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Micromorphological Characteristics of Polluted Soils in Tehran Petroleum Refinery

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ABSTRACT

In this study, micromorphological properties of some samples collected from pedons polluted with petroleum refinery wastes and some adjacent unpolluted pedons were studied. After description of the studied pedons, disturbed and undisturbed samples were collected for physicochemical and micromorphological analyses. The results showed that the physicochemical properties (i.e. structure, bulk density, pH, EC and organic matter) of the soils polluted with petroleum wastes were strongly changed. Prolonged exposure of soils to the petroleum wastes resulted in the formation of specific and distinctive micromorphological features. Strongly developed granular microstructure and infillings of solid petroleum wastes alone or mixed with soil aggregates were some of the most important pedofeatures which were observed in deeper horizons. The existence of excrement belonging to different soil micro and macro fauna, coatings, hypocoatings, quasicoatings, and zones depleted from petroleum dissolvable materials at different depths were the other features throughout the pedons. The type of developed pedofeatures was correlated with the state of petroleum wastes and their fluidity in penetration, deposition, or dissolving and removal of soil compounds. This study demonstrated that micromorphology can be used as a powerful technique in characterization of petroleum polluted soils.

Keywords: Oil contamination, Pedofeatures, Physico-chemical properties, Soil quality, Technosols.

INTRODUCTION

Excessive demands for the products of petroleum industries have led to their extensive development, even very close to the areas of dense population, thereby contributing to the increased petroleum related effluents, wastes, sludge, and other by-products. Their safe disposal is an important environmental problem of modern societies. The industrial and petroleum producer countries not only have to pay attention to the petroleum exploration, exploitation, transportation and refining activities, but also have to combat the resulting environmental problems. Soil is generally the final destination for such waste materials. Description, characterization, and surveying of such polluted and hazardous soils are therefore important priorities, and to draw the attention of land users and experts, Technosols have recently been introduced by the World Reference Base (WRB) for soil resources (FAO, 2014). They may form on wastes (sludge, cinders, mine spoils, landfills, and ashes), on pavements and their underlying unconsolidated materials, on soils with geomembranes and soils formed in human made materials.

There are several studies reported in the literature on the physical, chemical, and biological properties of petroleum polluted soils. The physicochemical quality of

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petroleum contaminated soils was studied by Pathak *et al*. (2011) and Onojake and Osuji (2012). They concluded that moisture status, pH, *EC*, and water holding capacity of soil play important roles in the degradation of soil pollutants. They reported very high organic carbon content in the studied contaminated soils compared to the unpolluted adjacent soils. Pathak *et al*. (2011) stated that particle size distribution was a very important parameter due to its roles in soil aeration, bulk density, vertical and lateral petroleum movements, the capability of soil for holding contaminants, and degradation of petroleum pollutants. They concluded that petroleum contamination lowered the soil quality and increased soil toxic and carcinogenic factors. According to Onojake, and Osuji (2012) morphological and anatomical aberrations were observed in the plants' growth due to the presence of hydrocarbon films in the epidermal and cortical regions of roots, stems, and leaves.

Effluents of petroleum refineries contain many different chemicals including sulfates, chlorides, hydrocarbons, and sodium that are harmful for seeds germination and vegetation cover (Gulshan and Dasti, 2012). Nwazue (2011) reported that the petroleum pollution severely affected soil and water chemistry (lower pH values and moisture contents and higher organic carbon contents) than the unpolluted soils as well as plants, animals and other inhabitants of both aquatic and terrestrial environments. Olalemi and Arotupin (2012) investigated the effects of refined petroleum byproducts on the bacterial population and physicochemical characteristics of cultivated agricultural soils. The toxic effects of total petroleum hydrocarbons (TPHs) of wastes from Tehran refinery on plant growth were investigated by Zand *et al*., (2010). The results of analyses showed that the soils contained different heavy metals such as Cd, Co, Cu, Ni and Pb in very high levels. Heidarzadeh *et al*., (2009) stated that the sludge of Tehran petroleum refinery did not contain detectable amounts of polycyclic aromatic hydrocarbons (PAHs) but that the mean concentrations of selected heavy metals, namely Ni, Pb, Cd and Zn were as follows: 2700, 850, 100, and 6100 ppm, respectively.

Despite considerable studies on physicochemical and biological properties of petroleum contaminated soils, their morphological and micromorphological characteristics have not yet been studied. Soil morphology and micromorphology are basic tools in diagnosing soil formation factors and the involved processes. Micromorphology is a tool for collecting more data from soils that may impose different changes (Stoops *et al*., 2010) including those caused by petroleum contaminants. Micromorphological studies reveal the exact pattern of movement and distribution, positioning and placement of petroleum compounds in soils. These studies can help soil scientists to better understand the effects of petroleum pollutants on soil behavior, horizon formation, and the exact classification of soils.

Despite severe disturbances of soils and environment caused by urbanization, their documentation has not been carried out sufficiently. Technosols and Anthroposols are the last introduced soil reference groups in the World Reference Base system (FAO, 2014). Human-altered and human-transported material classes also have been defined at the family level of the Keys to Soil Taxonomy (Soil Survey Staff, 2014). However, there are not sufficient data on their micromorphological characteristics, especially with respect to petroleum polluted soils. The aim of this study was to investigate the micromorphological properties of soils exposed to petroleum waste materials for a long time.

MATERIALS AND METHODS

Site and Profile Description

The Tehran petroleum refinery is one of the largest and oldest petroleum refineries in Iran, located in south of Tehran. Since the beginning of its activity in 1968, its waste materials (solid, semisolid and liquid) have been disposed in large lagoons next to the refinery site. During this long period, considerable changes in soil properties have occurred, which are of great research interest for soil and environmental scientists. The studied area (about 60 ha) was located in the south of Tehran (latitude: 35° 30.299' to 35° 30.814' N and longitude: 51° 25.682' to 51° 26.296' E). Six pedons, including four Technosols developed on the petroleum refinery waste materials (pedons no. 1, 3, 4 and 6) and two reference pedons (pedons no. 2 and 5) were fully described and sampled (Figure 1-a). Figure 1-b and Table 1 show some morphological and physicochemical properties of the unpolluted and polluted pedons. In total, 30 disturbed and 18 undisturbed samples were collected. Soil moisture and temperature regimes are aridic and thermic, respectively (USDA and NRCS, 2012). The studied area consists of almost smooth and flat geomorphic units including alluvial plains (calcareous and gypseous fine deposits) of which the surface layers (up to about one meter) have been reshaped into lagoons for deposition of the refinery waste materials. There was some sparse vegetation cover including drought resistant plants such as *Alhagi camelorum*, *Peganum harmala*, *Gundelia tournefortii* (Asadi and Heidari, 2012).

Diagnostic horizons were identified and finally the studied pedons were classified according to the Keys to Soil Taxonomy (Soil Survey Staff, 2014) and the World Reference Base (FAO, 2014).

Physical and Chemical Analyses

Due to the diversity of petroleum wastes as well as their unknown amount and disposal time, proper sampling or analysis and presenting practical results were not possible. However, the morphological and micromorphological effects of petroleum waste materials were studied. The collected soil samples were air-dried and ground to pass through 2 mm sieve. Particle size distribution (PSD) of gypsiferous samples was determined by the specific method for gypsiferous soils (Hesse, 1976). PSD of non-gypsiferous samples was determined according to the standard hydrometer method (Gee and Bauder, 1986), but the petroleum-polluted samples were analyzed according to the standard ultrasound method (Sawhney, 1996). Organic carbon content was determined by Walkley and Black (1934). pH and *EC* were measured in saturation extracts using Jenway *EC* and pH meter. Gypsum and $CaCO_3$ contents were determined using acetone (Sparks *et al.*, 1996), and calcimetry methods, respectively.

