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Oil Fractions Impact on Mexican Soils Evaluation Web Application

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Abstract. This paper presents an Evaluation Web Application designed to provide essential technical information about environmental damage caused by light fraction, medium fraction and heavy impact fraction contamination by oil and its effect on Mexican soils. According to NOM-138-SEMARNAT-2012 "Maximum permissible limits of hydrocarbons in soils and guidelines for sampling in the characterization and specification for remediation", published at Federation Official Gazette in Mexico on September 10th, 2013. The application developed on Java Script Object (JSON) technology for a non-relational database, shows effects on every different soil when a hydrocarbon spill happens, and suggest appropriate mitigation and remediation strategies for every soil present at Mexico municipalities.

Keywords: Oil fractions, polluted soils, web application, Mexican soils.

1 Introduction

In Petroleum Industry, it is of fundamental importance to minimize risks in industrial operation, maximizing occupational safety and health of all the processing work personnel, like storage and distribution facilities, at the wholesale or retail level of petroleum products and petrochemicals. as well as functional and operational integrity of facilities and related equipment [1]. In Mexico, gasoline and diesel clandestine takes in transportation pipelines are a serious problem with social, economic, environmental and operational safety impacts. As a result of the so-called Energy Reform of our country (2013-2014) [2], the responsibility for Industrial Hydrocarbons Sector Management was concentrated in specialized government agencies: National Hydrocarbons Commission (CNH) for oil resources exploration and exploitation; Energy Regulatory Commission (CRE) for petroleum and petrochemicals products operation, distribution and commercialization; besides Security, Energy and Environment Agency (ASEA) for Industrial Safety and Environmental Protection of the Hydrocarbons National Sector. The activities carried out in the Oil Value Chain (OVC) three segments, begin with the drilling of wells in land and seabed and the extraction of crude oil, going through natural resource industrial transformation to convert it into oil products and other derivatives; liquids and gases, which have to be stored, transported, distributed and marketed until they reach final consumers, which can be industries and the general public [6]. Dangerous substances are handled throughout activities sequence, since they are chemical compounds that can form explosive, flammable and toxic mixtures, consequences of an unexpected release into the environment can cause irreparable damage, as well as considerable economic losses [3].

Considering the magnitude and complexity of the activities carried out on a daily basis in the Petroleum Industry, major accidents related to the handling of hazardous substances and materials occur infrequently; however, social, environmental and economic cost is often high [8, 9]. The resulting loss depends on the capacity and resilience of the system and environment under study to withstand the disaster and, in turn, the disaster occurs when hazards and risks are linked to vulnerability [5].

Oil spills to the ground are conveniently studied by classifying them according to the activities carried out in a given segment of the oil value chain (OVC). The spills in the upstream segment focus on the effects on the soil and offshore water, due to the spillage of oil, drilling fluids and materials extracted from the subsoil by drilling bits in onshore and offshore producing reservoirs, as well as in transfer ports [12]. The spills in the intermediate current segment (midstream) correspond to those that occur at sites where oil, gas and its derivatives storage and distribution facilities are located, gas and liquid transportation pipelines and natural gas liquefaction and regasification facilities [7]. In this classification there are also mobile sources, freight trains and tank trucks. Spills in the downstream segment correspond to those that occur at sites where oil refineries and petrochemical facilities are located, including facilities with a large storage capacity for petroleum products and petrochemicals. Industrial facilities for processing petroleum derivatives called petrochemicals are also included in this segment [12].

Table 1. Distribution of fires and explosions in industries that use or process hydrocarbon [16].

Typology	Proportion %
Fire	32
Explosions inside equipment due to air input	11
Explosions within equipment due to uncontrolled reaction, or explosive decomposition	23
Explosions outside equipment, but inside building	24
Explosions outdoors	3
Container explosions (due to corrosion, third party damage, overheating or overpressure)	7

1.1 Explosions and Fire in the Oil and Gas Industry

An explosion can be defined as the generation of a pressure wave in the air as a consequence of the extremely rapid release of energy. Within this broad definition there are various physical and chemical phenomena that, with a certain probability, can occur in process industry that uses hazardous substances [13, 14, 15]. In these industries, explosions represent, together with fires, the most frequent and destructive accidents, highlighting those dedicated to the manufacture of explosives or pyrotechnic materials, those that use flammable gases or Installations that, without having capable substances If they cause an explosion by themselves, they have containers where high pressures can be generated which, when they explode, release the contained energy in a violent way. Table 1 provides an overview of the importance of explosions in the chemical industries [16].

