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Effects of Crude Oil Spillage on the Physico-chemical Properties of Soil, Tarjan, Kurdistan Region, Iraq

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Abstract
Kurdistan is a new oil producing region in the Middle East, and the oil wells are located in or near farm-lands. Crude oil spillage is a big threat to the soil fertility, which is especially important for farming. Spillage occurs due to the pipeline rupture, and traffic accidents involving tankers which are very common in Kurdistan. The physico-chemical properties of soil are susceptible to alteration when polluted with crude oil, and this issue is not been studied well in Kurdistan. The intent of this paper is to study the effects of crude oil spillage on the physico-chemical properties of soil in Tarjan village, Kurdistan region-Iraq. For this purpose soil samples were collected in the Tarjan area, tested in a laboratory, and compared to non-polluted soil sample. The pH values of the soil samples remained almost the same. The electrical conductivity, and salinity increased. The amount of sulfate increased, the amount of potassium decreased. The amount of lead increased. The changes in these parameters in the soil affected plant growth in the spillage area, as there was no sign of vegetation on the affected soils. There was a positive correlation between salinity and lead and negative correlation between pH, electrical conductivity, potassium ions and sulphate ions.
Keywords: Crude oil, Soil, pH, EC, Salinity, Sulfate, Potassium, Lead

1. Introduction

Crude oil spillage is a global issue in oil producing countries, and it has negative effects on environment and the regional biological ecosystem. A large number of studies has been carried out to determine the effects of this type of pollution on the environment, plants, animals, and humans. The world has seen many disasters caused by crude oil spillage. For instance, the crude oil spillage disaster of the Gulf of Mexico that resulted in many casualties of animals, and consumed a large amount of money. Crude oil spillage is usually caused by pipeline rupture, tanker accidents, and tankers or pipeline leakages. The Kurdistan region of Iraq is a new oil producing area in the Middle East, and just like other oil- rich countries, crude oil spillage is an emerging problem in the region. In majority of oil producing countries large amount of oil has been absorbed by agricultural land (Roseta & Ebomotei, 2011). Accidents involving trucks and leakage from storage tankers and pipelines are common causes of crude oil spillage in the Kurdistan region. The crude oil spillage phenomenon has not been studied well in Kurdistan. This study focuses on the effects of the crude oil spillage on the physico-chemical properties of soil in agricultural land. The physico- chemical properties of soil polluted by crude oil are different from soil that has not been polluted in this way (Abosede, 2013).The area investigated in this study is called Tarjan and is located 25 km southwest of Erbil. Tarjan is an agricultural, and oil producing area. Oil has spilled out from the rig site and flows through the crops, and other vegetated land. The site of the spillage is a death zone for plants, as there is no sign of vegetation in contrast to unpolluted areas. Crude oil can cause the reduction of the available nutrients in the soil and adds some toxic elements, and the results are the death of the plants and diminished soil fertility (Barua, et al., 2011). The study tries to identify which physico- chemical parameters of soil are subjected to alteration in the affected soil samples. The parameters that were considered are: pH value, electrical conductivity, concentration of potassium, and sulfate, salinity, and the concentration of lead. The pH value has a great effect on the fertility of the soil, as the pH value influences the availability of nutrients to the plants. A low (acidic) pH level and a high (alkaline) pH level both have adverse impacts on plant growth and soil fertility. The ideal pH value for many plants including crops is between 6.5to7.5 (Oyem & Lawrence, 2013). The electrical conductivity represents the concentration of ions in the soil. A high level of electrical conductivity indicates a high concentration of dissolved salt ions in the soil samples. Salinity is the concentration of dissolved salts stored in the soil, and when the salinity is high it can negatively affect plant growth by preventing water uptake by the plants. Salinity ranging from 326.4 ppm to 800 ppm is considered normal for plant growth, and concentration above 1280 ppm causes stunted growth, root damage and death (Sonon, et al., 2015). An extremely high salinity absorption ratio in soil that contains a high concentration of sodium prevents the formation of soil aggregates and seals the surface. Thereby preventing the infiltration of water into the soil. Potassium is one of the primary nutrients in the soil and it has an essential role in plant growth and crop yield. A good amount of potassium in the soil increases the productivity of farmland, as potassium increases the resistance of the crops to various diseases, increases the production of protein, and encourage early and rapid growth (Rehm & Schmitt, 2002). The content of potassium in the soil is ranked in the State of Manasota, USA ranging from very low to very high. (41-80 ppm) is considered as low level and (121-

