Pre-evaluation of contaminated soil for oil field reactivation in Moloacan, Veracruz, Mexico

Pre-evaluación de suelos contaminados para la reactivación de campo petrolero en Moloacán, Veracruz, México

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Abstract

This document presents studies to establish an Environmental Baseline for the oil sector in 13 wells in the Moloacán Field, in Veracruz, México regarding hydrocarbons in soils. Four factors were taken into account: visual soil assessment, methods for the hydrocarbon extraction (with two methods: the Soxhlet and the Petroflag), effects on fertility properties, and heavy metals content. The results show spills in every well with a high percentage of heavy fractions (mainly polar). However, these are not entirely visible because they are below or between the rhizosphere. Also, higher concentrations of hydrocarbons were found in specific sites such as old incinerators and waste pits. In the waste pits, pollutants had contact with the aquifer. In addition, in the determination of hydrocarbons, the Soxhlet method showed better results than the Petroflag one. Likewise, a relationship between these pollutants and the negative effects on soil properties, such as the increase in densities, electrical conductivity, and sands, as well as the decrease in field capacity and clays were found. Also, pH and salinity increased when the hydrocarbons exceeded the permissible limits (>4400 mg·kg^{-1}). Finally, metals such as Cr, V, Ba, Hg, Ni, Pb, and Cd were also found, but only Ni was found at dangerous levels for agricultural use.
Keywords: diagnostic, heavy metals, hydrocarbons, restauration, regulations.

Resumen

Este documento presenta los estudios utilizados para establecer una Línea Base Ambiental para el sector petrolero en 13 pozos en el Campo Moloacán, en Veracruz, México sobre hidrocarburos en suelos. Se tomaron en cuenta cuatro factores: valorización visual del suelo, métodos de extracción de hidrocarburos (con dos métodos: el Soxhlet y el Petroflag), efectos sobre las propiedades de fertilidad y contenido de metales pesados. Los resultados muestran derrames en todos los pozos con un alto porcentaje de fracciones pesadas (principalmente polares). Sin embargo, estas no son del todo visibles porque se encuentran por debajo o entre la rizosfera. Además, se encontraron concentraciones más altas de hidrocarburos en sitios específicos, como antiguos incineradores y pozos de desechos. En las fosas de desecho, estos contaminantes tuvieron contacto con el acuífero. Además, en la determinación de hidrocarburos, el método Soxhlet mostró mejores resultados que el Petroflag. Asimismo, se encontró una relación entre estos contaminantes y los efectos negativos sobre las propiedades del suelo, como el aumento de densidades, conductividad eléctrica y arenas, así como la disminución de la capacidad de campo y arcillas. Asimismo, el pH y la salinidad aumentaron cuando los hidrocarburos excedieron los límites permisibles (>4400 mg·kg^{-1}). Finalmente, también se encontraron metales como Cr, V, Ba, Hg, Ni, Pb y Cd, pero solo se encontró Ni en niveles peligrosos para uso agrícola.
Palabras clave: diagnóstico, metales pesados, hidrocarburos, restauración, regulaciones.

1 Introduction

The energy industry is one of the most profitable in the world, mainly because the rest of the productive sectors generally depend on it. However, the dumping of its products and waste has endangered the stability of the ecosystems (Thompson and Darwish, 2019). Recently, some organizations have expressed their concern because some oil-producing countries, after the health emergency derived from COVID-19, have decided to reactivate their economy by increasing the hydrocarbon production, but this, in parallel, might also increase the risks of spills (Norouzi and Fani, 2020).

In this matter, one of the great challenges is the regulation system for soil protection. Although, most of the norms consider a maximum concentration depending on the vocation of the soil, few of them include important parameters such as soil characteristics and changes in long-term pollutants (Kuppusamy *et al.*, 2020). For example, hydrocarbons can interact with biotic and abiotic factors in the system so their chemical composition can change, especially when exposed to the environment for a long time (Gómez-Mellado *et al.*, 2020).

Adams *et al.* (2016) and Vergeynst *et al.* (2019) found that the soil type could influence the response to the pollutant since when evaluating areas with old spills. They observed that forage grasses developed in fine-textured soils; in contrast to soils with coarse texture where grass could not develop. Varjani and Upasani (2019) and Zhang *et al.* (2020) reported this behavior to the specific characteristics of each region since they found a higher rate of degradation of hydrocarbons in tropical areas compared to colder zones (unlike temperate zones, in tropical, there is greater variability of temperatures and rainfall throughout the year which contributes to high biological activity that promote degradation). Other studies estimate that the degradation of a pollutant could vary according to the soil and the hydrocarbons properties since it has been observed that although light oils tend to move more easily on the soil matrix, they also tend to degrade faster than heavy oils (Ite and Ibok, 2019; Velázquez-Vázquez *et al.*, 2022).

In this sense, Haghollahi *et al.* (2016) evaluated contaminated sites based on the types of hydrocarbons: saturates, aromatics, resins, and asphaltenes (SARA) as a reference parameter and found that the degradation of each of them varies depending on the type of soil and the organisms present in it. Guzmán-Osorio *et al.* (2019) agree that the degradation of hydrocarbons in the soil is permanent but, in the long term it increases slowly. Additionally, they mention that there is always a residual fraction of hydrocarbons that has effects on the water capacity of the soil which also affects the development of some species. However, Fayeulle *et al.* (2019) and Domínguez-Rodríguez *et al.* (2020) reported that the change effects could also be related to the conditions to which any hydrocarbon spill is exposed. In general, in the long term, a greater number of variables are added. Hence, in many cases, it is difficult to establish adequate diagnoses to evaluate contaminated soils.

In this context, Varjani and Upasani (2019) and Al-Dhabaan (2019) recommend that, to make diagnoses, they should consider aspects such as hydrocarbon fractions, soil, environmental conditions, weathering time, and the analytical determination method. This last point has been widely discussed due to two associated aspects. The first one is related to a type of solvent, since it has been observed that treatment time plays an important role in the isolation of the analyte according to the type of soil, and the second one is related to a growing tendency to replace the gravimetric method by the spectrometric, since the latter have greater uncertainties (Guzmán-Osorio *et al.*, 2019). However, Hewelke and Gozdowski (2020) and Beck *et al.* (2020) have shown the various errors that these two methods can present, including the standard used in the calibration curve and variations in the absorption range, since these vary according to the abundance of the present fractions.