Micromorphological Analyses

Undisturbed blocks were sampled using Kubiëna boxes, air dried and then impregnated with a mixture of polyester resin. catalyst (hydrogen peroxide) and cobalt naphthenate as accelerator. In order to prevent the dissolution of petroleum waste materials, acetone was not used as diluter for the resin. More energy was needed for the required vacuum for the impregnation with non-diluted resin, and some non-impregnated parts were left in some blocks, but no obvious interactions were observed between the polyester resin and the petroleum wastes. The impregnated samples were dried, sawed, mounted on 60×90 mm slides, thinned and polished to about 25-30 μm thickness. Thin sections were studied using an Olympus polarizing microscope under plane (PPL) and crossed polarized (XPL) lights. Micromorphological descriptions were carried out using the terminology of Stoops (2003). Scanning electron microscopy (SEM) was used to compare the side effects of waste

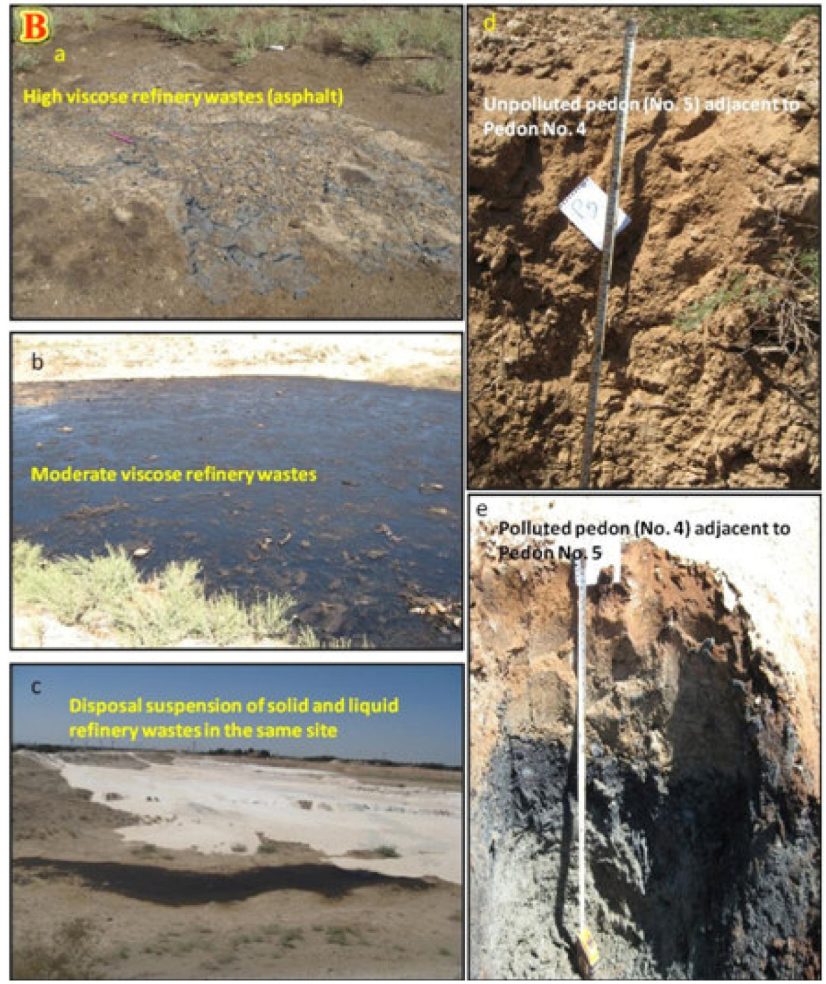

Figure 1- A (left) - Location of the studied area and the described and sampled pedons. B (right) - Different types of petroleum waste materials (a, b and c) and representative studied pedons unpolluted (d) and polluted (e) (pay attention to white colored solid waste and strongly reduced subsurface soil layers saturated with petroleum wastes that was strongly smelling due to presence of petroleum wastes)

Table 1- Physicochemical properties of the studied pedons.

Pedon No.	Depth (cm)	Horizon	Structure[a]	OM (%)	pH	EC (mS cm^{-1})	Gypsum (%)	$CaCO_3$ (%)	Clay	Silt (%)	Sand
	Coarse-loamy, smectitic, thermic, Typic Haplogypsids [Linic Technosols (Calcaric, Humic, Toxic)]										
1	0-20	Ap	Massive	8.67	7.75	4.08	2.10	15.48	18.16	30	51.84
	20-38	2Ap	1Csbk+Massive	8.59	7.77	5.50	3.45	14.19	12.16	22	65.84
	38-47	2AB	1Csbk	8.17	7.87	5.99	1.97	13.87	18.16	28	53.84
	47-60	2B1y	Massive	6.02	7.60	6.38	5.67	13.55	14.72	34	51.28
	60-90	2B2y	Massive	3.88	7.29	5.46	5.63	19.03	12.72	46	41.28
	90-115	2B3y	Massive	3.63	7.58	6.13	10.00	12.90	10.72	30	59.28
	115-150	2Byg	-	2.60	8.09	6.59	4.85	10.00	36.16	28	35.84
	Fine-loamy, smectitic,thermic,Typic Calcigypsids (Hypogypsic Gypsisols)										
2	0-18	Ap	Massive+2Fgr	1.32	8.16	2.93	1.68	17.42	32.16	28	39.84
	18-27	AB	3Mabk+ Platy	1.24	8.15	3.09	0.51	16.45	40.72	34	25.28
	27-40	Bk1	2Cabk	0.06	8.18	4.29	0.48	19.35	42.16	38	19.84
	40-65	Bk2	1Csbk	0.17	7.84	4.99	5.15	20.64	8.16	68	23.84
	65-100	By1	Massive	0.17	7.82	4.12	6.10	16.45	10.16	14	75.84
	100-150	By2	Massive	0.41	7.75	2.95	7.60	19.03	10.72	16	73.28
	150-200	By3	Massive	0.05	7.58	2.93	2.35	17.74	58.72	21.28	20
	Coarse-loamy, smectitic, thermic, Typic Calcigypsids (Linic Technosols (Calcaric, Humic, Toxic))										
3	0-18	Ap	Massive+1Cabk	10.65	6.97	8.56	1.03	14.84	12.16	18	69.84
	18-30	AC	Massive+ Cabk	6.17	7.71	8.67	1.12	17.42	10.16	26	63.84
	30-70	Cy1	Massive+1Cabk	5.42	7.81	6.83	1.52	20.32	12.16	28	59.84
	70-120	Cy2	Massive	2.76	8.05	6.83	1.46	18.38	10.72	38	51.28
	Fine-loamy, smectitic, thermic,Fluventic Aquicambids (Technic Fluvisols)										
4	0-10	Ap	Massive	9.60	7.55	5.60	2.62	12.90	12.16	4	83.84
	10_28	Bw	Massive	7.45	7.88	5.02	2.82	18.06	10.72	53.28	36
	28-43	C1	Massive	8.00	7.80	4.87	0.39	19.67	32.72	40	27.28
	43-70	C2	Massive	8.82	7.72	5.97	0.16	17.74	18.27	42	39.28
	Clayey, smectitic, thermic, Sodic Haplocalcids (Salic Solonetz (Aridic))										
5	0-20	Ap	Massive	0.50	7.96	3.86	2.48	14.84	32.72	36	31.28
	20-40	By	Massive	0.17	8.10	8.49	2.30	15.16	8.72	66	25.28
	40-67	2Bky	3Cabk	0.08	8.57	20.00	1.47	17.09	28.72	52	19.28
	67-120	2Bk	3Cabk+3Mabk	0.08	8.51	23.70	0.22	24.51	42.16	38	19.84
	Fine-loamy, smectitic, thermic, Typic Calcigypsids (Linic Technosols (Calcaric, Toxic, Humic))										
6	0-5	Ap1	-	12.05	6.71	5.23	2.71	8.06	8.16	2	89.84
	5_25	Ap2	-	8.66	7.47	4.34	7.30	12.26	10.72	18	71.28
	25-70	Cy1	-	8.45	7.61	7.04	8.27	16.77	10.16	40	49.84

