

Research Articles

Remediation of Contaminated Soil Using Soil Washing and Biopile Methodologies at a Field Level

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Abstract

Background, Aims and Scope. An out-of-service oil distribution and storage station (ODSS), which operated from 1966 to 2000 in Mexico, is contaminated mainly by gasoline and diesel, showing the presence of methyl-tert-butyl-ether, benzene, toluene, ethyl benzene, and xylenes. Nine of the 16 polycyclic aromatic hydrocarbons were found, as well as Fe, Pb, V, and Zn. The health risk assessment suggested the necessity of reducing of three PAHs [benzo(a)anthracene, benzo(a)pyrene, and benzo(b)fluoranthene], and vanadium. The aim of this work is to show that soil washing (*on-site*) and biopiles are excellent remediation methodologies to treat soils contaminated with petroleum derivatives and metals. Applying them, it is possible to reach the goal value of 2,000 mg TPH/kg in a few months, as requested by Mexican legislation.

Methods. More than 140 m³ were excavated from the ODSS. Three soil-washing dishes were built. 1540 m³ were treated by soil washing using a nonionic surfactant. A 100 m³ biopile was built to study the system capabilities in the biodegradation of around 4,500 mg/kg of TPH using the autochthonous microflora.

Results and Discussion. The soil washing, average TPH-removal value was 83%, but values up to ca. 93% were observed. Removal values resulted in a function of the TPH initial values. Biopile (100 m³) worked during 66 days, reaching a TPH-removal value of 85%. At the end of the processes, no PAHs were detected. The contaminated soil was treated successfully, reaching the legislation limits (TPH values under 2,000 mg/kg, and a significant reduction in PAH concentrations).

Conclusion and Recommendation. Both systems are suitable for remediation purposes, achieving high removal efficiencies at short and medium stages. It is highly recommended to proceed with soil washing studies, identifying new products, and mixtures, which could reduce costs and assure optimum operation.

Keywords: Biopiles; benzene, toluene, ethyl benzene and xylenes (BTEX); *ex-situ*; health risk assessment (HRA); hydrocarbons; *in-situ*; metals; methyl-tert-butyl-ether (MTBE); oil distribution and storage station (ODSS); polycyclic aromatic hydrocarbons (PAHs); remediation; soil washing; total petroleum hydrocarbons (TPHs)

Introduction

Petroleos Mexicanos (PEMEX) is the company in charge of exploration, extraction, transformation, storage, distribution, and sale of petroleum and derivatives in Mexico. PEMEX has a great concern regarding environmental protection

agenda, especially with the minimization of environmental impact due to water, soil and air discharge, and hazardous materials (PEMEX 2003). Beginning some years ago, an environmental auditing program has been developed in oil distribution and storage stations, refineries, and other kinds of petroleum-handling facilities.

An out-of-service oil distribution and storage station (ODSS), which operated in Mexico from 1966 to 2000, was characterized by our research group in 2000 (Iturbe et al. 2003). The main conclusions of that study were the following: ODSS was contaminated mainly by gasoline and diesel, showing the presence of methyl-tert-butyl-ether (MTBE), benzene, toluene, ethyl benzene and xylenes (BTEX). Nine of the 16 polycyclic aromatic hydrocarbons were found, as well as Fe, Pb, V, and Zn. The health risk assessment (HRA) suggested the necessity of reducing three of the PAHs [benzo(a)anthracene, benzo(a)pyrene, and benzo(b)fluoranthene], and vanadium. The estimated amount of contaminated soil was 1,640 m³. Of course, not all this soil had the same contaminants and concentrations (Iturbe et al. 2003).

There are many available soil remediation methodologies, such as vapor extraction systems, soil stabilization and solidification, thermal treatments, electrokinetic systems, flushing and washing of soils, and biological methods, i.e. land farming, biopiles, bioaugmentation, and phytoremediation (Iturbe et al. 1998). We have learned from our experience in soil washing treatments that this methodology is cost-effective and easy to apply in conditions similar to those found on the ODSS under study. We have explored the use of different anionic, and nonionic surfactants for washing highly contaminated sandy soils (Torres et al. 2003), and the successful use of *in-situ* flushing techniques (Iturbe et al. 2000b) for remediation of oil-contaminated soils.

On the other hand, biopiles have been shown to be an excellent option for treatment of oil-contaminated soil (Fahnestock 1998, Seklemova et al. 2001, Gogoi et al. 2001, Chaineau et al. 2002). We have experimented with small biopiles, and even with a 27 m³ biopile designed for the treatment of soils contaminated with approximately 40,000 mg TPH/kg of soil, aside from the presence of BTEX and PAHs (Iturbe et al. 2001).

The aim of this work is to show that soil washing (*on-site*) and biopiles are excellent remediation methodologies to treat soils contaminated with petroleum derivatives and metals. Applying them, it is possible to reach the goal value of 2,000 mg TPH/kg in a few months, as requested by Mexican legislation.

1 Materials and Methods

1.1 Soil excavation and characterization

As concluded by Iturbe et al. (2003), the referred ODSS is still contaminated by TPH, PAH, and gasoline fractions mainly in three localized zones. The first zone is where mobile-tanks were filled. The second zone corresponds to the railway, and the third zone is around the ODSS wastewater treatment plant (map not shown). After abandonment, pavement was retired, railway sleepers were removed and soil from these zones was excavated with the appropriate equipment (retro-excavators and frontal-loaders). Many times, rock was reached at about 0.5 m. Where necessary, excavated walls and floors were washed with surfactant solution (see above). Soils were widely characterized in a previous work (Iturbe et al. 2003), but soil to be treated by soil washing or biopiles was characterized only in terms of TPH and PAH concentrations, parameters whose minimization was suggested in the health risk assessment. In Table 1, some physical-chemical properties of the contaminated soil are shown.

