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Environmental Bases on the Exploitation of Crude Oil in Mexico

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1. Introduction

Oil is one of the most important energy resources for the global economy. Regarding this, Mexico has an economic dependency of the oil industry that has being going on for decades. Based on the current oil production, the proven and possible reserves might last for ten years; still, if we consider probable and possible oil reserves, Mexico could count with an oil production for more than 30 years. Under this consideration, Mexico requires state of the art technologies for exploring, exploiting and processing crude oil.

Nowadays the technological and industrial development has to be environmentally responsible in accordance with the global needs. That is why the creation of new technologies and resources exploitation must be based on a responsible energetic development. Regarding this matter, being environmental friendly is a main goal for the society (Rodríguez *et al*., 2009), and gets to our attention that Mexico –until the seventies– did not apply any environmental criteria while exercising its oil activities (Ortínez *et al*., 2003). In consequence, oil production, leading, transportation, storage and processing had a negative impact on soils (Trujillo *et al*., 1995; Rivera-Cruz & Trujillo-Narcía, 2004), waters (Adams *et al*., 1999), and ecosystems at the southeast of the country (Santos *et al*., 2011).

In Mexico there are environmental regulations about hydrocarbons pollution, although these bypass criteria about the hydrocarbons' chronic effects on the ecosystems. However, in accordance with the current development conditions, it is necessary to introduce the *environmental basis for the oil exploitation*, whose main goal is to analyze the effects of the traditional oil related activities. The aim is to lay down the foundations for the creation of new technologies that contribute to a responsible and affordable energetic development for the country.

2. Environmental effects of the oil exploitation in Mexico

The world's economic sustenance, as based on the oil industry, has originated serious environmental issues (Hall *et al*., 2003). In Mexico, the oil industry has worn down the Southeastern natural resources, thus altering properties of soils (Rivera-Cruz & Trujillo-Narcía, 2004), sub-soils (Iturbe *et al*., 2007) and water (Ortiz *et al*., 2005), as a consequence of problems related oil extraction, processing and transportation (George *et al*., 2011).

Most soils affected by hydrocarbons are located in tropical zones with high rain precipitation, augmenting the pollutants' dispersion through mangroves or zones with deficient drainage (Gutiérrez & Zavala, 2002; Rivera-Cruz & Trujillo-Narcía, 2004; García-López *et al*., 2006; Vega *et al*., 2009). Additionally, this situation gets worse due to the age of the oil facilities, their lack of maintenance, as well as clandestine oil valves that have caused chronic spills of already weathered oil (Rivera-Cruz *et al*., 2005) which contains compounds of high molecular weight, endangering the resource's sustainability. The affected states with the highest number of environmental emergencies occurred in Mexico are Veracruz, Campeche and Tabasco, representing 78.7% of the events related to PEMEX activities mainly because of its deteriorated pipelines, clandestine oil valves, corrosion and mechanical impacts (PEMEX, 2003; Olivera-Villaseñor & Rodríguez-Castellanos, 2005).

The water bodies and the coastal zone are also affected by wastes derived from oil exploring, offshore production, sea and submarine transportation, shipment and storage operations, accidents during operations such as submarine oil pipes cracks, tankers accidents, spill outs and explosions at oil rigs (García-Cuéllar *et al*., 2004; Mei & Yin, 2009).

During the seventies, Mexico developed oil exploitation technology and intensified its crude oil production and transportation via underwater pipelines to cargo floating buoys to storage ports located at Tabasco, as well as the oil's transformation and refining at Coatzacoalcos, Veracruz, and Salina Cruz. As a consequence, this created industrial networks all over the country that raised pollution issues at coastal zones, thus impacting the ecosystems of the Gulf of Mexico and the Pacific southeast coast (Carbajal & Chavira, 1985; Botello, 1996; González-Lozano *et al*., 2006; Salazar-Coria *et al*., 2007). Nevertheless, conscience was not made until the IXTOC-I accident regarding the potential risks of the industry's activities (Jernelöv, 2010). Currently the main oil and gas production zone is located at the Gulf of Mexico, in the Campeche maritime zone where there are severely affected ecosystems after more than three decades of oil exploitation (García-Cuéllar *et al*., 2004). The last Gulf of Mexico disaster was estimated three times that of the Valdez spill (Trevors & Saier, 2010).

On the other hand, in Mexico was installed the first and largest oil refinery (until 2004) in Latin America, dating from 1908; the environmental deterioration is evident after more than one hundred years of oil exploitation. The effects are observed at the lower Coatzacoalcos River (Toledo, 1995; González-Mille *et al*., 2010) as it has suffered the impacts of the oil refining and transportation processes since the swamp areas surrounding the oil refinery are used as waste traps. In addition, accidents related to carelessness during the load and cleaning of the tankers, as well as the discharge of the cooling water from the Minatitlán refinery into the river have created a complex mixture of hazardous materials that pollute the lower Coatzacoalcos River area directly, affecting both the fishing resources and the inhabitants (Toledo, 1983; Rosales-Hoz. & Carranza-Edwards, 1998; Cruz-Orea *et al*, 2004; Ruelas-Inzunza *et al*, 2009; Ruelas-Inzunza *et al*., 2011).