160) is considered as high (Rehm & Schmitt, 2002). There is no doubt that sulfate is one of the major secondary nutrients in the soil after the primary nutrients (P, N, and K), and it plays an essential role in plant growth and crop production, but high amounts of sulfate in the soil have many negative effects on plants and crops yields. A high sulfate content reduces the availability of suitable nutrients in the soil. The maximum concentration of sulfate as a fertilizer in the soil according to the Phozyn International Limit is approximately 18 ppm (Ben Mussa, et al., 2009). When a plant grows near the site of an oil spillage it may contain a high concentration of sulfate which has negative health effects on humans when consumed. Sulfate causes Cathartic disease in males, and high sulfate intake by humans may cause dehydration (Fawell & Mascarenhas, 2004). In addition to considerations of crops and human health, high concentration of sulfate negatively affect concrete foundations, and steel beams, causing structural failures, when its value reaches (3000 ppm).

2. Materials and Methods

2.1 Soil sampling

Four samples along with a control soil sample of the area were collected. The control sample was collected from cultivated soil near the spillage site. The samples were collected at 50 m intervals, southwest of Erbil. Each sample was taken at a depth of 10cm below the surface, and the samples are kept in plastic bags. All samples were very carefully labeled. The samples were air dried, and any stones or debris were removed. They were then sieved in the laboratory to make them all ready for analysis.

2.2 Determining pH value

The first step starts with adding nearly 30g of soil into the glass beaker, after that adding 30ml of distilled water to the glass beaker, and mixed well to produce soil slurry. The sample was held for about one hour in the glass beaker, and was stirred every 10 or 15 minutes. This process stabilized the pH of the soil flurry. Then the temperature of the sample was measured, and the temperature of the pH meter managed according to the temperature of the sample. The pH meter was calibrated by using the stand solutions. The soil slurry is stirred again, and the electrode of the pH meter was placed in the soil slurry. The beaker glass is turned around to provide a good contact between the electrode and the soil slurry, after that, the electrode is placed in the slurry for nearly 30 seconds. The PH value is obtained. Information acquired from (New York State Department of Transportation, 2015).

2.3 Determining electrical conductivity

The Electrical Conductivity Probe and Meter is used. The accuracy of EC meter is very high. The soil sample is dried, and well sieved (2mm). Nearly 25g of soil was mixed with 40 ml of pure water, and held for 4 hours to get the solution equilibrium. Without stirring, the mixture is filtered through a Whatman number. 40 filter paper into a flask. The probe is inserted into the solution and moved up and down for several times to avoid the air bubbles. The results are displayed on the EC meter. Information acquired from (Hanlon, 1993).

2.4 Determining salinity

The amount of salts, or salinity of soil has a great contact with the electrical conductivity of the soil sample. The more salts in the soil means the higher electrical conductivity value of the soil sample (Slinger, et al., 2005). The electrical conductivity data can be used to determine the salinity of soil samples. For example, we have about 1000 µS/cm of electrical conductivity. This value can be converted to ppm to indicate the value of salinity which is equal to 640ppm. Please note that 1000 µS/cm = 640ppm.

2.5 Determining available amount of potassium

2.5.1 Regents and chemicals

- Distilled water
- Ammonium acetate
- Standard potassium solution (1000ppm)
- Flame Photometer
- Laboratory sensitive balance
- Whatman number.40 filter paper
- Plastic flasks
- Glass flasks

2.5.2 Soil samples treatment

The soil sample is air dried, and sieved (2mm). Weighted 5g of soil sample.

2.5.3 Preparing the Ammonium acetate solution

Ammonium acetate solution (CH_3COONH_4) is needed. Preparing the Ammonium acetate: 77g of Ammonium acetate is mixed with 58ml of acetic acid, and the mixture is placed into the 1000 ml flask and distilled water is added slowly and we continuously shake of the flask till it is full.

2.5.4 The calibration of standard solution

A certain amount of standard solution of potassium (1000 ppm) is mixed with a certain amount of distilled water to prepare a standard solution of 30 ppm.

