era Hill University, Dehradun, Uttarakhand, India

Analyzing the heavy metal pollutants and physico-chemical properties of soil in areas degraded by oilfield activities

Kamal Kant Joshi

Abstract
The research investigated heavy metal and physicochemical parameters of soil samples in Ishiagu lead-zinc mining region. The soils are all somewhat alkaline, with moderate CEC, medium to high organic carbon. There is considerable possibility of heavy metal contamination of Oilfield from the tailing region owing to its low pH, whereas the increased clay concentration at the mining location may assist slow metal breakdown. Yet, the high quantity of these hazardous metals in the soil may have significant impacts on soil quality and on human health if they enter into the food chain. In order to limit the chance of this happening, unlawful artisanal mining and the eating of contaminated plant and Oil should be aggressively discouraged.

Keywords: Oilfield, Soil, heavy metal, environment, physicochemical

1. Introduction

Heavy metals are a persistent problem for soil quality since they are not broken down by soil organisms or by any other natural processes. Heavy metals may be divided into two categories: those that are needed for biological processes, and those that are not. When present in excess, essential heavy metals like Cu, Fe, Mn, Ni, and Zn may be hazardous to plants while being essential for a variety of physiological and biochemical activities throughout their life cycles. Heavy metals that are not essential to plant growth, such as lead, cadmium, arsenic, and mercury, are extremely poisonous to plants and serve no useful purpose in them. They are a potential source of environmental pollution and can have devastating effects on a wide range of physiological and biochemical processes in crops, leading to decreased yields. They pose a serious risk to human health because they may be ingested via crops and then biomagnified to dangerous levels once inside the body. Heavy metals in the environment have grown dramatically over the last several decades due to the spread of industrialization and urbanization, prompting widespread alarm. The term "heavy metal" refers to a class of chemical elements known for their high density, atomic weight, and atomic number.

Due to their toxicity, widespread distribution, and great migratory potential, oil and oil products are the environment's top priority contaminant. The contamination of natural ecosystems, especially soil cover, is a direct outcome of the development and exploitation of oil resources and the violation of hydrocarbon transportation restrictions. The Absheron peninsula in the Azerbaijan Republic is home to a large portion of the country's industrial potential and 60% of its onshore oil production, but it also shares the environmental degradation issues that plague other hydrocarbon producing locations throughout the globe. Vital oil and gas pipelines cross the area as well.

Literature Review

Nwankwoala HO, *et al* (2018) [1] We want to learn more about the soil and ground water quality in and around Okpoko, Anambra State, via this research. Fifteen samples of soil and groundwater were taken for testing to determine the presence of various heavy metals and hydrocarbons. We collected soil samples at 15 and 30 centimetres deep to gain a more complete view. Atomic absorption spectroscopy was used to determine the heavy metal content of soil and groundwater.

Except for Ni, the concentrations of all the other metals diminish as one descends into the earth. Topsoil and subsoil TPH levels in the region range from 109.43 to 2112.64 mg/kg and 105.57 to 1747.82 mg/kg, respectively. Topsoil and subsoil average 654.01 582.12 and 568.27 502.11 mg/kg of TPH, respectively, whereas the control site averages just 54.43 16.63 mg/kg. The greater TOC level near the gas station compared to the control location suggests the presence of human activity. The control had a lower TPH concentration than the area around the gas station and service station, suggesting that the TPH content declines with depth. In contrast to Fe and Mn, the concentrations of all the other metals are higher than in the control. The levels of metals were much below the DPR's maximum allowable levels for use in agricultural soils. It is advised to conduct regular soil and groundwater assessments to check for possible contamination.

John Pichtel (2016) [5] So-called "produced water" is the most abundant byproduct of oil and natural gas extraction. To further facilitate these oil and gas operations, hydraulic fracturing (HF) fluids are injected into the formation. Water that has been created may have hundreds of different chemicals, much as HF fluids, some of which are harmful to people and the environment. Wastewater from the oil and gas industry may have several uses, especially in dry areas, provided it is handled properly. Injection, discharge to the surface, and beneficial reuse are all feasible because to the wide range of treatment methods available today. Little is known about the impacts of oil and gas production wastewater (OGPW) on soil resources, despite the abundance of literature on the topic's effects on groundwater and surface water. The consequences of oil and gas development on soil are examined in this review study, which gathers background data on a wide range of chemicals utilized and generated in the industry. Moreover, OGPW-related pollution control solutions are discussed. Understanding how OGPW alters soil's chemical, physical, and biological properties might aid in its restoration. And there's potential for enhanced sustainable reuse of oil and gas water in agricultural and industrial settings.