1.2 Analytical methods

Soil samples were evaluated in accordance to EPA analytic techniques: EPA 418.1 for TPH; and the EPA 8100 method for PAHs.

1.3 Soil washing

Washing ditches construction. For the soil washing processes, three washing ditches were built. Thanks to the land availability, three units were built, two were identical, and the other was bigger. Fig. 1 shows the dimensions of ditches A, and B (8.7 m x 7.4 m x 1.25 m). Dimensions for ditch C are 10.4 m x 8.5 m x 1.25 m. Every ditch has one recycling and one sedimentation tank of about 4.3 m x 3.5 m x 1.25 m, as shown in Fig. 1. A 2-inch diameter and 87 m long piping was used for connecting the 47 m³ water storage tank, and the ditches for water recycling. Two ½ HP pumps were used for that purpose.

Soil washing. A non-ionic surfactant, previously characterized (Torres et al. 2003), was employed in this work – Canarcel TW80 (Canamex, S.A. de C.V., Mexico). The soil washing process was as follows. Approximately 104 tons (ditches A and B) or 143 tons (ditch C) of soil were poured into each ditch. 18 or 24.8 m³ of a 0.5% surfactant solution was intro-

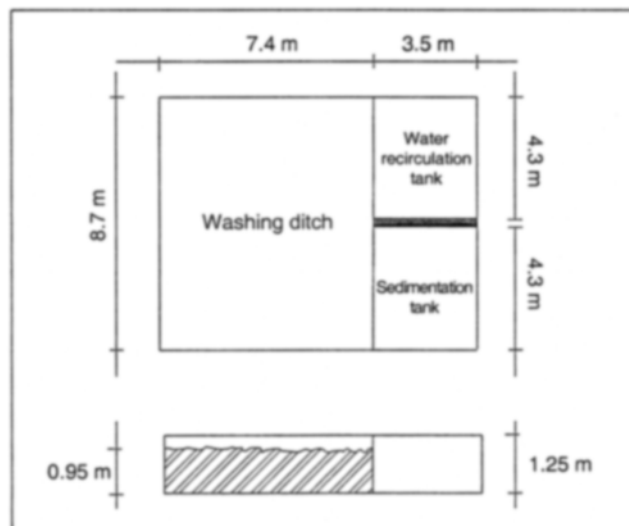


Fig. 1: Soil washing ditch diagram

duced to each basin (18 for ditches A and B, 24 for ditch C). Then, soil and surfactant solution were mechanically mixed. After that, the surfactant-dissolved hydrocarbon solution was pumped out to the sedimentation tank. When solids sedimented, the solution was transferred to the recycling tank, and then to the washing tank. The process was done three times. As a polishing stage, 18 (or 24.8) m³ of clean water were added to the soil. At the beginning, and after every stage, samples of soil were taken in order to evaluate TPH concentrations. Composed samples were analyzed for PAH-removal determination. Wastewater was pumped out, and mixed with the washing solution for its appropriate treatment.

1.4 Biopiles methodology

Microbial characterization. Heterotrophic bacteria present in contaminated soil were measured as follows. One gram of soil was diluted in peptonated solution. Different dilutions were prepared. Dilutions were plated on Petri dishes prepared with BHI media (Merk). Colonies were selected because of their color and/or morphology. Colonies were re-plated in Petri dishes with fresh BHI media. Pure colonies were characterized using the Gram technique for separation of gram-positive and gram-negative bacteria. A miniaturized biochemical system was employed: BBL CRYSTAL GP ID (Becton Dickinson S.A., France) for gram-positive bacteria. Some additional biochemical tests (i.e. oxidase, Simons citrate, motility, Voges-Proskauer) were developed when necessary. Microscope observations were used as an auxiliary tool. After this process, soil bacteria were grown in the presence of wasted heavy oil, diesel, and crude oil in 250 ml

Table 1: Physical-chemical properties of the contaminated soil

| Initial characterization ^a | | During remediation program | |
|---------------------------------------|---------------------------|----------------------------|-------------|
| Bulk density | 1.7 g/cm ³ | Water content | 37% |
| Porosity | 38% | Field capacity | 26% |
| Organic carbon fraction | 0.74% | Total N | 420 mg/kg |
| Hydraulic conductivity | 8.6x10 ⁻⁴ cm/s | Available P | 63.72 mg/kg |
| pH | 7.8 | pH | 7.8 |

^a from Iturbe et al. 2003

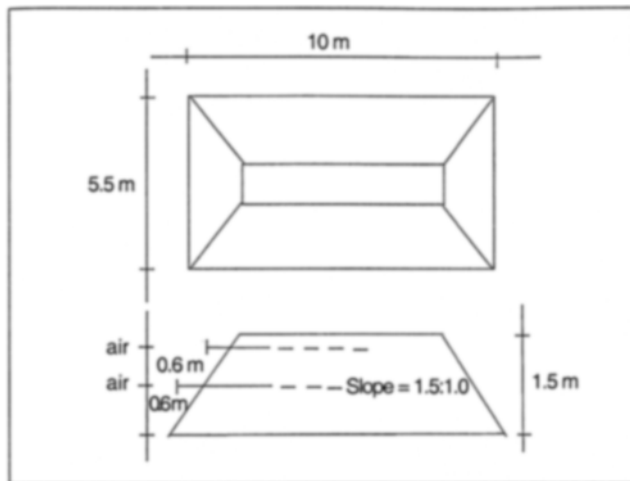


Fig. 2: Biopile diagram

Erlenmeyer flasks. For that, 50 ml of mineral medium were supplied with one ml of every hydrocarbon source and incubated during 48 hours at 20°C. After that, the entire identification process was repeated.