For example, in Mexico, the *Agencia de Seguridad, Energía y Ambiente* (ASEA) has established specific guidelines for the development of oil infrastructures in the Environmental Baseline Study (EBS). However, many cited regulations used for impact evaluations come from the *Secretaría del Medio Ambiente y Recursos Naturales* (SEMARNAT). Even though some of them need to be updated, such as the NOM-138-SEMARNAT-SSA1-2012 (SEMARNAT, 2013). Several reports have emphasized that this norm presents some errors, especially in the evaluation of old spills which present residual fractions of hydrocarbons (Morales-Bautista *et al.*, 2020).

Many of the oil fields in Mexico require EBS. However, it has to be considered that these fields might present two peculiarities. They have not been operated in decades ,as well as, they might have old

spills. That is why, it is of great relevance to have at hand the appropriate tools to avoid putting in risk any new activity in these fields that might affect the environmental services and public health (Rodríguez, 2019; Pulster *et al.*, 2020).

Besides, in similar studies of abandoned oil sites, infrastructure has been identified, such as valves, incinerators, separation batteries, wells, and waste pits (Trellu *et al.*, 2017), all with very low concentrations of hydrocarbons and, in some cases, spills have been covered by flora or soil (Ziarati *et al.*, 2019; Botello *et al.*, 2019; Saadati *et al.*, 2020). Due to these low concentrations, some of these sites have been declared below the permissible limits, but in some cases, environmental problems persist affecting the growth and development of plants (Sánchez *et al.*, 2017; Challenger *et al.*, 2018). Hence, Soto *et al.* (2018) and González-Mille *et al.* (2019) highlight the importance of considering methods of identification of these components since they relate them to negative effects on water potential, density, and porosity of the soil.

This study focused on the evaluation of the areas surrounding 13 wells at the Moloacán Oil Field, in Veracruz, México, where four aspects were considered: 1) visual soil assessment, 2) application of two methods for the extraction of hydrocarbons, 3) comparative analysis of the properties of soils contaminated by hydrocarbons against the fertility of a control soil and, 4) heavy metals concentrations. All of these parameters propose a basic comparative tool which may contribute to the standardization of these types of analysis and in the decision-making process, regarding the sampling and analysis of the entire oil field, as well as establishing an auxiliary background to work on diagnoses in similar sites.

2 Materials and methods

In every case, the sampling, in each of the 13 wells, was carried out within a radius of 20 to 30 meters from the center of each well. Some of these wells had waste pits and/or incinerators. The affected zone or the polygon was considered up to where hydrocarbons were no longer observed. Additionally, by using the same method, a control sample of soil was gathered in a site located outside Moloacán Oil Field. The location of every sample is specified in Figure I.
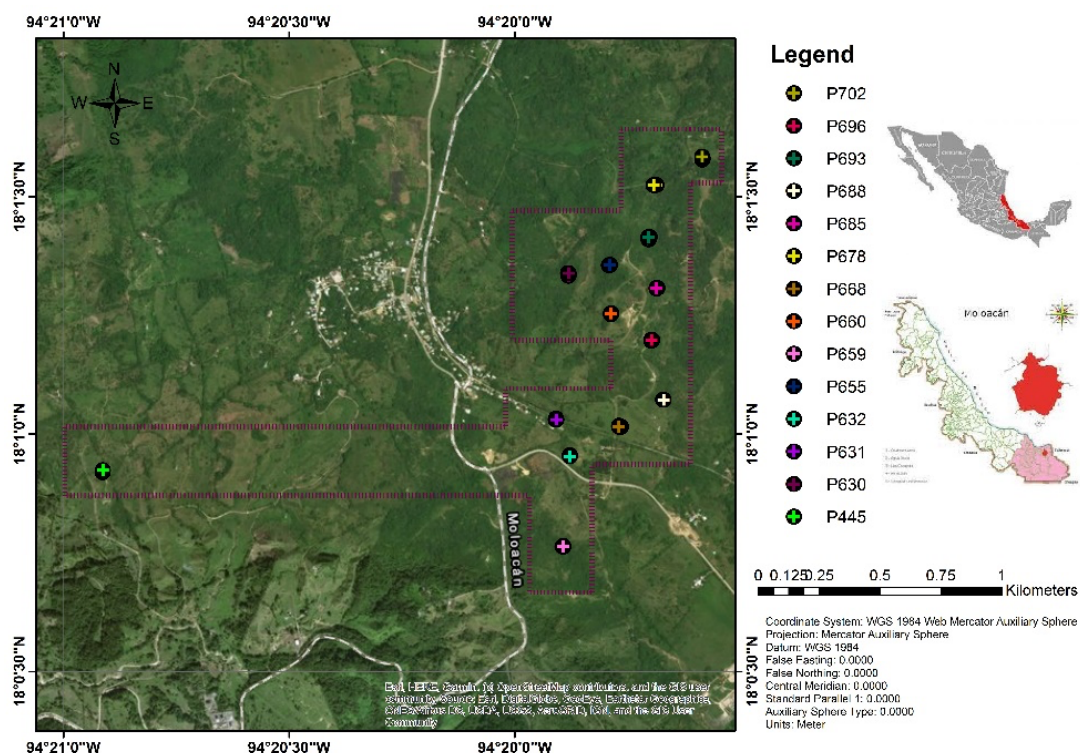

Figure I. Ubication of the wells and the sampling areas in Moloacán Oil Field.

A total of 14 (n=3) samples were collected in each polygon. Specific characteristics such as color (Munsell chart), texture (tact), aggregates, and presence of anthropogenic material were identified in each site. Subsequently, the samples were homogenized, a quartering was performed and, finally, three samples, of approximately 2 kg each were gathered (Palma-López *et al.*, 2017). In laboratory, a pretreatment was applied to each sample. This consisted of removing roots and rocks. Later they were dried at 60 °C, grounded and sieved. Subsequently, in order to evaluate the effects of the hydrocarbon on the properties of the soil, the following parameters were determined (NOM-021-SEMARNAT-2000 (SEMARNAT, 2002)):

- pH (Hydrogen potential, 1:2 soil-water ratio),

- Electrical conductivity (EC) of saturated extract in dS·m^{-1},

- Field capacity (%FC, per column of Colman),

- Texture through Bouyoucos method, expressed in percentages of silt (%L), clay (%R) and sand (%S),

- Apparent density (AD, by volumetric weight, in g·cm^{-3}),

- Percentage of porosity (Po, calculated by the ratio of RD and 2.6 g·cm^{-3}).