Ku. Smita Tale, *et al* (2015) [2] Soil provides for the three most basic human needs—food, clothing, and shelter. We rely heavily on soil for our agricultural production. Wheat, rice, jawar, lentils, sugarcane, vegetables, fruits, etc. are all grown in abundance in India, and the country has a preeminent position in agricultural production worldwide. The execution of the other management strategies relies on a thorough knowledge of the physical and chemical state of each soil. Soil's physical and chemical qualities, which determine its production, make physico-chemical studies crucial. Farmers will be more aware of the importance of economic productivity thanks to this information.

Nabanita Bhuyan *et al* (2015) [4] The soil in which plants grow is crucial to the survival of all living things, including people. Establishing the soil's properties is crucial for evaluating its quality. The current research makes an effort to examine the soil's physicochemical characteristics at a degraded site in comparison to a control site. Soil characteristics such as acidity, carbon content, water retention, bulk density, phosphorus, potassium, zinc, manganese, iron, copper, and many more were measured. Moisture levels might be anywhere from 12.68 and 19.15 percent, 10.51 and 18.06 percent, 1.32 and 1.31 percent, and 17.23 and 5.39 percent. Site 4 has the most capacity to store water, whereas site 3 has the least. The research found low concentrations of P, K, and Organic Matter as well. Subsequent soil depth was observed to result in a decline in chemical parameters. Lower subsoil often has a higher bulk density than topsoil. The results showed that nutrients and characteristics varied significantly across samples and between the numerous locations that were considered.

Debojit Barua (2011) [3] Total nitrogen, organic carbon, and exchangeable potassium all increase, whereas soil moisture, porosity, water holding capacity, soil pH, and extractable phosphorous all drop after a crude oil spill. Physical and chemical changes to soil are undeniably attributable to spilled crude oil.

Materials and Methods

The first hectare of farmland in each sample zone was chosen at random. On the side of the river where there was more irrigation activity, a 100-meter-long transect was taken using a stratified grid sample approach. Every 20 meters along the transect, from the surface down to around 20 centimeters, samples were taken. The same method of sampling was used to a further four 20-meter transects that were conducted immediately after the first. Twenty-five samples in all were collected, five from each of three distinct sections along the river's edge. After being air-dried, the samples were crushed and sieved through a 2-millimeter mesh before being sent to the lab for analysis. Testing at a soil-water ratio of 1:2.5 using an EL model 720 pH metre, we were able to calculate the pH level. Beckman Conductivity Bridge measurements of electrical conductivity (EC) were made using a soil-to-distilled-water ratio of 1:2.5. Hydrometer measurements were taken to determine particle size, as Jaiswal instructed (2004). To calculate organic carbon, we used the Walkley-Black wet oxidation approach, and to calculate CEC and exchangeable bases, we employed the ammonium acetate extraction and saturation procedures reported. The extraction procedure for total heavy metal content determination made use of the double acid digestion approach (Anderson, 1974). One gram of each sample was combined with one hundred centimeters three of de-ionized water to use.'s modified Tessier sequential extraction method to calculate the soluble and exchangeable heavy metal fractions. After being shaken for eight hours, sitting for a whole night, then centrifuged for 15 minutes at 10,000 rpm, the resulting mixture was ready for further analysis. The soil's concentration of soluble metals was calculated using the decanted supernatant liquid. The insoluble metal fraction residual was combined with 100cm3 of ammonium oxalate, agitated for eight hours at 10,000 rpm, allowed to rest for a full night, centrifuged for 15 minutes, and drained. Exchanging amounts of metals were calculated using the solution. All experiments were conducted in triplicate, and metal concentrations were determined using an atomic absorption spectrometer. Descriptive and inferential statistics were used to the collected data.

Results

Physico-chemical properties of the soil

The physicochemical characteristics of the soils in these three regions are summarized in Table 1. There were a wide variety of soil types, from loamy sand to sandy loam. Overall, the pH levels in all three locations are somewhat alkaline. There is a big disparity in the mean EC values of the three regions, with Jakara having the highest value. There were statistically significant differences (p 0.05) in the organic carbon concentrations at the three locations. Earlier, Esu noted that their rankings ranged from poor in Watari and Challawa to middle in Jakara (1991).

All three locations had potassium amounts that were high to very high. According to the rankings of Landon, both the sodium and CEC concentrations were rather typical for the middle to upper parts of their respective ranges (1991).

