Impact of crude oil contamination on soil physicochemical properties around the Sildubi oil spill, Borhola, Assam

ABSTRACT:

Crude oil pollution is a serious constraint on the rice ecosystem near the oil drilling sites.The objective of this study was to identify the effects of crude oil contamination through oil exploration on soil health and the horizontal distribution of soil nutrients in rice field soils in the Sildubi area, Jorhat district, Assam. Soil samples were collected at a depth of 0–15 cm from the drilling site and from the four directions (East, West, South and North) in a circular mode with a radius of 500 and 1000m away from the oil spill. Each sample was mounded with four replications. Samples were analyzed for physicochemical properties by using standard methods that reflect soil nutrient status.

The percentage of organic carbon, organic matter and soil pH are found to be higher at the drilling site compared to the results obtained in the rice field soils, apart by 500 and 1000m from the central zone. Similarly, bulk density, moisture percentage and electrical conductivity were found to be lowest in the soils of the drilling site. In our study, considerable variation in the horizontal distribution of soil nutrients was also observed. The highest P, Ca and nitrogen contents were recorded in the oil-contaminated soils compared to soils collected from 500 and 1000m radius. The total soil Fe was significantly higher in the samples collected at 1000m. Spilled crude oil is certainly responsible for alterations in soil physicochemical properties and the horizontal distribution of some plant-specific nutrients. High concentrations of Fe and P observed due to crude oil contamination have been developing Fe stress situations reducing crop production in neighbouring agricultural lands.

Keywords: Crude oil, physicochemical, bulk density, horizontal, Fe stress.

Abbreviation:

TOC = total organic carbon, TOM = total organic matters, THC = total petroleum hydrocarbon, EC = electrical conductivity, DL site = Drilling site

INTRODUCTION

Soil is one of the most important resources in nature, an important reservoir of nutrients and moisture for the plant's production. Healthy soil is indeed alive and dynamic, consisting of microorganisms. The top-most layer of soil is comparatively richer in nutrients and supports maximum crop production. Normally, soil physicochemical properties vary distinctly from place to place, particularly with respect todepth in the soil profile, climate, water content of the soil, and soil organic carbons.

Crude oil contamination is one of the most severe problems for soil health. Oil Contamination reduces the strength, permeability, maximum dryness and optimum moisture content (Salimnezha et al., 2021). Crude oil contamination of the soil environment can undoubtedly limit its protective function, disturb metabolic activity, adversely affect its physicochemical characteristics, reduce fertility and negatively influence crop production. The oil deposited on the leaves of the plants penetrates into the leaves and reduces transpiration and photosynthesis rate (Okafor, 2023).For upland oil spills, the effects become more serious in nearby low-land crop fields. Crude oil pollution is a serious constraint on the rice ecosystem near the oil drilling sites.

Oil leakage is inadvertent due to oil exploitation,transportation pipeline damage, coastal facility discharge and oil tank accident (Zhang et al., 2021).Such unintended crude oil contamination comprises contaminants like heavy metals (Borah and Deka, 2023)and aromatic hydrocarbons. For crude oil contamination, pore spaces might be blocked, which could reduce soil aeration and water infiltration and increase bulk density. Such a dramatic modification in crude oil-contaminated soil directly affects the growth and productivity of nearby rice fields. Moreover, oils that are denser than water might reduce and restrict soil permeability (Abosede, 2013). Crude oil-contaminated soils are hydrophobic compared to immaculate sites (Quyum*et al*.,2002). Hydrocarbon contamination can increase soil total organic carbon (Ekundayo and Obuekwe, 2000) and change soil chemical properties like pH, total organic matter and soil mineral nutrients such as sodium, potassium, sulphate, phosphate and nitrate, thus indirectly affecting the growth and development of plants and microorganisms (Kisicet al.,2009; Wang et al., 2010). Crude oil contamination may increase the soil pH up to 8.0 (Wanget al.,2013) and in alkaline soils crude oil adversely affects soil physicochemical properties,particularly soil available phosphorous concentration and causes deterioration of wetland soil health.

The effects of crude oil contamination on soil health may be explained by two probable mechanisms. It may penetrate the soil interlayer, where it directly affects the plant root system, microbial population and thus depletes soil oxygen content. Crude oil may also develop a pseudo nutrient deficiency through a reduction in the level of available plant nutrients or by elevating the concentration of certain elements to toxic levels, such as iron. Oil usually develops an anaerobic environment in soil by limiting soil particles and blocking air respiration in the soil pores. Such anoxic situations affect basic soil chemical and physical indicators and thus, the soil microbial communities (Sutton et al., 2013). Heavy crude oil contamination can cause the complete mortality of wetland vegetation (Lin and Mendelssohn, 2012).

