EnvironmentAsia
The international journal by the Thai Society of Higher Education Institutes on Environment

EnvironmentAsia 11(2) (2018) 109-117
DOI 10.14456/ea.2018.26
ISSN 1906-1714; ONLINE ISSN: 2586-8861

# Identification of Total Petroleum Hydrocarbon and Heavy Metals Levels in Crude Oil Contaminated Soil at Wonocolo Public Mining

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Received: November 2, 2017; Accepted: February 1, 2018

## ABSTRACT

The aims of this study were to determine the content of total petroleum hydrocarbon (TPH) and heavy metals in top soil at Wonocolo public crude oil mining. Three composite soil samples were collected from oil well (OW), refinery (R), and transportation line (T) areas. Quantification and identification of TPH were performed by Gravimetric method and Gas Chromatography-Mass Spectrometry (GC-MS), respectively. Heavy metals concentrations were analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The results showed that each soil samples contained $C_{14-36}$ of TPH with high concentration of 8.33; 12.30; and 4.35% in OW, R, and T soils, respectively. These values exceeded the limit of soil standard of 1.00% that indicated the top soils at Wonocolo public crude oil mining were highly polluted by TPH. Meanwhile, heavy metals such as Pb, Cr, and Hg have been detected in OW, R, and T soil at of 0.07-0.10, 0.02-0.03, and 0.05-0.06 mg/g, respectively. These values were below the soil quality standard and indexed as moderate-very severe contamination of heavy metal. Bioremediation may be recommended to reduce and manage the TPH pollution levels.

***Keywords;*** Heavy metal; Public crude oil mine; Soil polluted; Total petroleum hydrocarbon; Wonocolo Sub-district.

## 1. Introduction

Wonocolo is one of the sub-districts in Bojonegoro, East Java which has an area of 11.37 $km^2$. It lies between Banyu Urip, Kadewan, Ngantru, and Kali Gede to the east, west, south, and north, respectively. In Wonocolo Sub-district, some crude oil mining activities like drilling, refinery, and transportation are operated by the local community (Naumi and Trilaksana, 2002).

Since the Dutch colonial period at 1942, public mining activities in Wonocolo have been conducted using a simple equipment that caused crude oil spills and carried petroleum hydrocarbon contamination in soil (Handrianto et al., 2012; Xu and Liu, 2010; Liu et al., 2011; Wang et al., 2011; Agarry et al., 2013). Soil contamination of TPH becomes potential given the high production reaches 25,771 $m^3$/day of crude oil from 44 active wells (Handrianto et al., 2012). In the measurement, petroleum hydrocarbon, known as total petroleum hydrocarbon, TPH (Asquith et al., 2011). According to Indonesian Government Regulation No. 101 (2014), TPH was classified as hazardous waste which were toxic and carcinogenic. Thus, the distribution of TPH in soil was needed to be controlled. Hamilton and Sewell (1999); Indonesian Environment Ministry (2003) were reported that several countries included Indonesia, Texas, Lousiana, and Colorado have been established the maximum levels of TPH in soil of 1%.

Earlier study reported that soil in Wonocolo public crude oil mining has been highly polluted by TPH of 4.12% (Handrianto et al., 2012). It means, this site needs a remediation to reduce the TPH level below the soil quality standard. Nevertheless, the publication about TPH compounds content in crude oil polluted soil at Wonocolo public mining has not been found. This information is important to determine a remediation technique to reduce the TPH pollution level (Abdel-Moghny et al., 2012). Information of heavy metal presence in TPH polluted soil is also needed because crude oil can increase the concentrations (Adesina and Adelasoye, 2014). Therefore, the purposes of this study were to identify and determine the concentration of each compounds of TPH and heavy metal in OW, R, and T areas at Wonocolo public crude oil mining. In addition, some recommendations are proposed to manage the pollution.

## 2. Materials and Methods

### *2.1 Soil Sample Collection*

Thirty-two soil samples were collected from three different sites according to mining activity, i.e OW, R, and T. The soil was taken from 0-20 cm depth (Okop and Ekpo, 2012) with different patterns according to the point sources such as diagonal, random, and line for OW, R, and T, respectively (Margensin and Schinner, 2005). The soil sampling point locations were illustrated in Figure 1.

### *2.2 Total Petroleum Hydrocarbon Analysis*

The samples were homogenized by filtering the soil using 2 mm sieve. Soil samples were extracted using soxhlet and gravimetric method to obtain the hydrocarbon extract by APHA-AWWA (2005) standard No. 5520D and 5520F, respectively. Then, the hydrocarbon extract was used for TPH quantification in duplicate using FT-IR Spectrometer at 2930 $cm^{-1}$ of absorbance according to ASTM (2011) No. D7066-4. Furthermore, the compounds of TPH was identified using GC-MS with Agilent HP 1 MS column. Chromatographic resolution was achieved with a 30 m x 0.25 mm capillary column with a 0.25 μm film thickness. The carrier gas was helium at a flow rate of 3 mL/min. The temperature of the injection port was 310°C. The quantitative analysis was performed by internal calibration method, and TPH identification was performed by comparison of their peaks with standards.