Concurrently, we must add the petrochemical activity to the oil exploring and refining processes (Rao *et al.,* 2007a). With the creation of petrochemical complexes since 1960, these activities increased the impact of the area conditioning where the industrial zones were located (Ortiz *et al*., 2005). Additionally, huge amounts of materials were dredged in order to build the artificial dock of Pajaritos. The industrial plants operation, the numerous transportation networks (petrochemical ducts and pipelines) and the linking earth systems built at the lower areas caused other activities with an environmental impact for the zone (Toledo, 1995; Adams *et al*., 2008). Another environmental effect of the intensity of the oil exploitation has been the loss of swamps, mangroves, and other elements of the water coastal systems that must be attended given its importance for the environmental services (Gutiérrez & Zavala, 2002; Bahena-Manjarrez *et al*., 2002).

3. Crude oil toxicity

Toxicity is the ability of a chemical substance to damage and alter certain functions of the biological systems (Rivero *et al*., 2001). There are two toxicity criteria for the natural systems. *Acute toxicity* is produced by large, short-termed, accidental polluting agents' discharges (Roth & Baltz, 2009), although it may have long term effects. On the other hand, *chronic toxicity* is expressed by effects noticed on the long term due to relatively small amounts of a toxic compound found on air, water or soil (Scarlett *et al*., 2007).

Crude oil is constituted by a complex hydrocarbon mixture and a wide range of n-alkanes (C_6-C_{60}), alkenes, aromatic hydrocarbons, as well as polar fractions formed by asphaltene and resins (Salanitro *et al*., 2000). From these, hydrocarbons with of the highest molecular weight are the most persistent within the environment (Rivera-Cruz & Trujillo-Narcía, 2004; Kostecki *et al*., 2005). The oil toxicity within the ecosystems depends on the physical and chemical characteristics of former's components (Vega *et al*., 2009), discharges time and types (Romaniuk *et al*., 2007), weathered degree (Rivera-Cruz *et al*., 2005), biological (Rivera-Cruz *et al*., 2002) and environmental (King *et al*., 2006) factors. In this sense, oil can affect the natural systems differentially.

In Mexico, the main oil pollution sources are the oil-well pits and the deficiencies in their maintenance, the discharges of the processing facilities, petrochemical plants and oil ducts cracks since most of the facilities are sixty years ago (Botello, 1990). There is a systemic and synergic interaction of the effects of the hydrocarbon polluted soils; in this sense, all of the ecosystems' components are altered, which affects the soils' properties, the present microorganisms, and even the plants' growth and reproduction, endangering the ecosystems' sustainability (Palma-López *et al*., 2007).

3.1 Ground ecosystem: soil, microorganisms and plants

The oil affectations are due mainly to oil spills; the negative effects of crude oil depend on the spill type (Kolesnikov *et al*., 2010), the zone's ecological characteristics, the amount and type of spilled oil, as well as the time over the soil (Hernández-Acosta *et al*., 2004) and weathered degree (Rivera-Cruz *et al*., 2005). In this sense, the pollution levels vary in accordance with the hydrocarbons' source, the age of the oil facilities and their deterioration (Adams *et al*., 1999). Hydrocarbon polluted soils also experience physical, chemical and biological processes (Li *et al*., 1997; Martínez & López, 2001; Rivera-Cruz *et al*., 2002; Rivera-Cruz, 2004), altering the sustainability and productivity of the systems (FAO *et al*., 1980).

Nevertheless, there are properties inherent to soils that favor the fixation and toxicity of the pollutants (Charman & Murphy, 2007). For instance, soils with a clay texture take a long time to recover from an oil spill, while the thick texture soils recover in short time

(Hernández-Acosta *et al.*, 2006). Still, this last texture can favor mobility towards the phreatic surfaces by the infiltration of the pollutant (Iturbe *et al.*, 2007), thus widening the range of the hydrocarbon's toxicity (Srogi *et al.*, 2007) towards the water tables (Fig. 1). Therefore, the aquatic organisms and the trophic chain can be severely affected, in consequence, the inhabitants consuming these products.