North-eastern India, particularly Assam iswell-known in the production of petroleum oil. Crude oil pollution is a usual phenomenon in the oil drilling sites as well as the periphery areas through which oil transportation pipelines carry the crude oil to the oil collecting stations. Large, well-established reports are available regarding the effects of crude oil pollution on soil physicochemical properties and different stabilization methods have been proposed as a remedy for such soil to regain its properties at the regional level (Ezeokpube et al., 2022). However, the literature regarding the geographical position of oil drilling sites and the effects of crude oil on the horizontal distribution of soil chemical constituents is still inadequate.Hence, an effort has been made to investigate some realistic information regarding the effects of crude oil pollution on soil physicochemical properties and to compare the horizontal variation of different physicochemical parameters in paddy soil around the Sildubi oil spill in Borhola, Assam.

MATERIALS AND METHODS:

Study Location

The study area of this investigation was the Sildubi oil field in the Jorhat district of upper Assam, where oil exploration activities are conducted by Oil & Natural Gas Co-operation Limited (ONGCL). Geographically, the south-east side of this oil spill was hilly and the other sides were covered by low-land rice fields.

Collection of Soil Samples

Soil samples were collected at 0–15 cm depth from the top surface using a soil auger. Soil collected from the drilling site is represented as DL site. Four samples were collected from North (N), South (S), East (E) and West (W) zones at radius of 500 m from drilling site in circular mode and another set of four samples were collected at 1000 m radius in similar way. Each sample was mounted in replicate quadrants, from which samples were collected. The collected samples were put into polythene bags and taken to the laboratory for analysis after labelling.

Preparation of Soil Samples

In the laboratory, the samples were spread on brown paper and dried in open air and then ground with a mortar pestle, taking the precaution not to break down the ultimate particles of soil.

Analysis of Soil Physicochemical Properties

In this study, the analysis of soil samples was carried out according to standard methods using analytical-grade reagents. The analysis process of different parameters of the soil samples is discussed below:

The colour determination was made by visual observation. The pH was tested in deionised water at a 1:3 soil-water solution ratio by using a calibrated pH meterand moisture content was determined gravimetrically by weighing samples before and after oven-drying at 105°C for 24 h (Zhang et al., 2016). The bulk density (ρ_d) of the soil was determined from the core samples (Ma *et al.*,2013). Total organic carbon (TOC) and total organic matter (TOM) were also determined in the laboratory by the titrimetric method of Walkey and Black (1934). Available nitrogen was determined by the distillation method (Bremner, 1965). The K, Na and Ca were measured with a flame photometer (Jackson, 1973). Soil iron and phosphorous was determined by the spectrophotometric method as outlined by Jackson (1973) at 540 and 660 nm, respectively.

Statistical analyses of experimental data were carried out using SPSS software. An analysis of variance was carried out to test the significance of the treatment effect. The F-test, coefficient of variance and critical difference were calculated by the standard method (Cochran and Cox, 1963).

RSULTS AND DISCUSSION

Soil bulk density

Soil bulk density is a function of soil textures, structures, and organic matter content, but in a given soil type, it can be used to monitor the degree of soil compaction and peddling (Oyem and Oyem, 2013). Changes in soil bulk density may affect water and oxygen supply to the host. In this investigation, significant horizontal variations were observed in soil bulk density. Lower soil bulk density was recorded in the sample collected from the drilling site compared to the samples of 500and 100m radius (Table 1 and Figure 1A). Soil samples collected at 1000m radius showed high compactness (ρ_b = 1.243 g/cm^3) compared to soils at 500m radius (Table 1). In contrast to the results of previous studies (Agmi et al., 2021; Oyem and Oyem, 2013), a lower bulk density in crude oil-contaminated soil was recorded in our study. The effect of crude oil contamination on soil physicochemical properties may also fluctuate with sampling season (Wang et al., 2013) and location of the oil spills. In the case of upland oil spills, due to heavy rainfall in the summer season, the effect of crude oil pollution may be more pronounced in nearby lowland rice field soils. In this investigation, the geographical position of the Sildubi oil spill might be the major reason for the low bulk density value in the soils on the oil drilling side.

Moisture

Moisture content is an important physical indicator of fertile soil. Soils with very low moisture content show a stressful condition for plant growth. Particle size, void ratio, clay minerals, organic matter and groundwater conditions determine the soil moisture.