Fire is a chemical reaction that involves an element oxidation or rapid combustion causing contamination in Mexican soils, although there is no presence of fire, hydrocarbons also affect soils nature and contaminate them.

1.1.1 Contaminated Soils in Mexico

In Mexico there is a great variety of soils due to various factors interaction, such as complex topography caused by the Cenozoic volcanic activity, altitudinal gradient (from zero to 5,600 meters above sea level), the presence of four of the Five types of climates and the landscape diversity and rocks type in territory, in Mexico there are 26 of 32 soil groups recognized by International World Reference Base System for Soil Resources (IUSS). Leptosols (28.3% of territory), Regosols (13.7%), Phaeozems (11.7%), Calcisols (10.4%), Luvisols (9%) and Vertisols (8.6%) dominate all over the country, together occupy 81.7% of national surface [20].

Contaminated soil is all that whose characteristics have been negatively altered by the presence of dangerous chemical components of human origin, in a concentration such that it poses an unacceptable risk to human health or the environment. Oil spills affect the physical properties of soils and especially, natural populations of microorganisms. In particular, they cause a decrease in free-living nitrogen-fixing bacteria, responsible for assimilating and recycling nutrients in biogeochemical cycles [10].

In addition to soil contamination effects produced by hydrocarbons, oil interferes in parameters determination, such as texture, organic matter, real density and porosity

Table 2. Products associated with hydrocarbon spills, for which maximum permissible limits of contamination in soils are established [11].

Contaminant Product	Hydrocarbons				
	Heavy Fraction	Medium Fraction	HAP	Light Fraction	BTEX
Mix of unknown petroleum products	X	X	X	X	X
Crude Oil	X	X	X	X	X
Fuel Oil	X		X		
Paraffin	X		X		
Petrolatum	X		X		
Derived Oils	X		X		
Gas Oil		X	X		
Diesel		X	X		
Jet Fuel		X	X		
Kerosene		X	X		
Creosote		X	X		
Gas Plane				X	X
Solvent Gas				X	X
Gasoline				X	X
Naphta Gas				X	X

Table 3. Maximum permissible limits for hydrocarbon fractions in soils [11].

Hydrocarbons Fractions	Predominant Soil Usage (mg/kg) Dry Base			Analytic Method
	Agricultural, forestry, livestock and conservation	Residential and recreational	Industrial and commercial	
Light	200	200	500	NMX-AA-105-SCFI-2008
Medium	1200	1200	5000	NMX-AA-145-SCFI-2008
High	3000	3000	6000	NMX-AA-134-SCFI-2008

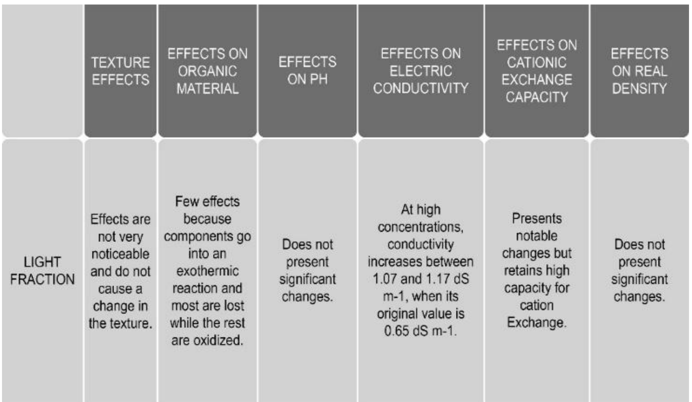
[18]. Therefore, soil pollutant's introduction can result in damage or some functions loss and affectation of water, particularly groundwater. The concentration of dangerous pollutants in soils above certain levels entails a large number of negative consequences for human health, as well as for all types of ecosystems and others.

For this reason, contaminated soils constitute the most urgent and important problem still unsolved in environmental matters [17].

