BEHAVIOR OF A DIESEL-CONTAMINATED UNCONSOLIDATED CLAYEY SOIL

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Abstract: A diesel-contaminated site in Mexico City has been characterized. The subsoil consists of unconsolidated clay and sandy clay with very low permeability. Its hydraulic conductivity is $10^{-7} - 10^{-8}$ m/s and the phreatic level is 2-m deep. Ground water moves very slowly and the saturated clay acts as an aquitard. Sixty two 19-mm diameter monitoring borings were drilled at the site to a depth from 3.00 to 3.50 m. Measurements of volatile hydrocarbons made in the vadose zone of each boring showed concentrations higher than 10,000 ppm in practically the whole area studied. Free product floating as a layer of up to 200 mm in thickness on the water table was encountered in some borings. Continuous undisturbed soil samples were recovered in 19 borings to perform chromatographic analyses; stratigraphical cross sections were developed from them. Results confirmed the presence of diesel fuel as the sole contaminant, with concentrations as high as 22,000 mg/kg in some points. Concentrations of polynuclear aromatic hydrocarbons, mainly fenatrene, were found to be equal to 0.030 mg/kg, as well as fluorene at a lower content (0.007 mg/kg). Seasonal fluctuations of the water table affect the thickness of the contaminated soil layer; this is why part of the clayey soil located below the water table evidences diesel adsorption. The migration of hydrocarbons to adjacent zones has been delayed because the clay is practically impervious. In spite of the diesel biodegradability properties, bioremediation techniques are difficult to implement at this site due to restrictions of mass transfer through the clayey soils.

1. INTRODUCTION

The subsoil of Mexico City shows unique characteristics because sediments from an extinct lake that have become dehydrated in the course of time comprise it and man-made constructions have been built upon them during many years. Sediments consist of unconsolidated clays and sandy clays that cover an area in excess of 400 km^2 with a thickness ranging from 40 to 60 m throughout most of the valley. This thickness tapers down to zero toward the border of the former lake whereas at its center the clay layers are interspersed with sand deposits down to depths of over 100 m. Clays in turn are underlain by alluvial deposits and pervious volcanic emissions that constitute the main aquifer of the region. With such a distribution, extraction of ground water induces a vertical downwards flow from the clays to the aquifer. Soil Mechanics tests performed in the past have shown values of permeability of $10^{-7} - 10^{-8}$ m/s (Carrillo, 1969; DGCOH, 1990); a void ratio varying from 2 to 15 (DGCOH, 1990), and a coefficient of consolidation of 0.05 mm^2/s (Carrillo, 1969). The saturated clays are not consolidated; the phreatic level is encountered at a depth of about 2 m and seasonal fluctuations are encountered. The hydraulic gradient is practically horizontal.

The site under study, 5645 m^2, is located in Mexico City and it was used during more than three decades as a diesel supply and distribution terminal for industries operating in the vecinity of the area. The daily fuel loading and unloading activities generated spills that in the course of time seeped vertically downwards through the subsoil until reaching the shallow phreatic level. The terminal closed its operations several years ago and the storage tanks are at present empty and abandoned, as well as yards and warehouses; no traces of recent handling of fuels were found. With the purpose of determining the degree of contamination of the subsoil within the site, a local characterization was performed by means of gasometric analysis at depths of 0.90 and 2.0 m, together with a sampling of undisturbed geologic material down to the phreatic level in order to obtain lithologic data and to determine the concentration of contaminants at different points and at different depths.

2. ANALYTICAL TECHNIQUES

***In-situ* diagnosis.** To measure volatile hydrocarbons 62 shallow borings located exclusively inside the premises were drilled. Borings were made with a KVA electric roto-hammer that "drives" 19-mm diameter steel rods. When a depth of 0.90 m was reached the rod was extracted and the volatile hydrocarbons (VHC) were measured; drilling was then resumed down to a depth of 2.00 m for a new measurement. Monitoring was made with a *Gastech* portable photo-ionizer with a measuring range from 0 to 10,000 ppm (Lesser, 1995). This device is calibrated with hexane, that is a typical component of diesel fuels (Riser-Roberts, 1992) and therefore the readings were indicative of the presence of fuel compounds in the subsoil.