In this study, soil moisture contents at the contaminated site were appreciably lower than the samples collected at 500 and 1000m radii. The samples collected from 1000m, showed comparatively high moisture content (Table 1 and Figure 1B). It is evident from the results that the crude oil, which penetrates the soil interlayer, prevents top-down movements of water. Similar results were reported by Rowell, (1977) and De Jong (1980) in their observations who advocated that the water-holding capacity of crude oil-contaminated soil was directly proportional to porosity. They recorded lower water holding capacity at the highly polluted site with reduced porosity. The formation of hydrophobic crude oil coating above the soil surface might have blocked soil pores and reduced the permeability of water and air (Baruah, 2007; Wang et al., 2013; Bennett et al., 1993; Roy et al., 1999; Khamehchiyan et al., 2007), thus affecting the soil water content.

Sample collection sites	Physical Properties					
	Colour		Bulk Density		% Moisture	
	500 m	1000 m	500 m	1000 m	500 m	1000 m
East	Light Brown	Pale Brown	1.168±0.005	1.396±0.002	6.213±0.028	17.255±0.03
West	Light Brown	Brown	1.287±0.003	1.372±0.002	9.135±0.027	16.66±.0.03
North	Light Brown	Light Brown	1.308±0.002	1.472±0.002	23.455±0.06	18.625±0.32
South	Brown	Brown	1.334±0.003	1.228±0.001	21.42±0.27	25.127±0.1
Drilling site	Black		0.763±0.01		3.855±0.02	
Mean			1.172±0.11	1.246±0.13	12.816±5.76	16.303±3.7
CV			1.11%	7.18%	7.73%	2.11%
F value			1790.87***	3217.72***	330.81***	2.23.61***
CD at 0.01%			0.04	0.027	3.024	1.049

Table 1: Effect of crude oil contamination onsoil physical parameters in the samples collected from different sites.*** represent the significance at 0.1% level of probability.

Soil pH

Surface soil pH plays a vital role in ensuring soil fertility and the availability of other plant nutrients like Fe, Mn, Zn and Cu, which are more available in acidic than alkaline soils.

Hence, pH is one of the most significant physical properties of soil and from a farmer's point of view; it is an important soil parameter for crop production.

The soil pH value at the drilling site was 7.85 and was significantly higher than the samples collected from 500m and 1000m radius(Figure 1C) and differs from the results of previous studies that showed an increase in petroleum hydrocarbon concentrations in soil could lower pH values (Kisic et al., 2009). There was significant horizontal variation on the soil pH values among the sampling sites except the samples collected from north. The pH values of the samples collected at the 1000m radius were lower than at the other sampling sites. The results of previous studies on oilfields (Wang et al., 2013; Wang et al., 2010) showed that oil pollution raised soil pH whichis supported by our results. The higher pH values in the soils of the drilling site in this study might be due to the hydrophobic nature of crude oil, which might induce a potential drought in the surface layers of polluted soil (Njoku et al., 2009; Wang et al., 2013). Moreover, crude oil contamination in soil may intensify the accumulation of exchangeable bases like Ca^{2+} or may reduce the exchangeable acidity (Wang et al., 2013; Osuji et al., 2006; Agbogidiet al., 2007), which also supports the increase of pH in crude oil-polluted soil.

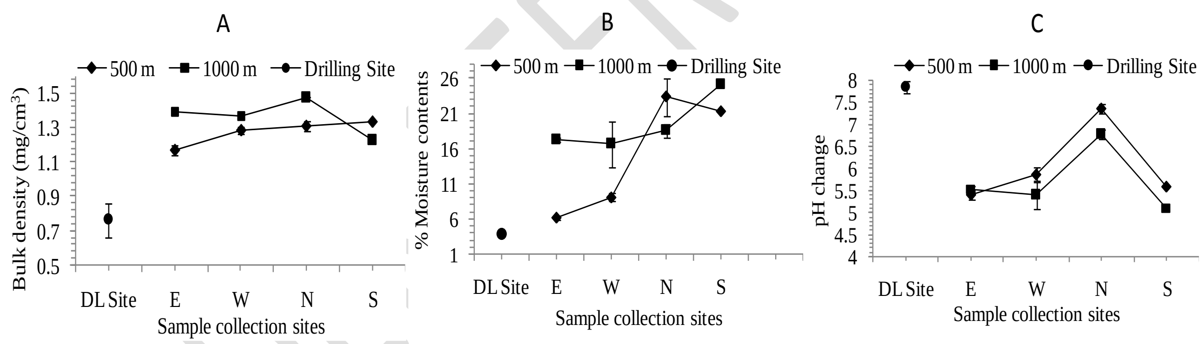

Figure 1: Effect of crude oil contaminationon (A) bulk density ($mg.cm^{-3}$), (B) % moisture content and(C) soil pH in the samples collected from different sites. The vertical bars represent the mean standard error. The ±SEM values in the error bars for (A) and (B) are shown as a multiple of 10.*** represent the significance at 0.1% level of probability.