[a] 1Csbk: Weak coarse subangular blocky; 1Cabk: Weak coarse angular blocky; 2Fgr: Moderate fine granular, 3Mabk: Strong medium angular blocky.

contaminants on resin polymerization in the thin sections and to recognize possible types of solid or viscous liquid materials entrapped between gypsum minerals or adsorbed to their surfaces (results not presented).

RESULTS AND DISCUSSION

Physical and Chemical Properties

Important morphological changes between the unpolluted (Figure 1-d) and polluted (Figure 1-e) pedons were observed in the studied area. Table 1 presents the results of physicochemical properties measured for the representative polluted (1, 3, 4 and 6) and unpolluted (2 and 5) soils. Horizons of both polluted and unpolluted soils were mostly gypseous and/or calcareous, especially in the middle parts. Considering the surface and subsurface diagnostic horizons and the aridic-thermic soil moisture and temperature regimes, the studied soils were classified as Gypsids, Calcids or Cambids (Soil Survey Staff, 2014) (Table 1). However, due to the added petroleum waste compounds and presence of impermeable geomembrane in some of the polluted pedons, they were classified as Technosols in the WRB system (FAO, 2014) (Table 1). The surface horizons of the unpolluted soils contained less than 2 percent organic matter which regularly decreased by depth. In some horizons of the polluted soils, however, soil organic matter exceeded 12 percent (Table 1). It is reported that waste materials can percolate through deeper soil horizons and even contaminate groundwater in some cases (Gitipour *et al*., 2004). pH decreased by increasing organic matter (petroleum waste compounds) possibly due to H^+ dissociation from the petroleum compounds (Laurent *et al*., 2012). Electrical conductivity throughout the polluted soil horizons showed more limited variability than the unpolluted ones, probably due to their higher capability of water and liquids dynamics. Khademi and Mermut (2003) reported similar phenomenon in gypsiferous soils of Iran.

Micromorphology of the Studied Soils

Micromorphological characteristics of all sampled pedons were described. The results for three selected pedons including two polluted pedons (1 and 3) and one unpolluted pedon (2) are illustrated in Table 2.

Microstructure

The most dominant microstructure in the polluted soils was moderate to well developed granular (Table 2, Figures 2-a and -b), while in the unpolluted ones, it was subangular blocky with some weak to moderately developed granular zones (Table 2, Figures 3-a and -b). This can be attributed to the effects of petroleum compounds on particles aggregation in the polluted soils. Inflow of petroleum compounds with low dielectric constant into soil leads to the decrease of electrostatic repulsion forces and the collapse of diffused double layer around soil particles, which causes the coagulation of soil particles to form a granular microstructure (Mesri and Olson, 1971; Mitchell, 1976; Bowders *et al*., 1985; Zhao, 1996; Kaya and Fang, 2005). Therefore, it can be concluded that the prolonged exposure of the studied soils to the petroleum waste materials resulted in the coagulation and formation of small domains of clay particles behaving similar to silt and fine sand sized grains (Olgun,

Table 2- Micromorphological properties of selected pedons.

Pedon/Horizon /Depth (cm)	Microstructure	$c/f_{(20\mu m)}$	Related distribution pattern	Voids and porosity (%)	Coarse fraction		Fine materials	Pedofeatures
					Minerals and rock Frag.	Organic matter		
P1 Ap (0-20)	Well developed granular	2/8	Open porphyric	Complex packing voids (50%), planar (30%), vugh and chamber (20%), channel few	Plagioclase Basalt-granite	Earthworm organs and root tissue residues	Grayish brown dotted (solid oil compounds) and waxy clay and calcite	Depletion zones of oil soluble compounds, excrements beside semi-decomposed solid oil compounds (OC), calcite nodule
2By1 (47-60)	Well developed granular	3/7	Double-spaced open porphyric	Complex packing voids (50%), planar (35%), chamber and vugh (15%),	Plagioclase, quartz		Grayish brown dotted (solid oil compounds) and waxy clay and calcite	Lenticular and microcrystalline gypsum as nested infillings and solid fragments of oil waste mixed with soil material and excrements
2By2 (60-90)	Well developed granular with subangular blocky	4/6	Double-spaced open porphyric	Complex packing voids (45%), vugh and chamber (35%), planar (20%)	Plagioclase, quartz		Grayish brown dotted (solid oil compounds) and waxy clay and calcite	Lenticular and microcrystalline gypsum as nested infillings and solid fragments of oil waste mixed with soil material and excrements
2By3 (90-115)	Well developed granular (60%) and subangular blocky (40%)	2/8	Open porphyric	Total porosity about 40 % including compound packing voids (40%),planar voids (40%), chamber and vughs (20%)	Plagioclase, quartz		Grayish brown dotted (solid oil compounds) and waxy clay and calcite	Lenticular and microcrystalline gypsum as nested infillings and individual gypsum crystals, solid fragments of oil waste mixed with soil material and excrements
P2 (control) BK1 (35-45)	Moderately developed granular and few subangular blocky	2.5/7.5	Double-spaced and open porphyric	Complex packing voids (45%), planar (40%) chamber and vugh (15%),	Plagioclase, quartz	Root tissue residues	Brown to dark brown clay and calcite	Hypocoatings, loose discontinuous infillings of pores with gypsum crystal, calcite nodule,
By3 (150-200)	Weakly developed angular and subangular blocky (70%) and granular (30%)	0.5/9.5	Fine monic	Planar (50%) chamber (25%), vugh (25%)	Plagioclase, quartz	-	Brown to dark brown clay and calcite	Hypocoating and quazicoating, excrements, loose discontinuous infilling of pores with gypsum crystals and microaggregates, calcite depletion,
P 3 Ap (10-20)	Well developed granular	2/8	Open porphyric	Complex packing voids (55%), planar (25%), vugh and chamber (20%),channel	Plagioclase, quartz	Earthworm organ and root tissue residues	Grayish brown dotted (solid oil compounds) and waxy clay and calcite	Hypocoating and quazicoating, excrements loose discontinuous infilling of pores with gypsur crystals and microaggregates, calcite depletion.
Cy1 (30-40)	Moderate developed granular and few subangular blocky	4/6	Open porphyric	Complex packing voids (45%) vugh and chamber (35%), planar (20%)	Plagioclase		Grayish brown dotted (solid oil compounds) and waxy clay and micritic calcite	Hypocoating and quazicoating, excrements,, loose discontinuous infilling of pores with gypsum crystals and microaggregates, calcite depletion,.
Cy1 (40-50)	Well to moderate developed granular	3/7	Open porphyric	Complex packing voids (50%), planar (35%), vugh and chamber (15%)	Plagioclase	-	Grayish brown dotted (solid oil compounds) and waxy clay and micritic calcite	Hypocoating and quazicoating, excrements loose discontinuous infilling of pores with gypsur crystals and microaggregates, calcite depletion.
Cy2 (100-150)	Moderate developed subangular blocky (90%) and granular (10%)	1.5/5.5	Open porphyric	Total Porosity about 30-35 % planar (50%), vugh, and chamber (50%)	Plagioclase, and quartz	-	Grayish brown dotted (solid oil compounds) and waxy clay and micritic calcite	Hypocoating and quazicoating, excrements,, loose discontinuous infilling of pores with gypsum crystals and microaggregates, calcite depletion.