Hydrocarbon content was measured in terms of TPH by two methods: the first one was modified according to the Petroflag Method (TPHP), which consists of mixing 5 g of a sample with hexane and put in constant agitation for 2 hours. Subsequently, it was leaked and the liquid extracted was passed through a packed column (silica-hexane, n=3). The obtained sample was compared with a calibration curve (wavelength range 360 nm in a UV-Vis GENESYS^{TM} 10S spectrophotometer) (Kong *et al.*, 2017; Arguijo-Portillo *et al.*, 2019), constructed from heavy crude oil (15 °API), which was obtained from the Lacamango Separation Battery and is characterized as specified by Morales-Bautista *et al.* (2013). The second method was the Soxhlet and gravimetry (TPHS) (n=3) which is described in NOM-138-SEMARNAT-SSA1-2012 (SEMARNAT, 2013). However, dichloromethane was used as an extraction solvent instead of hexane (solvent cited by the standard), since Morales-Bautista *et al.* (2020) observed that dichloromethane performs a higher percentage of extractions, especially in samples with weathered hydrocarbons.

Also, the extract obtained by the second method (TPHS) was analyzed by the SARA fractions in a packed silica column and with selectivity of solvents (Marín-García *et al.*, 2016). Besides, due to the fact that some studies estimate that there are differences between the methods for determining TPH, mainly between the functional groups present in the samples, it was decided to analyze the extracts of P445, P688, and P660 (control soil, and samples with low and high hydrocarbon content, respectively) in a Fourier transform infrared spectrometer (Biocompare IRAffinity-1S FTIR Shimadzu) (Guzmán-Osorio *et al.*, 2019). In order to establish a relationship between the content of metals and the concentration of hydrocarbons, for these same samples: P445, P688, and P660, the following metals: Cr, V, As, Ba, Hg, Ni, Pb, Cd, K, Na, Mg, Ca, Cu, Fe and Zn were determined in an Atomic Absorption Spectrophotometer (Model AA Varian 240 Fs) according to NOM-021-SEMARNAT-2000 (SEMARNAT, 2002), and NOM-147-SEMARNAT-SSA1-2004 (SEMARNAT, 2007).

Finally, all results were statistically analyzed using the Shapiro Wilks normality test (Critical Value or VC vs Statistical value W, considering a significance level of 5%), the ANOVA test (p-value, $\alpha = 0.05$), and the Tukey test (honestly significant difference or HSD), all using the R- program project (Luke *et al.*, 2017).

3 Results and discussions

3.1 *Visual soil assessment*

In the samples that were analyzed in the field, the presence of hydrocarbons in solid, semi-solid and liquid states was observed. It was also detected the neglect of the infrastructure due to: deterioration of materials, theft and environmental processes. These three conditions might have caused spills, some of them were visible and others were not. Most of these compounds were found near the wells and in the waste pits (a, b, and c of Figure II). Likewise, a frequent characteristic detected was that the contaminants were below the rhizosphere or mixed with it (d and e of Figure II). This phenomenon coincides with that reported by Filatov *et al.* (2018) who specify that the combination of environmental factors could favor the development of plants in contaminated soils.

(a) Highly weathered hydrocarbon (covering an area of ~1000 m²). No wells or debris pits were found however, hardened hydrocarbon cuttings were observed throughout the area, and the inhabitants use it as raw material for road fillings.
(b) Well, which was plugged, with the presence of forage grass and no waste pit in a radius of 30-35 m. It was recorded the presence of hydrocarbons in form of hardened aggregates (1-2 cm in diameter) and in form of highly viscous spots, all in contact with phreatic level (~40-50 cm).
(c) Sample inside the waste well, semi-solid and viscous hydrocarbons are observed after 10 cm and in contact with the water table (90-110 cm).

(d and e) Waste pits, hydrocarbons were observed outside, all in the form of hardened and viscous aggregates (2-5 cm) throughout the profile and until reaching the phreatic level (90-110 cm). High stoniness, roots do not go beyond 20 cm, hydrocarbon contact was also observed with groundwater outside the waste pit and near the well. Also, it was found a mixture of hydrocarbons and CaO, which was commonly used to stabilize drilling wastes and coincides with the location of these.
(f) Site adjacent to a set of redirection valves and an affluent, the slope (30°) conditions determined the level of infiltration, it was observed that in the soil near the infrastructure there was only a semisolid hydrocarbon layer of ~10 cm, in contrast, in the midpoints of the slope, the samples shown hydrocarbons in a viscous state with the ability to move through the walls of the hole (20-80 cm), at these points, it was found the contact of the contaminant with the layer water table (~80 cm) within a radius of 35 m adjacent to the well.

Figure II. Soil conditions observed in field.

Similarly, Adams *et al*. (2015) and Riveroll-Larios *et al*. (2015) observed that in sites with old spills, some species could develop through stolons above the contaminant. They have called this process "biological sequestration" (Mcintosh *et al*., 2017). In some areas, this process has allowed the soil to gradually recover (Antonio and Georgina, 2014; Aljuboury *et al*., 2017). However, other studies have shown that in old spills, hydrocarbon leaching can represent a risk factor since this can cause biomagnification (Trellu *et al*., 2017; Khudur *et al*., 2018).

In this sense, Gómez-Mellado *et al*. (2020) reported that the composition of the hydrocarbon could have changed due to a weathering process, because during that period several biotransformation, degradation and leaching processes took place.
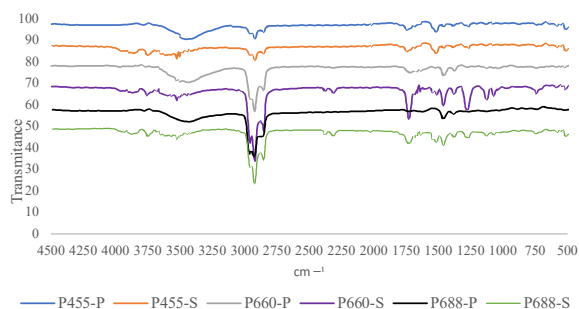
Figure III. FTIR of TPH extracts (both methods) from sites P445, P688 and P660 (where: P stands for Petroflag and S for Soxhlet extraction method).