Electrical Conductivity

Electrical conductivity is the measure of ions present in a soil solution. Usually, electrical conductivity varies with depth, but horizontally, the range of variation becomes more prominent between upland and nearby lowland profiles. This probably occurred due to the slope of the land surface, which is responsible for leaching out alkali and alkaline bases (Shehla et al., 2018). In this study, electrical conductivity is quite variable in the soil samples collected at different radii from the central drilling site (Figure 2D). Significant variations in horizontal electrical conductivity were recorded in the present study. The lowest electrical conductivity was recorded in oil-contaminated soils at the drilling site. Although high EC was recorded in the control soils collected at a 1000m radius to the west, the other results were quite lower in all other samples collected at this radius. Soils collected at a 500m radius recorded significantly higher EC than the samples from drilling and control sites. Exceptionally high EC was observed in the soils at a 500m radius to the north. This variation in soil EC might be due to the horizontal flow of alkali and alkaline bases from upland oil drilling sites to near-low-land rice fields for heavy rain in the summer season.

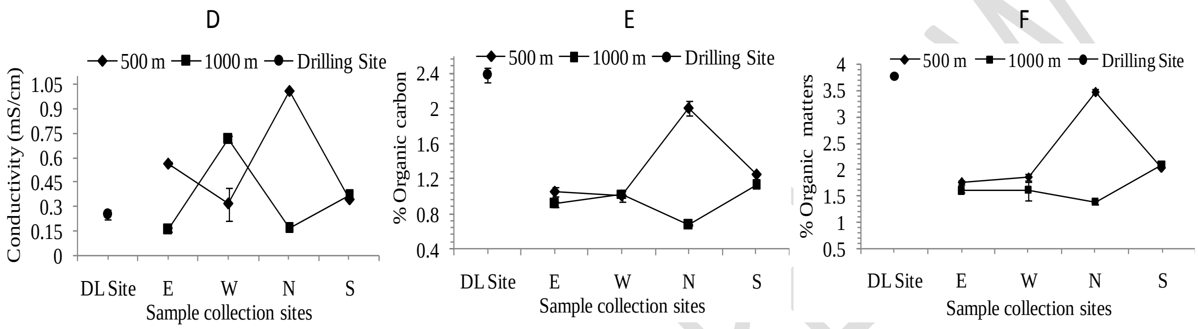

Figure 2: Effect of crude oil contaminationon (D) conductivity ($mS.cm^{-1}$), (E) % organic carbon and (F) % organic carbon in the samples collected from different sites.The vertical bars represent the mean standard errors. The ±SEM values in the error bars for (D) are shown as a multiple of 10.
*** represents the significance at the 0.1% level of probability.

Soil Organic Carbonand Organic Matter

Organic carbon content was found to be higher in the soils of crude oil-contaminated zones, while the soil samples collected at a 1000m radius were found to be the lowest. Significant horizontal variations in organic carbon content and percentage organic matterswere recorded in current investigation (Table 2).

Organic carbon decreases with an increase in horizontal distance. Organic carbon in the soil is generally derived from biota, such as peat formation with time, plant fine root turnover, microbial biomass, etc. However, crude oil contamination in oilfield marshes might also contribute to the TOC in the soil. In the present investigation, the observed increase in the total organic carbon in the soils of the drilling site may be attributed to the accumulation of high hydrocarbon content during oil exploration (Figure 2E and 2F).Wang et al. (2010), in their study, also reported that oil contamination significantly increased the TOC contents, most probably because of the much higher TPH concentration (Wang et al., 2013).Similar findings have been reported by Agbogidi et al. (2007) who concluded that high organic carbon in crude oil-contaminated soil might be due to the slow decomposition rate by soil organisms since contamination of soil with crude oil might have poor soil aeration.