2.5.5 Determining the K

The sample is placed into a plastic flask and 50ml of the Ammonium acetate solution is added to the flask. The mixture is vibrated for about 30 minutes by using a mechanical shaker. After the shaking is completed, the mixture is filtered into a flask by using a Whatman number.40.The standard solution of potassium 30ppm is used to calibrate the Flame Photometer instrument. After the calibration is done, the sample is measured by the instrument and the data is collected. Information obtained from (Patel, et al., 2014).

Note: After measuring each sample the instrument must be recalibrated for another sample by using a distilled water (the instrument must read the value of zero).

2.6 Determining the amount of available sulfate

2.6.1 Reagents and equipment

- Glycerol
- HCl
- Distilled water
- Ethanol
- NaCl
- Dry (Na_2SO_4)
- ($BaCl_2$) Crystal
- Whatman number. 40 filter paper
- Flasks
- Glass beakers
- UV-VIS spectrophotometer

2.6.2 Soil samples treatment

Soil samples are collected, and stored in the plastic bags. The sample is air dried, and sieved (2mm). 50g of each soil sample weighted, and transported into a glass beaker. 50 ml of distilled water is added to the soil sample, and stirred by using the mechanical shaker in the lab for the duration of 10 minutes. After shaking, the sample is held for about 30 minutes to reach the equilibrium. Without stirring the mixture is filtered through a Whatman number. 40 filter paper.

2.6.3 Conditional reagent

Conditional reagent is set by adding 50ml glycerol with 30ml HCl, 300ml distilled water, 100ml ethanol (95%), and 75g NaCl.

2.6.4 Standard sulfate solution

Standard sulfate solution is prepared by mixing 3.551g of dry Na_2SO_4 with 500ml of distilled water in the flask.

2.6.5 Determining Sulfate

5ml of the filtered sample solution is mixed with a 100ml of distilled water in a volumetric flask. The mixture is transferred to 250ml conical flask. 5ml of the conditional reagent is added and stirred, while stirring 0.3g of $BaCl_2$ crystal is added and stirred for one minutes at a constant speed (to obtain a constant stirring speed, using the mechanical shaker we recommend). After the stirring the solution was immediately placed into a 4cm silica cells, and was placed into the UV-VIS spectrophotometer. The absorbance was measured at 420nm. This procedure was followed from (Ben Mussa, et al., 2009).

2.7 Determining the amount of lead

The sample is air dried, and sieved (2mm). Accurately 1g of the sample is weighted and put it into the glass beaker. 10ml of Nitric acid is added to the sample, and heated till the mixture is completely dried. The dried sample is cooled to the room temperature and adding another 10ml of Nitric acid and this process was repeated. When the sample is dried again 10ml of Hydrochloric acid is added and heated till the sample become dry. Then preparing a 1mole of hydrochloric acid and adding it to the sample. The mixture is filtered into the 50ml flask by using Whatman number.40 filter papers. The solution was applied to the Atomic Absorption Spectrophotometer instrument. The procedure is followed from (Tavallali, et al., 2010).

3. Results

After finishing the data acquisition in the laboratory, the data are collected and analyzed. The data are expressed in the form of tables, chart, and graphs to provide the best expression and easy understanding. The sample number five in the below table represents the control soil (unpolluted).

Table **1**. The Physiochemical parameters of soil samples, and their ratio in each soil sample

Sample NO.	pH value	Electrical Conductivity, µS/cm	Salinity, ppm	Lead, ppm	Sulfate, ppm	Potassium, ppm
1	7.22	2620	1676.8	2.10703907	112.4469178	9.7
2	7.21	3050	1952	1.394817564	106.4195205	3.5
3	7.04	2360	1318.4	2.344446238	107.9263699	1.8
4	7.14	3080	1971.2	1.315681843	140.9400685	6.6
5	7.5	570	364.8	0.340868	9.296232877	46.8