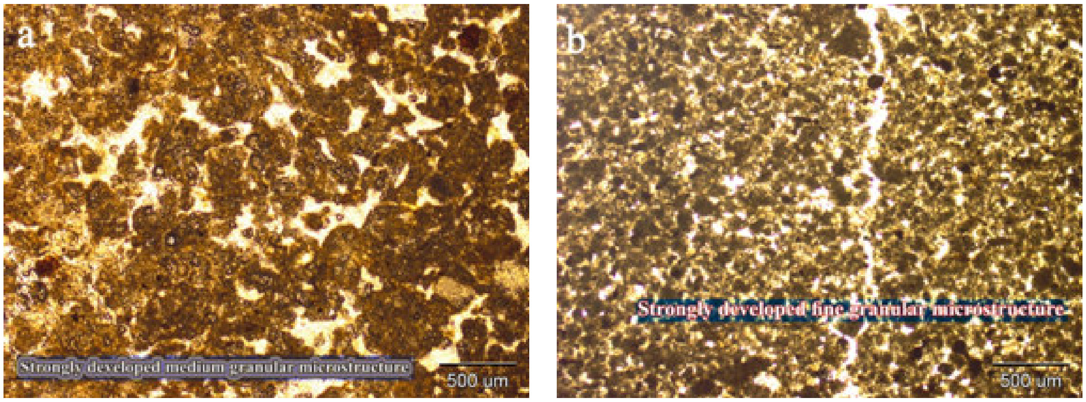

Figure 2. (a) strongly developed granular microstructure in pedon no. 3, 30-40 cm, and (b) pedon no. 4, 50-60 cm (both in PPL).

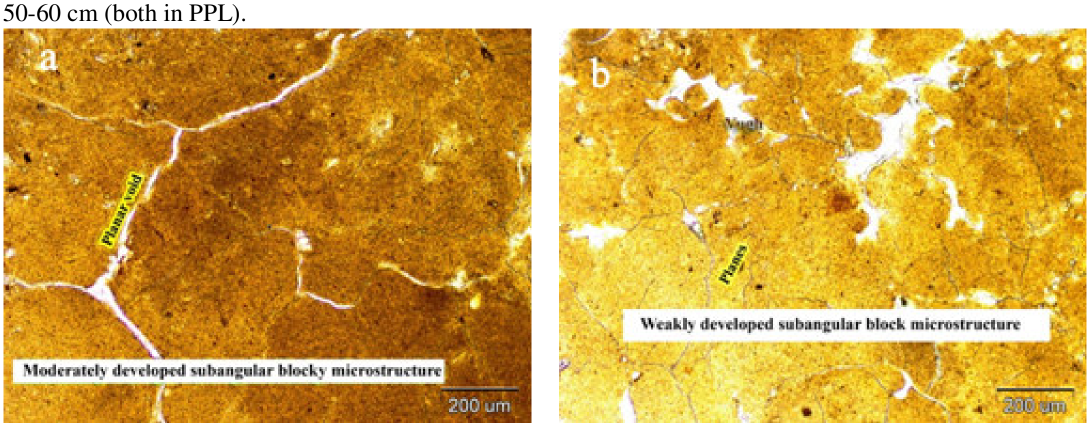

Figure 3. (a) Moderately and weakly developed subangular blocky microstructure in pedon no. 5, 30-60 cm, and (b) Pedon no. 2, 100-110 cm (both in PPL).

2008; Kaya and Fang, 2000) and even formation of a granular microstructure with enhanced total porosity (Ratnaweera and Meegoda, 2006) up to the depth that the petroleum compounds penetrated.

Micromorphological studies demonstrated that petroleum compounds also penetrated by horizontal seepage into pedons 2 and 5 which were described as references. Some effects of different petroleum compounds were observed in the thin sections of the unpolluted pedons (Table 2). Deep percolation of petroleum wastes leading to ground water contamination in the studied area was reported already by Gitipour *et al.* (2004).

c/f Related Distribution Pattern

Due to the origin of soil parent materials, which comprised fine alluvial and calcareous deposits, the most common *c/f* related distribution pattern in the studied thin sections were double-spaced to open porphyric (Table 2) and fine monic (Figures 3-a and b).

Fine material and b-fabric

The studied soils were highly calcareous resulting in the calcitic-crystallitic b-fabric (Table 2; Figures 4-a; 5-a, and -b). Micritic calcite (Figure 7-a) and dark colored

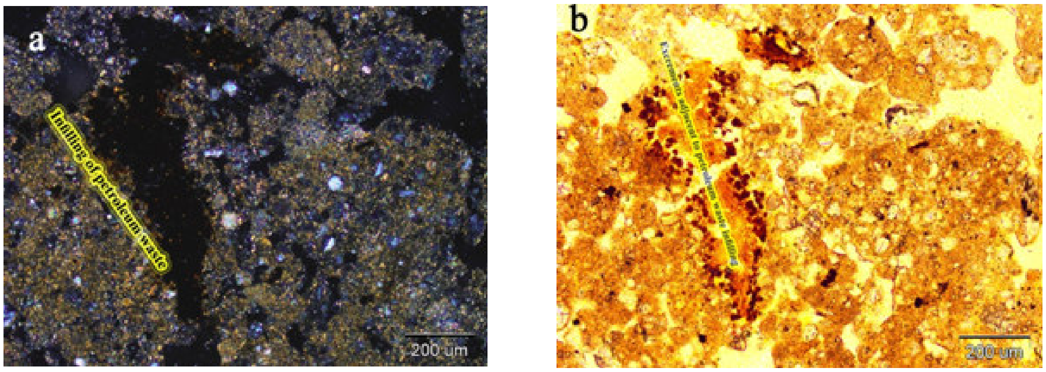

Figure 4. (a) Double spaced to open porphyric c/f related distribution pattern and crystallitic b-fabric (XPL), and (b) Granular and subangular blocky microstructure, infilling of petroleum waste and adjacent excrements showing biological activity, pedon no. 3,10-20 cm (PPL).

