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Analysis of Petroleum Products Spill Potential Impact (Gasoline and Diesel Fuels) on Soil Fertility Quality Around Pertamina Rewulu-Cilacap Pipeline Bantul-Yogyakarta

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ABSTRACT. This research focused on analyzing the potential impact of petroleum products spill (gasoline and diesel fuels) on soil fertility quality around PERTAMINA Rewulu-Cilacap Pipeline Bantul, Yogyakarta. The objectives of this study were to analyze the change of soil fertility parameters that are contaminated by gasoline and diesel fuel oils, compared to uncontaminated soil as control. Soil samples were collected from Pertamina Rewulu-Cilacap around the pipeline. Some physico-chemical properties that reflect soil fertility were determined using standard physico-chemical methods and Total Petroleum Hydrocarbon (TPH) using Gas Chromatography. Soil samples were divided into three points (I, II, and III) based on taken places. The study started with analysis of physical and chemical properties of the soil, then petroleum products (gasoline and diesel) were added to the soil samples. The contaminated soil and control then analyzed for identify the fertility quality and TPH content. The results showed that petroleum product contamination increases N, P, and reduces K concentrations in the soil. The sample in point III had the highest values of TPH concentration without any additional petroleum products. After addition of a dose of 13% gasoline, the concentration of TPH in point I, II, and III increased by 0.036%, 0.08% and 0.008%. With the addition of 15% diesel in the sample, the TPH concentration of point I, II, and III increased by 0.892 %, 1.198%, and 0.91%.

Keywords: Petroleum product, soil contamination, soil fertility, total petroleum hydrocarbon

INTRODUCTION

The distribution of petroleum through pipelines is one of the safest methods of fluid transfer due to the low frequency of accidents in pipelines, even though millions of pipelines are used worldwide (Adegboye et al., 2019). However, distribution through pipelines allows the risk of leakage due to work accidents or natural disasters. Several cases of soil pollution due to petroleum contamination that occurred in Indonesia include illegal oil drilling activities, leaking of oil pipelines due to corrosion, as well as due to illegal oil theft. The case of leakage of oil distribution pipelines due to illegal oil theft in Indonesia is increasing from year to year. The use of petroleum continues to increase along with the progress of civilization, this is also accompanied by the increasing number of petroleum pollutants into the environment (Panchenco et al., 2017). Pollution caused by petroleum and its derivatives is the most important environmental problem (Iqbal et al., 2016)

Petroleum is a highly hydrophobic material with most of the petroleum hydrocarbon components having low water solubility (Wang et al., 2019). In addition, petroleum hydrocarbons also affect soil minerals, physical, chemical, and biological properties of the soil, changes in pH, the amount of carbon and an increase in the salt content of the soil (Cruz et al., 2013). After the release of oil into the environment, petroleum hydrocarbons can bind strongly to soil particles and become non-bio-available to micro-organisms. The spillage of petroleum into the ground can reduce its permeability. This occurs due to the trapping of petroleum in the pore space of the soil (Akinwumi et al., 2014).

Oil pipe spill can be a problem and environmental pollution both have an impact on soil, groundwater, and surface water. To be able on determining the level of contamination impacted, it is necessary to know the properties of the soil, both physical and chemical properties. Several studies have been conducted to study the effect of petroleum hydrocarbon contamination on soil fertility. Wyszkowski, et al (2020) in their reported, the greater the number of diesel contaminants in the soil, the levels of N, K, Na decreased, and the P and Ca elements increased. Other research was also carried out by Wang et al. (2013) an increase in the amount of petroleum contaminants in the soil causes a decrease in P levels and an increase in soil pH.

Based on the above background, this study was conducted to determine the effect of uncontaminated and contaminated soil with petroleum products on soil fertility around the Pertamina pipeline (as National Energy Company) Rewulu-Cilacap route in Bantul, Yogyakarta.