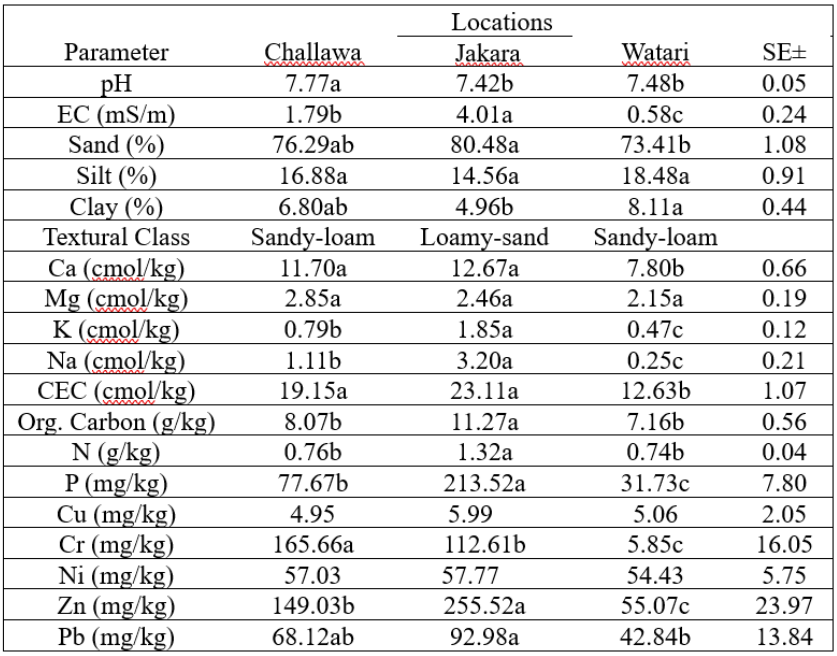
Landon (1991) reports that the soils contain high levels of Nitrogen, Jakara's value is substantially (p 0.05) greater than both Watari's and Challawa's. Compared to Jakara and Challawa, where Phosphorus levels were far too high, those in Watari were about normal. In terms of statistical significance (p 0.05), the Jakara site produced the highest average. One possible explanation for Jakara's high nutrient concentrations is because it serves as a dumping place for domestic waste.

Total heavy metals concentrations

In Table 1, we can see the overall metal soil concentrations. While the Jakara site had greater levels for both Cu and Ni, there was no discernible difference between the three locations. There was a large disparity in the mean Cr and Zn contents, The Challawa basin has the highest concentration of Cr, whereas the Jakara region has the highest concentration of Zn. The Jakara basin, in contrast to the Watari basin, has a much higher Pb content (92.98mg/kg).

There was a statistically significant difference (p 0.05) in the mean Cd concentrations at the three locations, with Jakara having the highest mean (11.81mg/kg). Maximum allowable levels of Zn, Cu, Cd, Pb, Cr, and Ni, as well as the corresponding threshold values proposed by the European Commission, are not exceeded in either Jakara or Challawa.

Table 1: Physicochemical Properties of the Soils of the Three Study Areas in Kano



		Locations		
Parameter	Challawa	Jakara	Watari	SE±
pH	7.77a	7.42b	7.48b	0.05
EC (mS/m)	1.79b	4.01a	0.58c	0.24
Sand (%)	76.29ab	80.48a	73.41b	1.08
Silt (%)	16.88a	14.56a	18.48a	0.91
Clay (%)	6.80ab	4.96b	8.11a	0.44
Textural Class	Sandy-loam	Loamy-sand	Sandy-loam	
Ca (cmol/kg)	11.70a	12.67a	7.80b	0.66
Mg (cmol/kg)	2.85a	2.46a	2.15a	0.19
K (cmol/kg)	0.79b	1.85a	0.47c	0.12
Na (cmol/kg)	1.11b	3.20a	0.25c	0.21
CEC (cmol/kg)	19.15a	23.11a	12.63b	1.07
Org. Carbon (g/kg)	8.07b	11.27a	7.16b	0.56
N (g/kg)	0.76b	1.32a	0.74b	0.04
P (mg/kg)	77.67b	213.52a	31.73c	7.80
Cu (mg/kg)	4.95	5.99	5.06	2.05
Cr (mg/kg)	165.66a	112.61b	5.85c	16.05
Ni (mg/kg)	57.03	57.77	54.43	5.75
Zn (mg/kg)	149.03b	255.52a	55.07c	23.97
Pb (mg/kg)	68.12ab	92.98a	42.84b	13.84

No statistically significant difference exists (p> 0.05) between the means in adjacent rows that are labelled with the same letter. Although there was some variation, the results are consistent with those of Audu and Peacock (2005), where Ni, Cu, Cr, and Pb were discovered in soils at alarmingly high concentrations at the Jakara dam irrigation site, and where Ni and Zn were discovered at alarmingly high concentrations in the Challawa valley, reaching 99.50 and 204.00mg/kg, respectively. These elements were found at high concentrations in the research areas for a few main reasons: fertilisers, agrochemicals, batteries, alloys, pigments, plastics, and tannery effluent are all sources of nitrous oxide.