### *2.3 Heavy Metal Analysis*

Heavy metal analysis was performed using ICP-AES (Margensin and Schinner, 2005; Horwitz and Latimer, 2005). Heavy metals included arsenic (As), cadmium (Cd), lead (Pb), chromium (Cr), and mercury (Hg) were analyzed using digestion method following AOAC standard No. 9.2.39 (Horwitz and Latimer, 2005).

## 3. Results and Discussion

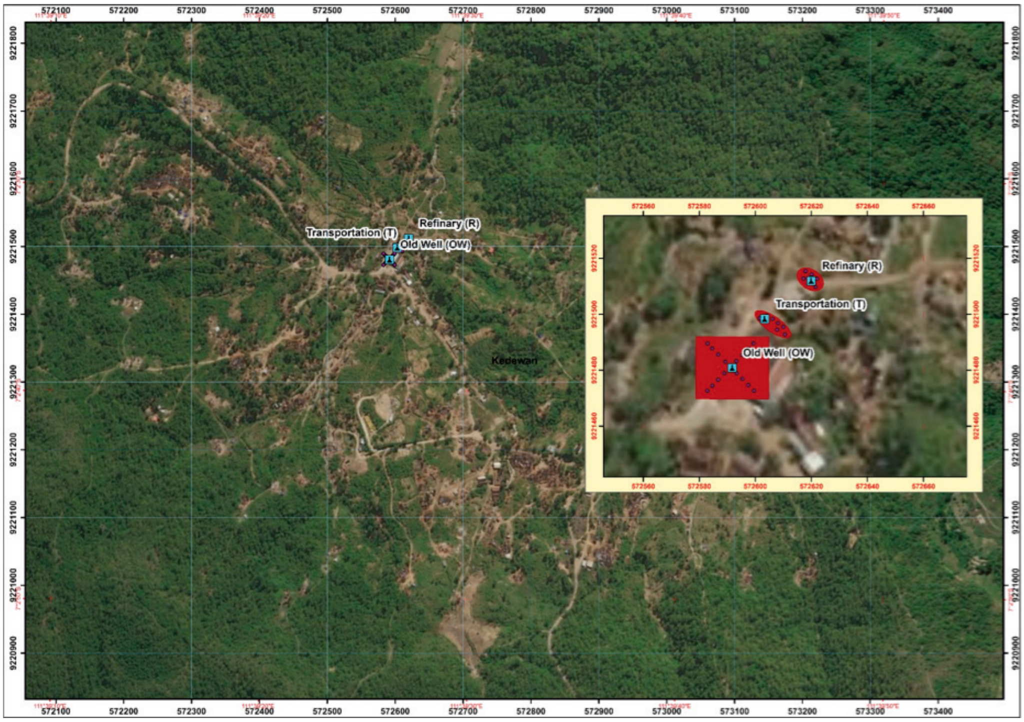
### *3.1 TPH Concentration and Distribution in Soils*

The results showed that there was high concentration of TPH in OW, R, and T soils were 8.33, 12.31, and 4.35%, respectively (Table 1). These values were higher than the concentration

**Table 1.** Distribution of TPH Compounds in Crude Oil Contaminated Soil

| TPH Compound(s) | TPH Concentrations (%) | | | |
|---|---|---|---|---|
| | OW | R | T | Total in soil |
| $C_{14}$ | 0.08 | 0.04 | nd | 0.12 |
| $C_{15}$ | 0.05 | 1.13 | 0.33 | 1.51 |
| $C_{16}$ | 0.58 | 0.17 | 0.35 | 1.10 |
| $C_{17}$ | nd | 0.06 | 0.20 | 0.26 |
| $C_{18}$ | 0.06 | 0.01 | nd | 0.07 |
| $C_{19}$ | 0.63 | 0.32 | 0.04 | 0.99 |
| **$C_{20}$** | **1.74** | **1.33** | **1.11** | **4.18** |
| $C_{21}$ | 0.38 | 0.08 | nd | 0.46 |
| **$C_{22}$** | **nd** | **2.05** | **nd** | **2.05** |
| $C_{23}$ | 0.03 | 1.08 | 0.28 | 1.39 |
| $C_{24}$ | 0.07 | 0.19 | nd | 0.26 |
| **$C_{25}$** | **3.39** | **5.08** | **0.82** | **9.29** |
| $C_{26}$ | 0.02 | 0.07 | nd | 0.09 |
| $C_{28}$ | 0.78 | 0.51 | 0.76 | 2.05 |
| $C_{29}$ | 0.03 | 0.05 | nd | 0.08 |
| $C_{36}$ | 0.49 | 0.15 | 0.46 | 1.10 |
| Total | 8.33 | 12.31 | 4.35 | 24.99 |