Stout *et al*. (2016) and Asghar *et al*. (2016) observed that some of these components in water, of which Yildiz *et al*. (2021) warn about the risk to public health. Likewise, Morales-Bautista *et al*. (2013) and Pérez-Hernández *et al*. (2017) found that in old discharges, the residual fraction of hydrocarbons has low mobility and is difficult to degrade, but these compounds cause a reduction in water potential that is related to the reduction in crop production.

3.2 TPH determination methods and SARA fractions

In terms of solubility, Pikovskii *et al*., (2017) and Morales-Bautista *et al*. (2020) mention that heavier crude oils tend to be more related to polar solvents compared to non-polar ones. These studies can explain why the values of the TPH extracts are higher in the Soxhlet method (TPHS) (40-50%) which were isolated with dichloromethane compared to those of Petroflag (TPHP) (Table I) which were isolated with hexane. Likewise, the SARA analysis shows that the main fractions in the extracts are resins and asphaltenes (60-80%) (Table I), which are more akin to halogenated solvents (Morales-Bautista *et al*., 2020).

Table I. Total hydrocarbons of petroleum (HTP) and SARA fractions in samples of contaminated sites.

ID	TPHP	TPHS	Hydrocarbon fractions			
			% Sat	% Ar	% Res	% As
P445	0	0	0	0	0	0
P630	23899.16 ± 9.35	51716.09 ± 1.98	0	15 ± 0.41	25 ± 0.11	60 ± 0.31
P631	2144.37 ± 8.97	4559.61 ± 1.78	0	10 ± 0.32	24 ± 0.41	66 ± 0.22
P632	11944.01 ± 4.91	26667.68 ± 1.04	0	13 ± 0.21	28 ± 0.12	59 ± 0.14
P655	466.65 ± 8.27	994.03 ± 3.84	0	11 ± 0.18	19 ± 0.13	70 ± 0.12
P659	122.22 ± 4.78	259.82 ±1.01	0	11 ± 082	34 ± 0.22	55 ± 0.11
P660	10488.52 ± 4.71	22277.03 ± 8.73	0	11 ± 0.31	45 ± 0.31	40 ± 0.14
P668	633.31 ± 2.47	1396.32 ± 5.27	0	10 ± 0.23	45 ± 0.15	45 ± 0.15
P678	15966.11 ± 6.25	33751.56 ±1.32	0	12 ± 0.30	33 ± 0.20	55 ± 0.22
P685	1866.6 ± 7.09	3998.12 ±1.55	0	13 ± 0.70	26 ± 0.16	61 ± 0.21
P688	3144.33 ±1.23	6694.39 ± 2.61	0	11 ± 0.33	23 ± 0.11	66 ± 0.30
P693	5177.6 ± 2.027	11500.8 ± 4.31	0	10 ± 0.41	30 ± 0.31	60 ± 0.33
P696	15866.11 ± 6.21	35718.98 ±1.320	0	9 ± 0.07	25 ± 0.12	66 ± 0.20
P702	3188.78 ± 1.24	6468.86 ± 2.65	0	8 ± 0.09	21 ± 0.13	70 ± 0.13
W	0.896	0.937	NA	3.114	1.781	2.861
p-value	———— $p < 0.05$ ————		NA	———— $p < 0.05$ ————		
HSD	16.81	10.27	NA	1.71	6.81	4.86

Where: P445 is control sample, NA is not applicable, TPHP is Petroflag method and TPHS is Soxhlet test. % Sat = Saturated, %Ar = Aromatic fractions, %Res = Resins fractions and, %As=Asphaltenes fractions. The value For Shapiro-Wilk test VC = 0.866.

In addition, the infrared spectra (FTIR) of Figure III, confirm that the TPHS extracts have more defined C=O signals (~2850 and ~1600-1800 cm^{-1}) with respect to the TPHP and coincide with the reports of Hung and Fini (2019) and Guzmán-Osorio *et al.* (2019) who associate them with fractions of polar resins. Although TPHS presents a greater amount of extract in the TPHP campaign, it does not mean that they are the same, since when comparing the FTIR spectral with each other for the same sample, TPHS shows a greater number of signals, thus the composition between the two of them may be different as expressed by Wang *et al.* (2018) and Cipullo *et al.* (2019).

In addition, it was observed that the extracts of soils treated with dichloromethane show signals for aromatics whereas those from hexane do not (ca. 3000 cm^{-1}, 2000-2300 cm^{-1}, 1785-1874 cm^{-1}, and 1122-1070 cm^{-1} of Figure III) which coincides with the reports of Varjani and Upasani (2019). This could be related to some reports that warn about possible errors in the determination of TPH by spectrometric methods since when evaluating the same extract in different calibration curves, constructed at different wavelengths, the concentrations obtained differ from each other (Douglas *et al.*, 2019). Hence, it has deduced that if a calibration curve is built to a single signal of a functional group, it would be estimated just this one in particular and the rest could have left out of quantification (Webster *et al.*, 2016; Rakhmatullin *et al.*, 2018).

In this sense, since the Petroflag readings are made in the UV-Vis range, with a single beam equipment that makes readings between 300-350 nm, these wavelengths would only be reading aromatics (Arguijo-Portillo *et al.*, 2019). Other studies that have worked with wavelengths between 700-800 nm have been able to estimate heavy (polar) fractions (Samaniego *et al.*, 2017). Hence, in sites with weathered hydrocarbons, it was considered that the Petroflag method presents low extraction percentages, but if this tool is chosen due to its practicality in the field, it is necessary to complement it with the samples in the laboratory made by the Soxhlet method. In addition, the Petroflag method could be improved if, through experimentally contaminated soil samples, they are contrasted with the Soxhlet method.

Thus, it is suggested to consider evaluating oil spills in soils, the SARA fractions and the date of the spill. On the one hand, the results show that the type of solvent defines the amount of isolated analyte, which varies its solubility (González-Mille *et al.*, 2019); and on the other hand, although the samples are located within the same study area, the differences between the SARA fractions and the FTIR show that the time and conditions of the spill could influence the transformation of the hydrocarbon (Xu *et al.*, 2019; Xing *et al.*, 2019). An example of the above is that according to the values in Table I, with TPHP the samples P631, P655, P659, P668, P685, P688 and P702 do not exceed the Maximum Permissible Limit (MLP) of TPH established for agricultural use in Mexico (4400 mg kg^{-1}), whereas with TPHS values, only P655, P659, P668 and P685 would comply with the MLP.