Sample collection sites	Soil Chemical Properties							
	Soil pH		Conductivity		% Organic Carbon		% Organic Matters	
	500 m	1000 m	500 m	1000 m	500 m	1000 m	500 m	1000 m
East	5.4±0.12	5.53±0.1	0.562±0.001	0.156±0.002	1.05±0.03	0.916±0.01	1.752±0.04	1.588±0.02
West	5.87±0.1	5.38±0.06	0.214±0.001	0.711±0.001	1.007±0.05	1.03±0.03	1.857±0.03	1.595±0.02
North	7.35±0.16	6.78±0.63	1.11±0.01	0.165±0.002	2.004±0.06	0.676±.004	3.467±0.06	1.37±0.18
South	5.57±0.1	5.1±0.1	0.342±0.001	0.364±0.001	1.255±0.08	1.13±0.01	2.022±0.05	2.085±0.04
Drilling site	7.85±0.14		0.248±0.003		2.383±0.09		3.777±0.02	
Mean	6.41±0.5	6.12±0.52	0.495±0.165	0.327±0.1	1.54±0.27	1.23±0.3	2.575±0.43	2.083±0.44
CV	4.16%	2.53%	1.54%	2.82%	5.81%	6.80%	2.75%	8.03%
F value	69.79***	229.14***	9412***	2500.98***	185.31***	252.33***	718.04***	139.45***
CD at 0.1%	0.814	0.473	0.023	0.027	0.273	0.255	0.216	0.518

Table 2: Effect of crude oil contamination on soil chemical properties in the samples collected from different sites. *** represent the significance at 0.1% level of probability.

Our study also agrees with the results of Ekundayo and Obuekwe (1997), who reported an increase in the organic carbon content of oil-polluted soils in southern Nigeria. Udo&Faymei (1975) also reported that an increase in organic carbon is directly proportional to an increase in crude oil levels in the soil (Baruah, 2007).

Nitrogen

In the present investigation, the total nitrogen content in the soils of the drilling site was found to be higher than the samples collected from 500 and 1000m radii (Table 3 and Figure 3P). The increase in total nitrogen in the crude oil-contaminated soil is attributed to the impact of crude oil, which promotes the organic carbon content in the soil. Agmi et al., (2012), Akamigbo (1999), and Essienand John (2010) also found a positive relationship between soil organic carbon and total nitrogen in soils. Udo and Fayemi (1975) also reported that available nitrogen increases with increased crude oil contamination in the soil. The present results sustain the results ofAgim et al. (2021)**;** however, Obasi et al. (2013) and Onuh et al. (2008) reported a decrease in total nitrogen with an increase in crude oil pollution in the soil. Significant horizontal variations in total nitrogen were observed in the present study. Soil samples collected at a 1000m radius recorded the lowest nitrogen content compared to those observed at a 500m radius from the drilling site.

Phosphorous

Phosphorus is one of the key micronutrients essential for plant growth and helps in the transfer of energy. Most of the activities of plants, such as growth, respiration andreproduction, depend on the phosphorus levels of the soil where the plants are grown.Soils with high organic matter content have better supplies of organic phosphate for plant uptake.

Sample collection sites	Concentration of different elements in soil					
	Soil Nitrgen (µg / gm)		Soil K (µg / gm)		Soil P (µg / gm)	
	500m	1000m	500m	1000m	500m	1000m
East	469.25±13.8	502.85±3.85	2.322±.02	2.187±.02	2050.09±6.53	1068.54±5.7
West	441.5±10.18	407.25±4.34	2.89±.04	2.797±.05	1867.9±3.37	1160.22±5.5
North	541.25±10.5	324.5±9.07	3.86±.032	2.865±.05	1780.99±9.66	1264.24±15.8
South	501.5±5.2	475.25±3.47	2.225±.03	2.710±.045	2488.02±11.38	2185.09±4.7
Drilling site	994.75±7.8		1.945±.07		2214.22±10.4	
Mean	589.65	540.92	2.649	2.501	2080.24	1578.46
CV	2.33%	13.59	3.15%	3.99%	8.85%	2.10%
F value	1112.02***	51.15***	309.82***	67.84***	942.75***	1188.07***
CD at 0.01%	42.02	224.46	0.255	0.305	56.23	101.23

Table 3: Effect of crude oil contamination on soil macronutrient concentrations in the samples collected from different sites. *** represent the significance at 0.1% level of probability.