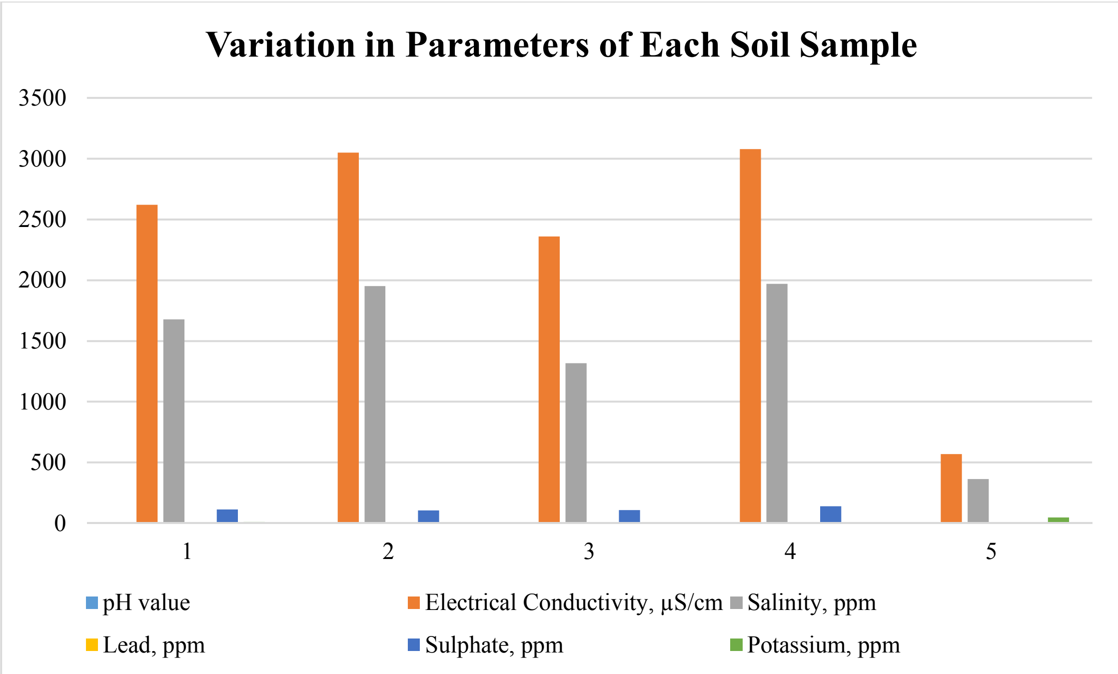

Figure **1.** The variation of parameters studied in the soil samples

3.1 pH value

The control soil sample of Tarjan area had a pH value of (7.5) which is within the range of the ideal pH value for plants growth. Other soil samples of the same area which are from the crude oil contaminated soils were still in the ideal pH value. Crude oil spillage on the farmlands in Tarjan area have not influenced the pH level in the soil. Average pH value of the crude oil contaminated soils was (7.15) which is an ideal value for plants to grow. This outcome indicate that the disappearance of plants and crops in the crude oil spillage areas is not due to the decrease or increase in the pH level.

3.2 Electrical conductivity

Electrical conductivity of crude oil polluted soil was found increased in contrast to control soil. In the control soil the ratio of electrical conductivity was (570 µS/cm), while the average ratio in the affected soil samples was (2777.5 µS/cm). The high value of electrical conductivity of crude oil polluted soil may refer to a high presence of charged ions (cations, and anions) in the soil (8). The value of electrical conductivity represents the ratio of soil salinity, so the key to determine salinity of soil is to obtain the electrical conductivity.

3.3 Salinity

Ratio of salinity in the affected soil samples was found increased in comparison to the control soil sample. The ratio of salinity in crude oil polluted soil was (1729.55 ppm), while its ratio in the control soil was (364.8 ppm). The ratio of salinity in the control soil was found between that range and it is normal for plants growth, but in the affected soil the ratio of salinity has produced a killing zone for plants. This outcome was a strong reason for unavailability of any kind of vegetation in the spillage area. The high amount accumulated salts in the soil can be treated by water leaching to the soil in order to migrate the salts down below the roots zone. The chemical treatment is relevant when the salinity ratio is extremely high like the polluted soil samples.

3.4 Sulfate

Results show that the concentration of sulfate was very high in the crude oil polluted soil samples in contrast to the control soil (unpolluted soil sample). This may refer to the high amount of sulfur presence in the crude oil of the area which has oxidized to sulfate when exposed to the surface. The average concentration of sulfate in the crude oil polluted soil samples of Tarjan was (116.932 ppm) which is a very high concentration in contrast to the Phozyn International Limit standard. The ratio of this high needs to be dealt with, but all the suggestions are recommend to avoid the sulfate pollution than dealing with its aftermath.