3.3 *Contaminated soil*

Concerning the effects of hydrocarbons on soils, some studies show that one of the most affected parameters is texture (Rodríguez *et al.*, 2015). However, it has also been found that they could retain some contaminants (Morales-Bautista *et al.*, 2016). For example, some wettability studies indicate that carbonate rocks are preferentially oil-wet and sandstones are preferentially water-wet (Castillo-Campos *et al.*, 2021). Other studies mention that the desorption and disposal mechanisms of hydrocarbons also depend on organic matter and clay (Álvarez-Coronel *et al.*, 2020; Velázquez-Vázquez *et al.*, 2022). However, there is little evidence from these studies on old spill sites. It is estimated that clay soils tend to retain hydrocarbons and its leaching is lower compared to other soils with coarser fractions (Mao *et al.*, 2019). However, there are those who suggest that this could depend on the amount and type of clay, since the size of the pore can vary between them (Kumar *et al.*, 2022). In addition, the behavior of the aggregates has not yet been defined, since in some cases the soils are repellent but not in all of them (Hewelke and Gozdowski, 2020). Recently, it was found that these effects could depend on the stability of the aggregates and, that in old spills, this phenomenon could favor the elimination, deposition or washing of contaminants (Gautam *et al.*, 2020).

In these sense, Morales-Bautista *et al.* (2016) mention that when the contaminants come into contact with the soil, the hydrocarbons form aggregates that can represent a higher percentage of sand (%S) and a lower content of clay (%R). This coincides with the data observed in Table II, that shows that the contaminated samples present a higher fraction of %S.

Table II. Proprieties of soil in contaminated sites.

ID	pH	EC	AD	%Porosity	FC	%L	%R	%S	T
P445*	4.38 ± 0.08	0.56 ± 0.09	1.06 ± 0.02	48.64 ± 1.41	26.32 ± 0.58	13.39 ± 0.61	28.85 ± 0.19	55.31 ± 0.3	SCL
P630	7.12 ± 0.15	2.57 ± 0.05	1.17 ± 0.03	47.87 ± 1.693	29.29 ± 0.65	17.22 ± 0.79	0 ± 0	80.98 ± 0.44	LS
P631	4.70 ± 0.12	5.04 ± 0.11	1.14 ± 0.05	47.95 ± 2.22	34.22 ± 0.76	16.27 ± 0.74	24.32 ± 0.61	57.27 ± 0.31	SCL
P632	6.10 ± 0.14	2.37 ± 0.05	1.33 ± 0.05	38.52 ± 2.52	26.72 ± 0.59	16.27 ± 0.75	8.76 ± 0.22	73.08 ± 0.4p	LS
P655	5.51 ± 0.13	6.43 ± 0.13	1.16 ± 0.02	46.08 ± 1.33	39.59 ± 0.88	16.28 ± 0.74	32.11 ± 0.8	49.38 ± 0.27	SCL
P659	4.50 ± 0.12	2.37 ± 0.01	1.30 ± 0.04	41.04 ±2.05	37.79 ± 0.87	13.40 ± 0.61	35.03 ± 0.87	49.38 ± 0.27	SCL
P660	4.53 ± 0.09	3.17 ± 0.63	1.10 ± 0.08	49.98 ±3.65	26.32 ± 0.58	17.22 ± 0.79	3.89 ± 0.09	77.03 ± 0.42	LS
P668	4.80 ± 0.12	2.87 ± 0.06	1.16 ± 0.03	45.35 ± 1.74	37.99 ± 0.84	16.27 ± 0.74	28.2 ± 0.7	53.33 ± 0.29	SCL
P678	5.80 ± 0.14	0.99 ± 0.02	1.20 ± 0.02	36.07 ± 1.63	38.73 ± 0.86	17.12 ± 0.78	0.97 ± 0.02	79.99 ± 0.44	LS
P685	6.20 ± 0.15	5.54 ± 0.11	1.25 ± 0.03	40.05 ± 1.72	22.59 ± 0.5	19.11 ± 0.87	22.38 ± 0.56	56.29 ± 0.31	SCL
P688	5.91 ± 0.14	1.08 ± 0.02	1.07 ± 0.02	48.48 ± 1.25	26.04 ± 0.59	19.13 ± 0.87	16.54 ± 0.41	62.21 ± 0.34	SL
P693	5.90 ± 0.12	0.50 ± 0.01	1.17 ± 0.04	47.41 ± 2.03	36.55 ± 0.81	19.14 ± 0.87	11.68 ±0.29	67.15 ± 0.37	SL
P696	5.81 ± 0.14	0.79 ± 0.02	1.37 ± 0.03	41.67 ± 1.62	33.61 ± 0.74	19.10 ± 0.87	0 ± 0	79 ± 0.44	LS
P702	5.60 ± 0.13	1.01 ± 0.02	1.20 ± 0.02	45.85 ± 1.55	34.22 ± 0.76	19.12 ± 0.87	14.59 ± 0.36	64.19 ± 0.36	SL
W	0.921	0.876	0.944	0.901	0.9	0.875	0.924	0.905	
p-value				$p < 0.05$					
HSD	0.22	0.31	0.07	3.42	1.25	2.34	1.38	1.07	

Where: * is control sample. SCL is Sandy-Clay-Loam, SL is Sandy-Loam, LS is Loamy-Sand and T is the Classification of United States Department of Agriculture or USDA (USDA, 2018). The value for Shapiro-Wilk test VC = 0.874.

However, although some contaminated samples show significant differences in the percentages of %S and %R (HSD lower than the calculated one), their textural classification is the same as that of the control. Ite and Ibok (2019) and Zahermand *et al*. (2020) mention that some soils may contain low concentrations of hydrocarbons without having major effects on the texture, which could explain why samples P631, P655, P659, P668 and P685 have an SCL classification since their concentrations of hydrocarbon are relatively low.

However, although the percentages of clay in the soil may be similar, it does not mean that the soils have similar properties in the rest of them. For example, soils with a similar textural classification have been reported in the study area, but some of them have expandable clays and others do not (Palma-López *et al*., 2017). Some comparative studies observed that in tropical soils with residual fractions of hydrocarbons, in alluvial zones (mostly with expandable clays) crops have been established, while in the terraced zone (similar to the study zone), management must be higher in order to improve field capacity (Oliaei and Heidarpoor, 2015; Álvarez-Coronel *et al*., 2020). Although the reports of these authors coincide with the results found in most of the soils of the study area, except in the waste pits, because in the samples, the hydrocarbon was in a semi-liquid state and in contact with phreatic level. Hence, the conditions of degradation in these small areas are different from the rest. Ukpaka *et al*. (2020) suggest to identify the types of aromatic hydrocarbons present, especially because they could biomagnify.

