ABSTRACT: A diesel-contaminated site in Mexico City has been characterised. The mineral consists of unconsolidated clay and sandy clay with very low permeability. Its hydraulic conductivity is $10^{-10}$ to $10^{-12}$ m/s and the phreatic level is 2 m deep. Ground water moves very slowly and the saturated clay acts as an aquifer. Sixty two 19-mm diameter multihole borings were drilled at the site to a depth of 3.00 to 3.50 m. Measurements of volumes, hydraulic heads, in the vadose zone of each boring showed concentrations higher than 10,000 ppm in pacity, the whole area studied. Free product flowing at a layer of up to 200 cm in thickness on the water table was encountered in some borings. Continuous unconfined soil samples were recovered in 19 borings to perform chromatographic analysis; petrographic 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 heptacene, were found to be equal to 0.039 mg/kg, as well as fluorine, as a lower content (0.007 mg/kg). Seasonal fluctuations of the water table affect the thickness of the contaminated soil layer, due to the strong of the clay layers located below the water level evidences diesel adoption. The migration of hydrocarbons to adjacent zones has been reduced because the clay is practically impervious. In some of the direct biodegradability properties, bioaugmentation treatments are difficult to implement at this site due to restrictions of man-made structures through the clayey soils.

1. INTRODUCTION

The island of Mexico City shows unique characteristics because sediments from an extinct lake that have become dehydrated in the course of time complete it and man-made constructions have been built upon them during many years. Sediments consist of unconsolidated Clay and sandy clays that cover an area in excess of 400 km², with a thickness ranging from 40 to 60 m throughout most of the valley. This thickness tapers down, in areas toward the forer of the former lake, whereas at its inner the clay thick are intermixed with sand deposits down to depths of over 100 m. Clays to sands are overlain by alluvial deposits and pervasive volcanic emissions that constitute the main aquifer of the region. With such a distribution, extraction of ground water reduces a vertical downward flow from the clays to the aquifer. A site mechanics test performed in the past have shown values of permeability of $10^{-10}$ to $10^{-12}$ m/s (Carrillo, 1969; DOCHO, 1990); a void ratio varying from 2 to 13 (DOCHO, 1990) and a coefficient of consolidation of 0.05 m/s (Carrillo, 1969). The saturated clays are not consolidated; the phreatic level is encountered as a depth of about 5 m in seasonal fluctuations we encountered. The hydraulic gradient is practically horizontal.
The site under study, 5645 m², is located in Mexico City and it was used during more than three decades as a debris supply and disposal terminal for industrial operating in the vicinity of the area. The daily load hauling and unloading activities generated spills that in the course of time spread vertically downwards through the substrata until reaching the shallow phreatic level. The terminal closed by 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 solids were found. With the purpose of determining the degree of contamination of the substrata within the site, a local characterization was performed by means of geotechnical analysis at depths of 0.90 and 2.0 m, together with a sampling of undisturbed geologic material down to the phreatic level in situ, 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 perimeter were drilled. Borings were made with a KVA electric into-hammer that “drives” 15 cm diameter steel rods. When a depth of 5.00 m was reached the rod was extracted and the volatile hydrocarbons (VHCs) were measured; drilling was then resumed down to a depth of 2.00 m for a new measurement. Monitoring was made with a Gaertner portable photo-ionizer with a measuring range from 0 to 10,000 ppm (Levy, 1995). This device is calibrated with benzene, that is a typical component of diesel fuels (Ozsoy-Butun, 1992) and therefore the readings were indicative of the presence of fuel compounds in the substrata.

To have an assurance of the completeness of the water table level and of the search for free product flowing in it, drilling 0.02-meters were continued until a depth from 2.00 to 3.50 m was reached. The thickness of the free water was measured with the help of a glass pipe. 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 acrylic tubes (measuring 0.64 m in length by 35 mm in diameter). Once the samples were recovered, they were hermetically sealed and kept in cold storage until used. A description of these samples was made to obtain stratigraphic profiles.

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

Physicochemical and microbiological characterization of soil. Citoplane 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 Kure and Lee (1988). The total count of heterotrophic bacteria was determined in a PYU medium (Carter, 1993), whereas the count of industrial diesel degrading bacteria was carried out by means of a technique developed at the laboratory (Siral and Dayta, in preparation).

3. RESULTS AND DISCUSSION

Figure 1 shows the contour 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 burnings, i.e. its influence practically covers the perimeter as a whole and especially toward the eastern and southeastern zones. These results evidence the fact that the contamination effects 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 phreatic level zones 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 0.78-1.00 m, generally corresponds to a fill, underlain by clay and sandy clay strata that in some cases showed dark spots that correspond to abandoned hydrocarbons. Cross section A-A' depicted in Fig. 3 was built from the topographical profiles obtained; it includes the ground water elevation, the thickness of the free product and the areas where spots of hydrocarbons adhered by the clay were observed. If these spots are considered among all the burnings, a distribution fitting can be plotted as shown in Fig. 4, that also depicts the thickness of the free product that in burnings 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 adhered by the clay; when the phreatic level recovers, free product moves upwards although part of the hydrocarbons adhered by the clay remain below the main 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 its oily consistency and a darker product color.
The presence of diesel fuel was detected at all of the points analyzed, even close to the access door to the site, where about 3000 mg/kg was determined at a depth ranging from 1.80 to 2.25 m. Toward the west and at a depth from 1.80 to 2.80 m, very high concentrations of diesel were observed (close to 14,000 mg/kg) that could be attributed to improper spills during filling of tank trucks.

The contaminants detected correspond to the east and northeast areas of the site, at levels 5.39, 5.53, 5.57, and 5.99 with 22.166, 21.509, 14.641 and 16.945 mg/kg, respectively. The two first bores reached depths from 1.25 and 200 m, whereas the two latter bores reached depths ranging from 2.20 to 2.60 m. The deepest boring analyzed (5.45) with a depth from 2.30 to 2.80 m is located toward the south and a hydrocarbon content of over 8000 mg/kg was determined.

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

The analyses made in the polynuclear aromatic hydrocarbons evidence the presence of four of their in low concentrations. Phenanthrene was found at the most contaminated area toward the east and southeast with concentrations of up to 0.030 mg/kg, whereas the highest concentration of fluorescence reached a value of 0.067 mg/kg. No carcinogenic hydrocarbons were detected.

In what refers to the physical-chemical properties of the soil, the pH was found to be slightly alkaline varying from 8.1 to 8.3. The total nitrogen was high (from 720 to 1240 mg/kg) whereas a low phosphate content from 3.59 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 autochthonous bacteria that for this particular case a cause equal to 167.8 kg/d was determined. It was found that this proportion corresponded to degrading bacteria of industrial diesel fuel. The fact of having isolated ammonia nitrogen, that can be regarded as the most expedient assimilation procedure for the microbial metabolism, provide an assurance that the existing bacteria are metabolically active. This situation became more evident during the anaerobic 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 (Kasal, 1997, 1999). In fact, several applications have shown successful results through hydrocarbon degradation by microbial consortia (AUSTY and BARRA, 1992; ROGERS et al., 1993; COOKMAN, 1995; SUIHEMAN, 1997).
4. CONCLUSIONS

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

The fact that the subsoil contains basically clay soils 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.

ACKNOWLEDGEMENT

To Francisco Mercado and Roberto Manrique for their technical assistance. This project was financed by Perenco Refinacion.

REFERENCES


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