EXPERIMENTAL SECTION

Materials

The soil sample used in this study was soil taken from around the Pertamina Rewulu-Cilacap pipeline in Bantul, Yogyakarta namely sampling point I, II, and III (**Figure 1**). The samples were topsoil with a depth of 0-30 cm. Potassium chloride (KCl), calcium chloride dihydrate ($CaCl_2.2H_2O$), barium chloride dihydrate ($BaCl_2.2H_2O$), magnesium sulfate pentahydrate ($MgSO_4.7H_2O$), lead(II) nitrate ($Pb(NO_3)_2$), copper(II) nitrate ($Cu(NO_3)_2$), cobalt(II) chloride ($CoCl_2$), nickel sulfate ($NiSO_4$), Cr solution 1.000 mg L^{-1}, Cu solution 1.000 mg L^{-1}, Zn solution 1.000 mg L^{-1}, Co Solution 1.000 mg L^{-1}, Ni solution 1.000 mg L^{-1}, iron(II) ammonium sulfate (FAS, $Fe(NH_4)_2(SO_4)2.6H_2O$), potassium dichromate ($K_2Cr_2O_7$), acid fluoride (HF) 40%, nitric acid (HNO_3) 65%, hydrochloric acid (HCl) 37%, sulfuric acid (H_2SO_4) 96%, phosphoric acid (H_3PO_4) 85%, *n*-hexane, *n*-pentane and ferroin indicator.

Instrumentations

Some instrumentations used in this study is spectrophotometer UV-VIS (Shimadzu UV-1800), Scanning Electron Microscope (SEM JSM-6510 LA) and spectrophotometer Fourier Transform InfraRed (FTIR Thermo Nicolet iS10), Gas Chromatography-Flame Ionization Detector.

Determination of Physicochemical Properties in the Soil Sample

Water content was determined by ISO 11465 (1993) method, pH content was determined by ISO 10390 (2005) method, the ash content was determined by Deutsches Institut für Normung European Committee for standardization/Technical Specification (DIN CEN/TS) 14775 (2004), Total Organic Carbon (TOC) was determined by the titration method of Walkey and Black, the cation exchange capacity was determined by DIN ISO 11260 (1997), electrical conductivity was determined by DIN CEN/TS 15937 (2013) method, analysis of heavy metals was determined by British Standards European Norm (BS EN) 13656 (2002) method, total nitrogen was measured by Kjeldahl digestion, phosphorus and potassium were determined by extraction using HCl 25%, and total petroleum hydrocarbon was determined using GC/FID.

Study of the Effect of Spilled Oil Products (Gasoline and Diesel) on Soil Fertility and Total Petroleum Hydrocarbons (TPH)

The gasoline (1 mL) and diesel (1 mL) were added to 5 g of soil sample by spraying and then stood for 24 hours. Soil samples were then analyzed to determine the concentration of N, P, K and total petroleum hydrocarbons. The contaminated soil sample then also analyzed using FT-IR, and SEM.