1.2 NOM-138-SEMARNAT/SSA1-2012

This standard establishes the maximum permissible limits for hydrocarbons in soils and sampling guidelines for characterization and specifications for remediation, as well as, products associated with oil spills, for which maximum limits are established are listed in Table 2 [11].

Maximum permissible limits for hydrocarbons fractions in soils listed in Table 3 [11], and Maximum Permissible Limits for specific hydrocarbons in the soil in Table 4 [11].



	TEXTURE EFFECTS	EFFECTS ON ORGANIC MATERIAL	EFFECTS ON PH	EFFECTS ON ELECTRIC CONDUCTIVITY	EFFECTS ON CATIONIC EXCHANGE CAPACITY	EFFECTS ON REAL DENSITY
LIGHT FRACTION	Effects are not very noticeable and do not cause a change in the texture.	Few effects because components go into an exothermic reaction and most are lost while the rest are oxidized.	Does not present significant changes.	At high concentrations, conductivity increases between 1.07 and 1.17 dS m-1, when its original value is 0.65 dS m-1.	Presents notable changes but retains high capacity for cation Exchange.	Does not present significant changes.

Fig. 1. Oil Impacts effects on soils.

Table 4. Maximum permissible limits for specific hydrocarbons in soils [11].

Specific Hydrocarbons	Predominant Soil Usage (mg/kg) Dry Base			Analytic Method
	Agricultural, forestry, livestock and conservation	**Residential and recreational**	**Industrial and commercial**	
Benzene	6	6	500	NMX-AA-141-SCFI-2007
Toluene	40	40	5000	NMX-AA-141-SCFI-2007
Ethylbenzene	10	10	6000	NMX-AA-141-SCFI-2007
Xylenes (sum of isomers)	40	40		NMX-AA-141-SCFI-2007
Benzo [a] pyrene	2	2		NMX-AA-146-SCFI-2008
Dibenzo [a, h] anthracene	2	2		NMX-AA-146-SCFI-2008
Benzo [a] anthracene	2	2		NMX-AA-146-SCFI-2008
Benzo [b] fluoranthene	2	2		NMX-AA-146-SCFI-2008
Benzo [k] fluoranthene	8	8		NMX-AA-146-SCFI-2008
Indene (1,2,3-cd) pyrene	2	2		NMX-AA-146-SCFI-2008

2 Oil Fractions Impact on Mexican Soils Evaluation Web Application Development

In order to be able to develop the correlation between oil fractions impact and the effect on the soils, a characterization study was used to determine soil damage [18]. It was decided that based on the effects produced according to oil fractions, it would be classified according to most noticeable changes that have occurred in soils, such a texture effects, organic matter effects, pH effects, electrical conductivity effects, cation exchange capacity effects, real density effects, apparent density effects and porosity effects, as shown in Figure 1.

In general, no matter soil type, sand values tend to increase and clay to decrease in medium and heavy fraction presence, variance between clay and concentration factors and hydrocarbon type indicates a non-significant difference. ($P < 0.05$) due to type of hydrocarbon effect that can be observed when comparing effects caused by the three types of fraction that is manifested when the concentration of hydrocarbon in the soil is very high. The texture is modified due to the adsorption of the middle fraction and the heavy fraction by the soil particles through electrostatic interactions of the type of Van der Waals forces, hydrogen bridges, water bridges and cationic bridges, causing effects on the sedimentation rate, which affects the density of the mud formed by the soil and water during the analysis, inducing a reading of particles. with the Bouyocos hydrometer, which is interpreted as altered.

Organic matter is one of the parameters with important variations that increase in proportion to the fraction's concentration, whether light, medium or heavy. It can also be seen that for the middle fraction there is a greater increase when hydrocarbons concentrations are present. Statistically between the organic matter parameter and the hydrocarbon type and concentration factors, it was determined that there is a significant difference ($P < 0.05$) for both factors, which is corroborated with the levels that increase in direct proportion to the concentration of hydrocarbons of light fraction ($r = 0.97$), medium fraction ($r = 0.88$) and heavy fraction ($r = 0.97$). Increase in organic matter is not beneficial, since said increase is due to petrogenic and not biogenic material. This may actually represent an ecotoxic risk due to the presence of polynuclear aromatic hydrocarbons contained in a greater proportion in medium and heavy fraction.