The results of the present study have recorded distinct horizontal variations in soil phosphorous concentration (Figure 3Q). The phosphorous concentrations in the soils of the drilling site (2214.22μg/g) were significantly higher than the mean phosphorous concentration in the samples collected at 500m (2080.24μg/g) and 1000m radius (1578.46μg/g). Samples collected at 1000m radius from the drilling site recorded the lowest phosphorous content. Moreover, in this study, the highest phosphorous concentrations were detected in the samples collected from the south direction at 500m (2488.02μg/g) and at 1000m (2185.09μg/g). This southern sampling site is a low-land area suitable for rice cultivation. The increase in phosphorus content in the soils of the drilling site might be due to the increase in soil organic matter and pH. Organic matter is an important factor in controlling phosphorus availability. With the increase in organic matter, the availability of phosphorus increases, this can be explained in two ways. Firstly, the mineralization of organic matter releases plant-available forms of phosphorus into soils, and secondly, organic molecules will compete with phosphate adsorbed to soil surfaces and reduce phosphorus retention. This process will increase the availability of phosphorus. Soil pH between 6 and 7 will result in maximum phosphorous availability. At low pH, soils have greater amounts of iron, which form very strong bonds with phosphate. At high pH, when calcium is the dominant cation, phosphate tends to precipitate with calcium. Higher Ca concentrations in the drilling site, as observed in this investigation, may precipitate phosphorous in the form of phosphates on the soil surface, which were spilled over by petroleum waste frequently. The poor microbial activities to degrade the crude oil hydrocarbons in such anoxic soil conditions might be another reason for the higher concentration of available phosphorous at the drilling site. Similar findings have been reported by Agbogidi et al. (2007) and they concluded that the increase in available phosphorous content of the crude oil-contaminated soil might be due to the increase in soil pH resulting from amendment applications. However, Da-Silva and Fitzsimmons (2016) reported that alkaline pH could cause flocculation of Ca, Mg and Fe with phosphorus and reduce their availability to plants.

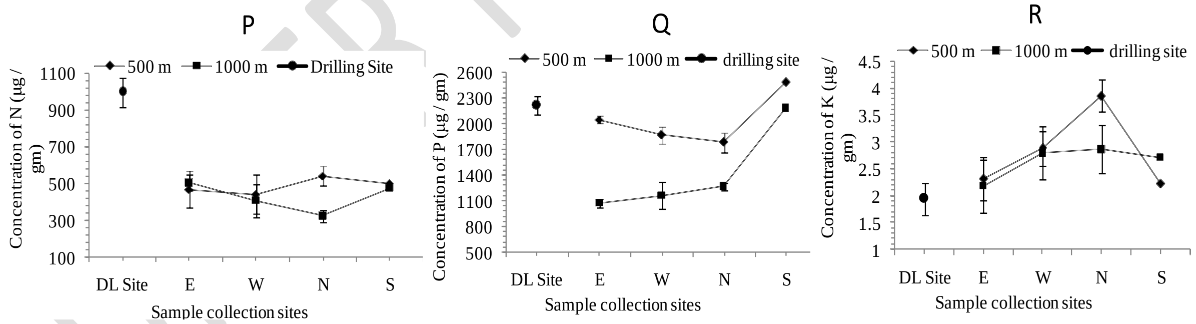

Figure 3: Effect of crude oil contaminationon (P) soil nitrogen (μg/g), (Q) available phosphorous (μg/g) and (R) potassium concentration (μg/g) in the samples collected from different sites. The vertical bars represent the mean standard errors. The ±SEM values in the error bars are shown as a multiple of 10. *** Significant at 0.1% level of probability.

The result of this investigation agrees with the observation of Siddiqui and Adams (2002), who reported an increase in phosphorous concentration with increasing concentrations of oil up to a certain limit, and then it declined. Bielski and Ferguson (1983) also noted that increasing pH increases weathering and mineralization rates. This could have increased phosphorous availability.

Potassium

Potassium is considered an important nutrient for plants and plays a key role in a vast array of physiological processes vital to plant growth, from protein synthesis to the maintenance of plant water balance (Agbogidi and Eshegbeyi, 2006). In the current study, the concentration of available potassium was found to be the lowest at the oil drilling site (1.945µg/g). The mean potassium content in the soils at 500m radius was found to be highest (2.694µg/g), while the soils at 1000m radius recorded 2.501µg/g available potassium. Except for the sample of North direction collected at 500m (3.86µg/g), comparable results of the available potassium content were recorded at other sampling sites (Table 3 and Figure 3R). The significant variations in the horizontal distribution of available potassium content might be due to excessive rainfall during the summer season, which accelerates the rate of parallel nutrient flow from the upland drilling site to the lowland paddy field. Agbogidiet al. (2007) had also recorded lower levels of K^+ and Na^+ in crude oil-contaminated soil and reported that the reduction of K^+ and Na^+ might be due to nutrient immobilization, consequent on the formation of complexes in the soil after degradation and uptake.