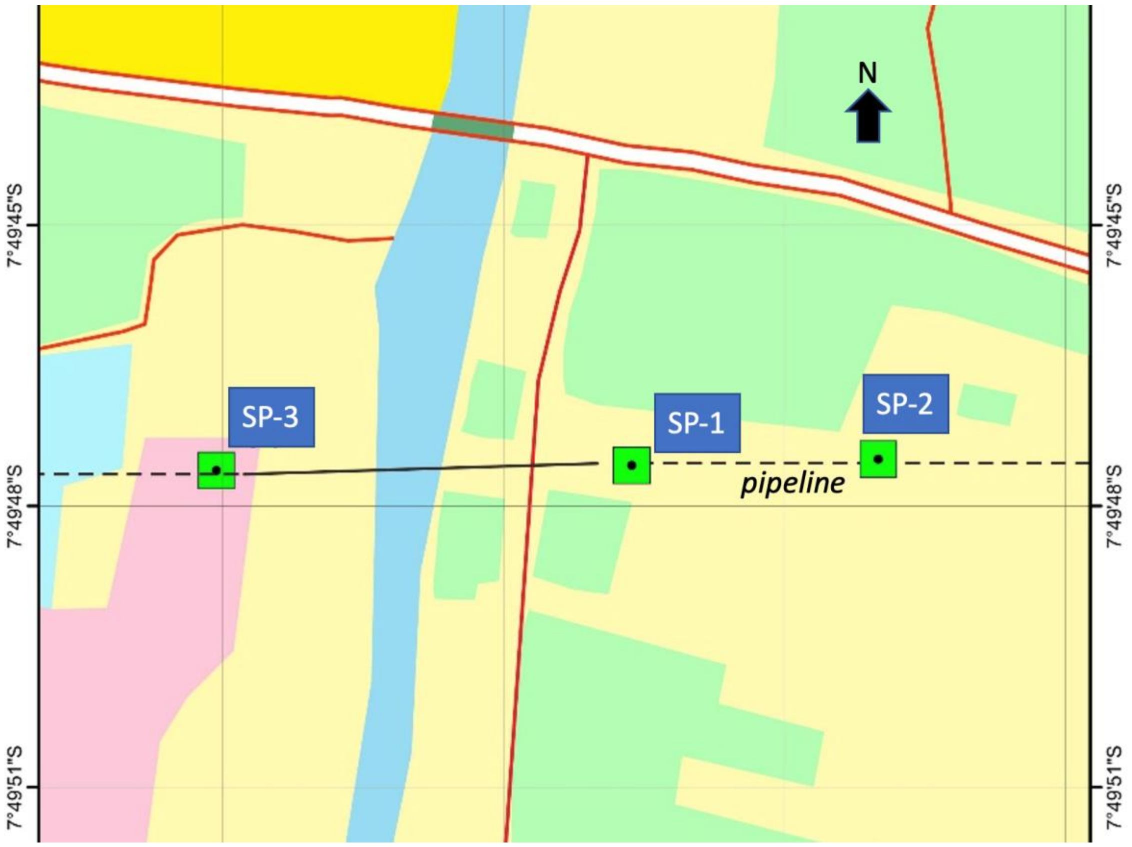

Figure 1. Sampling location (sampling point/SP) around pipeline of Pertamina Rewulu-Cilacap

RESULTS AND DISCUSSION

Characterization of Physicochemical Properties of Soil Samples

The soil sample used in this study was a soil sample taken from the soil around the Pertamina Cilacap-Rewulu pipeline in Yogyakarta (**Figure1**). The results of the characterization of the physicochemical properties of each soil sample are presented in **Table 1**.

In **Table 1** it is known that the samples from the three points have low water content. Sample point I has lower water content than sample point II and III. The difference in water content of each sample is due to differences in the ability of the soil sample to save water.

The ability of the soil to save water is related to the surface area of the soil, the larger the surface area, the greater the capacity of the soil to save water. Sample point I has the lowest water content; this is because the particle size of the sample point is larger, so it has a smaller surface area.

The ability of the soil to bind water is also influenced by organic matter in the soil. Organic carbon (C-organic) is the main component of organic matter in the soil, which is 58% (de Brogniez et al., 2015). Soils containing high organic matter indicate more negative charge of oxygen which will bind to hydrogen atoms from water, due to the presence of reactive groups such as carboxylate and phenol that make up soil organic matter (Essington, 2004). The possible bond between water and soil is through hydrogen bonds and van der Waals forces. This is in accordance with the results shown in **Table 1**, sample point I contains the lowest total organic carbon and water content while sample point II has the highest total organic carbon content and water content. From the results of the C-organic content and soil organic matter, it can determine the level of soil fertility.

Determination of the pH value in the soil sample was carried out by adding H_2O, KCl, and $CaCl_2$ so that a pH value was obtained which was in accordance with its natural conditions and due to pressure from other cations. The addition of KCl and $CaCl_2$ salts will cause the release of cations which will replace hydrogen ions in the soil. The hydrogen ions will later be pushed into the solution which results in their concentration approaching natural conditions, because these two cations are the cations with the highest content in the soil solution (Gavriloaiei, 2012).

Table 1. Physicochemical properties of the soil around the Pertamina Cilacap – Rewulu pipeline Bantul-Yogyakarta