PH practically does not have a variation in any concentration presence and hydrocarbon type, so it remains medium to slightly acidic. The analysis of variance between the pH parameter, against the factors concentration and type of hydrocarbon, determined that there is no significant difference ($P < 0.05$), that is, the soil subjected to different levels of contamination from the different fractions, produces minimal effects on pH, in such a way that no effect is perceived in this variable. Electrical conductivity has an irregular variation, since values increase and decrease in the presence of the three types of fractions at different concentrations. However, there is a slight tendency to increase when the pollutant is light fraction. When analyzing the variance between the electrical conductivity against the factors concentration and fraction, it was determined that there is no significant difference ($P < 0.05$), this means that the contaminated soil at different levels of contamination by different hydrocarbons does not they prevent the solubilization of the salts present in the soil, which is manifested in the similar determinations of conductivity in the extract, similar determinations of conductivity in the extract of the saturation paste.

There is an irregular variation in the cationic exchange capacity values, since they increase and decrease regardless of the concentration and type of hydrocarbon, so the trend is indefinite. The most notable changes correspond to the soil contaminated with gasoline, still retaining a high cation exchange capacity. The variations are related to the effect of the adsorption of hydrocarbons on the surface of the mineral soil particles, interfering in the cation exchange sites and by electrostatic interactions. It was determined that there is no significant difference ($P < 0.05$) between the cation exchange capacity parameter against the concentration factors and type of fraction, which is observed as an effect on the values with an irregular tendency to increase and decrease around the average value of uncontaminated soil, clay soil real density variation with respect to the concentration and type of hydrocarbon, where the medium fraction and the light fraction show minimal variation even in high concentrations of hydrocarbon.

It should be noted that the heavy fraction does cause a variation in the real density tending to decrease from high concentrations, causing a downward trend. This value must be considered with great care for the purpose of selecting some soil remediation technology, however, between real density against the factors concentration and type of hydrocarbon, there is no significant difference ($P < 0.05$). This is due to the relationship with the determination process, since it takes into account the weight and volume only of the mineral particles in the soil, which at the time of determining their weight, this is modified by the combination of particles with higher density with the hydrocarbide with lower density. Variations in apparent density are minimal, so different fractions at different concentrations do not influence this parameter, the analysis between variance between the apparent density parameter against the concentration factors by fraction type, they indicate that there is no significant difference ($P < 0.05$) for the type of hydro-carbide.

Porosity does not vary significantly when the soil is contaminated with light fraction or medium fraction hydrocarbons, however, with heavy fraction hydrocarbons, this parameter decreases drastically. This trend originates from the effect on the decrease in the real density, since there is a mathematical relationship between both parameters. Statistically between porosity and hydrocarbon type, there is no significant difference ($P < 0.05$) for light fraction and medium fraction.

2.1 Database Construction

The necessary information was obtained for the creation of the database in Excel® software by consulting NOM-138-SEMARNAT/SSA1-2012 rule [11]. Because Excel® is a registered trademark of Microsoft®, the use of freeware was considered for database migration, it was necessary to import all data with help of simple text format for data exchange JSON and will be linked to a Mexican edaphology database [19]. It is important to mention that it is due to this data collection that a non-relational database will be generated.

As a first phase, maximum permissible limits for hydrocarbon fractions in soils were obtained from PROFEPA, although the type of pollutant, in this case, oil derivatives [4]. including hydrological information, edaphologic information, geologic information and economic information of every place, production modes among other facts. Only the necessary information that would be required for the database elaboration had to be captured and some fields that help to its exploration in order to obtain desired results, once information had been reviewed, it was then synthesized into State, number of municipalities and soils percentage, classified in an edaphological way by each of them, as well as the use of land in corresponding municipality (urban, agriculture and pasture). as shown in Figure 2.