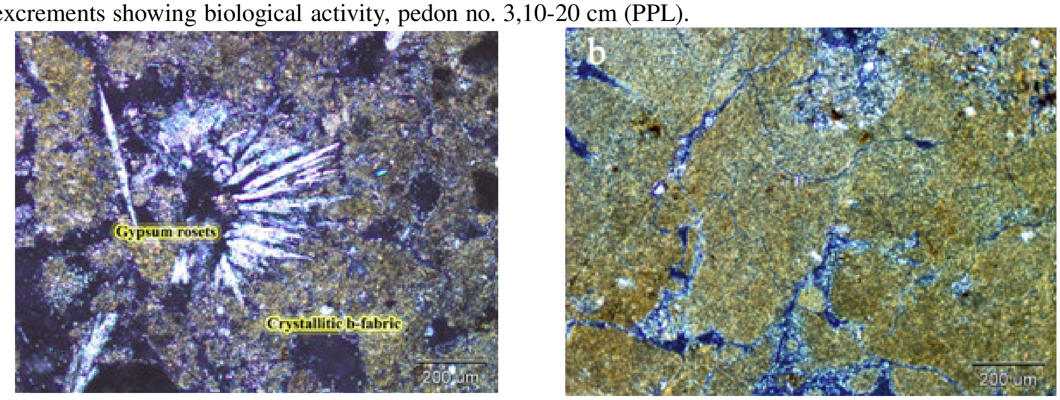

Figure 5. (a) Gypsum rosettes and crystallitic b-fabric, pedon no. 1, 60-90 cm, and (b) Pedon no. 5, 0-20 cm (both in XPL).

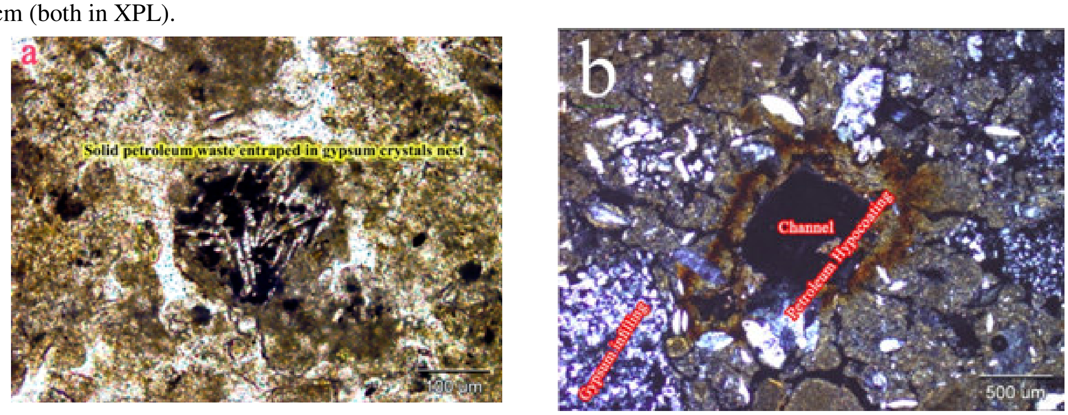

Figure 6. (a) Interactions between gypsum crystals aggregate and petroleum waste materials in pedon no.3, 40-50 cm (PPL), and (b) Petroleum quasicoating plus gypsum crystals infilling in pedon no. 6, 10-20 cm (XPL).

petroleum compounds (Figures 4-a; 6-b; 8-a; 10-a, and 11-b) masked fine materials making it difficult to observe the possible b-fabrics due to their lower transparency. There have been many reports indicating micritic calcite as a component of micromass and masking factor of pedofeatures (Stoops, 2003, Heidari *et al*., 2005), but there is no report on the role of petroleum compounds as a component of

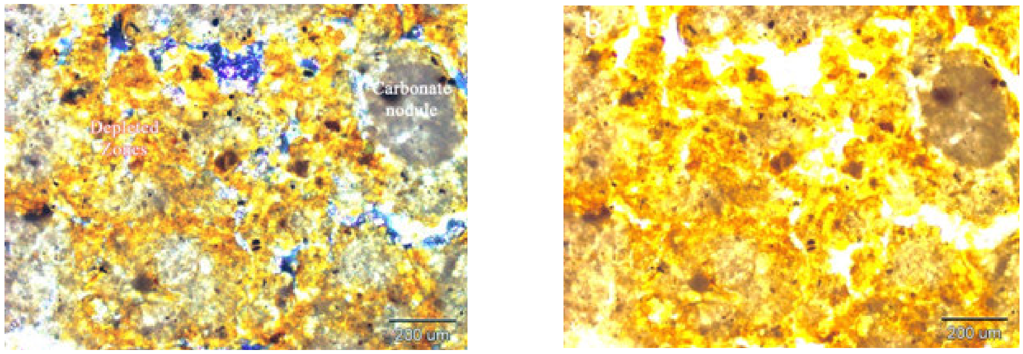

Figure 7. (a) Petroleum and water soluble compounds depletion zones at the margins of aggregates pedon no. 3, 100-150 cm (XPL), and (b) The same in (PPL).

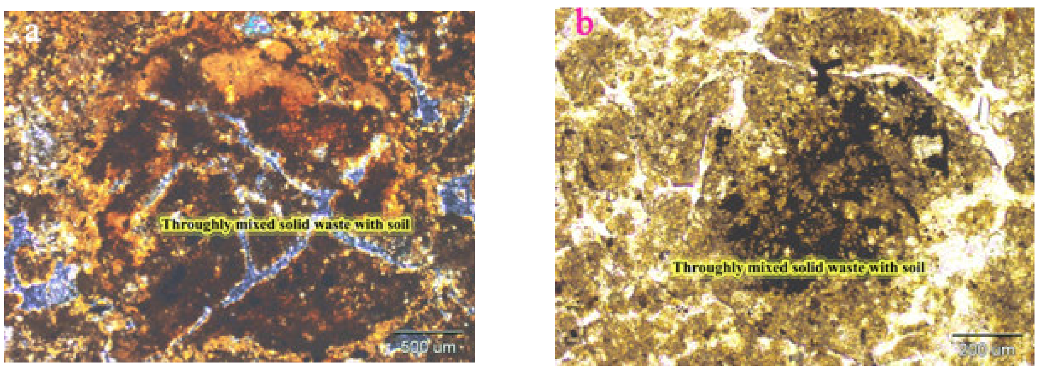

Figure 8. Thoroughly mixed petroleum waste with soil aggregates pedon no. 3, 50-90 cm (XPL), and (b) Pedon no. 4, 0-10 cm (PPL).

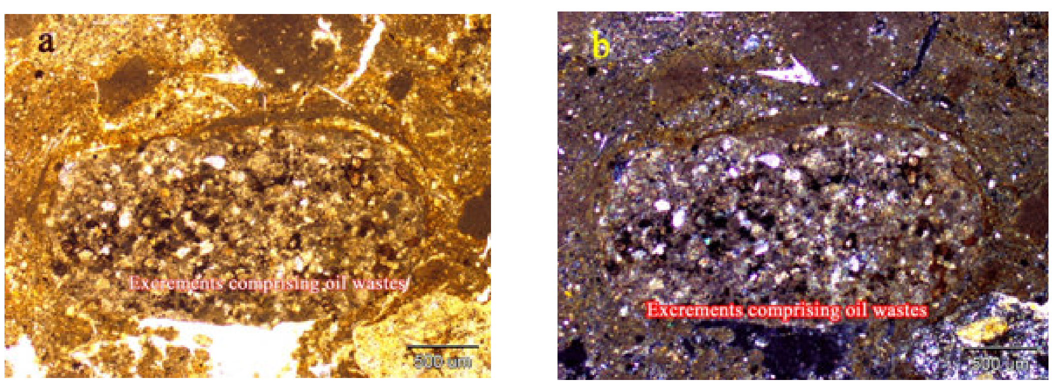

Figure 9. (a) Large excrements comprising oil wastes mixed with soil components pedon no. 4, 10-20 cm (PPL), and (b) The same in (XPL).

fine materials and masking agent of pedofeatures. Incorporation of petroleum compounds into the soil fine fraction and their interactions produced waxy and dark spots in some parts of micromass (Table 2; Figures 4-a; 6-b; 8-a; 10-a; 11-b, and 12-a).