Parameter	Sampling Point I	Sampling Point II	Sampling Point III
Water content (%)			
a. Dried at room temperature	6.64 ± 0.23	9.93 ± 1.05	9.55 ± 0.12
b. Dried at 105 °C	7.90 ± 0.07	12.42 ± 0.06	12.93 ± 0.21
pH			
a. H_2O	6.48 ± 0.02	6.93 ± 0.10	6.20 ± 0.01
b. KCl	5.65 ± 0.01	5.97 ± 0.01	5.22 ± 0.01
c. $CaCl_2$	5.92 ± 0.00	6.40 ± 0.01	5.59 ± 0.02
Ash content (%)	95.00 ± 0.07	89.40 ± 0.18	89.92 ± 1.94
TOC (mg g^{-1})	56.09 ± 0.06	56.78 ± 0.27	56.60 ± 0.11
Soil Organic Ingredients (mg BOT g^{-1} Soil)	96.72 ± 0.11	97.91 ± 0.47	97.59 ± 0.19
KTK (meg/100g)	1.41 ± 0.06	1.60 ± 0.09	1.51 ± 0.08
Electrical Conductivity (μS cm^{-1})	38.27 ± 0.23	84.97 ± 3.28	44.13 ± 5.34
NPK content			
N (%)	0.0633	0.0625	0.0622
P (mg/100g)	4.16 ± 0.00	4.82 ± 0.02	5.04 ± 0.00
K (mg/100g)	53.74 ± 1.96	31.22 ± 0.39	3.17 ± 0.46
Metal content (ppm)			
a. Cu	30.96	35.49	29.05
b. Zn	133.40	131.92	167.56
c. Co	51.87	54.07	46.73
d. Cr	5.11	5.11	5.40
e. Ni	52.47	51.29	56.59

In **Table 1**. the pH values measured using the H_2O extractor have a higher pH value than the KCl and $CaCl_2$ extractors. This is due to the large number of H^+ ions released in solution due to the pressure of K^+ and Ca^{2+} ions, thereby lowering the pH value. The pH value in the soil sample was in the range of 5.22-6.93 with the lowest pH value being owned by sample point III. The pH value also affects the presence of soil nutrients such as N, P, and K. In sample I, the levels of N and K have the highest values compared to samples II and III this is because at pH 6.5 is the optimum pH value for the presence of nutrients N, P, and K in the soil. The high concentration of H^+ and the high solubility of Al^+ in acidic conditions causes K to compete for cation exchange, especially in coarse sandy soils. In sample II, the P level was greater than that in sample I, which had a lower pH. The magnitude of the pH affects the solubility of P in the soil, where in acid soils, phosphorus precipitates with aluminum and/or iron or phosphorus bound to iron/aluminum oxide and clay mineral surfaces. In neutral and calcareous soils, which consist mostly of calcium carbonate, phosphorus precipitates with calcium or is retained on the soil surface from clay minerals and calcium carbonate. However, in this study, sample III with a pH of 6.2 had a higher availability of phosphorus, which was 5.04 mg/100g. This is the same in the research conducted by Sawyer et al. (2002) where the availability of high phosphorus at pH 6.2.

Sample point I has the highest ash content and sample point II has the lowest ash content. If it is related to the organic C content in the soil, the ash content is the opposite of the organic C content (Suherman et al., 2013). From **Table 1**. It is known that the highest organic C-level is owned by sample point II and the lowest is sample point I.

Soil organic matter in sample II was higher than the others. The levels of organic C in sample II 56.78 mg C g-1 showed moderate fertility. Soil organic matter is important in soil fertility and other needs such as minimizing erosion, exchange of water and air through the soil pores, therefore soil organic matter content have a direct effect on soil fertility. Soil can contain up to 95% organic matter, but the ideal organic matter content for plants is 5-15% of the total weight of the soil (Piccolo, 2002) this affects sample I which has low organic matter content so that the fertility level is also low.

Effect of Spilled Petroleum Products (Gasoline and Diesel) on NPK Levels and Total Petroleum Hydrocarbons (TPH)

In this study, the effect of spilled petroleum products (Gasoline and Diesel) on NPK and Total Petroleum Hydrocarbons (TPH) levels was studied. Each soil sample was added with a dose of 13% gasoline and 15% diesel fuel. The results are presented in **Figure 2**. Based on **Figure 2**. Soil samples increased in N, P, and TPH levels while K levels decreased. The increase in nitrogen levels in soil contaminated with gasoline and diesel fuel occurs due to the addition of gasoline and diesel contaminants where both gasoline and diesel contain a certain amount of nitrogen (Slavica et al., 2003). This is supported by research conducted by Ujowundu et al. (2011) on nitrogen levels in diesel-contaminated soil in southeastern Nigeria where N levels increase with the increase in pollutant oil concentrations.