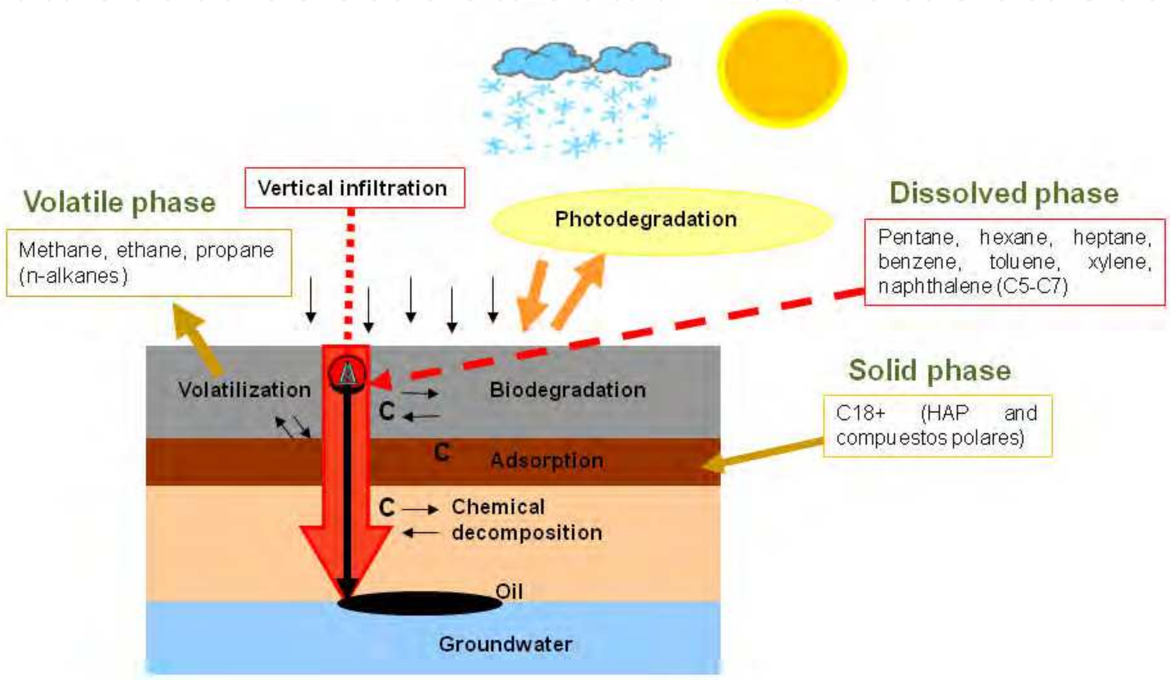

Fig. 1.Vertical infiltration process of crude oil (Eweis *et al.*, 1998).

There are synergic effects due to the crude oil soil pollution, since the oil blocks the gas interchange with the atmosphere –given its anoxic properties– (Leitgi *et al.*, 2008) and the change of the physical and chemical properties of the soils (Martínez & López, 2001) severely diminish the microbial communities benefic to the soil (Labud *et al.*, 2007). These microbiological variables are indeed a good indicator of the impact of a pollutant on the soil (Eibes *et al.*, 2006).

The toxicity mechanisms caused by the oil on soils is not limited to the microorganisms, since it also includes plants that suffer from hydric stress (Chaîneau *et al.*, 1997) due to the lack of water and nutrients. Concurrently, the lipid structures within the cells of the plants may be affected if the former are not quickly metabolized. In this sense, the oil has diverse effects over the plants since it inhibits the germination, growth and the biomass accumulation, reflecting these effects on a smaller plants production and, with time, in detriment of the natural resources sustainability.

The variables that have a determining effect over the plants affected by the soil hydrocarbons pollution are the soil ecology, the rhizosphere, emergence and germination, aerial and radical growth, biomass accumulation and salts present on the soil (Fig. 2).

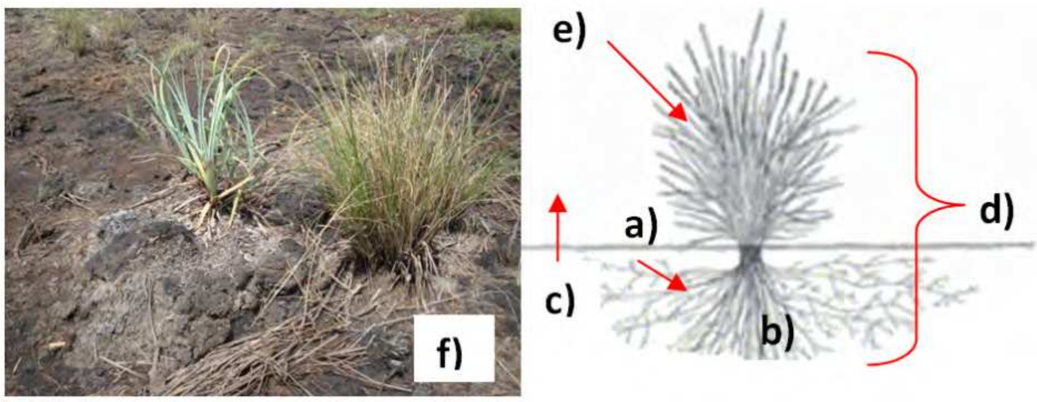

Fig. 2. Variables that have a determining effect over the plants affected by hydrocarbon polluted soils are: a) soil ecology, b) rhizosphere, c) emergence and germination, d) aerial and radical growth, e) biomass accumulation and f) salts presence.