3.5 Potassium

Concentration of potassium in the crude oil polluted soil samples of Tarjan area was found reduced in contrast to the concentration of potassium in the non-polluted soil sample. The reduction of potassium was found very high as compared to the control soil (non-polluted) the amount of potassium was (46.8 ppm) while in the polluted soil samples the average concentration of potassium was found (5.4 ppm). The level of potassium in each polluted soil sample in Tarjan area was below the very low level of normal concentration ranges, even the concentration of potassium in the control soil least down in the low level. This may refer to the sensitivity of potassium to the crude oil that might have affected the soil of the entire area. In this case to increase the concentration of potassium in the soils potassium fertilizer methods should be applied in the soil of the farmlands.

3.6 Lead

According to the results the concentration of lead in the crude oil polluted soil in Tarjan area was found increased in contrast to the control soil (non-polluted soil). The average amount of the lead in the crude oil polluted soil was (1.79 ppm), while in the control soil of the same area was (0.34 ppm). This refers to the availability of the lead elements in the crude oil of the area in a certain amount that increased the lead levels in the soil, just like adding a salty water to the flour, and the outcome is of course the salty slurry. Fortunately the amount of lead in all the soil samples was not too high than the normal ratio.

4. Discussion

Table **2**: The correlation table of soil samples parameters.

	pH value	*Electrical Conductivity (µS/cm)*	*Salinity (ppm)*	*Lead (ppm)*	*Sulphate (ppm)*	*Potassium (ppm)*
pH value	1					
Electrical Conductivity (µS/cm)	-0.79968	1				
Salinity (ppm)	-0.71763	0.991635	1			
Lead (ppm)	-0.85605	0.624758	0.54309	1		
Sulfate (ppm)	-0.87695	0.960825	0.936381	0.705387	1	
Potassium (ppm)	0.940182	-0.93511	-0.88316	-0.82185	-0.93103	1

In the above table the turbidity, pH and electrical conductivity is negatively correlated. It means that if pH decreases then the electrical conductivity decreases. There is positive correlation between salinity and concentration of Lead metal. It means that if the concentration of lead increases then the salinity increases. There is also negative correlation between the sulphate and potassium ions. It means the concentration of potassium decreases with increasing sulfate concentration.

5. Conclusion

Crude oil spillage problem is big threat to the agriculture and human health in all oil producing countries. Many crude oil related disasters are recorded worldwide, and resulted in a huge losses. Kurdistan region of Iraq is subjected to this type of pollution and unfortunately it has not been studied well. Tarjan is one of the examples in Kurdistan that crude oil spillage is occurred and still occurring in a very big amount and is resulting in the elimination of vegetation in large farmlands. Crude oil spillage has affected the physico-chemical properties of the soil in a bad way. Salinity of the affected soil has strongly increased in a way that plants yield and growth is unmanageable, and has caused the contaminated area to be vanished from vegetation. The concentration of lead was not that high to be dangerous, but the study of lead in the soil near oil wells should be carried out, as lead is very toxic and hazardous for plants, humans, and animals. Concentration of sulfate has intensely increased in the polluted soil, and has many negative effects on plants and humans. Concentration of potassium was found decreased in the polluted soils which prevents the yield and growth of plants. Crude oil spillage has been found affecting negatively the regional environment, and this problem should be dealt with, immediately.

Recommendation

Crude oil spillage on the agricultural land is a big threat on production, and health. It is suggested to deal with the spillage prevention, than fronting the consequences. Crude oil spillage phenomenon in Kurdistan region should be stopped. Government needs to create a modern and professional environmental policy, and should strictly prevent the climatic disturbances. The treatment of the contaminated soil with crude oil is very complex, and costly operation. Contaminated soil excavation, and soil washing are mechanical technique that are recommended for practicing. The Bioremediation technique is effective for polluted soil treatment. It concerns the addition of fertilizers to the soil. For example, adding chloride potassium to increase potassium content. Adding calcium with water can be used to reduce the salinity of the soil. High sulfate content in the soil can be managed by covering the surface by non-sulfate content soils, and calcium based stabilizer also reduces the sulfate in the soil.

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