Biopile construction and operation. 100 m³ of soil from the abandoned ODSS, contaminated with approximately 4,600 mg/kg of TPH, and four PAHs at concentrations shown in Table 2, were employed for the biopile construction. Di-

mensions are shown in Fig. 2. The biopile was built over a paved and impermeabilized base. A one-brick high wall was used as the biopile limit. The biopile was built using consecutive 0.3 m layers. After the second and fourth soil layers, aeration pipes were installed. This piping was connected to an air compressor. After finishing the biopiles, a 0.05 m layer of coarse gravel was added to prevent erosion. The biopile was operating during 8 weeks and was evaluated taking two samples of soil on four occasions. Air was supplied one hour a day. No water was added during biopile operation.

2 Results and Discussion

2.1 Soil washing

Table 3 shows TPH concentrations for the soil washing of experimental batches (i.e. 1, 2, 3, and 4), for every ditch (i.e. A, B, and C). Initial concentrations C₀, are compared with the TPH values found at the end of stages 1, 2, and 3. As observed, only 3 of the washing experiments required 3 stages (1A, 1B, and 1C). Most of the batches required 2 stages, and only two of them needed only one washing stage (4A, and 4B). The TPH initial concentrations were quite different (from 3,037 to 17,238 mg/kg soil, average = 9,172 mg/kg). At the end of the washing process, the TPH concentrations were quite variable, from 942 to 2,317 mg/kg (average = 1,520 mg/kg). For this reason, removal values fluctuated from 50.3 to 92.8% (average = 83.42%).

Table 2: PAHs detected on soil before biopile treatment

| PAH | Concentration (mg/kg) | Number of aromatic rings | Solubility in water ^a (25°C) mg/l | Required cleaning level (mg/kg) |
|--------------|-----------------------|--------------------------|--|---------------------------------|
| Phenanthrene | 5.98 | 3 | 1.1 | 170 |
| Naphthalene | 4.63 | 2 | 31.0 | 58.000 |
| Fluorene | 1.81 | 3 | 1.9 | NR |
| Pyrene | 0.65 | 4 | 0.13 | 45 |
| Total | 13.07 | - | - | - |

^afrom Eriksson et al. 2000

Table 3: Soil washing experimental runs and main results

| Batch/ Ditch | C ₀ (mg/kg) | C1 (mg/kg) | C2 (mg/kg) | C3 (mg/kg) | Removal (%) | TPH = a exp (b*number of stages) | | | Removal efficiency (g TPH/g surfactant) | |
|---------------------|---------------------------|-------------------|---------------|---------------|----------------|----------------------------------|---------|----------------|--|--|
| | | | | | | a | b | R ² | | |
| First batch | | | | | | | | | | |
| 1A | 17.238 | 4.121 | 1.475 | 1.242 | 92.8 | 31.400 | -0.8919 | 0.9073 | 55.45 | |
| 1B | 12.224 | 4.656 | 2.780 | 1.580 | 87.0 | 20.984 | -0.6654 | 0.9768 | 36.90 | |
| 1C | 4.252 | 2.000 | 2.639 | 1.901 | 55.3 | 4.361 | -0.2138 | 0.5602 | 8.13 | |
| Second batch | | | | | | | | | | |
| 2A | 9.438 | 1.787 | 942 | - | 90.0 | 25.348 | -1.1546 | 0.938 | 29.61 | |
| 2B | 9.483 | 2.875 | 1.740 | - | 81.6 | 19.729 | -0.8478 | 0.9475 | 26.84 | |
| 2C | 4.666 | 3.200 | 2.317 | - | 50.3 | 6.561 | -0.3500 | 0.9980 | 8.13 | |
| Third batch | | | | | | | | | | |
| 3A | 8.171 | 2.053 | 1.825 | - | 77.6 | 14.006 | -0.7495 | 0.8085 | 22.00 | |
| 3B | 12.989 | 2.208 | 1.661 | - | 87.2 | 28.348 | -1.0283 | 0.8516 | 39.27 | |
| 3C | 10.291 | 3.530 | 1.521 | - | 85.2 | 25.770 | -0.956 | 0.9953 | 30.34 | |
| Fourth batch | | | | | | | | | | |
| 4A | 3.037 | 1.075 | - | - | 64.6 | - | - | - | 6.80 | |
| 4B | 3.261 | 987 | - | - | 69.7 | - | - | - | 7.88 | |
| 4C | 15.064 | 4.419 | 1.448 | - | 90.4 | 47.700 | -1.1711 | 0.9993 | 47.11 | |
| Average | 9.172 | Last stage: 1.520 | | | 83.42 | 22.420 | 0.8028 | 0.8982 | 26.53 | |