a. **Soil ecology**: Oil also has an effect over the soil's biological composition (Tang *et al.*, 2011), since toxic concentrations of oil on the soil inhibit the development of different species of nematodes, protozoa, rotifers, algae, fungi, bacteria and actinomycetes (Chaîneau *et al.*, 2003; Ilarionov *et al.*, 2003). Likewise, it induces the **loss of biodiversity** of microbial communities, which are of significant relevance in the biogeochemical cycles of the ecosystem affecting, as a consequence, its productivity (Rhodes & Hendricks, 1990) and the nutrients availability.
b. **Rhizosphere**: It is the soil area surrounding the plant's root containing, 10 to 100 times more exudates than a soil lacking plants (Rao *et al.*, 2007b). The root exudates (sugars, alcohols, and enzymes) provide enough carbon and energy for the rhizospheric microorganisms (Olguín *et al.*, 2007; Muñoz *et al.*, 2010) and it is precisely on this region where the intense and complex interactions between the roots systems, the microorganisms and the environment occur, with an increase of the total microbial activity (De la Garza *et al.*, 2008). Oil blocks the gases interchange between the soil and the atmosphere, causing death or diminishment of the bacteria and nematodes (Tynybaeva *et al.*, 2008). Nevertheless, Freedman (1989) and Germida *et al.* (2002) report some microorganisms can increase its population in the presence of hydrocarbons thanks to their capabilities for surviving under such conditions.
c. **Emergence and germination**: Oil forms a hydrophobic layer diminishing the hygroscopic water retention (Quiñones *et al.*, 2003). This reduces the plants' water retention capability, directly affecting the seeds emergence and germination (Vázquez-Luna *et al.*, 2010a). Other effect is reflected due to the volatile oil fractions that penetrate and damage the seeds embryo (Banks & Schultz, 2005), diminishing its viability (Chaîneau *et al.*, 1997) and affecting the ecosystem balance (Labud *et al.*, 2007).
d. **Aerial and radical growth**. Recent researches find out that high hydrocarbons concentrations damage the plants growth and development since the pollutants diminish the radicle elongation and the vegetative growth (Vázquez-Luna *et al.*, 2010a). García (2005) found a growth and dry weight reduction in rice seedlings after a 25 day exposure to 90,000 mg·kg^{-1} of weathered oil. This effect could be attributed to the oil since it forms a hydrophobic layer, limiting the root's water and nutriments absorption.

e. **Biomass accumulation**. When the plant grows and its needs increase, the lack of absorbed water diminishes the cellular swelling, reduces or inhibits the nutriments incorporation processes and affects the vegetative growth (Inckot *et al*., 2011), and the later grains or fruits harvest. On this regard, researches by Rivera-Cruz & Trujillo Narcía (2004) found that the exposure to oil hydrocarbons concentrations of 2791, 9025 and 79,457 $mg \cdot kg^{-1}$ on the soil inhibited the vegetative growth and reduced the plants biomass in the seedlings of Echinochloa polystachya, Brachiaria mutica and Cyperus spp grasses. The biomass reduction is due to the damage caused in the root system (Langer *et al*., 2010), making more difficult the plants' growth and, consequently, reducing their biomass (Zavala-Cruz *et al*., 2005) (Fig. 3). Additionally, there are visual reports of chlorosis and reddish hues characteristic of phenolic compounds on the leaves, due to the roots' stress and damages (Harvey *et al*., 2001; Peña-Castro *et al*., 2006) as shown on Figure 4.

f. **Salts presence**. Regarding salts presence, Adams *et al*. (2008) state that, when an oil spill occurs, high salinity is commonly associated to the production water or to the formation of the oil well. Soluble salts of calcium carbonates, nitrates and sulfates increase in presence of hydrocarbons (Ke *et al*., 2011), as shown on Figure 5.