Although describe significant releases from home sewages and slaughterhouse waste waters, Jakara's high Zn and Pb levels may be attributable to the ever-increasing number of automobiles in the city, as well as contributions from exhaust emissions from these vehicles.

Exchangeable and soluble metals concentrations

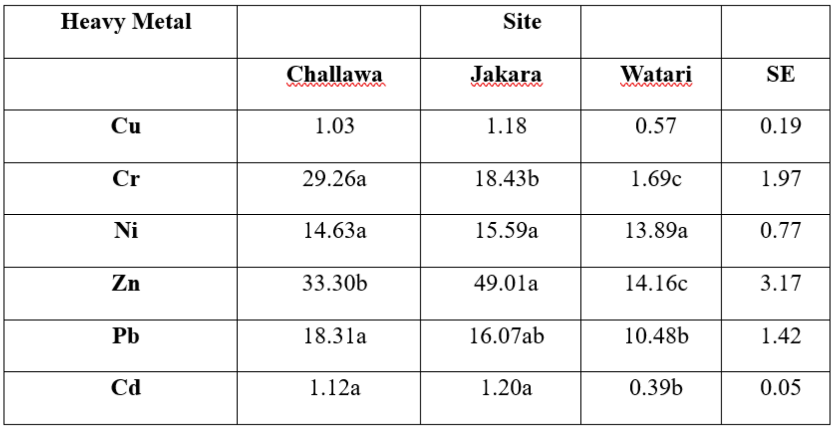
Tables 2 and 3 show the concentrations of soluble and exchangeable metals. The two types of Cu did not vary in their overall average concentration throughout the locations, although the average exchangeable Cr concentration was lowest in Watari and highest in Jakara. Jakara has much greater exchangeable and soluble Ni, Zn, and Pb concentrations than either Challawa or Watari (p <0.05). Cd was not discovered in solution, and the mean exchangeable Cd was much lower in the Watari site compared to Jakara and Challawa.

Soil pH, the type and quantity of clays and related oxides, organic matter, and the presence and composition of humic substances are the primary variables that influence the behavior of metals in the soil. Although higher values in the total concentration, the soluble and exchangeable concentrations are low. Most soil components that influence the solubility and exchange behaviour of the metals are quite rare, which is likely the case here.

The Jakara site has a lot of organic material, but not much tradable Pb. If Pb is taken up by the organic part, then less of it will be accessible at the exchange complex. Research by Yusuf (2007) and Adekola *et al*. demonstrates that the quantity of Pb sorbed by organic matter exceeds the amount discovered in exchangeable form (2010). In view of its total and exchangeable concentrations, the Jakara site's low levels of soluble Pb are notably notable. Total and exchangeable

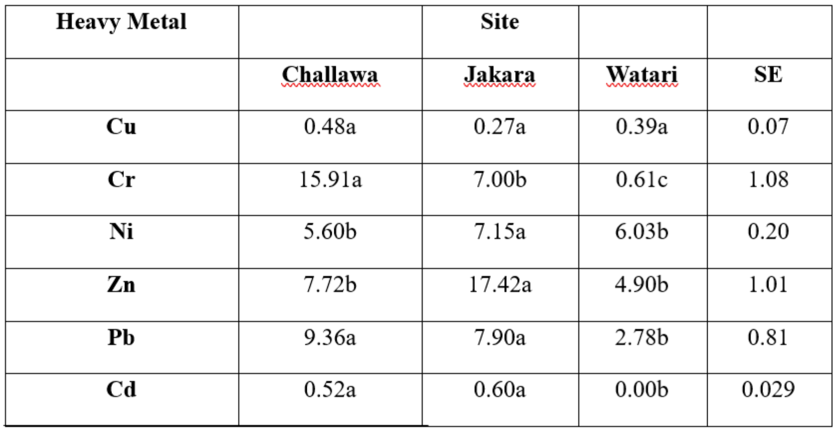
Pb concentrations at this site were higher than those at the Challawa site, as shown in Tables 1 and 2, although the Challawa site had higher concentrations of soluble Pb. Pb's unusual behavior is likely due to the fact that it is bound to the very high levels of phosphorus (P) found in the Jakara region (Table 1). Lead phosphate minerals, most stable form of lead minerals in soils over a broad variety of environmental conditions, may be effectively immobilised using phosphate (Cao *et al*., 2009).