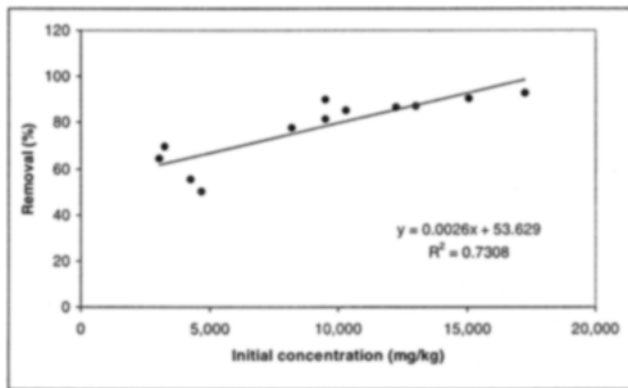


Fig. 3: TPH Removal as a function of TPH initial concentrations

In Fig. 3, the relationship between initial concentration and removal efficiencies is shown. As observed, the higher the initial soil TPH concentration, the higher the removal value. This behavior is well represented by the equation:

$$\text{Removal\%} = 0.0026 \text{ TPH initial concentration} + 53.629, R^2 = 0.7308 \dots (1)$$

Figs. 4a, 4b, 4c, and 4d (Fig. 4) show the TPH concentrations for the different washing batches in the three ditches. It is important to keep in mind that the washing process was carried out until reaching a TPH concentration equal to or below 2,000 mg/kg, as suggested by PROFEPA (2000). Note

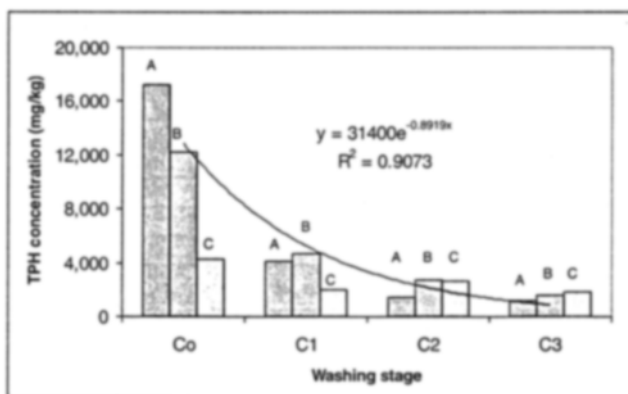


Fig. 4a: TPH concentrations. Batch 1, ditch A, B, and C, showing exponential decaying curve

that batch 1 required 3 washing stages, batches 2, and 3 needed two stages, and batch 4 required only one stage, except for ditch 4C, which required of 2 stages.

In the same figures, it is noticeable that TPH concentration decaying curves have the form of an exponential curve (see Fig. 4a, as an example). Values were fitted to the form:

$$\text{TPH} = a \exp (b \cdot \text{number of washing stages}), R^2 = 0.8565 \quad (2)$$

Values of a, b, and r (correlation factor) for every batch/ditch are shown in Table 3. As noted, the higher the initial soil TPH concentration, the higher the value of a and b. Experiments 4A and 4B were not considered, as they consisted of only one stage. Correlation factors are good enough, except for experiment 1C (0.5602). This kind of expression could help as a rule of thumb for anticipating how many washing stages are necessary in order to get a desired final TPH concentration during the washing process.

It is possible to estimate the amount of TPH removed from soil for every washing process using the initial and final TPH concentrations, and the amount of soil. During the washing process, 104 tons of soils were processed on ditches A, and B, while approximately 143 tons of soils were processed in ditch C (average soil density of 1.7 g/cm³). On the other hand, it can be assumed that the amount of surfactant employed in every washing process is 0.18 m³ water x 5 kg/m³