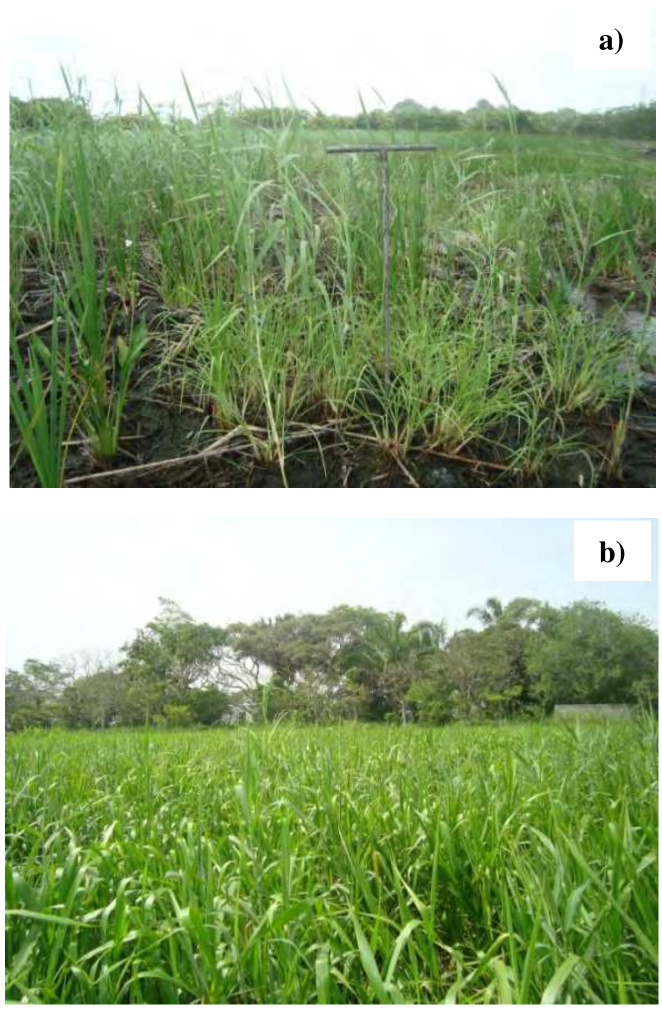

Fig. 3. Differences in grasses growth and biomass accumulation in a) polluted zone with 12,276 $mg \cdot kg^{-1}$ of TPH and b) zone with 82 $mg \cdot kg^{-1}$.

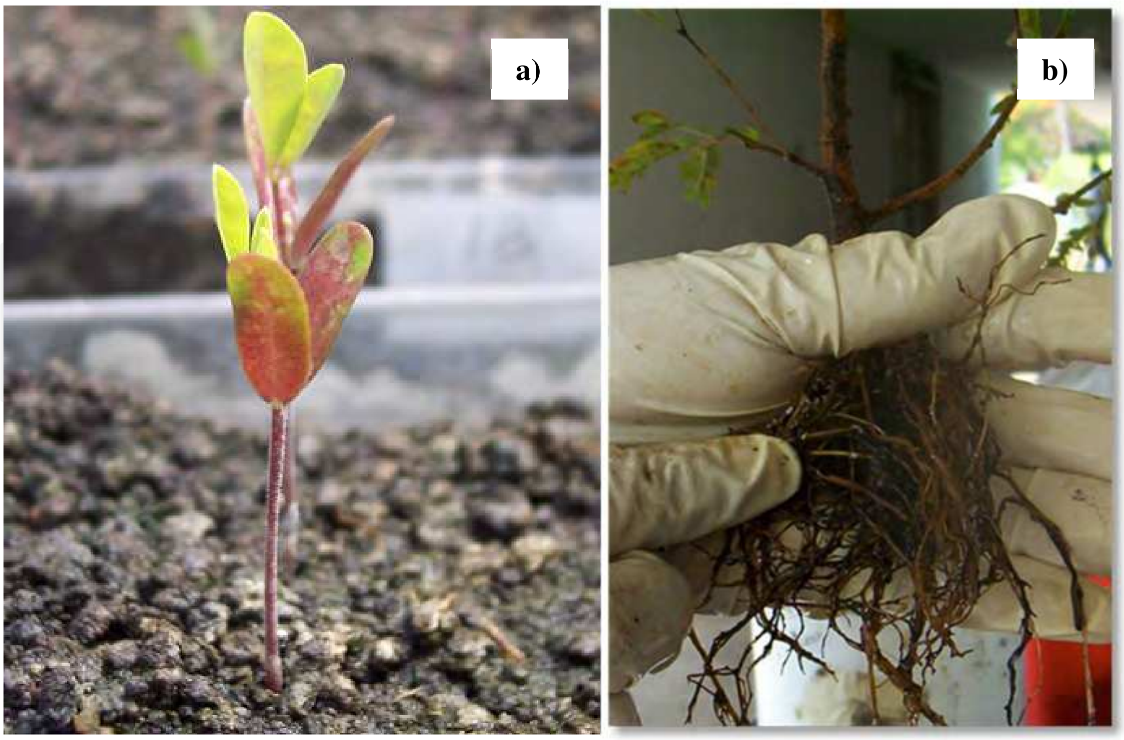

Fig. 4. Oil toxicity visible effects due to: a) chlorosis and reddish hues in cotyledons (*Crotalia incana)* and b) damages in *Leucaena leucocephala* roots exposed to 80,000 mg·kg^{-1} of HTP.

Fig. 5. Salts presence in polluted soils (with 12,276 mg·kg^{-1} of HTP) as a collateral effect of the oil industry pollution.

3.2 Marine ecosystems

The oil toxicity in the marine environment is very complex due to the great diversity of factors intervening during an environmental risk event. When oil is spilled or introduced to the marine ecosystem (Mercer & Trevors, 2011), it becomes weathered (Fig. 6), during which several processes take place, such as the **evaporation** of the volatile compounds, **dispersion** by means of waves, winds and turbulences (Chang *et al.*, 2011), **emulsification**, which constitutes the main cause of the persistence of light and medium crude oils on the sea surface, **dilution** depending of the crude oil type, temperature, turbulence and dispersion, **sedimentation** or sinking of the particles by adhesion to the sediments or organic matter, and **biodegradation** (Botello, 1995; Nikolopoulou & Kalogerakis, 2010; Prince, 2010). In Mexico, the Tonalá River in Veracruz and the Laguna de Términos in Campeche have shown the highest levels of dissolved hydrocarbons in the Gulf of Mexico (Botello *et al.*, 1996).