Regarding the pH values, the ANOVA test shows significant differences between the values of the samples ($p < 0.05$). In this sense, when performing the contrast of means using the Tukey test, it was observed that the samples P445 (control) P659, P660, and P631 do not present significant differences between them (mean differences less than the calculated HSD). These values coincide with those of Palma-López *et al*. (2017) who report that the soils in this area have an acidic pH and associate them with the presence of aluminum or iron. However, samples 660 and 631 have a pH similar to the soil control and both contain hydrocarbons in different concentrations. In this context, there are studies that mention that acidity is associated with the minerals present such as clays and that hydrocarbons are preferentially deposited in them and that this could influence changes in pH (Álvarez-Coronel *et al*., 2020). This can also be seen in the reduction of the %R fraction and the increase in pH in various samples (Table II). But when evaluating all the samples, we do not observe a direct relationship between both parameters. These variations have been reported and mention that the

effects on soil properties depend on the type of crude oil and the amount spilled (°API) (Morales-Bautista *et al.*, 2016). Likewise, the values of the samples P688, P685, P693, P696, P678, and P702 do not present significant differences between them (mean differences less than the calculated HSD).

Adams *et al.* (2004) reported other changes in pH at remediated sites near the study area and mentioned that CaO was added to contaminated sites and waste pits to stabilize, and Interiano-López *et al.* (2019) observed that the drill cuttings may contain limestone, which has alkaline properties. Domínguez-Rodríguez *et al.* (2020) mention that these practices also modified the pH, increased the percentage of %S and RD, as well as provoked a decrease in porosity. These reports coincide with the properties such as pH and porosity of some contaminated samples, in which, some of them change from very acid to acid with respect to the control sample. Zamora *et al.* (2012 and Guarino *et al.* (2017) have found that on fresh spills hydrocarbon has no effect on pH.

However, McIntosh *et al.* (2017) and Kudhur *et al.* (2018) evaluated contaminated soils with hydrocarbons. They detected some errors in the parameter determination such as density, porosity and field capacity related to the water repellency. Besides, Guzman-Osorio, (2020) relate repellency to the asphaltenes + resins fractions. Hence, the TPH values are contrasted with those of the soil properties (clay, sand, field capacity and porosity) (Figure IV).

The trends in Figure IV show that as the hydrocarbon concentration increases, the sand content also increases and the clay content decreases (in range of 8,800-18,000 mg kg^{-1}), which coincides with the literature (Vogel *et al.*, 2020). In addition, these trends show that these changes depend on the concentration, since in samples with concentrations below ~5000 mg kg^{-1} (polygon a, close to the MLP for agricultural use) the textural classification similar to the control is preserved and, from these concentrations and in those below ~25,000 mg kg^{-1}, the classification is transformed to coarser textures (polygon b) and, for samples with concentrations higher than this last value, clays are ~5% and sands are greater than ~90% (polygon c).

Other effects observed in Figure IV are in the field capacity (FC) which decreases with the increase in hydrocarbon concentration. Although these results coincide with some reports such as those of Mao *et al.* (2019), the Colman assay could have errors due to the formation of agglomerates known as amphipathic micelles of high or low molecular weight, since these aggregates can form a waterproof film that does not allow the passage of water by gravity, being retained in the upper part of the column (Rakhmatullin *et al.*, 2018). In this sense, when comparing the TPHS values between P678 and P696 samples, the concentrations are similar and not significant differences are observed (HSD is lower than calculated). Likewise, the sum of the fractions %Res and %As is similar, but when comparing their FC values with that of the control (P445), no significant differences are observed for P678 (HSD lower than calculated).
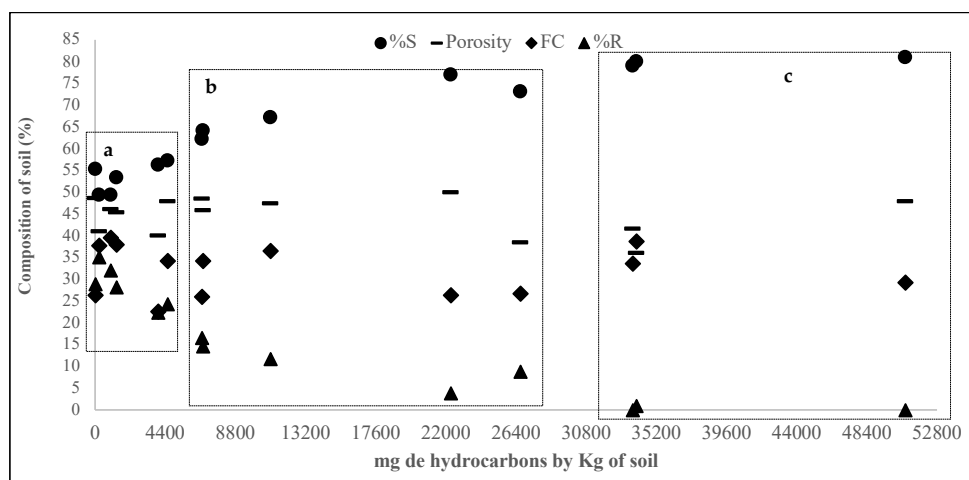

Figure IV. Changes in soil properties in relation to the concentration of total hydrocarbons of petroleum.

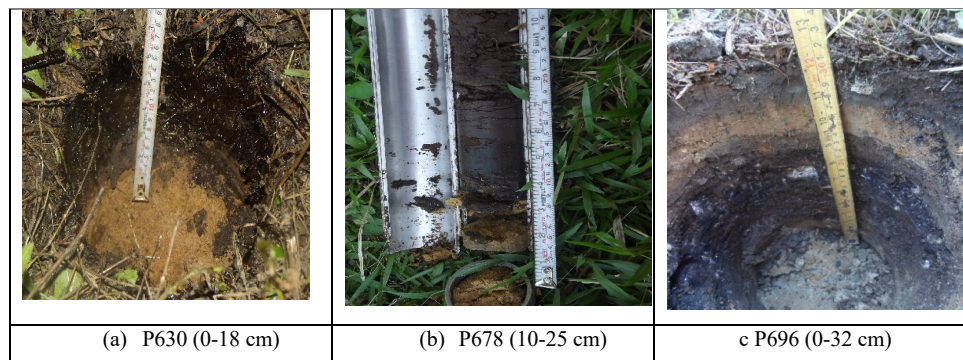| (a) P630 (0-18 cm) | (b) P678 (10-25 cm) | c P696 (0-32 cm) |

Figure V. Conditions in soil according to density of hydrocarbon.