Depletion and removal of soluble compounds from the fine materials at the margins of aggregates by seepage of less viscous and more fluid petroleum compounds resulted in the limpid fine

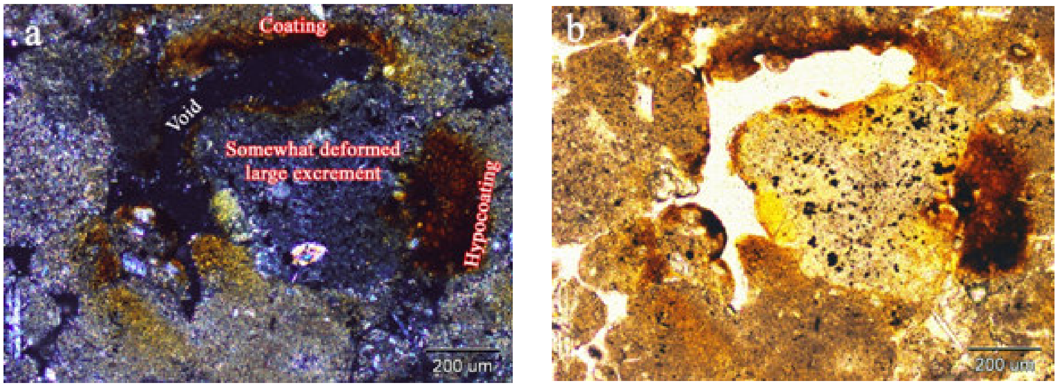

Figure 10. (a) Different hypocoatings, coatings, depletions and mixed oil wastes in a somewhat deformed large excrement microcrystalline pedon no. 4, 10-20 (XPL), and (b) The same in (PPL) .

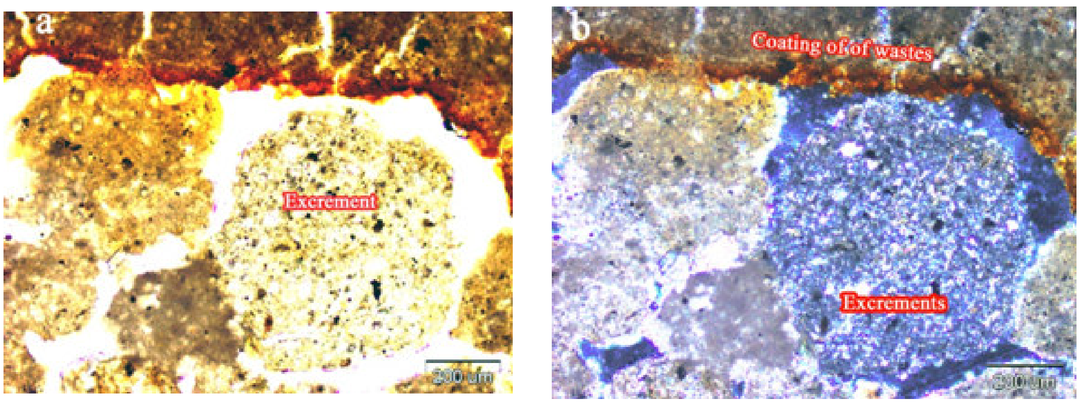

Figure 11. (a) Large partly deformed excrements comprising soil components and oil waste materials, coating of oil compounds and depletion zone pedon no. 4, 30-40 cm (PPL), and (b) The same in (XPL).

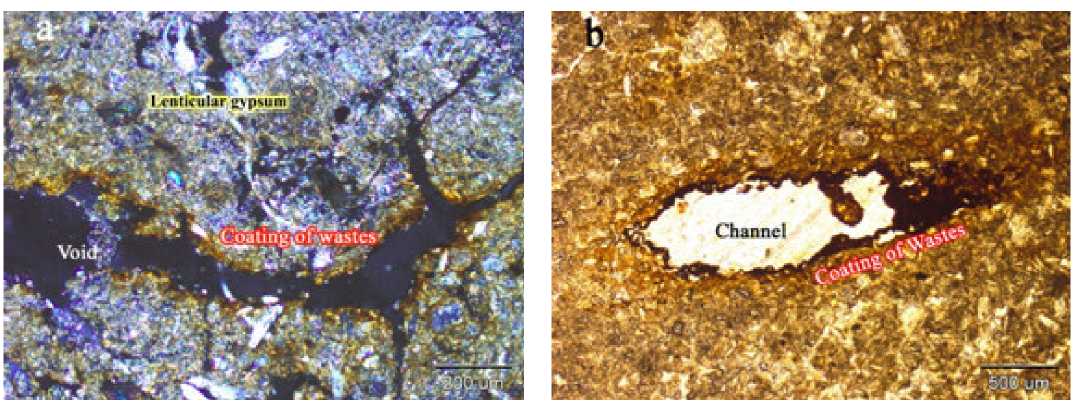

Figure 12. (a) Thin coatings of oil waste on voids in pedon no. 6, 10-20 cm (XPL), (b) Coating of oil compound in pedon no. 6, 10-20 cm (PPL).

materials in the depleted zones revealed (Figures 7-a and -b).

Coarse Materials

As shown in Table 2, the *c/f* related distribution pattern ratios varied from fine monic to double spaced porphyric. The mineral coarse fraction mainly comprised rock fragments (about 2-5 %), a few basaltoids and granitoids and minerals such as orthoclase and quartz. A few (less than 1-3 percent) remnants of coarse organic residues including plant and animal organs and tissue residues (Table 2; Figure 3-a) were observed. The existence of almost fresh remnants of earthworms' organs in the polluted pedons and their absence in the unpolluted pedons indicated that they died from waste materials and their intact remains in the period of waste discharging caused by the saturation of soil and limited aeration. These residues greatly adsorbed petroleum contaminants and discolored to brown and blackish colors.