Sodium

Sodium is not considered an essential nutrient for the growth of plants; instead, high sodium concentrations build up salt stress in the soil and adversely affect the plants' growth. However, it acts as a counter-ion in the soil where the potassium concentration is very low. In this study, significant horizontal variations in the Na^+ concentration were recorded at different sampling points (Figure 4X). The sodium concentration at the drilling site was 6.492µg/g. The average value for samples at 500m radius was 13.113µg/g, and at 1000m radius it was 6.738µg/g. The highest Na^+ and K^+ concentrations were recorded in the sample collected from north direction at a radius of 500 m. The higher soil pH (pH = 7.35) and electrical conductivity (1.1mS/cm) in this sample might be the reason for the high accumulation of exchangeable bases like Na^+ and K^+ ions (Agbogidi et al., 2007). The alkaline pH of the soils contaminated with crude oil might be attributed to the accumulation of high sodium content that entered the nearby rice fields during heavy rains. The observed increase in salt concentration at 500m may be due to the leaching of Na^+ and K^+ ions from the drilling site to the neighbouring rice field area during the summer season.

Sample collection sites	Concentration of different elements in soil					
	Soil Ca (µg / gm)		Soil Na (µg / gm)		Soil Fe (µg / gm)	
	500m	1000m	500m	1000m	500m	1000m
East	394.778±6.12	210.81±.68	15.56±.52	5.415±.23	3990.67±6.1	7659.46±0.5
West	285.9±6.37	275.848±4.66	14.745±.2	6.703±.168	2690.05±6.53	8176.54±0.95
North	283.595±6.55	189.793±5.78	16.768±.15	6.255±.045	2050.85±5.6	7239.59±23.9
South	324.735±2.86	218.853±4.53	11.997±.06	8.823±.12	2646.82±8.65	8078±24.49
Drilling site	402.71±8.27		6.492±.14		2859.17±16.5	
Mean	338.344	259.603	13.113	6.738	2847.91	6802.55
CV	3.54%	4.55%	5.08%	5.03%	3.81%	2.78%
F value	92.248***	212.20***	269.525***	56.724***	169.9***	18927.2***
CD at 0.01%	36.608	36.096	1.72	1.035	331.55	99.23

Table 4: Effect of crude oil contamination on calcium, sodium and total iron concentrations in the soil samples collected from different sites. *** represent the significance at 0.1% level of probability.

Calcium

Calcium is present in sufficient amounts in most soils. Calcium is a component of several primary and secondary minerals in soil that are essentially insoluble for agricultural purposes. However, calcium is also present in relatively soluble forms as cations adsorbed to the soil colloidal complex, which is considered to be available to crops. Crude oil contamination may increase the concentration of Ca in the soil (Shehla et al., 2018; Agbogidi et al., 2007). In this study, significant horizontal variation in soil Ca concentrations was recorded (Figure 4Y). The highest Ca concentration (402.71µg/g) was detected in the soils of the drilling site, which were heavily contaminated with crude oil waste. The average values of Ca content in the samples collected at 500 and 1000m radius were 338.344µg/g and 259.603µg/g, respectively. The results of this study support the findings of Agbogidi et al. (2007), Konwar and Jha (2010), and Wang et al. (2013). In that study, the maximum calcium content was estimated in highly contaminated soil and the minimum in control soil. The result of the current study supports the findings of Onojake and Osuji (2012), who recorded lower Ca content in soils contaminated with petroleum waste.

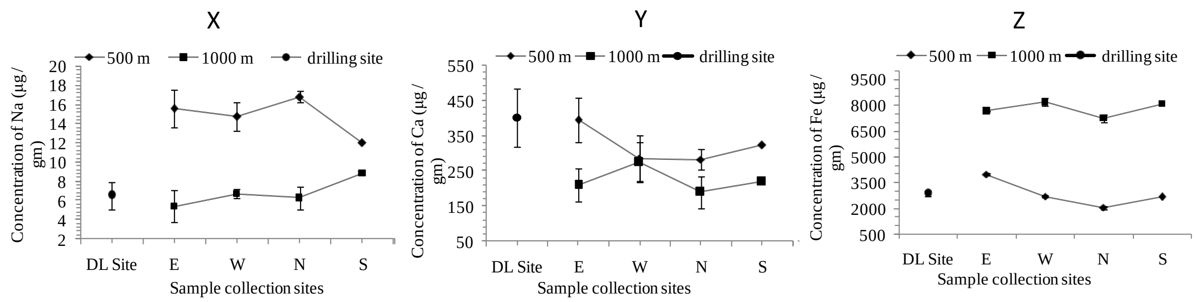

Figure 4: Effect of crude oil contaminationon (X) sodium concentration (µg/g), (Y) soil Ca concentration (µg/g) and (Z) total iron (µg/g) in the samples collected from different sites. The vertical bars represent the mean standard errors. The ±SEM values in the error bars are shown as a multiple of 10. *** Significant at 0.1% level of probability.