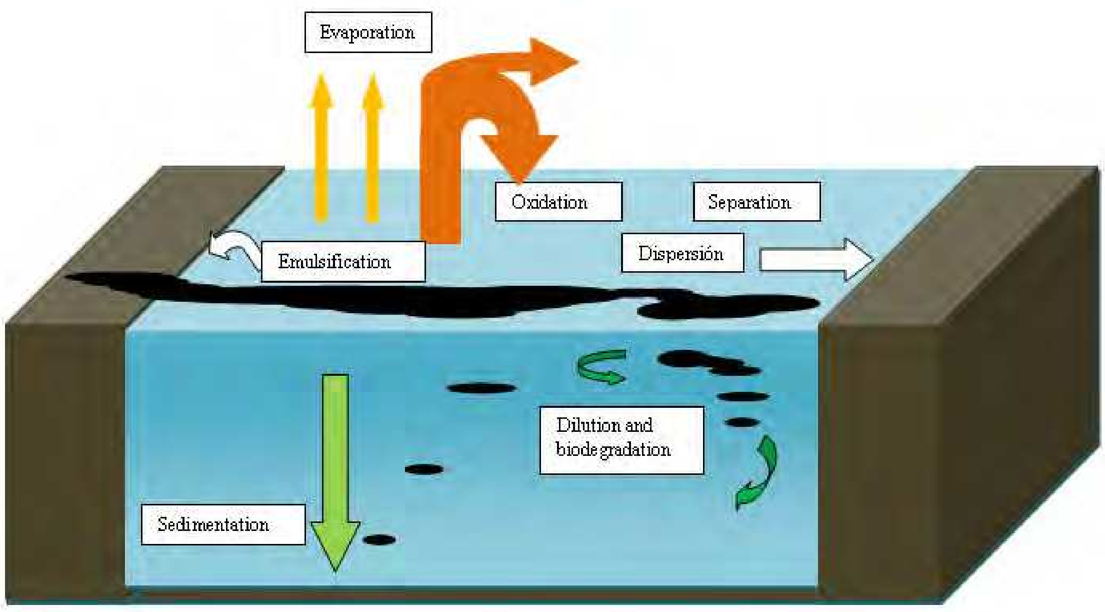

Fig. 6. Weathering process of the oil spilled in the sea, taken from Botello (1995).

Regarding the hydrocarbons assessment in the lower Coatzacoalcos River basin, the classical works of Botello & Páez (1986) are outstanding since they found the highest polycyclic aromatic hydrocarbons (PAH) levels at the zones of fixed discharges or of intense oil activity (García-Ruelas *et al.*, 2004). Other studies determined the presence of PAH on 19 organic species such as fish, crustaceans and mollusks (sea bass, native sea bream, scallop and prawns) and the presence of benzo(a)pyrene and benzo(ghi)perylene, which are the most hazardous given its carcinogenic potential (Sharma *et al.*, 2002). On the other hand, oil refinement and processing also contribute to broadening the range of toxicity caused to the fishing industry.

The marine oil pollution effects are harder to estimate (Trevors & Saier, 2010), since there is no information previous to the beginning of the oil-industry activities over the effects on the ecosystems and its components; as a consequence, it is not possible to measure the magnitude of the oil industry in the marine seaway. Additionally, it has not been possible to determine the chronic effects of pollution over the ecosystems since the data available is very precise in a given time and determined concentrations (García-Cuéllar *et al.*, 2004). Currently, there are studies proving the existence of considerable disturbances in the environment (Scarlett *et al.*, 2007; Denoyelle *et al.*, 2012); however, it is important to highlight that pollutants bioaccumulate in water organisms destined to human consumption (Webb, 2011).

3.3 Human beings

Mexico's oil industry history has been characterized by conflicts, power clashes, interests differences, competence between diverse companies, oilers and political leaders discrepancies, jealous preservation of the acquired rights by foreign interests, international consumer interest to have access a strategic product to a low cost, struggle for applying the 1917 Constitution over a given industry and the pressure from the workers to obtain a higher participation of the profit sharing (Brown, 2005).

The social conflicts attributed to the oil-zones development has been studied by different researchers; among them, Bustamante & Jarrín (2005) point that the presence of oil-related activities does not improve the population life standard nor destroys it, although it must be said that such study did not consider the analysis of violence indicators nor the environment toxicity. On this regard, Avellaneda (2004) expresses that there cannot be an "environmental conflict" study which excludes the social dimension and vice versa, since the critics toward the oil-industry activities shall be discussed from several social, political, economic and cultural angles (Avellaneda, 2005). About this, a recent study by Vázquez *et al.* (2010b) found negative effects over the equitable development in areas near oil zones and considers the population health as a primordial entity for development. Regarding this, Elliot (1994) says that when the degree of residues generation exceeds the atmosphere, oceans, vegetation and soils natural capacity, these are absorbed affecting human health and the ecological systems.