HYDROCARBONS FRACTIONS	PREDOMINANT SOIL USE (mg/kg DRY BASE)			ANALYTIC METHOD
	Agricultural, forestry, livestock and conservation	Residential and recreational	Industrial and commercial	
Light	200	200	500	NMX-AA-105-SCFI-2008
Medium	1 200	1 200	5 000	NMX-AA-145-SCFI-2008
Heavy	3 000	3 000	6 000	NMX-AA-134-SCFI-2006

Fig. 2. NOM-138-SEMARNAT/SSA1-2012 Database created in Excel®.

```
<head>
    <meta charset="utf-8">
    <meta http-equiv="X-UA-Compatible" content="IE=edge">
    <title></title>
    <meta name="description" content="">
    <meta name="viewport" content="width=device-width, initial-scale=1">
    <link rel="stylesheet" href="lib/materialize/css/materialize.css">
    <link rel="stylesheet" href="css/estilos.css">
</head>

<body>
    <!--[if lt IE 7]>
            <p class="browsehappy">You are using an <strong>outdated</strong> browser. Please <a href="#">upgrade your browser</a> to improve your experience.</p>
        <![endif]-->
    <nav>
        <div class="nav-wrapper lime accent-4 ">
            <a href="#" class="brand-logo blue-grey-text text-darken-3"><img src="img/tierra.png" class="logo responsive-img" />
                <B>EDAFOLOGÍA MEXICANA</B>
            </a>

            <ul id="nav-mobile" class="right hide-on-med-and-down ">
                <li><a class="blue-grey-text text-darken-3" href="sass.html">Salir</a></li>
            </ul>
        </div>
    </nav>
    <section class="blue lighten-5">

            <div class="row">
                <div class="col s4 m3 ">
                    <ul class="collection white-text ">
                        <li class="collection-item blue-grey lighten-3 center-align lime accent-4">Estado</li>
                        <li class="collection-item blue-grey lighten-3 blue-grey lighten-3 truncate">Aguascalientes</li>
                        <li id="bc" class="collection-item blue-grey lighten-3 blue-grey lighten-3">Baja California</li>
                        <li class="collection-item blue-grey lighten-3  blue-grey lighten-3">Baja California Sur</li>
                        <li class="collection-item blue-grey lighten-3  blue-grey lighten-3">Campeche</li>
                        <li class="collection-item blue-grey lighten-3">Coahuila</li>
                        <li class="collection-item blue-grey lighten-3">Colima</li>
                        <li class="collection-item blue-grey lighten-3">Chiapas</li>
                        <li class="collection-item blue-grey lighten-3">Chihuahua</li>
                        <li class="collection-item blue-grey lighten-3">Distrito Federal</li>
                        <li class="collection-item blue-grey lighten-3">Durango</li>
                        <li class="collection-item blue-grey lighten-3">Guanajuato</li>
                        <li class="collection-item blue-grey lighten-3">Guerrero</li>
                        <li class="collection-item blue-grey lighten-3">Hidalgo</li>
                        <li class="collection-item blue-grey lighten-3">Jalisco</li>
                        <li class="collection-item blue-grey lighten-3">México</li>
                        <li class="collection-item blue-grey lighten-3">Michoacán</li>
                        <li class="collection-item blue-grey lighten-3">Morelos</li>
```

Fig. 3. Converting Excel® to JSON format using JavaScript®.

The first step will be to convert the Excel® database to Java Script Object (JSON), format. JSON is a simple text format that is used for data exchange because it is open source and has no cost, it is also a subset of the independent - language JavaScript object literal notation and has many advantages as it is used as a data exchange format.

In order to add the values contained in the Excel® database to the compilation code, it must be carried out through transformation and adaptation to JSON, constructing and referencing the values contained in each cell linearly so that they can be represented in the tool.