Soil Iron

Iron is the most abundant element in the earth crust, which plays an important role in the mobilization of toxic elements in the environment and functions as an electron carrier in many complex red-ox reactions in the plant body. Iron is a co-factor of many enzymes involved in plant defence systems. The study of soil iron is very significant because its deficiency or toxicity in soil may cause many physiological and biochemical disorders in the plant body. Above 6,000 soils Fe may cause iron toxicity in paddy rice (Saikia and Baruah, 2012).

Significant variations in the horizontal distribution of soil Fe contents were recorded in this study (Figure 4Z). The samples collected at 1000m away from the drilling site recorded the highest mean Fe concentration (6802.55µg/g). The Fe concentrations in the samples collected from the east, west,north and south directions at a 1000m radius were 7659.46µg/g, 8176.54µg/g, 7239.59µg/g and 8078µg/g, respectively. A considerable increase in total Fe concentrations in the samples collected at 1000m radius might be due to artificial flooding and the spontaneous flow of rainwater from upland oil spill during rainy season. The total Fe concentrations (2844.59µg/g) in the soils at a 500m radius were lower than the results of the drilling site. Although the amounts of major elements such as Ca, K, Na, Mg and Fe in petroleum waste-contaminated soils primarily depend on the extent of petroleum waste, the effects of other parameters like soil pH, precipitation of these elements in the form of phosphates, hydroxides, oxy-hydroxides and the geographical position of the oil-contaminated area also play an important role in the availability of these elements. In the current study, significant increase in total Fe in the samples collected from 1000m radius might also be attributed to the horizontal flow of the element either through flooding or by soil osmotic properties. Soil heavily contaminated with crude oil shows threshold levels of major elements (Shehla et al., 2018). Moreover, there are positive correlations between soil pH, available P content and soil Fe concentrations. Ch'ng et al. (2014) reported that in an acidic soil environment, if phosphate ion concentrations are high, they compete with Fe and thus Fe becomes unavailable to plants, while pH greater than 7 may cause the flocculation of Ca and Fe with phosphorus in the form of their phosphates, thus reducing their availability to plants. In this study, the high concentration of available phosphorous and alkaline elements in the soil of the drilling site might be the cause for higher concentration of total Fe in the neighbouringagricultural soils. The high concentration of Fe under acidic pH in the peripheral rice field around the oil drilling site might be the reason for severe oxidative stress in rice leaves called 'leaf bronzing',which in turns deplete crop productivity(Saikia and Baruah, 2012).

CONCLUSION:

From the results of current study, it can beconcluded that the test results obtained from the soil analysis of the oil-spilled impacted sites and compared to the results of the soil samples collected from 500 and 1000 m, indicate that the total hydrocarbon levels observed at the soils of the oil-spilled locations have provided evidence of severe hydrocarbon contamination of the site. The alteration in soil physical and chemical properties under such conditions lowers crop productivity on neighbouring agricultural lands. Significant variations in the results of different parameters were observed among the soil samples collected from different collection zones. Sol pH, organic carbon and organic matter were significantly higher at the drilling site, while other studied parameters were higher in the samples collected from nearby agricultural lands. The significant horizontal variations in soil physical and chemical properties primarily depend on the extent of petroleum waste. Moreover, the effects of other parameters like soil pH, precipitation of elements in the form of phosphates, hydroxides, oxy-hydroxides and the geographical position also accelerate the nutrient alteration in the oil-contaminated area. Among the different mechanisms available to explain the variability in nutrient concentration upon crude oil contamination, flooding, soil osmotic properties, and the formation of hydrophobic crude oil layers over the root surface also play important roles in nutrient modification and their availability for plants' uptake. Similarly, antagonistic relationships among the nutrients and their competitive absorption and mobilization by the plant's chelators might also be the cause of specific nutrients unavailability under crude oil contamination. In this study, high concentrations of Fe and phosphorous observed due to crude oil contamination have been developing Fe stress situations, either by Fe deficiency in alkaline pH or by toxicity in acidic pH, thus sinking crop production in neighbouring agricultural lands.

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