Table 2: Heavy Metal Exchange Concentrations (mg/kg) in Kano's Three Research Areas



Heavy Metal		Site		
	Challawa	Jakara	Watari	SE
Cu	1.03	1.18	0.57	0.19
Cr	29.26a	18.43b	1.69c	1.97
Ni	14.63a	15.59a	13.89a	0.77
Zn	33.30b	49.01a	14.16c	3.17
Pb	18.31a	16.07ab	10.48b	1.42
Cd	1.12a	1.20a	0.39b	0.05

Table 3: Salivary Heavy Metal Concentrations (mg/kg) in Three Kano Study Areas



Heavy Metal		Site		
	Challawa	Jakara	Watari	SE
Cu	0.48a	0.27a	0.39a	0.07
Cr	15.91a	7.00b	0.61c	1.08
Ni	5.60b	7.15a	6.03b	0.20
Zn	7.72b	17.42a	4.90b	1.01
Pb	9.36a	7.90a	2.78b	0.81
Cd	0.52a	0.60a	0.00b	0.029

Experiments conducted at the Challawa and Jakara sites showed that clay, organic matter, and pH all have a role in influencing the concentrations of exchangeable and soluble Cd. Along with the overall concentration, the Jakara site's concentrations of exchangeable and soluble species were influenced by this variable as well. Both high concentration of organic compounds and clay had the same effects. *Tokaliolu et al*. (2003) found that cadmium (Cd) is a highly mobile ion, but that its mobility to the exchange complex was low in comparison to the total quantity in the soil at all locations. Cd may alter its behaviour after sorption by organic materials, especially in soils with a slightly alkaline to alkaline pH, and this may be the reason for the comparatively low quantities found in this investigation (Basta *et al*, 2005).

Adsorption of Cu by clay and/or organic matter close to the soil surface rises with increasing pH, as it does for other metals. (Wild, 1996). This may lend credence to the findings, particularly when contrasted to the organic matter concentrations in the respective regions as reported in Table 1. Since the pH of the water at most of the sample sites was somewhat alkaline and there was abundant organic matter present, the metal exchangeable values were likewise rather high.

The concentration's impact on Ni's exchangeable form was comparable. Ni's commercial form shows a high degree of specialisation within sectors. The presence of clay and organic matter has altered not only the overall concentration of this metal but also its exchange property. In spite of having less organic matter than the other two sites, because to its much better clay composition, the Watari site has significant quantities of Ni in exchange complex. More Ni is available for exchange because of concentration, increased organic matter content, and favourable clay composition in certain areas of the Jakara basin. Nickel is more mobile both within the soil matrix and into other media when pH is low. This is by far the most noticeable characteristic that influences its solvability in this setting. Although though there is a fair quantity of this metal in all of the sites' sectors and it is readily exchangeable, fewer than expected levels were found everywhere. This is because the pH tends to tilt toward alkalinity everywhere, which does not favor Ni solubility. Increases in soil pH, as documented by McBride *et al*. (2004), decrease Ni solubility and, thus, its extractability from the bio-available fraction.

It seems that organic matter and total concentration have a greater impact on the exchangeable Zn concentration as the levels decline from high in Jakara to low in Challawa and finally to low in Watari. According to Zhao *et al*. (2010) [6], as concentration increased, so did the amount of Zn that could be exchanged. Exchangeable Zn and CO32-associated Zn were high in areas with abundant organic matter in the study of Yusuf (2007), despite a large concentration of it being discovered bonded (sorbed) to the organic matter.

Relationship between metals and soil properties

Table 4 displays the metals that were found and how they were linked to observable soil characteristics. Total and exchangeable metals were demonstrated to be associated with clay content, pH, total nitrogen, organic carbon, accessible phosphorus, calcium, magnesium, potassium, sodium, and cation exchange capacity. There was a strong negative relationship between clay content and total Zn, Pb, and Cd, as well as all exchangeable forms except Cu. The pH ranged from around 5.5 to 8.5, with the exception of a slightly upward trend in the exchangeable Cr and Ni. Nonetheless, there was a statistically significant negative relationship between pH and total Cu, Zn, Pb, and Ex. Zn. With the exception of Ex, Total N, organic carbon, and P were positively and statistically significantly correlated with both forms of metal. Ni and Ex. Pb. There was a strong positive relationship between cations and CEC and a weak negative relationship between sodium, calcium, magnesium, sodium, cation exchange capacity (CEC), and total copper, nickel, and nickle.

