Remediation of TPH/PAHs Contaminated Soil Using Soil Washing

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ABSTRACT

This work deals with the treatment of a site contaminated mainly by gasoline and diesel, showing the presence of PAHs, MTBE, and BTEX. Soil washing was applied in three washing ditches of approximately 100 m^3. Every ditch had one recycling and one sedimentation tank.

A non-ionic surfactant, previously characterized, was employed in this work. Approximately 104 tons of soil were poured into each ditch and 18 m^3 of a 0.5% surfactant solution was introduced to each basin. Then, soil and surfactant solution were mechanically agitated. After that, the surfactant solution with dissolved hydrocarbons 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 repeated three times. As a polishing stage, 18 m^3 of water were added to the soil.

At the beginning and after every stage, samples of soil were taken and analyzed in accordance to EPA analytic techniques. Average soil washing TPH removal was 83%. The soil treated reached the legislation limits (TPH values under 2,000 mg/kg) and had a significant reduction in PAHs concentrations. At the end of the process the washed soil was poured at the original site.

INTRODUCTION

A contaminated industrial site, which operated in Mexico from 1966 to 2000, was contaminated with hydrocarbons. The site was characterized by our research group in 2000 (Iturbe *et al.* 2003a). The main conclusions were that the soil 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 soil contaminated was 1,640 m^3.

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 site 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.* 2003b) for remediation of oil-contaminated soils.

The aim of this work is to show that soil washing is an excellent remediation methodology to treat soils contaminated with petroleum derivates and metals. Applying them, it is possible to reach the goal value of 2,000 mg TPH/kg, requested by Mexican legislation, in a few months.

MATERIALS AND METHODS

Soil excavation and characterization

Three zones were mainly contaminated by TPH, PAH, and gasoline fractions. The first zone is where mobile-tanks were filled. The second zone corresponds to the railway, and the third zone is around the 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 (backhoe/loader and skid steer-loaders). Many times, rock was reached at about 0.5 m. Where necessary, extracted stones, walls and floors were washed with surfactant solution. On table 1, some physical-chemical properties of the contaminated soil are shown.

Analytical methods

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

Soil washing

For the soil washing processes, three washing ditches were built. Figure 1 shows the dimensions of ditches (8.7 m x 7.4 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.

A non-ionic surfactant, previously characterized (Torres *et al*., 2003) was employed in this work (Canarcel TW80). Soil washing process was as follows. Approximately 104 tons of soil were poured into each ditch and 18 m^3 of a 0.5% surfactant solution was introduced to each basin. Then, soil and surfactant solution were mechanically mixed. After that, the surfactant dissolved hydrocarbons 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 repeated three times. As a polishing stage, 18 m^3 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.

RESULTS AND DISCUSSION

Table 2 shows TPH concentrations for soil washing experimental batches (*i.e.,* 1, 2, 3, and 4), for every ditch. Initial concentrations Co, 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 (form 3,037 to 17,238 mg/kg soil). An average of 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 form 50.3 to 92.8 % (average = 83.42%). As observed, the higher the initial soil TPH concentration, the higher the removal value. On figure 2, the relationship between initial concentration and removal efficiencies is shown. This behavior is well represented by the equation:

Removal %= 0.0026 TPH initial concentration + 53.629 R^2 = 0.7308 … (1)

Figures 3a and 3b show the TPH concentrations for the first and final washing batches respectively in the three ditches. The washing process was carried out until reaching a TPH concentration equal or below 2,000 mg/kg, as suggested by PROFEPA (2000). Note 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. On the same figures, it is noticeable that TPH concentration decaying curves have the form of an exponential curve (figure 3a, as an example). Values were fitted to the form:

TPH=a exp (b*number of washing stages), R^2 =0.8565 (2)

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 washing process, 104 tons of soils were processed on ditches A, and B, while approximately 143 tons of soils were processed at ditch C (average soil density of 1.7 g/cm^3). On the other hand, it can be assumed that the amount of surfactant employed in every washing process is 0.18 m^3 water x 5 kg/m^3 surfactant = 90 kg of surfactant, for ditches A and B. As every surfactant solution is employed thrice, 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 2. Note that, in general, the higher the initial TPH soil concentration, the higher the removal efficiency as g TPH/g surfactant.

Figure 4 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, but the function is no linear. Data were adjusted to an exponential curve, giving the following equation:

$$\textbf{Removal efficiency} = \mathbf{0.4305 \exp(0.05*removal)},\ \mathbf{R^2=0.8565} \qquad \textbf{(3)}$$

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 soil initial TPHs concentration affects the whole washing process. Three blocks were considered. The first one shows the experiences within a high concentration range (12,000-18,00 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) include the 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 TPG amount to remove.