*nd: not detected




**Δ Sample point**

**Figure 1.** Map of Soil Sampling Locations

of TPH at earlier study by Handrianto et al. (2012) of 4.12%. This indicated that TPH accumulation occurs all the time. Various TPH concentrations at these sites were influenced by oil spills volume (Abioye, 2011). The highest concentration was recorded in R soil because the refining process was daily operated with high capacity production of 200 L/day of heavy diesel. In contrast, drilling and transportation process were operated every 3-7 days. Compared to the maximum limit of TPH in the soil by the Indonesian Environmental Ministry Decree No. 128 (2003), at 1.00%, these sites have been polluted by TPH. According to Indonesian Government Regulation No. 101 (2014), the soils classified as TK-A (serious polluted), which contain $C_{14-36}$ more than 4% (see Table 1). Therefore, a remediation is needed to avoid the increase of pollution loads and minimize the human hazard risk to miners.

Highly concentration of TPH in Wonocolo public mining soil was influenced by long chain hydrocarbon present and soil texture. It can be seen in Table 1, that those soil samples contained $C_{20}$, $C_{22}$, and $C_{25}$ as dominance compounds with total concentrations of 4.18, 2.05, and 9.29%, respectively. Soil texture were classified as silty clay loam by USDA standard, which were consist of sand, dust, and clay in the soil are 20; 56; and 26%, respectively. The clay tends to associated with long chain hydrocarbons which were hydrophobic and have been strongly bound in soil matrix (Abdel-Moghny et al., 2012; US-EPA, 1996). Thus, the TPH becomes difficult to degrade and persistent in soil (Nicolotti and Egli, 1998; Lueprom-Chai et al., 2007; Ezeonu et al., 2012; Chijioke-Osuji et al., 2014). This condition is also influenced by clogged pores by crude oil spillages that caused oxygen depletion. Low oxygen in the soil will inhibit the growth and proliferation of bacteria even plants that can reduce the levels of TPH (Abosede, 2013).

## *3.2 Heavy Metals Concentration and Distribution in Soil*

The results showed that three (Pb, Cr, and Hg) of five heavy metals were detected in OW, R, and T soils. The values of Pb, Cr, and Hg in OW soil were 0.09, 0.03, and 0.05 mg/g, respectively. In T soil, the concentration of Pb, Cr, and Hg were observed of 0.10, 0.03, and 0.06 mg/g. Meanwhile, the concentration of three heavy metals in R soil were 0.07, 0.02, and 0.05 mg/g. However, at those locations the other heavy metals of As and Cd were not found.

Several studies in Nigeria showed various heavy metals were identified to contain higher concentration than this research. In Warri-Kaduna near The Effurun Round, Delta State, were obtained high concentration of Pb, Cd, Cr, Ni, Zn, and Cu in the crude oil contaminated soil i.e 5680, 4800, 11680, 24340, 223090, and 18960 mg/g, respectively (Abdel-Moghny et al., 2012). High concentration of Pb, Cu, Cd, Cr, Ni, and Zn were also found in crude oil contaminated soil from Abara and Ozuzu, Niger Delta of 2380, 3100, 20, 60, 170, and 18500 mg/g, respectively (Ideriah et al., 2013).

Indonesian Government has not established the specific national standard for heavy metal content in oil mining area. Generally, the assessment of soil pollution by heavy metals refers to WHO/FAO standards (Chen et al., 2014; Duressa and Letta., 2015) where the permitted limits of Pb, Cr, and Hg are 0.10 mg/g (WHO/FAO, 2001). Based on the standard, almost all concentration of Pb, Cr, and Hg in Wonocolo public crude oil mining soils were below the limit. Only Pb in OW soil has same concentration with WHO/FAO standard. The comparative of heavy metals concentration in soil samples with the WHO/FAO standard were illustrated in Figure 2.