The phosphorus content in samples I, II, and III which were not contaminated with gasoline and diesel were 4.16 mg/100g, 4.82 mg/100g, and 5.04 mg/100g, respectively. After adding 13% gasoline, the levels of soil samples I, II, and III increased to 8.31 mg/100gr, 9.07 mg/100gr, and 11.79 mg/100gr, as well as the addition of 15% phosphorus content of diesel fuel. increased to 13.36 mg/100gr, 16.13 mg/100gr, 15.97 mg/100gr this is in line with research conducted by Wyszkowski (2020) that phosphorus increases as the concentration of diesel contaminants in the soil increases.

Potassium levels in the samples I, II and III were comparable before and after contaminated gasoline and diesel fuels. However, regarding the previous research from Khan et al. (2013) and Devatha et al. (2019), potassium levels will decrease as the concentration of oil contaminants increases. **Figure 2**(**c**) possibly due to the limitation of hydrocarbon in soil structure, thus not affected in the existence of potassium significantly.

Characterization of Functional Groups of Soil Samples Before and After Adding Oil

Soil samples before and after the addition of gasoline contaminants at a dose of 13% and diesel fuel 15% were characterized using an FTIR spectrophotometer to determine the characteristics of functional groups in soil samples. Gasoline has aliphatic bonds so that the presence of bonds between C, H atoms is the basis for using an infrared spectrophotometer to characterize soil samples.

Figure 3 showed the spectra of gasoline, soil samples before and after the addition of gasoline. The spectra of the soil sample before gasoline addition showed an absorption at wave number of 3456 cm^{-1} indicating the absorption area for the –OH group, wave number 2924 cm^{-1} indicating absorption of the C-H functional group. Absorption in the area around 1635 cm^{-1} indicates the region of the water H-O-H buckling vibration. The wavenumber of 1033 cm^{-1} indicates the absorption area for the stretching vibration of Si–O clay minerals.

The wave number of 540 cm^{-1} is estimated as the absorption region for the Si–O–Al group. In the spectra of gasoline there is a typical absorption of hydrocarbons, namely at a wavelength of 2924 – 2870 cm^{-1} which indicates the C-H stretching vibration functional group. The wavelength of 1458 cm^{-1} shows the C-H bending vibration. In the soil sample after the addition of gasoline, the intensity of the typical