Pedofeatures

Infillings, rosettes, nests and lenticular and microcrystalline gypsum crystals embedded in soil matrix, were the most easily detectable pedofeatures in most of the studied soils (Figures 5-a; 6-a and -b; 9-a and -b; 12-a, and 14-b). These pedofeatures were attributed to the pedogenesis prior to the addition of petroleum wastes. Micritic

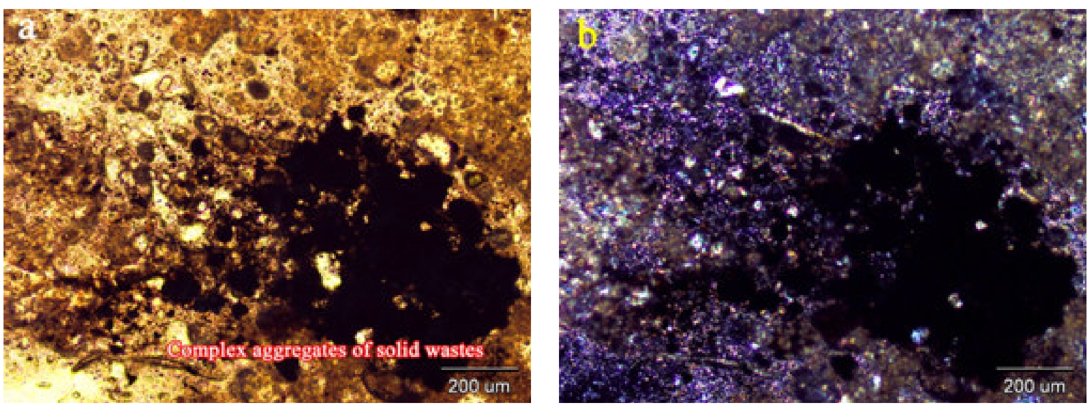

Figure 13. (a) Complex aggregate of waste materials pedon no. 4, 50-60 cm (PPL), and (b) The same in (XPL).

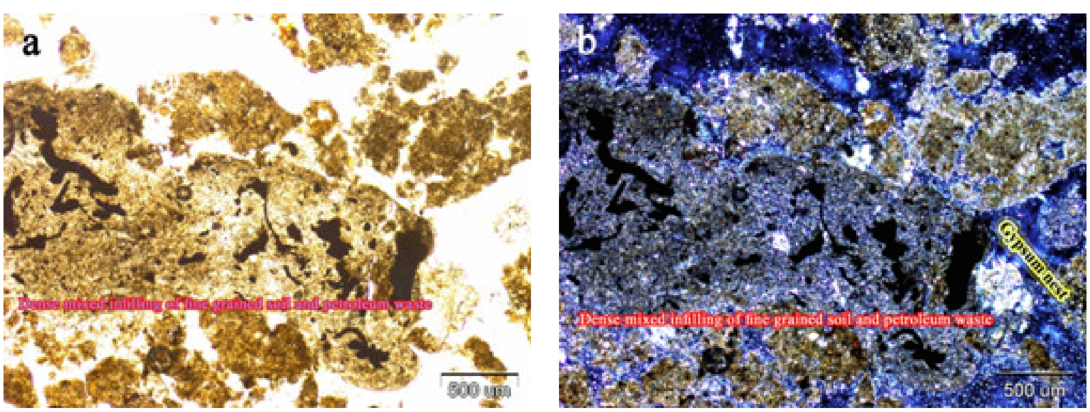

Figure 14- (a) Dense mixed infilling of fine grained soil and petroleum waste material in pedon no. 1, 90-115 cm, and (b) The same in (XPL).

calcite nodules were the other important pedofeatures formed before using the studied area for petroleum waste disposal (Figures 7-a and -b). As shown in Figures 4-a and -b, dense infillings of petroleum compounds with moderate viscosity were observed in some voids. The existence of many excrement of soil fauna having approximately spherical and elliptical shapes very close to the infillings demonstrated that these compounds were used as food sources by soil fauna (Figures 4-a and -b). Figure 6-a displays the entrapped granules of solid petroleum wastes between the infillings of acicular gypsum crystals. Figure 6-b shows the hypocoating of petroleum materials with moderate viscosity precisely stopped beneath the void surface. Other types of pedofeatures resulting from a more fluid fraction of petroleum wastes are the depleted zones of soil matrix and the margins of soil peds. Figures 8-a and -b show solid wastes thoroughly mixed with soil aggregates of different depths in pedons 3 and 4 that were possibly formed by biological activities or physical mixing of soil materials.

The existence of large droppings comprising chewed petroleum wastes excreted along with soil materials demonstrated that mice or other soil animals fed on the petroleum wastes (Figures 9-11). Burrows made by these animals formed big holes down to the deeper horizons that could cause deep percolation of the liquid phase and also infilling of the solid petroleum phases mixed with soil materials (Figures 14-a and -b).

Dark colored coatings of petroleum compounds with different thickness were the other important pedofeatures observed in the studied polluted pedons (Figures 12-a and -b). Complex aggregates of waste materials (Figures 13-a and -b) were observed in relatively deep horizons that could possibly be formed by falling of the semisolid phase into larger voids or burrows. Different types of infillings of surface materials into voids caused the translocation of petroleum compounds down to very deep soil horizons as shown in Figures 14-a and -b.

CONCLUSIONS

As observed in the studied soils, their morphological, physico-chemical and micro-morphological properties were adversely affected by the petroleum wastes. Long-term disposal of petroleum refinery wastes formed very distinct surface and subsurface morphological layers with special features due to enrichment with petroleum compounds that need to be introduced for Technosols (FAO, 2014). In addition to the morphological features, the physico-chemical properties also changed during wastes disposal. Soil structure, bulk density, and water retention were the most important physical properties influenced by petroleum wastes. pH and *EC* of saturated paste extract and organic matter content also were severely affected by the petroleum contamination.

Micromorphological studies showed that the microstructure and pedality were strongly affected by petroleum refinery waste compounds from surface down to the deeper soil horizons. Composition and viscosity of petroleum compounds may cause different impacts on soil micromorphological features. Low viscosity compounds which easily penetrated into deeper soil layers moved soluble compounds (e.g. organic matter) from the soil matrix or edges of aggregates and left specific depletion zones. Petroleum compounds with moderate viscosity could penetrate and stay in the middle depths beneath the soil surface possibly due to their bigger molecular size, and form coatings on voids. The high viscosity part of petroleum compounds which could not penetrate into the soil matrix formed coatings and aggregated nodules. Infillings of solid petroleum wastes mixed with fine soil aggregates in the deep subsurface horizons beside fine to large excrements containing solid petroleum wastes demonstrated considerable biological activities and consumption of the wastes, probably as a food source by the soil organisms. This study showed that micromorphology can play an important role to characterize the petroleum polluted soils.