A study made at the Ecuador's Amazonia found that women living near oil wells zones (up to 5 km) presented symptoms such as tiredness, nasal and throat irritation, headache, eye irritation, earache, diarrhea and gastritis; these were associated with the proximity to oil wells and stations (San Sebastián *et al*., 2001). The main effects found in other studies regarding the acute exposure to oil after an oil spill at sea have been headache, throat and eyes irritation, tiredness, in addition to disorders such as anxiety and depression (Lyons *et al*., 1999). However, a repeated or long (chronic) exposure to low concentrations of oil volatile compounds can produce nausea, drowsiness, and headache (Kaplan *et al*., 1993). In accordance with Sánchez (2003), certain cases of pediatric intoxications are due to short chain hydrocarbons acting as asphyxiating agents given their high volatility and low viscosity, replacing the alveolar gas and producing hypoxia. When going through the alveolar membrane, they create symptoms such as the diminishment of the conscience threshold progressing towards convulsions, epileptic status or coma; additionally they induce the apparition of arrhythmias. On their side, the long chain hydrocarbons have a lower toxic power and large amounts are needed for them to produce central depression. The symptoms related range from symmetric sensorial dysfunction in the distal zones of the extremities, weakness of fingers and toes, loss of deep sensitive reflexes, to central nervous system depression, drowsiness and motor incoordination.

The hydrocarbons pollution might have teratogenic, mutagenic and carcinogen effects on human health (Neff, 2004). The oil hydrocarbons toxicology has been reviewed by the Agency for Toxic Substances and Diseases Registry (ATSDR) in the USA. According to this environmental agency, a major part of the total repercussion over the human health of all the chemical products on the soil is due to specific compounds called *worrying chemical substances* with a significant toxicological power. The worrying chemical products for gasoline, kerosene, and overall fuel polluted areas are benzene, toluene, ethilbenzene and xylene (BTEX) depending on the spill and the oilfield nature, which may contain heavy metals such as nickel and vanadium (López *et al.*, 2008). Additional to the polycyclic (or polynuclear) aromatic hydrocarbons such as benzo(a)pyrene (EA, 2003), most of these hydrocarbons of high-molecular weight are present in soils with weathered oil or previous spills (Rivera-Cruz, 2004; Rivera-Cruz & Trujillo-Narcía, 2004). About this, the International Agency for Research on Cancer (IARC), dependent of the World Health Organization (WHO), assessed benzo(a)anthracene, benzo(a)pyrene, and dibenz(a,h)anthracene as probable human carcinogens, and benzo(b)fluoranthene, benzo(k)fluoranthene, indene, pyrene, and naphthalene as possible human carcinogens (Kirkeleit *et al.*, 2008).

Some compounds act as xenoestrogens, having the ability of stimulating the mammary gland tissue (De Celis *et al.*, 2006); others may work as endocrine disruptors having effects on the reproduction (Chichizola, 2003). On this regard, cancer is the third cause of death on people aged 1 to 19 years; while only 5 to 10% of the malign tumors have been actually related to genetic causes; the rest might be influenced by a wide range of environmental factors (Anderson, 2001).

Because of this, it is important to regulate the oil refinement processes since they can pour into the atmosphere a large number of chemical compounds such as naphthalene, considered a dangerous airborne compound in accordance with the US Environmental Protection Agency (USEPA) since it can cause eye, skin and respiratory tract irritation. If inhaled for long periods it can damage the kidneys and the liver, in addition to skin allergies and dermatitis (Baars, 2002), cataracts, retina damage and also can attack the central nervous system. In high concentrations it can destroy red blood cells, causing hemolytic anemia (USEPA, 2003); as well, it is considered as a possible human carcinogen (Carmichael *et al.*, 1991; ATSDR, 2004).

The main health risks are due to contact, inhalation and ingestion, and may increase depending on age, gender and exposure degree (Chen & Liao, 2006). Some surveys show that among the 13 fractions of TPH, the aliphactics EC8-16 and aromatics EC10-21 are the main contributors to human health risks along all of the exposure routes (Park & Park, 2010).

4. The challenge: responsible energy development

The Responsible Energy Development in Mexico is an immediate need in view of the holistic analysis of the effects of the oil industry over the natural resources (Patín, 2004). For a proposal to work, it is required the joint efforts of the scientific, technological, industrial, political, regulatory, legal and social sectors. In this sense, the environmental problems must be attacked from different angles, involving all of its elements (Fig. 7).

Mexico needs a holistic political view of the oil hydrocarbons pollution including the social, ecological and economical aspects, and –most of all– to create the conditions required for the Responsible Energy Development with an integral regulatory, economical and legislative frame.