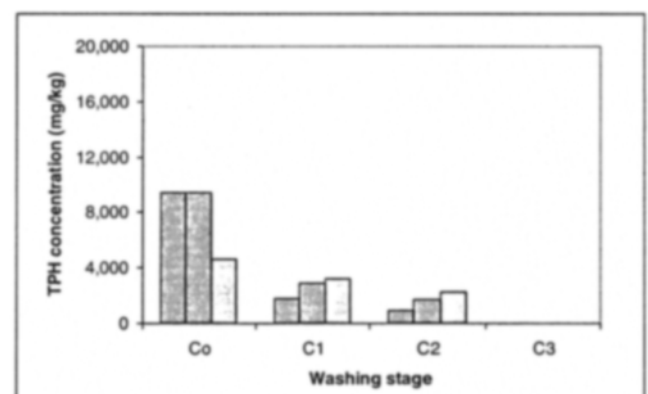


Fig. 4b: TPH concentrations. Batch 2, ditch A, B, and C

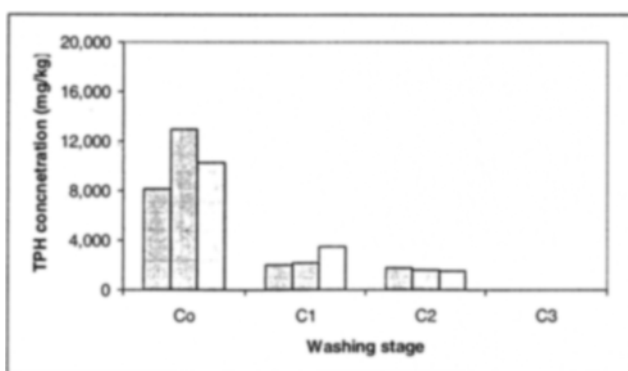


Fig. 4c: TPH concentrations. Batch 3, ditch A, B, and C

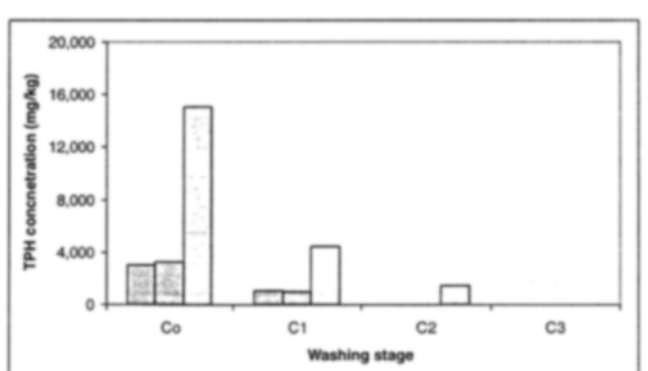


Fig. 4d: TPH concentrations. Batch 4, ditch A, B, and C

surfactant = 90 kg of surfactant, for ditches A and B. As every surfactant solution is employed three times, it can be assumed that every batch consumes 30 kg of surfactant. For ditch C, the amount of employed water is 24.8 tons, giving a total of 123 kg and 123/4 kg per batch process. Defining a new removal efficiency as the amount (in grams) of TPH removed per g of employed surfactant, values between 7.88 and 55.45 mg TPH/mg surfactant can be achieved, as observed in Table 4. Note that, in general, the higher the initial TPH soil concentration, the higher the removal efficiency as g TPH/g surfactant.

Fig. 5 shows the relationship between that removal efficiency (g TPH/g surfactant), and the percent removal.

It is remarkable that the higher the percent removal, the higher the amount in g of TPH removed by g of surfactant,

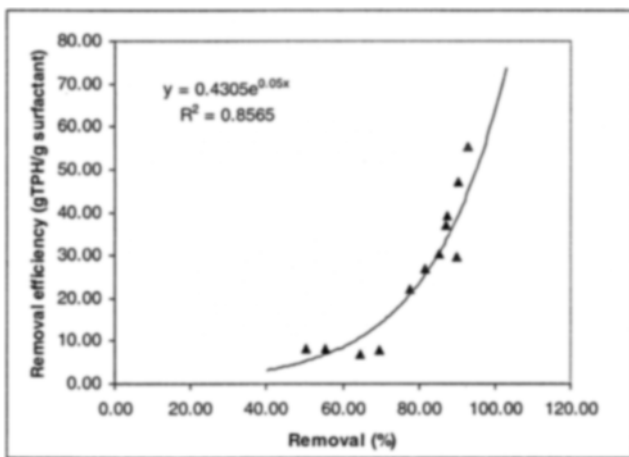


Fig. 5: Removal efficiency as a function of TPH removal

but the function is not linear. Data were adjusted to an exponential curve, giving the following equation:

$$\text{Removal efficiency} = 0.4305 \exp(0.05 \cdot \text{removal}), R^2 = 0.8565 \quad (3)$$

This means that with the washing of soils with low TPH concentrations by means of a 0.5% surfactant solution, low percent removals are obtained, besides with very low removal efficiencies, therefore wasting a lot of surfactant.

It is noteworthy that the initial soil TPH concentration affects the whole washing process. Because of that, some values from Table 3 were re-arranged in Table 4, according to the initial soil TPH concentration. Three blocks were considered. The first one shows the experiences within a high concentration range (12,000–18,000 mg/kg). Runs 1A, 4C, 3B, and 1B were included. They had an average initial concentration of 14,379, an average percent removal of 89.35%, and a removal efficiency of 44 g TPH/g surfactant. The second block considers the moderate concentration range (8,000–11,000 mg/kg), runs 3C, 2B, 2A, and 3A. As noted, they had an initial soil TPH concentration of 9,346, an average percent removal of 83.6%, and an average removal efficiency of 28.62 g TPH/g surfactant. At the end, the block of low range concentrations (3,000–5,000 mg/kg) includes runs 2C, 1C, 4B, and 4A. They had an average initial concentration of 3,804 mg/kg, an average percent removal of 60%, and average removal efficiency of 11.63 g TPH/g surfactant. This means that using a 0.5% surfactant solution for washing low TPH concentration soils, losses in removal efficiency of 16 and 32 mg TPH/g surfactant are obtained, if compared with the moderate TPH concentration and high TPH concentration soils, respectively. These figures suggest the future use of surfactant solutions with lower concentrations, appropriated for the TPH amount to remove.