Table 3 shows the PAHs 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. PAHs 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 less removed 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 in a 100%.

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/m^3 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 \$/m^3. Finally, if volume of NAPL removed is the target parameter, costs between 6 and 63 \$/L are the typical. As noted, the costs involved in the washing process are on the range of the typical costs for *in situ* flushing methodologies.

CONCLUSIONS

- Soil washing process (approximately 1,540 m^3) started with TPH average concentrations of 10 138 mg/kg. Percent removals in the range of 55.3 to 92.8% were observed (83.4% in 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 a quadratic function of the percent removal values.

- The contaminated soil was treated successfully, reaching the legislation limits *i.e.,* TPH values under 2,000 mg/kg, and a significant reduction in PAHs 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/$m^{3,}$ or \$67/kg TPH removed.

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Table 1. Physical-chemical properties of the contaminated soil

Initial characterization (Iturbe *et al.*, 2003a)	
Bulk density	1.7 g/cm^3
Porosity	0.38
Organic carbon fraction	0.0074
Hydraulic conductivity	8.6x10^{-4} cm/s
pH	7.8

Table 2. 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 (gTPH/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 3. PAH concentrations in a composed sample of soil before and after soil washing process

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

ND, not detected, NR not reported, **carcinogenic PAHs in bold**

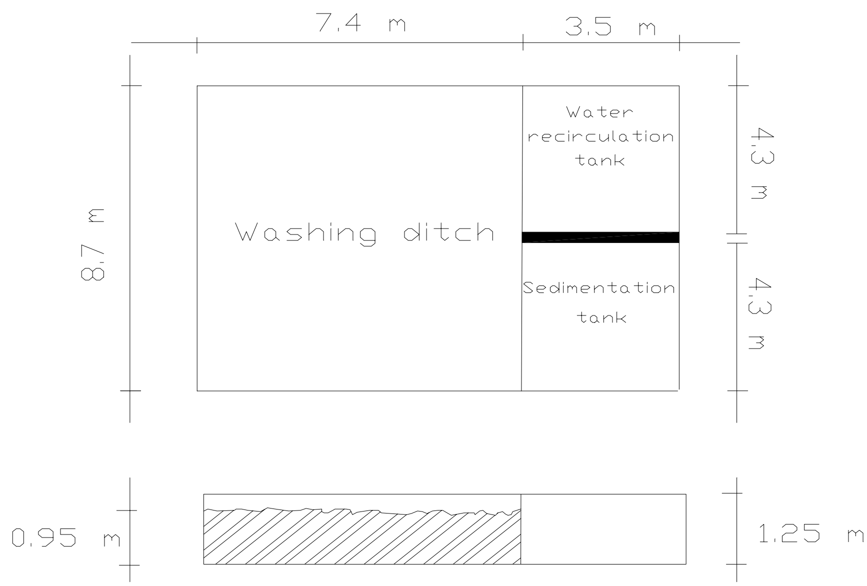

Figure 1. Soil washing ditch diagram

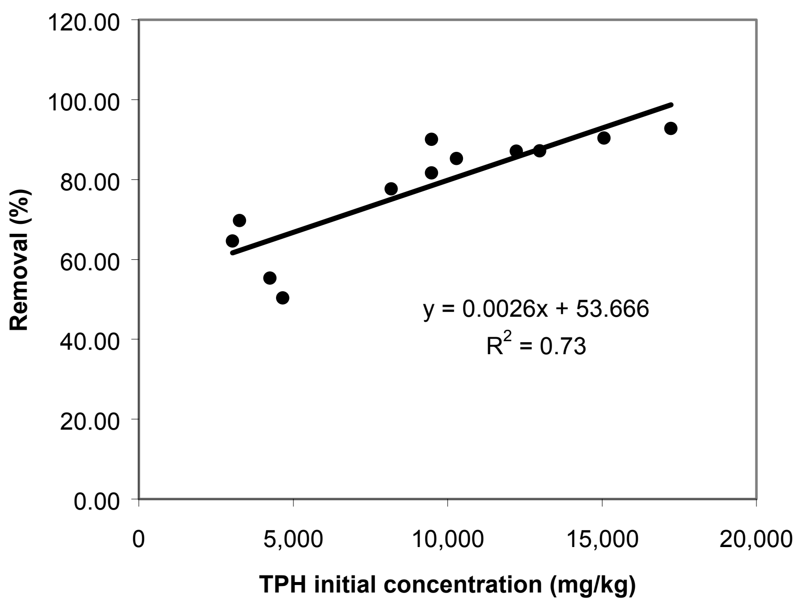

Figure 2. TPH Removal as a function of TPH initial concentrations

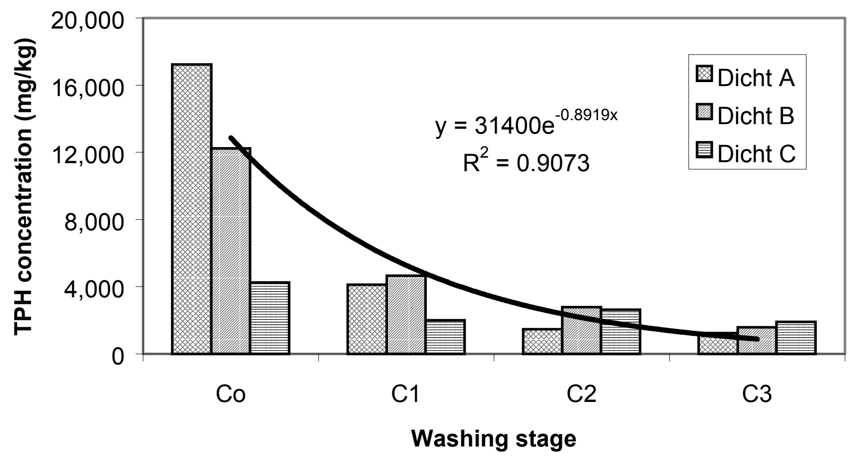

Figure 3 a. TPH concentrations. Batch 1, ditch A, B, and C

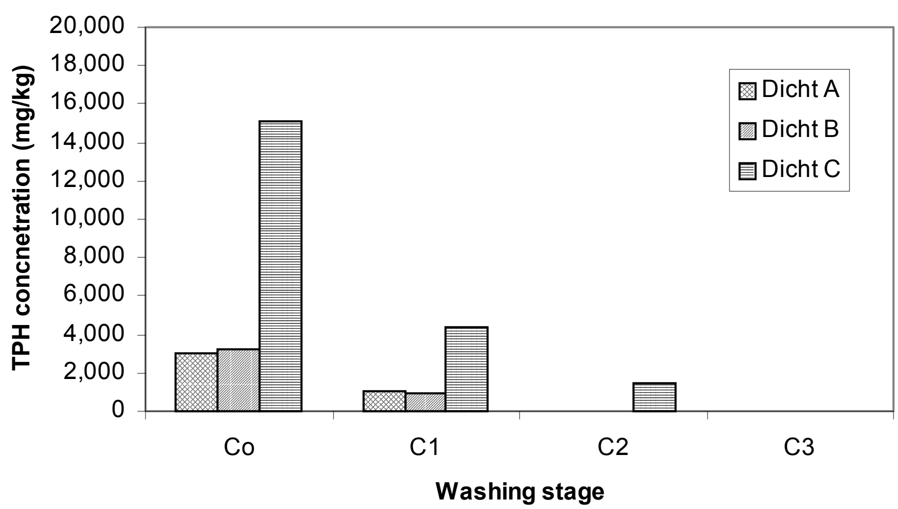

Figure 3b. TPH concentrations. Batch 4, ditch A, B, and C

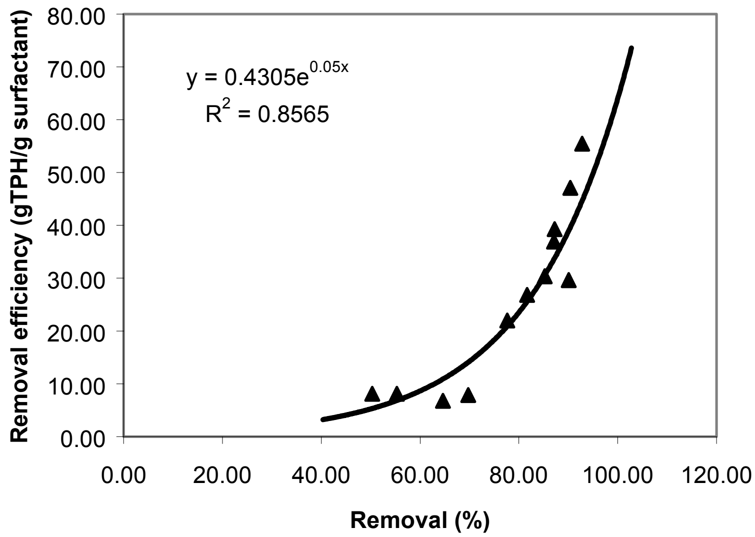

Figure 4. Removal efficiency as a function of TPH removal