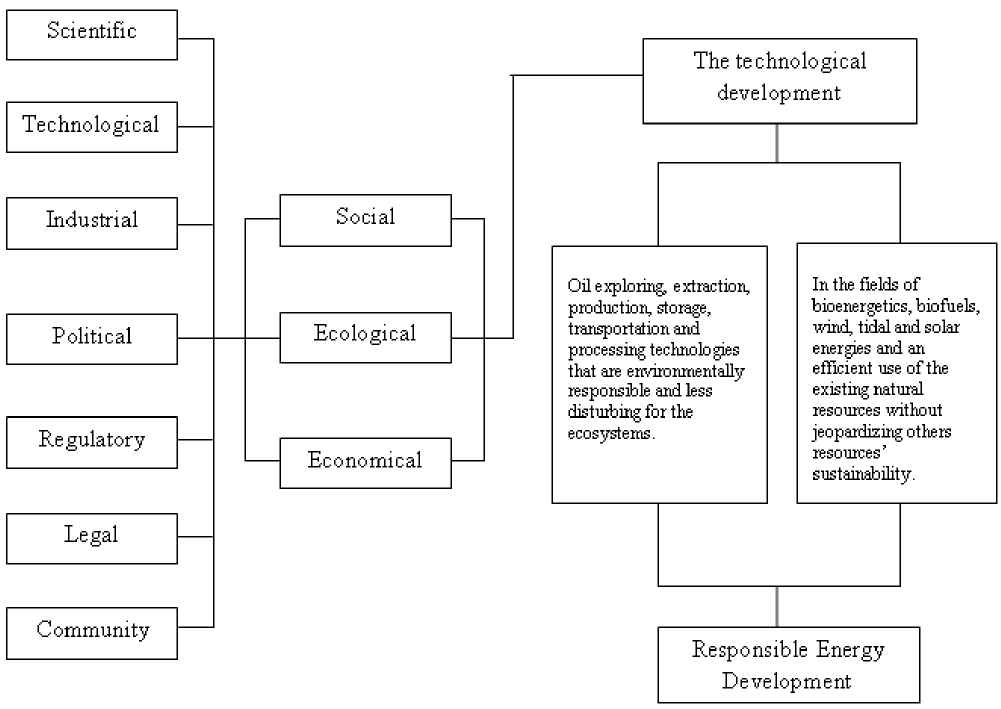

Fig. 7. Holistic approach in order to achieve a Responsible Energy Development.

On one hand, the oil spills and accidents that may occur due to maintenance deficiencies can be prevented with the proper maintenance and technological design on the side of the industry. On the other hand, citizens must avoid the clandestine oil valves and inform the authorities about fails; this information has been added into the environmental Mexican regulations. Nevertheless, there is still the need to increase the ecosystems protection due to the chronic effects of the polluting agents via strict legislation and regulations regarding the industrial wastes poured into the atmosphere, water bodies and soils, incorporating the periodic evaluation to the fishing resources for human consumption.

The economy is a subsystem within the whole development system and it is necessary that part of the oil surplus is used to finance research as well as for the technological development of adequate oil exploring, extraction, production, storage, transportation and processing technologies that are environmentally responsible and less disturbing for the ecosystems.

Finally, it is urgent to invest in the creation, research and development of new alternative energy sources for them to be gradually introduced within the country's energetic development. Such investments would enable the exploitation of profitable and sustainable energy sources, as well as the technological development in the fields of bioenergetics, biofuels, wind, tidal and solar energies and an efficient use of the existing natural resources without jeopardizing others resources' sustainability.

5. Conclusion

The environmental bases for the oil exploitation are the mainstays in order to analyze the effects of the traditional exploitation of oil in Mexico. The technological and scientific advances must be built over these bases, towards the development of new and better technologies for the resources exploitation. Consequently, this must cover the knowledge of the effects of pollution and thus promote the energetic sustainability without compromising human health, the environmental balance and the national economy.

Oil is fundamental for the economy of many countries. Therefore, it is not convenient to propose a radical change in the energetic system; rather, the proposal should consider the scientific and technological development based on two actions. The first one must focus on the exploring, extraction, processing, storage and transportation of crude oil with less risk and minimal disturbances of the natural resources. The second must bear in mind the gradual and integrated incorporation of the sustainable energies, allowing the efficient exploitation of resources without endangering others.

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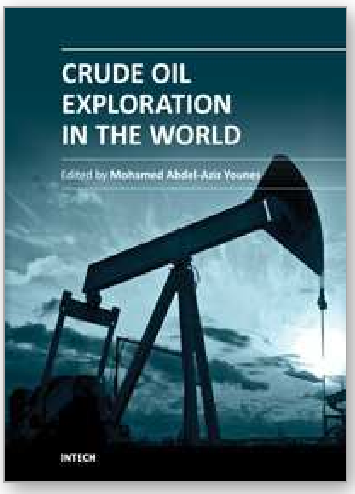

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