Table 4: Analysis of the washing of soils as a function of the soil TPH-concentration range

| Concentration range (mg/kg) | Batch/Ditch | Initial concentration (mg/kg) | Removal (%) | Removal efficiency (g TPH/g surfactant) |
|-----------------------------|-------------|-------------------------------|-------------|---|
| High (12.000–18.000) | 1A | 17.238 | 92.8 | 55.45 |
| | 4C | 15.064 | 90.4 | 47.11 |
| | 3B | 12.989 | 87.2 | 39.27 |
| | 1B | 12.224 | 87.0 | 36.90 |
| | Average | 14.379 | 89.3 | 44.68 |
| Moderate (8.000–12.000) | 3C | 10.291 | 85.2 | 30.34 |
| | 2B | 9.483 | 81.6 | 26.84 |
| | 2A | 9.438 | 90.0 | 29.61 |
| | 3A | 8.171 | 77.6 | 22.00 |
| | Average | 9.346 | 83.6 | 27.20 |
| Low (3.000–8.000) | 2C | 4.666 | 50.3 | 8.13 |
| | 1C | 4.252 | 55.3 | 8.13 |
| | 4B | 3.261 | 69.7 | 7.88 |
| | 4A | 3.037 | 64.6 | 6.80 |
| | Average | 3.804 | 60.0 | 7.73 |

Table 5: PAH concentrations in a composed sample of soil before and after soil washing process

| Compound | Initial concentration (mg/kg) | Final concentration (mg/kg) | Removal (%) | Required cleaning level (mg/kg) |
|-------------------------------|-------------------------------|-----------------------------|-------------|---------------------------------|
| Pyrene | 9.88 | 1.08 | 89 | 45 |
| Naphthalene | 6.69 | ND | 100 | 58.000 |
| <i>Benzo(a)anthracene</i> | 6.69 | 0.57 | 91.5 | 0.55 |
| Benzo(g,h,i)perylene | 6.42 | ND | 100 | NR |
| Anthracene | 4.43 | 0.39 | 91.2 | 4.7 |
| Fluorene | 4.25 | ND | 100 | NR |
| Phenanthrene | 3.14 | 1.08 | 65.6 | 170 |
| <i>Benzo(b)fluoranthene</i> | 2.35 | 0.76 | 67.6 | 0.55 |
| <i>Chrysene</i> | 2.03 | 1.06 | 47.8 | NR |
| <i>Dibenzo(ah)anthracene</i> | 1.94 | ND | 100 | 0.032 |
| <i>Benzo(a)pyrene</i> | 1.42 | 0.56 | 60.6 | 0.054 |
| Fluoranthene | 0.767 | 1.02 | -33.0 | 58 |
| <i>Indene(1,2,3-cd)pyrene</i> | 0.414 | ND | 100 | 0.55 |
| Acenaphthene | 0.102 | ND | 100 | NR |
| Acenaphthylene | ND | ND | - | NR |
| <i>Benzo(k)fluoranthene</i> | ND | ND | - | NR |
| Total PAHs | 50.52 | 6.52 | 87.1 | - |

ND, not detected, NR not reported, carcinogenic PAHs in Italics

Table 5 shows the PAH concentrations in a composed sample of soil, before and after the soil washing process. Carcinogenic PAHs are highlighted in italics. In addition, the percent removals, and required cleaning levels suggested by the health risk assessment (PROFEPA 2000), are included for comparison purposes. As noted, from the 16 PAH considered by USEPA, 14 were found in the soil under treatment. Only acenaphthylene, and benzo(k)fluoranthene were not detected. The PAH which appeared in higher concentrations were pyrene (9.88 mg/kg), naphthalene, and benzo(a)anthracene, both with 6.69 mg/kg. PAH removals due to the soil washing process were in the range of 47.8 to 100%. The case of fluoranthene is quite unusual, since an increase of 33% was observed due to the washing process. This fact could be related with soil heterogeneities. The PAH removed less from soils was chrysene (47.8%), but no required cleaning level is suggested for this aromatic hydrocarbon. On the other hand, naphthalene, benzo(g,h,i)perylene, fluorene, dibenzo(a,h)anthracene, indene(1,2,3-cd)pyrene, and acenaphthene were removed to 100%.

There are only two PAHs out of the required cleaning level. Benzo(a)anthracene should be in a concentration equal to or less than 0.55 mg/kg, and it was found in a concentration value of 0.57 mg/kg (1.036 times the goal value). Benzo(a)pyrene had a final concentration of 0.56 mg/kg, 10.37 times the goal value (0.054 mg/kg). Finally, a total amount of PAHs around 50.5 mg/kg was found before the washing process. At the end of the process, only 6.52 mg/kg remained. This means an average PAH removal of 87.1%. Very few works have reported the PAH suggested by USEPA removal efficiencies.

A very rough calculation of washing soil process costs, including labor, building materials, pumping and tubing, ditch construction, storage tanks, and surfactant costs, among others, gives a total cost of \$140/m³ or \$67/kg TPH removed. Lowe et al. (1999) report cost estimations for flushing technologies in the following ranges: the minimum and maximum are between 84 and \$774/m³. Finally, if the volume of NAPL removed is the target parameter, costs between 6 and \$63/L are typical. As noted, the costs involved in the washing process are on the range of the typical costs for *in-situ* flushing methodologies.

2.2 Biopile development

Soil to be treated by means of a biopile was characterized in terms of its bacterial count. As noted in Table 6, the amount of heterotrophs found in that soil, i.e. 1.8×10^8 UFC/g soil, is quite high. Regarding the specific hydrocarbon degraders, it was found that bacteria with the capability of degrading oil, diesel, and crude oil were detected in the same soil, in amounts of 5.6×10^8 , 5.4×10^8 , and 1.0×10^8 , respectively (see Table 6). Fahnestock (1998) considers that 1×10^3 UFC/g soil of heterotrophic bacteria are enough for correct biopile function.