REFERENCES

1. Asadi, P. and Heidari, A. 2012. Mineralogical and Physicochemical Properties of Some Oil Polluted Soils. *First National Conference for Guidelines Achieving Sustainable Development,* Tehran, Iran.
2. Bowders, J. J., Daniel, D. E., Broderick, G. P. and Liljestrand, H. M. 1985. Methods for Testing the Compressibility of Clay Liners with Landfill Leachate. In: "*Hazardous and Industrial Solid Waste Testing, Fourth Symposium*", (Ed.): ASTM STP 886. American Society for Testing Materials, pp. 233–250.
3. FAO. 2014. World Reference Base for Soil Resources, International Soil Classification System for Naming Soils and Creating Legends for Soil Maps: World Soil Resources Reports No. 106. FAO, Rome.
4. Gee, G. W. and Bauder, J. W. 1986. Particle-Size Analysis. In: Methods of Soil Analysis. Part 1. "*Physical and Mineralogical Methods*", (Ed.): Klute, A.. American Society of Agronomy, PP. 383–411.
5. Gitipour, S., Nabi, Gh. and Gorji, M. A. 2004. Soils Contaminated by Leaking Petroleum Compounds in South of Tehran Refinery. *J. Ecol.,* **34**: 39-45.
6. Gulshan, A. B. and Dasti, A. A. 2012. Role of Soil Texture and Depths on the Emergence of Buried Weed Seeds. *ARPN J. Agric. Biolog. Sci.,* **7**: 223-228.
7. Heidari, A., Mahmoodi, Sh., Stoops, G. and Mees, F. 2005. Micromorphological Characteristics of Vertisols of Iran, Including Non-smectitic Soils, *ALRM*, **19:** 29-46.
8. Heidarzadeh, N., Gitipour, S. and Abdoli, M. A. 2009. Statistical Sampling and Sludge Characterization at Tehran Oil Refinery. *Res. J. Chem. Environ.,* **13(4).**
9. Hesse, P.R. 1976. Particle Size Distribution in Gypsic Soils. *Plant Soil,* **44:** 241-247.
10. Kaya, A. and Fang, H. Y. 2000. The Effects of Organic Fluids on Physicochemical Parameters of Fine-grained Soils. *Can. Geotech. J.,* **37:** 943–950.
11. Kaya, A. and Fang, H. Y. 2005. Experimental Evidence of Reduction in Attractive and Repulsive Forces between Clay Particles Permeated with Organic Fluids: Technical Note. *Can. Geotech. J.,* **42**: 632–640.
12. Khademi, H. and Mermut, A. R. 2003. Micromorphology and Classification of Argids and Associated Gypsiferous Aridisols from Central Iran. *Catena,* **54:** 439–455.
13. Laurent, F., Cebron, A., Schwartz, C. and Leyval, C. 2012. Oxidation of a PAH Polluted Soil Using Modified Fenton Reaction in Unsaturated Condition Affects Biological and Physico-chemical Properties. *Chemosphere,* **86:** 659–664.
14. Mesri, G. and Olson, R. E. 1971. Mechanisms Controlling the Permeability of Clays. *Clay. Clay Mineral.,* **19(3):** 151–158.
15. Mitchell, J. K. 1976. *Fundamentals of Soil Behaviour.* John Wiley, New York.
16. Nwazue, N. R. 2011. The Effect of Crude Oil Spill on the Ascorbic Acid Content of Some Selected Vegetable Species in an Oil Polluted Soil. *Pak. J. Nutr.,* **10(3):** 274-281.
17. Olalemi, A. S. and Arotupin, D. J. 2012. Effect of Refined Petroleum Products Contamination on Bacterial Population and Physicochemical Characteristics of Cultivated Agricultural Soil. *J. Microbiol. Biotech. Food Sci.,* **2(2):** 684-700.
18. Olgun, M. 2008. The Investigation of Shear Strength and Consolidation Behaviors of Clay Soils Consolidated with Chemicals of Various Concentrations. PhD. Thesis, Selcuk University, Konya.
19. Onojake, M. C. and Osuji, L. C. 2012. Assessment of the Physico-chemical Properties of Hydrocarbon Contaminated Soil. *Arch. Appl. Sci. Res.,* **4(1)**: 48-58.
20. Pathak, H., Bhatnagar, K. and Jaroli, D. P. 2011. Physico-chemical Properties of Petroleum Polluted Soil Collected from Transport Nagar (Jaipur). *IJ FALS,* **1(3):** 84-89.
21. Ratnaweera, P. and Meegoda, J. N. 2006. Shear Strength and Stress–strain Behaviour of Contaminated Soils. *ASTM Geotech. Test. J.,* **29(2):** 133–140.
22. Sawhney, B. L. 1996. The Connecticut Agricultural Experiment Station: New Haven, Connecticut, Extraction of Organic Chemical. Part 3. Chemical Methods. In: "*Methods of Soil Analysis*", (Eds.): Sparks, D. L., Page, A. L. Helmke, P. A. and Loeppert, R. H.. Soil Science Society of America, Inc. Madison, Wisconsin, USA, **1.**
23. Soil Survey Staff. 2014. *Keys to Soil Taxonomy*. 12th Edition, USDA- NRCS.

24. Sparks, D. L. Page, A. L. Helmke, P. A. and Loeppert, R. H. 1996. *Method of Soil Analysis. Part 3. Chemical Methods.* American Society of Agronomy, Inc. Madison, Wisconsin, USA.
25. Stoops, G. 2003. Guidelines for the Analysis and Description of Soil and Regolith Thin Sections. SSSA, Madison, WI.
26. Stoops, G., Marcelino, V. and Mees, F., 2010. *Interpretation of Micromorphological Features of Soils and Regoliths.* Elsevier, Amsterdam, Netherlands.
27. USDA and NRCS. 2012. *Java Newhall Simulation Model (JNSM 1.6.0)*. Available at: (http://soils.usda.gov/technical/classification/jNSM/index.html).
28. Walkley, A. and Black, I. A. 1934. An Examination of the Degtjareff Method for Determining Soil Organic Matter, and a Proposed Modification of the Chromic Acid Titration Method. *Soil Sci.*, **34:** 29-38.
29. Zand, D. A., Nabibidhendi, Gh., Mehrdadi, N., Shirdam, R. and Mikaeili Tabrizi A. 2010. Total Petroleum Hydrocarbon (TPHs) Dissipation through Rhizoremediation by Plant Species. *Polish J. Environ. Stud.,* **19**: 115-122.
30. Zhao, D. 1996. Experimental Study of Stress–strain and Shear Strength Behaviour of Contaminated Cohesive Soils. PhD. Dissertation, The Johns Hopkins University, Baltimore, Maryland.

بررسی خصوصیات میکرومورفولوژیکی خاکهای آلوده در پالایشگاه نفت تهران

ا. حیدری و پ. اسدی

چکیده

در این مطالعه، خصوصیات میکرومورفولوژیک برخی از خاک های آلوده به مواد زائد نفتی پالایشگاهی نمونه برداری شده از جنوب تهران مورد مطالعه قرار گرفتند. پدون های غیر آلوده مجاور با پدون های آلوده نیز به عنوان مرجع و برای مقایسه نمونه برداری شدند. پس از تشریح پدون های مورد مطالعه، نمونه های دست نخورده برای تعیین خصوصیات میکروموفولوژیکی و نمونه های دست خورده برای تعیین خصوصیات فیزیکی و شیمیایی تهیه گردید.کلیه خصوصیات فیزیکی و شیمیایی با استفاده از روشهای استاندارد اندازه گیری شدند. نتایج نشان داد که خواص فیزیکی و شیمیایی (به عنوان مثال ساختمان ، جرم مخصوص، pHو EC و مواد آلی) خاک های آلوده به مواد نفتی به شدت تحت تاثیر قرار گرفته اند .قرار گرفتن طولانی مدت خاک در معرض ضایعات نفتی منجر به شکل گیری ویژگی های میکرومورفولوژیکی خاصی در خاکهای مورد مطالعه شده است. برخی از عوارض خاکساخت مهم شامل ساختمان دانه ای قوی، پرشدگی های حفرات از ضایعات نفتی جامد، به تنهایی و یا مخلوط با خاکدانه ها، حتی در افق های عمیق خاک مشاهده شد. وجود مواد دفعی مربوط به جانوران کوچک و بزرگ خاک، پوشش ها، پوشش های زیر سطحی و پوشش های در امتداد سطح و مناطق تخلیه شده از مواد محلول درنفت در اعماق مختلف مشاهده شد. نوع عوارض خاکساخت توسعه یافته به وضعیت مواد زائد نفتی و سیالیت آنها برای نفوذ، رسوب یا انحلال و انتقال ترکیبات خاک نسبت داده شد.