It is important to mention that the no relational database or the NoSQL query language, works under the principle that they do not contain an identifier that serves as

```html
<head>
    <meta charset="utf-8">
    <meta http-equiv="X-UA-Compatible" content="IE=edge">
    <title></title>
    <meta name="description" content="">
    <meta name="viewport" content="width=device-width, initial-scale=1">
    <link rel="stylesheet" href="lib/materialize/css/materialize.css">
    <link rel="stylesheet" href="css/estilos.css">
</head>

<body>
    <!--[if lt IE 7]>
            <p class="browsehappy">You are using an <strong>outdated</strong> browser. Please <a href="#">upgrade your browser</a> to improve your experience.</p>
        <![endif]-->
    <nav>
        <div class="nav-wrapper lime accent-4 ">
            <a href="#" class="brand-logo blue-grey-text text-darken-3"><img src="img/tierra.png" class="logo responsive-img" />
                <B>EDAFOLOGÍA MEXICANA</B>
            </a>

            <ul id="nav-mobile" class="right hide-on-med-and-down ">
                <li><a class="blue-grey-text text-darken-3" href="sass.html">Salir</a></li>
            </ul>
        </div>
    </nav>
    <section class="blue lighten-5">

            <div class="row">
                <div class="col s4 m3 ">
                    <ul class="collection white-text ">
                        <li class="collection-item blue-grey lighten-3 center-align lime accent-4">Estado</li>
                        <li class="collection-item blue-grey lighten-3 blue-grey lighten-3 truncate">Aguascalientes</li>
                        <li id="bc" class="collection-item blue-grey lighten-3 blue-grey lighten-3">Baja California</li>
                        <li class="collection-item blue-grey lighten-3  blue-grey lighten-3">Baja California Sur</li>
                        <li class="collection-item blue-grey lighten-3  blue-grey lighten-3">Campeche</li>
                        <li class="collection-item blue-grey lighten-3">Coahuila</li>
                        <li class="collection-item blue-grey lighten-3">Colima</li>
                        <li class="collection-item blue-grey lighten-3">Chiapas</li>
                        <li class="collection-item blue-grey lighten-3">Chihuahua</li>
                        <li class="collection-item blue-grey lighten-3">Distrito Federal</li>
                        <li class="collection-item blue-grey lighten-3">Durango</li>
                        <li class="collection-item blue-grey lighten-3">Guanajuato</li>
                        <li class="collection-item blue-grey lighten-3">Guerrero</li>
                        <li class="collection-item blue-grey lighten-3">Hidalgo</li>
                        <li class="collection-item blue-grey lighten-3">Jalisco</li>
                        <li class="collection-item blue-grey lighten-3">México</li>
                        <li class="collection-item blue-grey lighten-3">Michoacán</li>
                        <li class="collection-item blue-grey lighten-3">Morelos</li>
```

Fig. 4. Edaphology and NOM-138-SEMARNAT/SSA1-2012 non-relational database.

a data set and others, the information is organized in tables or documents and it is very useful when there is not an exact scheme of what is going to be stored, the program code is simple, as shown in Figure 3.

Next, the Materialize® Software is used, Materialize® is a modern responsive front-end framework based on Material Design, specially conceived for projects that make Material Design their flag. This CSS framework allows you to save time and effort when implementing and optimizing web projects. Not only does it contain a multitude of CSS classes already configured, but by incorporating JavaScript® code, the values from the database can be added to our interface.

On the one hand, the advantages of Materialize® CSS framework are:

– The development time is less, since most of the code is already written.

– A CSS framework is applied to achieve a better aesthetic in future projects.

– Design is more robust and the final aesthetic is more homogeneous.

– Materialize® occupies only 140 KB with its CSS, to which must be added 180 KB with Java Script® for a low space and resources demand.

At present, edaphology and NOM-138-SEMARNAT/SSA1-2012 non-relational database is fully operational and is available online via http://148.204.111.72/edafologia2/ web page as shown in Figure 4.

3 Conclusions

Depending on the type of hydrocarbons that are handled in each state and municipality of the country, the authorities must know what type of unwanted event may occur, that is, fire, explosion, formation of toxic clouds (leak) or spill, in order to locate the population near risk areas and determine the resources they have, in addition to the emergency services available to develop an emergency response plan based on computer tools such as the one developed for this purpose.

Information systems allow making decisions as a timely manner to mitigate the unwanted events effects.

Although NOM-138-SEMARNAT-2012 and NOM-138-SEMARNAT / SSA1-2012 standards contemplate techniques to determine soil impact by heavy, medium or light fractions, the amount of petroleum products is quite significant, so this standard should be expanded with more information to be applied in storage plants that spill pollutants on the ground.

Being a knowledge tool that helps to improve the understanding of all types of hydrocarbons pollution effects on soils over the Mexican republic in order to mitigate them will reduce population affectation.

This type of information systems will serve as a reference for design of remediation and restoration processes on refineries, gas stations, storage and distribution plants adjacent land, as well as lands where these types of facilities have existed and could have affected soils, in addition to serving as a reference for the development of standards related to characterization and sanitation of soils in the proximity of gas stations, refineries and storage and distribution terminals.

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