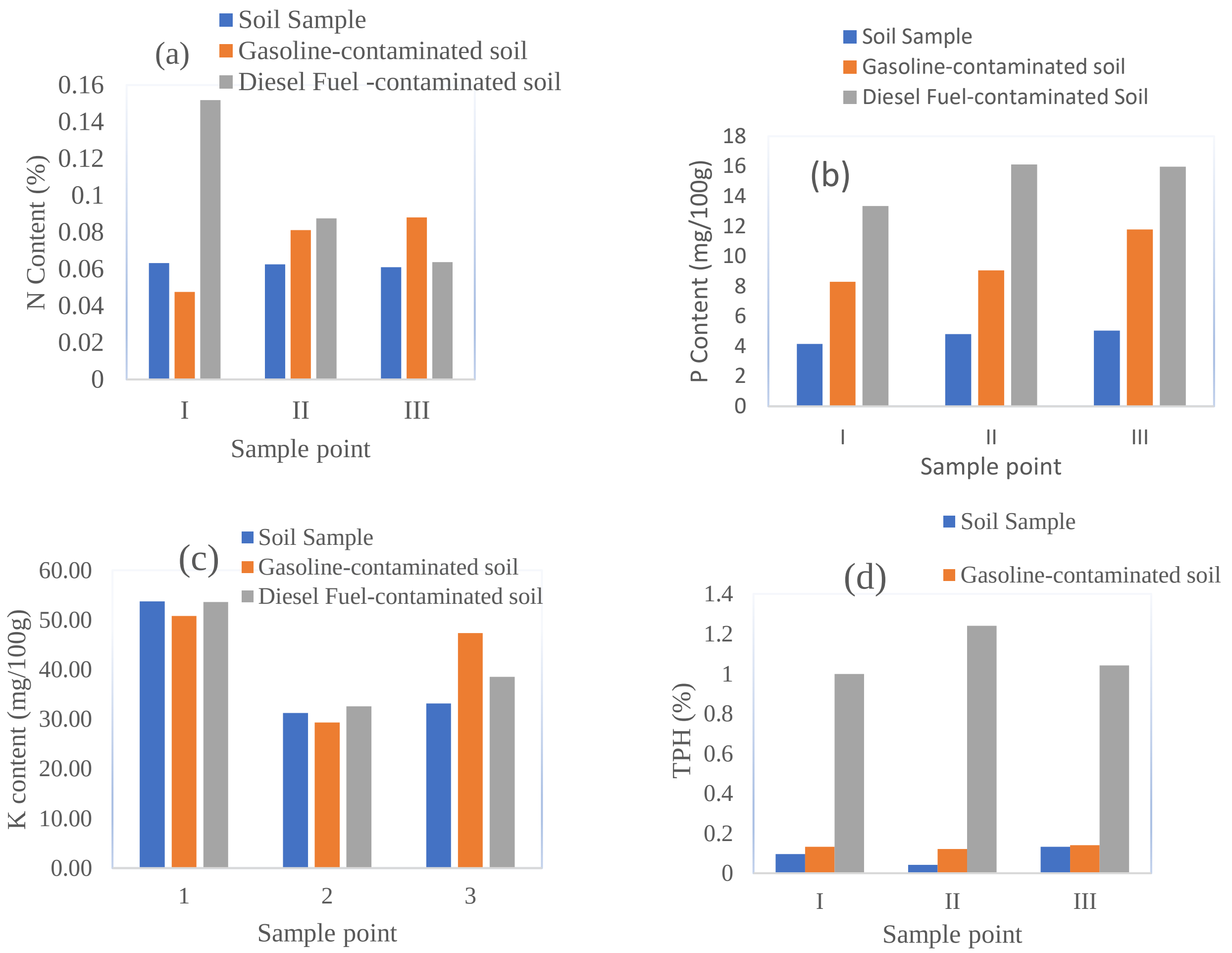

Figure 2. Graph of changes in levels of N (a), P (b), K (c), and TPH (d) after being contaminated with gasoline and diesel fuels.

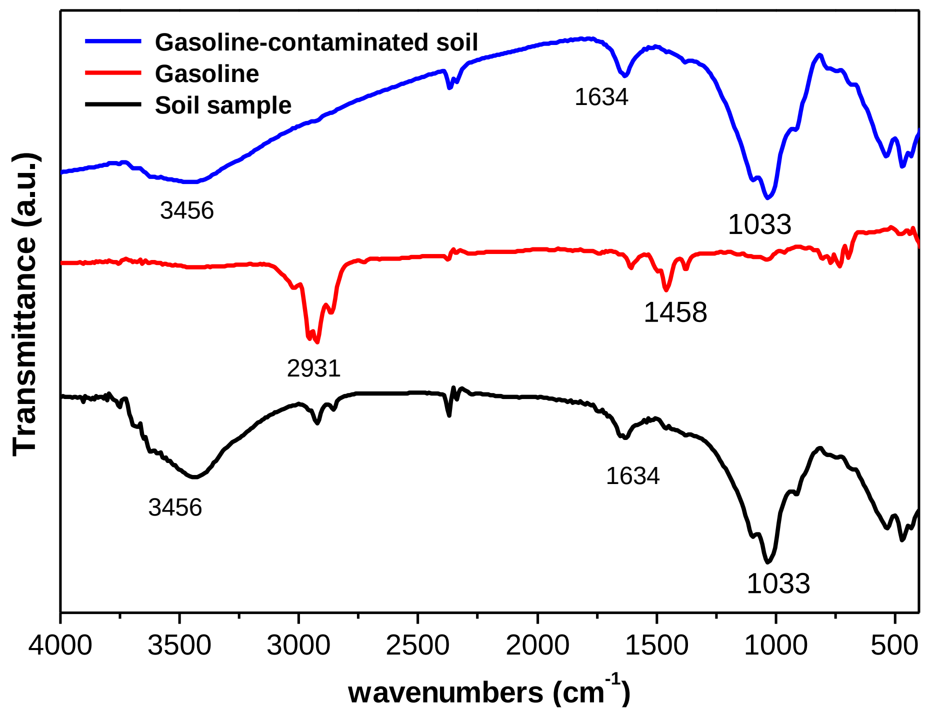

Figure 3. FTIR spectra of gasoline, soil samples before and after addition of gasoline

