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Subsoil TPH contamination in two oil pipeline pumping stations and one pipeline right-of-way in north Mexico

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ABSTRACT

This investigation deals with the characterization carried out in zones around two pipeline pumping stations and one pipeline right-of-way in the north of Mexico. In particular those areas where contamination was evaluated: (a) south area of the separation ditch in the *Avalos* station, (b) the area between the separation ditch at the *Avalos* station, (c) km 194 + 420 of the *Moctuzma* station, and (d) km 286 + 900 in the *Candelaria* station. Results of this investigation showed that only four samples showed TPH values higher than the Mexican limit for 2004: AVA 1B, with 21,191 mg kg^{-1}; AVA 1C, with 9348 mg kg^{-1}; AVA 2B, with 13,970 mg kg^{-1}; and MOC 2A, with 4108 mg kg^{-1}.None of the sampled points showed the presence of PAHs at values higher than those found in the Mexican or American legislations. PAH were detected in the range of 0.0004 and 13.05 mg kg^{-1}.It is suggested to implement surfactant soil washing as a remediation technique for the approximately 600 m^3 that need to be treated.

1. Introduction

There are some reports on the degree of contamination of sites where oil exploration, production, refining, storage, etc., are carried out (as an example, see some work produced by our research team: Iturbe et al. (1998, 2003a, 2003b, 2004, 2005, 2006a, 2006b)). Very seldom, the transportation of crude oil and oil products from the production zones or refining facilities to petrochemical plants, storage and distribution stations, etc., is taken into account as a potential risk. During the transportation of crude oil and its derivates, accidents are frequent, causing oil spills. Transport operations use tank-cars, ships, trains, and pipelines. The latter is used very much because of the huge amounts of oil and oil products that can be transported long distances. Nevertheless, pipelines show risks that must be taken into account. Because of the age of pipeline installations and weathering, they can fail and leak oil. Another problem with oil pipelines is the low level of maintenance operations, aside from the clandestine poaching mainly of refined products (gasolines and diesel). Unfortunately, in Mexico, this is still a common practice. We have discussed this issue in previous works related with pipelines sites (Iturbe et al., 2006c, 2007).

It is difficult to get information regarding the incidence of pipeline accidents. According to Olivera-Villaseñor and Rodriguez (2005), for the pipelines built between 1970 and 1995 in Europe, there were 500 incidents, with 3000 people damaged, 2000 deaths in 97 countries. From these incidents, 53% were reported in natural gas pipelines, 18% with LP Gas, 17% with crude oil, and 7% with gasolines.

In the case of Mexico the situation is not much better. For the year 1996, 366 incidents related with clandestine poaching of oil products (i.e., gasoline, diesel) were reported; 159 in 1997, and 240 in 1998. For the year 2003 (last reported figure), there were 136 events (Olivera-Villaseñor and Rodriguez, 2007).

Consequences of clandestine poaching of oil products and failure of pipelines is not only restricted to economical damages, or to soil, water, and air pollution, but with worse consequences, such as fires (because of the presence of flammable liquids), explosions (idem), exposure to thermal energy, etc. (Olivera-Villaseñor and Rodriguez, 2007).

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PEMEX, the Mexican national industry in charge of exploration, production, refining, and distribution of oil and oil products, is very concerned about the environmental agenda and has developed programs oriented to diminish contamination levels in oil facilities. The aim of this investigation is to show the characterization regarding Total petroleum hydrocarbons (TPHs) and Polycyclic aromatic hydrocarbons (PAHs) carried out in zones around two pipeline pumping stations and one pipeline right-of-way in north Mexico. In particular, the areas where contamination was evaluated are: (a) South area of the separation ditch in the *Avalos* station, (b) The area between the separation ditch at the *Avalos* station, (c) km 194 + 420 of the *Moctuzma* station, and (d) km 286 + 900 in the *Candelaria* station. All these areas were suggested by the Mexican Federal Agency in charge of environmental matters (Procuraduria Federal de Proteccion al Ambiente, PROFEPA). Due to the confidentiality of the information the authors are not allowed to present exact geographic coordinates.

Candelaria and *Moctezuma* stations are located in the *Municipio de Ahumada*. Chihuahua, north of the *Avalos* station (which is located in the *Municipio de Chihuahua*). Climate for this zone is extreme-arid, with maximum temperatures of 43 °C and minimum temperatures of −23 °C, with an average of 14 °C. Annual rain precipitation is about 275 mm. The zone is located in the Physiographic Province of *Sierras y Llanuras del Norte*, in the subprovince of *Llanuras y Medanos del Norte*. The average altitude for these locations is 1200 m above sea level.