Table 6: Soil bacterial count (heterotrophs and degraders)

| Heterotrophs | Specific degraders | |
|-------------------|--------------------|-------------------|
| | Waste oil | Diesel |
| 1.8×10^8 | Crude | 5.6×10^8 |
| | Diesel | 5.4×10^8 |
| | Crude | 1.0×10^8 |

Table 7: Soil bacterial identification

| Pristine soil – Gram positive | | | Contaminated soil – Gram positive | | |
|-------------------------------|-----------------------|--------------------|-----------------------------------|-----------------------|------------------------|
| <i>Bacillus</i> | <i>Micrococcus</i> | <i>Turicela</i> | <i>Staphylococcus</i> | <i>Micrococcus</i> | <i>Corynebacterium</i> |
| <i>B. licheniformis</i> | <i>M. sedentarius</i> | <i>T. otitidis</i> | <i>S. schleiferi</i> | <i>M. sedentarius</i> | <i>C. renale</i> |
| <i>B. brevis</i> | <i>M. luteus</i> | | | | |

In the pristine soil, only gram-positive bacteria were identified (Table 7). Three genera were detected specifically: *Bacillus*, *Micrococcus*, and *Turicela*. The species recognized were *B. brevis*, *B. licheniformis*, *M. luteus*, *M. sedentarius*, and *T. otitidis*. Contaminated soil showed the presence of three genera and species, all gram-positive too. Bacteria were *Staphylococcus schleiferi*, *Micrococcus sedentarius*, and *Corynebacterium renale*. There is no explanation for the presence of only gram-positive bacteria. Genera found in hydrocarbon-contaminated soils by other researchers are *Xanthomonas sp.*, *Bacillus sp.*, *Hyphomicrobiu sp.* (Li et al. 2000), *Sphingomonas pacimobillis*, *Sphingobacterium multivorum* (Jorgensen et al. 2000), *Stenotrophomonas maltophilia* (Boochnan et al. 1998), and *Rhodococcus sp.* (Sharma and Pant 2000), among others. Besides, some microorganisms have been reported because of their capability of producing biosurfactants. Among the microorganisms reported for that feature are some species of *Pseudomonas*, *Corynebacterium*, and *Bacillus* (two of them reported in this work), as well as *Arthrobacter*, *Mycobacterium*, *Rhodococcus*, *Candida*, *Rhodotorula*, and *Streptomices*, among many others (Mulligan et al. 2001).

Biopile was operated for 66 days, during the months of October, November and December. For these months, average temperatures are 13.1, 12.2, and 10.0°C, respectively (annual average temperature = 13.5°C) (CONAGUA 2000). Fig. 6 shows the biodegradation kinetic at the biopile. Though data are scarce, the high TPH degradation rate is remarkable. Process started with 4,666 mg/kg of TPH, and at the end of day 66, only 691 mg/kg were present on average. This means an 85.2% removal, and a 60.22 mg/kg/day degradation rate. Biopile was no longer operated, since the goal of 2,000 mg/kg was clearly reached. Regarding the PAHs, Table 2 shows the four PAH found in a composed sample before the biopile treatment. Phenathrene (5.98 mg/kg), naphthalene (4.63 mg/kg), fluorene (1.81 mg/kg) and pyrene (0.65 mg/kg) were found in the composed sample, giving a total PAH concentration of around 13 mg/kg. At the end of the biopile treatment, none of

the 16 PAHs considered by USEPA were found in the composed sample. This means 100% efficiency in PAH removals. It has been reported that PAH with three aromatic rings are easily bio-degraded (Eriksson et al. 2000). Guerin (2000) also found that the bioremediation of PAH contaminated soils is affected by the number of aromatic rings. In a process lasting 224 days, approximately 90% of the 4-ring PAH, and 70% of the 5- and 6-ring PAH were reported as biodegraded. As shown in Table 5, except pyrene (4 rings), all the PAHs present in the composed sample had 2 and 3 rings. The number of rings in a PAH has an effect on the compound physico-chemical properties. As an example, PAH water solubilities are highly affected by the number of rings in the PAH. While phenathrene, naphthalene, and fluorene have water solubilities of 1.1, 31, and 1.9 mg/l, respectively; pyrene has a water solubility value of 0.13 mg/l (Eriksson et al. 2000). This parameter is closely related with availability and biodegradation issues.

Seklemova et al. (2001) reported their work with three 0.6 m³ biopiles. They were contaminated with 2,000, 4,000, and 6,000 mg/kg of hydrocarbons. Biopiles were bio-stimulated with nutrients, but not aerated (only stirred once a month). They observed removal efficiencies of 66, 75, and 75% after 373 days of operation, respectively. Regarding the degradation rates, values of 4, 8, and 11 mg/kg/day were reached. Gogoi et al. (2003) worked with 500 kg cells with different treatments. They reported an initial TPH concentration of 44,000 mg/kg. Soil was amended with nutrients, and a consortium, isolated from hydrocarbon-contaminated soils, was inoculated. The system was aerated 1 hour a day at a rate of 100 m³/h. At the end of 365 operation days, the removal for the cell was 75%, with a degradation rate of 90 mg/kg/day. Finally, Chaineau et al. (2003) reported experiences with a 30 m³ biopile with an initial hydrocarbon concentration of 15,000 mg/kg. Temperature was in the range of 5–25°C during the experiments. The system was amended with nutrients and mixed with straw to enhance textural characteristics. The pile was aerated at a 10 m³/h rate. In 500 days, they reached a removal of 50%, which means a degradation value of 15 mg/kg/day. As observed, the 100 m³ biopile operated successfully, reaching quite high removal percentages and degradation rates, if compared with similar biopiles reported in the literature. Note that operation temperature was quite low (10–13.1°C).