To have an assurance of the measurement of the static water level and of the search for free product floating on it, drilling operations were continued until a depth from 3.00 to 3.50 m was reached. The thickness of the free product was measured with the help of a glass pipette. Samples of the free product were stored in perfectly airtight vials sealed with a Teflon cover and aluminum ring; the vials were preserved in a cold environment to retain their original characteristics prior to their analysis.

The depth of the phreatic level was determined with an electric probe. A topographic survey of the site was also executed by means of differential leveling of each of the borings. Undisturbed samples of the geologic material were recovered during drilling into transparent acetate cartridges (measuring 0.46 m in length by 25 mm in diameter). Once the samples were recovered, they were hermetically sealed and kept in cold storage until tested. A description of these samples was made to obtain stratigraphical profiles.

Chemical analysis. The quantification of diesel contained by the samples was made by applying EPA method 8015 by GC/FID. Two samples of the free product were also analyzed with this method (Potter, 1993). The polynuclear aromatic hydrocarbons were analyzed with EPA method 8310.

Physicochemical and microbiological characterization of soils. Composite samples were prepared with soil recovered from several borings in order to determine: pH, total nitrogen, ammonia nitrogen and phosphates, according to Carter (1993) and to Kute and Lee (1986). The total count of heterotrophic bacteria was determined in a PYG medium (Carter, 1993), whereas the count of industrial diesel degrading bacteria was carried out by means of a technique developed at the laboratory (Saval and Deyta, in preparation).

3. RESULTS AND DISCUSSION

Figure 1 shows the contours of equal values of the VHC measurements at a depth of 0.90 m; it can be observed that the most contaminated area with values in excess of 10,000 ppm corresponds to the center part of the site. At a depth of 2.00 m the VHC readings exceeded the value of 10,000 ppm in practically all of the borings, i.e. its influence practically covers the premises as a whole and especially toward the eastern and southeastern zones. These results evidence the fact that the contamination affects an important depth and it has encroached beyond the site boundaries.

The phreatic level is found at a depth of about 2 m in most parts of the site. Two piezometric cones exist in which slightly higher depths equal to approximately 2.30 m were encountered. These zones toward which the ground water tends to flow are located close to the center of the site. In general terms, the zones where the phreatic surface Is at its lowest level correspond to those areas where the largest concentrations of the free product of up to 200 mm in thickness were detected (Fig. 2). The variations shown by the phreatic level that were observed in all cases are indicative of the different permeability coefficients of the geologic materials; this effect induces a slow movement of both water and free product through the subsoil.

The material encountered at shallow depths, from soil surface to 0.70-1.00 m, generally corresponds to a fill, underlain by clay and sandy clay strata that in some cases showed dark spots that correspond to adsorbed hydrocarbons. Cross section A-A' depicted in Fig. 3 was built from the stratigraphical profiles obtained; it includes the ground water elevation, the thickness of the free product and the areas where spots of hydrocarbons adsorbed by the clay were observed. If these spots are correlated among all the borings, a distribution fringe can be plotted as shown in Fig. 4, that also depicts the thickness of the free product that in borings S-47 and S-51 was equal to 200 mm.

The existence of hydrocarbon spots above and below the phreatic level is a consequence of its fluctuations during the dry and wet seasons. In the dry season, water level draws down as well as hydrocarbons adsorbed by the clay; when the phreatic level recovers, free product moves upwards although part of the hydrocarbons adsorbed by the clay remain below the static water level.

In the samples of free product, the presence of diesel fuel as a contaminant with a certain degree of weathering was confirmed, although the existence of hydrocarbons with a higher molecular weight became evident as indicated by an oily consistency and a darker product color.