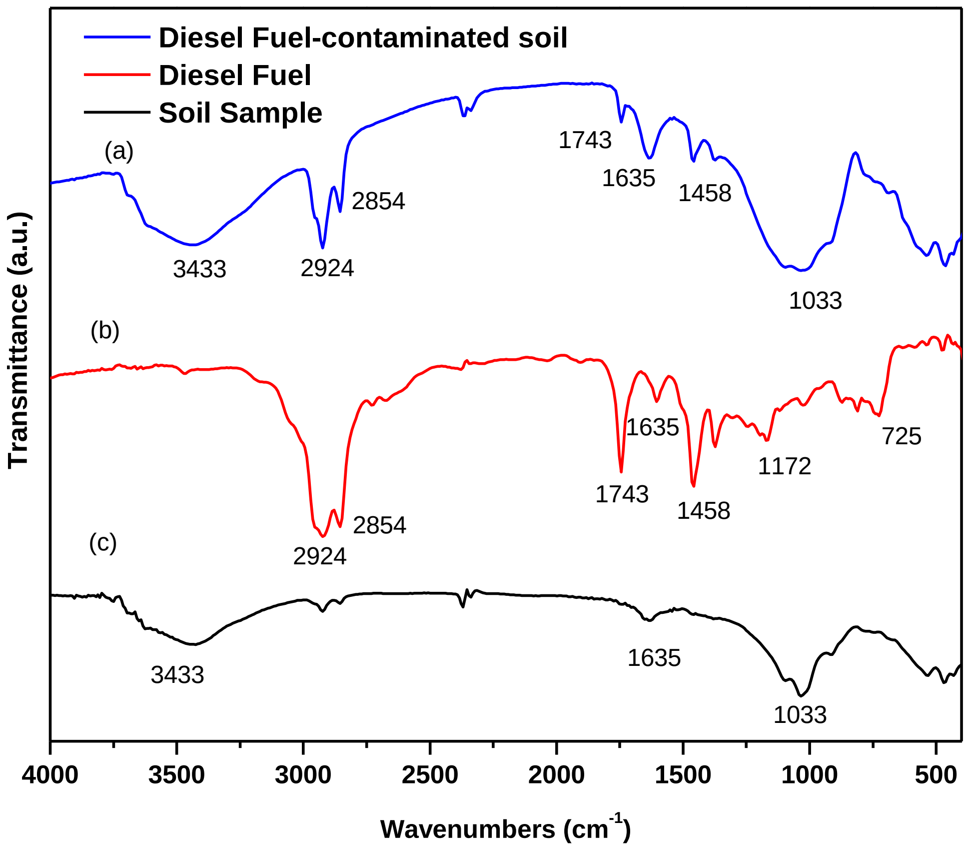

Figure 4. FTIR spectra of diesel oil, soil samples before and after addition of diesel