The findings presented suggest that the elements exhibit a wide range of behaviors. Based on Table 1, it is clear that the soil's low clay content has a major impact on the exchangeable forms of metals, which were predicted to have a closer association with the soil. The richness of the soil in organic materials, however, somewhat offset this favorable association. Metals have a strong preference for either organic matter or clay in terms of their exchangeability and retention, therefore the relative abundance of the two in the soil has a major impact on the concentration of the two metal forms. In the soil, Ni's correlation with clay concentration may be influenced by Ni's specific preference for clay locations. The increased clay concentration of Abdu's soil is a major factor in why his conclusion differs from that of other researchers who have studied comparable soils. This area's slightly alkaline soil acted as a powerful moderator between the metals and the soil's pH. This is due to the fact that found that a soil's exchangeable and other types of heavy metals were more abundant at a moderately acidic pH. (2006). Connections between the parent material and nutrient incorporation and release, respectively, may have promoted the generally strong interaction between metals and cations, on the one hand, and metals and P and N, on the other. In light of the diverse make-up of the basement complex formation and the soil's high concentration of organic materials, especially at the Jakara sites, (Ahmad, 2008), it is likely that this link exists (Table 1). Often found in mildly acidic to mildly alkaline soil, metallic associations with other cations and anions are a widespread phenomenon. It was Abdu who made a similar observation (2010).

Table 4: Relationship between total (T) and exchangeable (Ex.) metals with some soil parameters

	T. Cu	T. Cr	T. Zn	T. Ni	T. Pb	T. Cd	Ex. Cu	Ex. Cr	Ex. Zn	Ex. Ni	Ex. Pb	Ex. Cd
Clay	-0.024	-0.158	-0.429**	0.115	-0.344**	-0.327**	-0.050	-0.187*	-0.388**	0.178*	-0.217*	-0.225**
pH	-0.204*	0.142	-0.273**	-0.062	-0.248**	-0.046	-0.158	0.158	-0.303**	0.109	-0.079	-0.020
TN	0.174*	0.226**	0.594**	0.201*	0.359**	0.445**	0.225**	0.192*	0.571**	-0.038	0.144	0.375**
OC	0.193*	0.195*	0.478**	0.045	0.246**	0.403**	0.245**	0.132	0.422**	-0.137	0.102	0.310**
P	0.216*	0.345**	0.835**	0.091	0.464**	0.675**	0.277**	0.317**	0.743**	-0.109	0.148	0.485**
Ca	-0.023	0.451**	0.509**	-0.142	0.368**	0.493**	0.027	0.496**	0.533**	-0.356**	0.362**	0.448**
Mg	0.069	0.315**	0.246**	-0.089	0.251**	0.183*	0.075	0.367**	0.312**	-0.273**	0.325**	0.146
K	0.190*	0.337**	0.729**	0.080	0.508**	0.646**	0.225**	0.308**	0.655**	-0.072	0.230**	0.516**
Na	-0.020	0.353**	0.758**	-0.008	0.422**	0.646**	0.064	0.374**	0.655**	-0.175*	0.177*	0.448**
CEC	0.027	0.505**	0.657**	-0.057	0.440**	0.600**	0.079	0.541**	0.654**	-0.299**	0.363**	0.506**
				** Significant at $p \le 0.01$			* Significant at $p \le 0.05$					

Conclusion

The findings reveal that the soils of the examined areas are vulnerable to contamination because large total quantities are gradually released into exchange, solution, and probable absorption by the plant system. Many study sites had higher metal concentrations, but their soil was otherwise unsuitable for farming due to low to medium levels of CEC, organic matter, clay, and pH. Particularly, it shows that oil pollution decreased soil conductivity by 10%. Chromolaena odorata treated the soil at site-1 for 7 weeks, and it eliminated 53% of the petroleum hydrocarbons. Site 1's weed was more successful at removing oil from soil at 5% contamination than at 10% contamination, whereas Site 2's weed was more effective at removing oil from soil at 10% contamination than at 5% contamination, and this difference may be attributed to the soil types at each location.

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