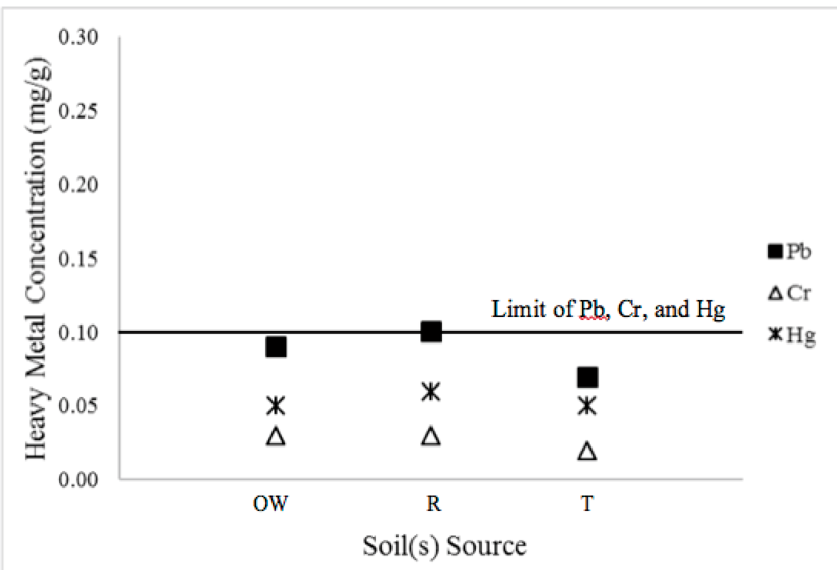



**Figure 2.** Heavy Metals Concentration in Soil

Several studies were reported that soil contamination by heavy metal could be classified by metal index (Lacatusu, 2000; Tamasi and Cini, 2004; Balakrishnan and Ramu, 2016). The index can be expressed by ratio of heavy metals concentration and the limit standard (Lacatusu, 2000; Tamasi and Cini, 2004).

Based on the metal index, soils in Wonocolo public crude oil mining have shown varied ratio from 0.20 to 1.00 that indicated the contamination of Pb, Cr, and Hg were moderate-very severe (see Table 2). Moderate-very severe contaminations mean the concentration of Pb, Cr, and Hg have no negative effect to soil, plant, and environment (Lacatusu, 2000). Nevertheless, the presence of heavy metals in soils still requires more attention. This is due to the potential accumulation of Pb, Cr, and Hg (heavy metals cannot degrade) and its ability to associate with TPH in the soil (Abdel-Moghny et al., 2012; Adesina and Adelasoye, 2014; Margensin and Schinner, 2005; Chijioke-Osuji et al., 2014). Thus, causes depletion of nutrient, inhibition of microbial activity, raises the level of toxicity and pollution loads in soil (Abdel-Moghny et al., 2012; Adesina and Adelasoye, 2014).

## 4. Recommendations for TPH-Polluted Soil Management

The authors suggest that the Government should conduct remediation immediately on inactive sites in Wonocolo public crude oil mining to avoid long-term pollution of TPH. Refers to Indonesian Environment Ministry Decree No. 128 (2003), soil remediation can conduct through biological process (as known as bioremediation) such as composting and land farming because the concentration in all soils are below of 15%. In addition, the Government should provide some training programs about environmentally crude oil exploitation process for local community to control the distribution of TPH in soil.

**Table 2.** Soil Quality Classification Using Metal Index

| Metal index | Classification | Soil(s) Source | | |
|---|---|---|---|---|
| | | OW | R | T |
| <0.10 | Very slight contamination | - | - | - |
| 0.10-0.25 | Slight contamination | - | - | - |
| 0.26-0.50 | Moderate contamination | Cr (0.30)<br>Hg (0.50) | Cr (0.30) | Cr (0.20)<br>Hg (0.50) |
| 0.51-0.75 | Severe contamination | - | Hg (0.60) | Pb (0.70) |
| 0.76-1.00 | Very severe contamination | Pb (0.90) | Pb (1.00) | - |
| 1.10-2.00 | Slight pollution | - | - | - |
| 2.10-4.00 | Moderate pollution | - | - | - |
| 4.10-8.00 | Severe pollution | - | - | - |
| 8.10-16.00 | Very severe pollution | - | - | - |
| >16.00 | Excessive pollution | - | - | - |

Adapted from Lacatusu (2000)

## 5. Conclusion

The TPH content of $C_{14-36}$ in OW, R, and T soil samples were 8.33, 12.31, and 4.35%. The finding of $C_{14-36}$ has relationship with the product of refining process which was heavy diesel. The measured concentrations exceeded the limit of Indonesian standard and classified as serious pollution. Heavy metals were also observed in all soils including Pb, Cr, and Hg with low concentration in each range of 0.07-0.10, 0.02-0.03, and 0.05-0.06 mg/g, respectively. These values have been indexed as slightly-moderate for contaminated soil. Therefore, it is necessary that the government conduct a bioremediation process to reduce the pollution levels of TPH in soils. Technically, to apply the bioremediation in Wonocolo public mining it is also needed the information about pollution and migration of TPH based on the soil depth. The data could be obtained by further research.

## Acknowledgment

The authors gratefully thank to the research and public Service of Universitas Singaperbangsa Karawang for the research grant Contract No. 0890/SP2H/UN64/V/2017, which made this study to work out. We also wish to thank Mr. Aditya N. Rakhmad and Ms. Rizkiy A. Barakwan for their support during the crude oil contaminated soil sampling process.

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