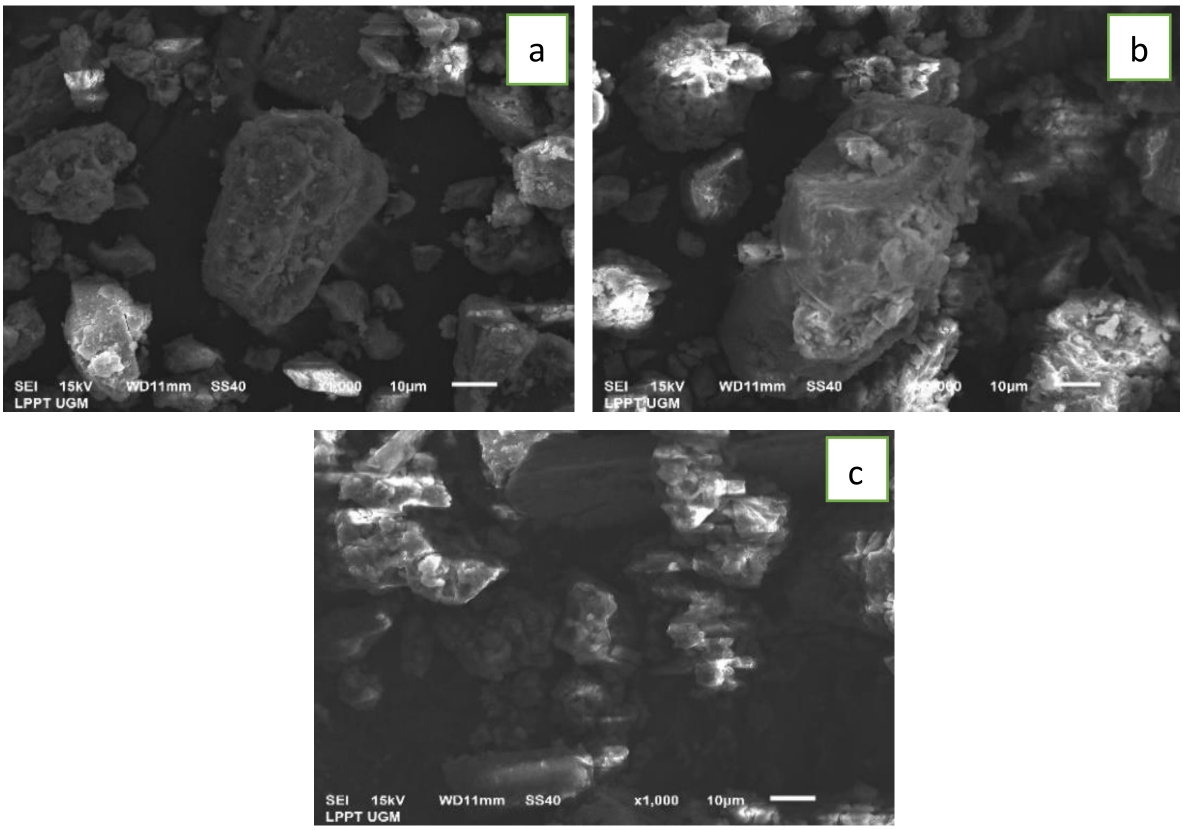

Figure 5. SEM images of (**a**) soil sample (**b**) gasoline-contaminated soil (**c**) diesel fuel-contaminated soil

hydrocarbon absorption at a wavelength of 2924 – 2870 cm $^{-1}$ decreased. It is possible that a lot of oil evaporates due to the volatile nature of the gasoline.

The IR spectra in **Figure 4** revealed typical hydrocarbon wavelength after diesel fuel contamination, namely at a wavelength of 2924-2854 cm $^{-1}$ which shows the stretching vibrational functional groups CH_3 and CH_2. While at a wavelength of 1743 cm $^{-1}$, 1458 cm $^{-1}$, 1172 cm $^{-1}$, and 725 cm $^{-1}$ shows the absorption of C=O stretching vibration, C-H bending vibration, C-N group, and alkyl halide vibration respectively. In soil samples that have been contaminated with diesel, absorption appears in 2924-2854 cm $^{-1}$ which shows the CH stretching vibration functional group with a high intensity, and absorption of 1743 cm $^{-1}$, 1458 cm $^{-1}$, each of which shows a stretching vibration of C=O. C-H bending vibration indicates that the oil has been adsorbed with the soil.

Surface morphological characteristics of soil samples before and after adding oil

Characterization of soil samples using SEM aims to see the characteristics of the morphology of soil samples before and after the addition of oil. **Figure 5** showed the morphology of the soil samples before and after the addition of 13% gasoline and 15% diesel fuel. The analysis was carried out at 1000x magnification for each sample. The surface morphology before and after contamination seems comparable each other's, this possibly due to less existences of fuel hydrocarbon in soil structure caused by evaporation.

CONCLUSIONS

Based on the results, it can be concluded that the petroleum product contamination increases the concentration of N, P, but slightly reduces K in the soil sample. The sample point III has the highest values of TPH concentration without addition of petroleum products. The concentration of TPH increased by 0.036%, 0.08% and 0.008% in the sample I, II and III after the addition of 13% gasoline. Finally, by the addition of 15% diesel dose, the TPH concentration of soil samples I, II, and III all increased significantly.

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