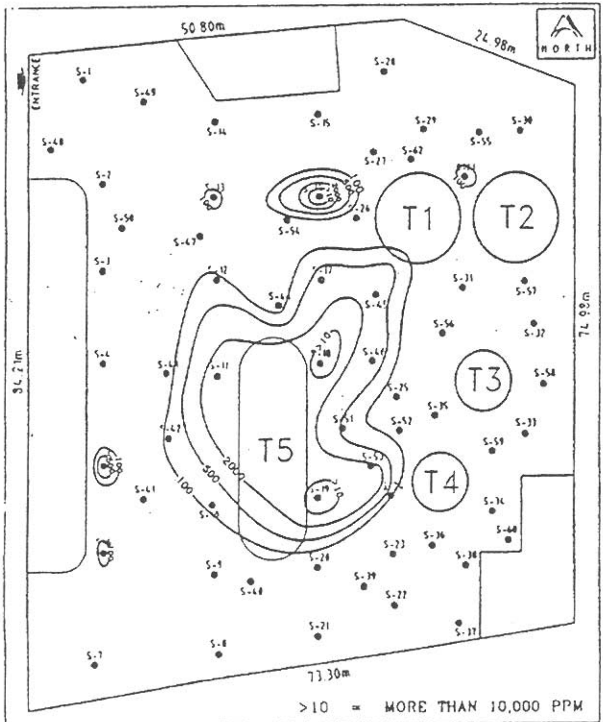

FIGURE 1.-VOLATILE HYDROCARBONS IN THE UNSATURED ZONE, IN PPM

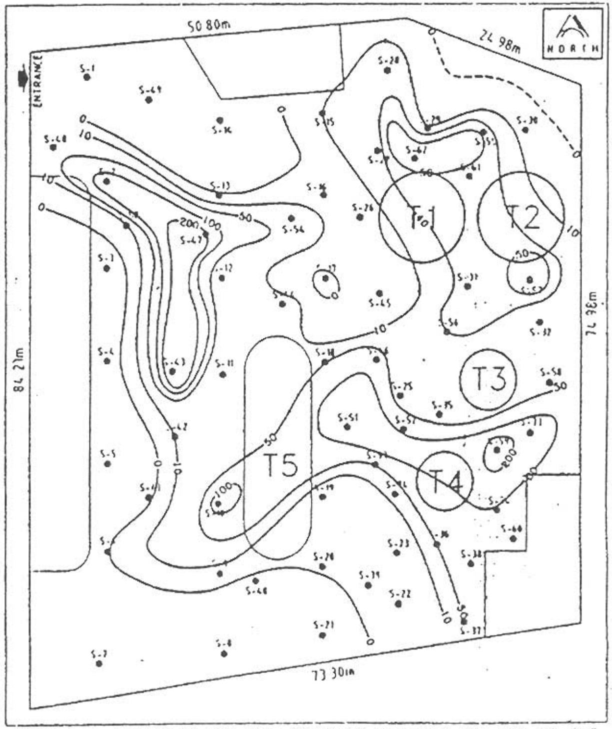

FIGURE 2.-THICKNESS OF FREE PRODUCT FLOATING ON TOP OF THE

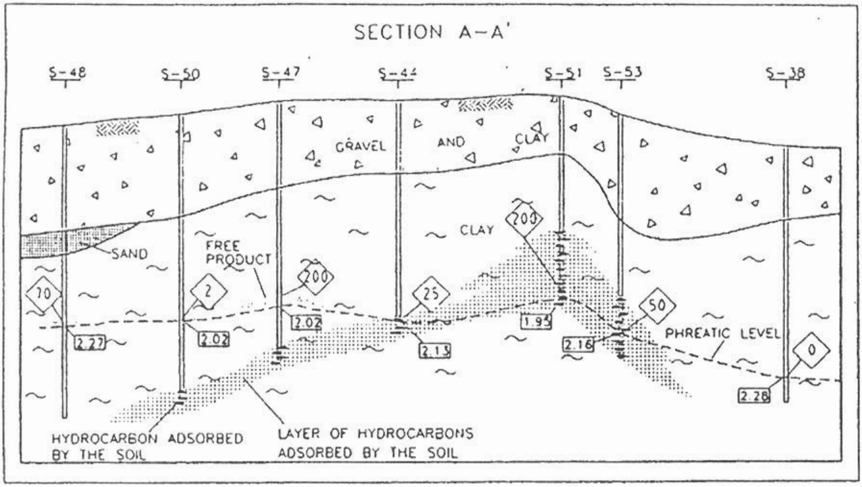

FIGURE 3.-FLUCTUATION OF THE PHREATIC LEVEL INDICATES LOW PERMEABILITY AND INFLUENCES THE THICKNESS OF THE SOIL WITH ADSORBED HYDROCARBONS; ⟨25⟩ THICKNESS OF FREE PRODUCT FLOATING ON THE PHREATIC LEVEL (mm); [2.02] DEPTH OF PHREATIC LEVEL (m)