Since the concentration and the density of hydrocarbons play an important role in environmental diagnostics, it was tried to exemplify these differences by using three samples of soil with similar concentrations but with different hydrocarbon density, which was calculated using the indirect method proposed by Morales-Bautista *et al.* (2013) (Figure V). Due to the °API values found (less than 15) and according report of Marín-García *et al.* (2016), all the samples would present water repellency. However, on one hand, "a" and "b" represent a greater risk because uniformity could favor the retention of water in the first horizons. On the other hand, "c" denotes that the hydrocarbons are solidified and that allow the development of roots (Adams *et al.*, 2016; Morales-Bautista *et al.*, 2016).

The results above, can also explain the FC variations in samples greater than 27000 mg kg^{-1} since there are no significant differences between the FC values of the P696 and P631 samples (the mean difference is less than the calculated HSD), but when comparing the TPHP and TPHS values, significant differences were found (the mean difference is greater than the calculated HSD). In addition, by preventing the passage of water towards the lower horizons (a and b) and if the soil is exposed to high temperatures, the water evaporates more quickly. Consequently, the plants could suffer water stress, especially in times of drought (Valle *et al.*, 2020).

In contrast, although it has been shown that soils have a great buffering capacity for salts, the excess of these can reduce the osmotic potential and thus reduce the yield in some vegetables (Gómez- Mellado *et al.*, 2020). Kuppusamy *et al.* (2020) have established that the level of impact can be measured through electrical conductivity (EC) or the percentage of exchangeable sodium (PSI). SEMARNAT (2002) agrees that to the negligible effects of salinity in levels of EC < 4 dS m^{-1}, PSI < 15%. In this sense, in EC only samples P631, P685, and P655 present values above 4 dS m^{-1}. The rest have values below this indicator. However, the ANOVA test indicates differences between them (p< 0.05). Later, when performing the Tukey test, the differences of the means indicate that between P630, P659, P632, and P668 do not present significant differences among themselves (differences of means less than the calculated HSD). Likewise, no significant differences are observed between the values of the samples P445 (control), P693, P696, P688, P678, and P702 (differences of means less than the calculated HSD).

Ukpaka *et al.* (2020) and Gomez-Mellado *et al.* (2020) mention that produced water and drilling cuttings can contribute to the presence of EC in soils contaminated with hydrocarbons, both studies also agree with the results of Botello *et al.* (2019) and Ziarati *et al.* (2019) who add the presence of heavy metals in low areas and sediments of oil spills, of which Reyes *et al.* (2016) have emphasized their effects on health. Also, other studies have observed effects from 0.02 eq L^{-1} of Na (from the extract of the saturated pasta), since the study area has a vocation for agricultural use, it is necessary to establish pastures and vegetables that can be tolerant to this indicator (Soto *et al.*, 2018; Mendoza-Carranza *et al.*, 2016).

3.4 Metals content

The extraction of crude petroleum is usually accompanied by produced waters and drilling cuts. Currently, these are treated in separation batteries or dehydrators in order to bring certain pollutants (mainly metals and hydrocarbons) to regulatory concentrations and finally give them final disposal (Xu *et al.*, 2018). Although this treatment has been used for decades, it

was not until a few years ago that well pretreatments (dehydrators, decanters, and furnaces) and parallel conduction systems were implemented. This is why, impacts related to heavy metals are very common in oil areas (Ziarati *et al.*, 2019; Saadati *et al.*, 2020).

For example, some studies like the one of Wang *et al.* (2017) have reported the presence of V, Cr, Pb, and Ni in the rivers sediments and the coastal areas of sites adjacent to oil facilities. These reports are consistent with studies carried out at two oil assets: at Cinco Presidentes in Veracruz, and at Samaria-Luna in Tabasco, in which Pb, Zn, Na, and Ni outside of regulatory ranges have been detected, as well as V, Cr, and Cd have been observed in different concentrations (Ruiz-Fernández *et al.*, 2019; Gómez-Mellado *et al.*, 2020; Machain-Castillo *et al.*, 2020). In addition, in some spills of crude oil and added asphalt, concentrations of Hg, Cd, Ni, As, Ba, Be, Ag, Se, and Ta were observed by Mendoza-Carranza *et al.* (2016) and Saadati *et al.* (2020).

The results of Table III show that in all the analyzed soils, metals Cd, and As were not detected. Likewise, only Cr, and V were found in the sample with the highest hydrocarbon content (P660). Similarly, metals such as Ba and Hg were not detected

in the control soil, but they were found in the samples contaminated with hydrocarbons whose Hg values show significant differences between them. However, the Ba content is similar in both samples (no significant differences between them).

In addition, no differences were observed between K concentrations in P445 and P688 (mean difference less than HSD). However, both values are different from P660 (mean differences greater than HSD). In contrast, there are no significant differences between Na, Mg, and Zn values of the contaminated samples (P688 and P660, the mean difference is less than the calculated HSD), but both samples present differences with the control (P445). For the rest of the metals (Ca, Cu, and Fe) as well as for the %PSI, all values differ from each other (mean difference greater than corresponding HSD).

To estimate the level of contamination and its possible effects, the values found (Table III) were compared with the normal and dangerous ranges of the soil fertility standard. In this sense, some metals such as Cr, V, As, Ba, Hg, Ni, Pb, and Cd are considered pollutants, for Mexico and their MLP are listed in NOM-147-SEMARNAT-2004 (SEMARNAT, 2007).

Table III. Quantification of heavy metals in control and contaminated sites according to the hydrocarbon content.