A rough calculation of building and operation costs for the 100 m³ biopile, gives a total cost of \$94.2/m³. There are no many authors who report the field costs of bioremediation though biopile methodologies. Fahnestok et al. (1998) reported a cost analysis for biopile construction and operation. They distinguished between temporary and permanent installations. For both, costs are an inverse function of total volume. For temporary biopiles (as the biopile operated along this work), costs fluctuated between 135.4 and \$60.5/m³, for biopiles with volumes of 500 and 5,000 yd³ (382 and 3,822 m³), respectively. As noted, the total cost reported here is quite near the range mentioned.

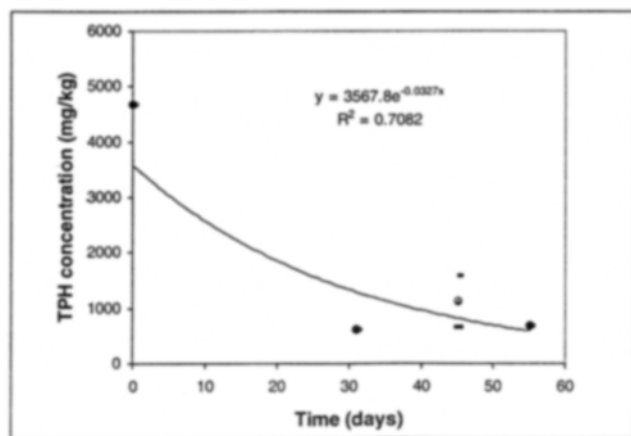


Fig. 6: TPH degradation kinetics in the biopile

2.3 General considerations

Clean soil was mixed and stored in piles. An evaluation of the TPH concentration (10 random samples) yielded an average of 1,390 mg/kg (standard deviation of 283 mg/kg). Considering an initial average TPH concentration of 10,000 mg/kg, the main features of the cleaning process were:

| | |
|---------------------------------------|----------------------|
| - Total volume of remediated soil | 1,642 m ³ |
| - Total mass of remediated soil | 2,463 ton |
| - Total mass of initial TPH in soil | 24.63 ton |
| - Total mass of final TPH in soil | 3.42 ton |
| - Total mass of removed TPH | 21.21 ton |
| - Average TPH removal efficiency | 84% |
| - Total amount of employed surfactant | 1.77 ton |

Regarding the waste waters generated by the process, ferric chloride (8 mg/l) was added to wastewaters in order to promote surfactant flocculation and sedimentation. Water samples were evaluated before and after treatment. Water was recycled to the washing process (data not published). The sludges generated in this treatment process were stored in metallic drums and sent to a hazardous waste confinement (less than 120 kg).

3 Conclusions

Remediation using soil washing/biopiles is a viable process for treating 1,640 m³ of soils contaminated by TPHs/PAHs. Specifically, the following conclusions can be made:

- Soil washing process (approximately 1,540 m³) started with TPH concentrations between 3,037 and 17,238 mg/kg. Percent removals in the range of 55.3 to 92.8% were observed (83.4% on average). Removal resulted in a direct function of the initial TPH concentration. The ratio g TPH/g surfactant showed values between 6.8 and 55.4 for the different washing batches, and resulted in a quadratic function of the percent removal values.
- Pristine soil showed the presence of *Bacillus*, *Micrococcus*, and *Turicela* genera. The species recognized were *B. brevis*, *B. licheniformis*, *M. luteus*, *M. sedentarius*, and *T. otitidis*. Contaminated soil showed the presence of three genera and species, all gram-positive. Bacteria were *Staphylococcus schleiferi*, *Micrococcus sedentarius*, and *Corynebacterium renale*. Microorganisms (heterotrophs and degraders) were in concentrations enough for the biodegradation process.
- Biopile process (100 m³) started with 4,666 mg/kg of TPH, and at the end of day 66, only 691 mg/kg were present on average. This means an 85.2% removal, and a 60.2 mg/kg/day degradation rate.
- The contaminated soil was treated successfully, reaching the legislation limits, i.e. TPH values under 2,000 mg/kg, and a significant reduction in PAH concentrations.
- A very rough calculation of washing soil process costs, including labor, building materials, pumping and tubing, ditches construction, storage tanks, and surfactant costs, among others, gives a total cost of \$140/m³, or \$67/kg TPH removed. A rough calculation of building and operation costs for the 100 m³ biopile, gives a total cost of 94.23 \$/m³.

Based on the land availability for washing ditches and biopiles construction, it would be possible to treat TPHs/PAHs contaminated soils in both systems in parallel. More than one biopile can be constructed besides a set of washing ditches for soil treatment. Both process are not time consuming proce-

dures, since soil washing operations can be in the order of weeks, and biopile treatment could last as much as 2–3 months.

4 Recommendation

It is highly recommended to perform soil washing studies, identifying new products, and mixtures, which could reduce costs and assure optimum operation. Besides, it would be useful to determine the effect of soil washing on metals and some nutrients (phosphorus, nitrogen, Na, K, Ca, Mg), as well as other soil physical-chemical and microbiological characteristics.

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