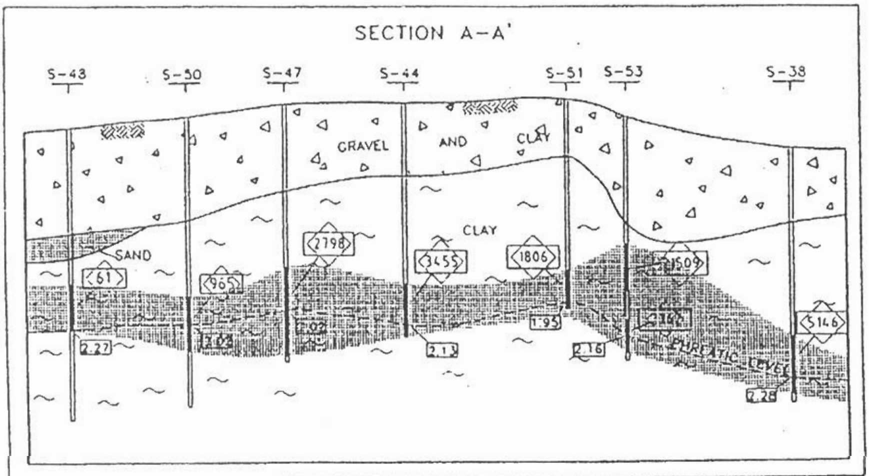

FIGURE 4.-DISTRIBUTION OF ADSORBED HYDROCARBONS; [2.13] DEPTH OF PHREATIC LEVEL; ⟨3455⟩ DIESEL CONCENTRATION IN SOIL (mg/kg)

The presence of diesel fuel was detected at all of the points analyzed, even close to the access door to the site, where about 3,000 mg/kg were determined at a depth ranging from 1.80 to 2.25 m. Toward the west and at a depth from 1.65 to 2.00 m a very high concentration of diesel was encountered (close to 14,000 mg/kg) that could be attributed to important spills during filling of tank trucks.

The most contaminated points correspond to the east and southeast areas of the site, at borings S-39, S-53, S-57 and S-59 with 22,160, 21,509, 14,641 and 16,345 mg/kg, respectively. The two first borings reached depths from 1.25 and 2.00 m, whereas the two latter borings correspond to depths ranging from 2.20 to 2.60 m. The deepest boring analyzed (S-45) with a depth from 2.30 to 2.80 m is located toward the north and a hydrocarbon content of over 5000 mg/kg was determined.

Figure 4 shows the same cross section A-A' but now in terms of the diesel concentrations obtained at the depths analyzed. It can be therefore confirmed that adsorbed diesel do exist at the clay strata encountered below the existing phreatic level.

The analyses made in the polynuclear aromatic hydrocarbons evidence the presence of two of them in low concentrations. Fenatrene was found at the most contaminated areas toward the east and southeast with concentrations of up to 0.030 mg/kg, whereas the highest concentration of fluorene reached a value of 0.007 mg/kg. No carcinogenic hydrocarbons were detected.

In what refers to the physicochemical properties of the soil, the pH was found to be slightly alkaline varying from 8 to 8.5. The total nitrogen was high (from 720 to 1240 mg/kg) whereas a low phosphate content from 2.59 to 4.75 mg/kg was determined.

The presence of nutrients, a pH-value with a trend toward alkalinity, and a moisture content of about 30% have promoted the preferential survival of heterotrophic bacteria that for this particular case a count equal to 10^6 cfu/g was determined. It was found that the largest proportion corresponded to degrading bacteria of industrial diesel fuel. The fact of having found ammonia nitrogen, that can be regarded as the most expedited assimilation procedure for the microbial metabolism, provides an assurance that the existing bacteria are metabolically active; this situation became evident during the respirometric tests carried out.

These results may suggest the possibility of implementing a bioremediation technique to clean-up of the site by exploiting the metabolic potential of the native bacterial flora (Saval, 1997; 1998). In fact, several applications have shown successful results through hydrocarbon degradation by microbial sources (Autry and Ellis, 1992; Rogers *et al.*, 1993; Cookson, 1995; Suthersan, 1997).

4. CONCLUSIONS

Even though it was not possible to delimit the lower boundary of the contamination stain, it could be demonstrated that the movement of contaminants through the subsoil has been influenced by the low permeability of the clays and that the extent is bounded along a vertical direction by the phreatic level and along a horizontal direction by the low permeability of the clays that hinders the dynamic conveyance of the contaminant to far-reaching areas.

The fact that the subsoil contains basically clay strata with a porosity of 55% and a low permeability will represent a major feature to be taken into account when defining the strategy for bioremediation of the contaminated site.

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