ID	As	Cd	Cr	V	Hg	Ba	Ni	Pb
	mg·kg^{-1}							
P445	< LD	< LD	< LD	< LD	< LD	< LD	14 ± 0.05	37 ± 0.16
P688	< LD	< LD	< LD	< LD	0.049 ± 0.001	114 ± 0.46	51 ± 0.21	40 ± 0.14
P660	< LD	< LD	92 ± 0.21	53.1 ± 0.15	0.046 ± 0.001	264 ± 0.10	232 ± 0.92	85 ± 0.34
W					0.795	0.993	0.873	0.796
p-value			NA		p > 0.05	——— p < 0.05 ———		
HSD					NA	0.004	13.77	5.44
MF		0.35					50	35
MP	22	37	280	78	23	5400	1600	400

ID	K	Na	Mg	Ca	Cu	Fe	Zn	PSI
	Cmol+·kg^{-1}				mg·kg^{-1}			%
P445	0.168 ± 0.004	0.155 ± 0.005	1.731 ± 0.059	21.85 ± 0.081	0.280 ± 0.009	3.15 ± 0.012	0.410 ± 0.010	0.19 ± 0.073
P688	0.168 ± 0.002	0.751 ± 0.021	0.330 ± 0.011	16.65 ± 0.066	0.038 ± 0.001	6.45 ± 0.025	0.983 ± 0.003	1.44 ± 0.001
P660	0.041 ± 0.001	0.793 ± 0.001	0.321± 0.010	2.50 ± 0.010	0.094 ± 0.002	10.21 ± 0.040	0.971 ± 0.002	18.35 ± 0.690
W	20.631	1.251	0.768	0.933	0.912	1.001	0.874	1.247
p-value		——————— p < 0.05 ———————						
HSD	0.014	0.064	0.103	1.596	0.007	0.017	0.722	0.083
MF	< 0.2		< 0.5	< 2	< 0.2	< 2.5	< 0.5	15

Where: DL: Detection Limit (Cr = 0.0086, V=0.048, As = 0.032, Ba = 0.045, Hg = 0.022, Ni = 0.0138, Pb = 0.0197, Cd = 0.0014, K = 0.0028, Na = 0.0011, Mg = 0.001, Ca= 0.028, Cu = 0.0037, Fe = 0.0061 and, Zn =0.0033); NA these are cases in which statistical tests were not performed. PSI stands for percentage of exchangeable sodium. The value for Shapiro-Wilk test is VC = 0.767. MF and MP are the LMP for soils by agricultural use marked by the standards the NOM-021-SEMARNAT-2000 and NOM-147-SEMARNAT-SSA1-2004 , respectively (SEMARNAT, 2002a, 2007b).

Likewise, the soil fertility standard NOM-021-SEMARNAT-2000 (SEMARNAT, 2002) establishes the following metals: Cu, Fe and Zn as nutrients in deficient ranges and in suitable ranges. Also, it estimates the concentrations of Cd, Pb, and Ni in two terms: normal and dangerous.

In these terms, no metal is above the MLP set by NOM-147-SEMARNAT-2004. However, there is a relationship between the amount of hydrocarbons and the concentrations for Cr, V, Ni, and Pb, which coincide with some reports where they found these metals in sites under industrial influence (Ziarati *et al.*, 2019; Agrelli *et al.*, 2020). A special case is Ba, which is used as a stabilizer in drilling cuttings (Iryna and Leonid, 2016). Although it is found in low concentrations, it could represent a problem since the waste pits were intended to confine them (Kujawska and Pawlowaska, 2018).

In contrast, with respect to the fertility norm, only the control soil presents deficiencies in Zn, the rest present adequate concentrations. However, Pb, Cd, and Ni are outside of the normal range, but only Ni is in dangerous ranges; despite the fact that only Ni represents a risk, some studies have related the presence of Pb and Ni with health problems in similar concentrations. Hence, it would be necessary to carry out studies of disposition and presence of other matrices and to consider the sites as environmental liabilities (Khudur *et al.*, 2018; Saadati *et al.*, 2020).

In addition, although NOM-021-SEMARNAT-2000 (SEMARNAT, 2002) establishes the criteria for fertility (according to metal contentand), and the range of exchangeable cations, most farmers continue to establish measures according to the type of crop. Throughout the southeast of Mexico, it is very common to find corn (Tuxpeño) in the state of Veracruz as well as banana and sugar cane in the state of Tabasco (Palma-López *et al.*, 2017). In the study area, it was observed that small producers combine their plots. Hence, next to the crops, there are meadows for raising cattle which is fed with resistant grasses such as Brachiaria humidicola (Pérez-Hernandez *et al.*, 2017).

When comparing the concentrations of Mg, Ca, and K in contaminated soils, these are lower with respect to the control soil, it is even appreciated that in both cases the hydrocarbon could affect their disposal (since the test is carried out the extract of the saturated paste). This is inverse for Na, and % PSI since both are higher in contaminated soils and are related to spills of congenital waters and hydrocarbons (Gómez-Mellado *et al.*, 2020). In this context, various authors report that the deficiency of these nutrients can affect the quality of food, some of them, like corn and beans, are very important in the Mexican diet (Asghar *et al.*, 2016; Tosquy-Valle *et al.*, 2020; Rodríguez *et al.*, 2019).

Conclusions

Hydrocarbon spills were identified in the study area, mainly in waste pits and areas surrounding the wells. Hydrocarbon fractions, mainly resins and asphaltenes, were also identified, both fractions could reduce the water potential of the soil and affect the development of crops. However, since the area is mostly cattle, this problem could be reduced with the induction of drought-tolerant grasses. To identify them, it is concluded that solvents should preferably be used for these fractions, since from the used methods, Soxhlet showed better results than Petroflag. Besides, some samples present values in higher yields than MLP and in higher concentrations than the established by the Mexican standard. In addition, a relationship was found between the concentration of hydrocarbons and the effects on soil properties, such as textures, of which the sands are directly related to the concentration of hydrocarbons. However, the changes in the textural classification depend on the concentration of hydrocarbons. Likewise, there is no relationship between properties such as field capacity (CF), apparent density (AD), and percentage of porosity (%Porosity). Although literature establishes that CF and %Porosity could have reductions, increases in their values were found. Consequently, the hypothesis of this study establishes that the methods for determining these properties could be interfered because of water repellency. Consequently, it is not recommended to consider these parameters since they would have errors in the EBS. It was also found that there is a slight increase in soil pH, but this could be more related to the materials used for soil stabilization. Likewise, the presence of Ni in the soils was identified at dangerous levels as established by the fertility standard, but like V and Cr, they are below the MLP for agricultural and industrial use according to the Mexican reference standard. However, since these metals are bioaccumulative, it is important to complement soil analyzes with those of other matrices such as water and vegetation and, in this way, determine the level of risk to which the population could be exposed. Also, because these metals have been found in the lower part of the basin,

it is suggested to carry out studies in the lower parts of the oil field.

Acknowledgments

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