The stratigraphy of the zone is represented by alluvial deposits, flooding plains and soils of recent age. Subjacent to these deposits, are gravels, probably from the Plio-Pleistocene era, that fill the *Santa Clara* river basin. Interstratified gravels with undifferentiated basaltic igneous stones are observed. They consist of ignimbrites, rhyolites, domes, and lavas. The Triassic period is represented by gravels, constituted by fragments of diverse size and roundness, with interstratified clays. This unit is widely distributed in all the area subject of this study, from the south to the north, constituting the lower zones and forming soft hills, tables, with pronounced slopes and big extension plains. During the Quaternary age, deposits of alluvium and flooding plains were originated (CNA, 2002a). Soil on these sites presented bulk densities between 1130 and 1121 kg m^{-3}, which classified the soils as loam according to the Mexican standard for soil classification (NOM-021-RECNAT-2000, DOF, 2002a). More physicochemical information about the soils is presented in Section 3.

Avalos. Climate for this zone is extreme-semiarid, average annual temperature is 18.2 °C with a maximum of 37.7 °C and a minimum of −7.4 °C. The annual average rain precipitation value is 387.5 mm. The *Avalos* station is located in the Province of *Sierras y Llanuras del Norte*, in the subprovince of *Bolson de Mapimi*. The altitude of this location is 1440 m above sea level.

The geologic frame of the site is composed by stones of varied age and composition, product of a series of geological events that started from the Jurassic period up to the Recent era. They comprehend marine and continental sedimentary stones, as well as intrusive and extrusive igneous stones. The Jurassic period is represented by alternancies of slates, lutites, sandstones, and quartzites. The low Cretacic is constituted by marine sedimentary stones (shales). The high Cretacic is designed by continental sediments and volcanic stones. The Quaternary comprehends the most recent continental sediments, which cover the low and central parts of the study area, including clays, sands, silts, and gravels, which form alluvial fans, hill deposits, alluvial deposits, fluvial deposits, and eolic deposits (CNA, 2002b). Subsoil of this area of study was fine textured (clay, according to the Mexican standard NOM-021-RECNAT-2000) More physicochemical information about the soil is presented in Section 3.

2. Material and methods

Sampling of sites was carried out following the suggestions of an Environmental Audit performed at the site by PROFEPA. Different pumping stations were sampled to assess the subsoil contamination levels. A simplified map showing the three pumping stations as well as the pipeline ways is found at Fig. 1. For the *Avalos pipeline pumping station* it was decided to collect 14 samples from 8 sampling points (see Fig. 2; depths between 1.5 and 4.2 m for this location). Six points were sampled at the *Candelaria pipeline pumping station* (CAN) (see Fig. 3; samples from sampling point CAN 1 were missed, so this point is not shown on this figure); a total of seven samples were collected between 0.4 and 2.2 m. Four samples from four different points were collected from the *Moctezuma pipeline right-of-way* (MOC) (see Fig. 4; depths between 1.4 and 1.8 m). Sampling equipment consisted basically of pneumatic systems, one semi-portable (12 HP and variable perforation speed), and one standing equipment, Longyear model 34, mounted on a pick-up. More details regarding the sampling procedures are found in Iturbe et al. (2006b).

TPHs were analyzed according to NOM-EM-138-ECOL 2002 using EPA 418.1-1995 method (DOF, 2002b), which was in force by the time the study was performed (2004). True density was evaluated using the pycnometer method (C-128-93-ASTM), bulk density was assessed through the probe method (FC 1990), pH according to the Mexican standard NOM-021-RECNAT-2000 (DOF, 2002a), and the 16 priority PAHs, considered by USEPA (1985), were assessed according to EPA-8310-1996.

For some samples, the rate of CO_2 production, called from this point on respirometry, was measured based on the method described by Gauger (1999). Basically, the procedure consists in the use of jars or closed bottles, where a portion of soil with or without any additions is placed, together with a small amount of a NaOH solution. This solution absorbs the CO_2 generated during 4, 24, or 48 h. After the process, the NaOH solutions from the experimental and blank jars are titrated with HCl, under the same conditions. Respiration rates are expressed as milligrams of CO_2 per kilogram of soil per hour.

The organic carbon fraction was measured in some samples using the method of Walkley–Black and included in the Mexican legislation (NOM-021-RECNAT-2000). Plate count method was employed to estimate the amount of heterotrophic bacteria in some samples. For that purpose, the method described in NOM-092-SSA1-1994 (DOF, 1995a) was used, after preparation and dilution of samples (NOM-110-SSA1-1994; DOF, 1995b). Finally, the pH was determined in some samples using the potentiometric method, reported in ASTM (1993), D 4972-89; 1985.

3. Results and discussion

3.1. TPH and PAH concentrations

Fig. 1 shows a map where the pipeline pumping stations and pipeline right-of-way are located, along the extent of the pipeline. These three sites were sampled as described in the previous section and the results of those analyses are shown in Table 1. This table depicts the identification for every sampled point, the place where the sample was taken, the correspondent depth, the TPH concentration (in mg kg^{-1}) including mean and standard deviation values, and some observations made during the sampling procedure. As observed, the most sampled site was *Avalos*; 8 points were sampled at depths between 1.5 and 4.2 m, obtaining a total of 14 samples. It is noticeable that 9 from the 14 samples showed TPH concentrations, as detected by the chosen method. Higher concentrations were found at deeper samples. Mexican legislation for the year