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An In-Situ Soil Washing System for Diesel Fuel Contaminated Soils

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ABSTRACT

The increasing production and use of fossil fuels increase the probability of soil source contamination by oil and petroleum products, and pose a hazard to life. There are over 43,000 chemical contaminated sites in Canada and USA, with 2,200 of them classified as high risk. In the US, over $10 billion are spent annually on the cleanup of contaminated sites. The primary objective of this study was to develop and test an innovative *in situ* soil washing system that could extract contaminants from the soil, quickly and effectively, without causing any threat to water sources. We proposed the use of an organic solvent in our system that is not only lighter than water but is also immiscible with water. It was introduced into the soil profile from below using a system of horizontal, underground perforated pipes, and collected from the soil surface. Since the solvent was being introduced from the bottom, it "wete" the soil completely and thus removed the contaminant effectively. To understand and evaluate the performance of the system for remediation, a preliminary experiment was performed using two stainless steel columns (1m long x 0.2m diameter) packed with two diesel fuel contaminated soils (fresh and old contamination). The proposed technique is innovative, unique and very fast for the remediation of diesel fuel contaminated soils. It is the first study of its kind employing a subirrigation system for delivering organic solvents (lighter than water and immiscible in water) for *in situ* soil washing. Some preliminary applications of the system to diesel fuel contaminated sand soils have proved very promising for both fresh and old contaminated sites. The method could be equally suited for other contaminants also.

Keyword: Diesel Contamination, *In Situ,* Soil Washing, Solvent.

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INTRODUCTION

The Canadian public is becoming increasingly concerned with the high risk of environmental pollution from wastes, industrial landfill sites, petroleum companies, coal gas production and utilization, mining industries, military activities, and accidental spills of industrial chemicals. The waste generated from industrial activities has increased fifteen times since the Industrial Revolution of 1945 (Hawkes, 1989). In the US, over $10 billion is spent annually on the cleanup of contaminated sites (Bredehoeft, 1994) and there are over 43,000 chemically contaminated sites in Canada and USA, with 2,200 of them classified as high risk (Smith, 1991). In the US, there are over 750,000 underground chemical storage facilities with over two million tanks (Caplan, 1993), used in places such as: gasoline stations, agricultural farms, residential areas, car rental companies, military bases, hospitals, fleet facilities, trucking terminals, and even national park services. Caplan (1993) also reported that over 50% of these tanks are leaking and the estimated cleanup cost is between $10,000 and $20,000 per tank. Some of the contaminants consist of compounds, such as polycyclic aromatic hydrocarbons (PAH), which are carcinogens and not only tend to resist microbial decomposition but also may physically, chemically or biologically be-

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come transformed to more hazardous compounds, thus leading to increased risk of environmental pollution.

Both *in situ* and *ex situ* methods are used to remediate soils around leaking gasoline storage tanks. For *ex situ* cleanups, the tank and the soil are excavated and about 5,000 tons of gasoline-contaminated soil per tank is removed and transported to a treatment site. The contaminated soil may be cleaned up in four possible ways: thermal treatment, which requires off-site transport of contaminants, is risky as well as expensive; burying in landfill sites is a temporary solution and requires long-term monitoring of the site; physical treatment methods, including washing of the contaminated soil, are considered to be quite expensive; and bioremediation, which uses indigenous or implanted microorganisms to remediate, is lately getting a lot of attention. The last two methods can be effected either on-site or off-site or, better still, *in situ*.

One of the *in situ* extraction methods involves the flushing of contaminated soil with water and/or solvents. This method is fast, requiring considerably less time to remediate than other methods based on biological degradation. It may become the method of choice if remediation costs and the risk of water pollution could somehow be minimized. Enhanced removal of diesel by solvents can result in contamination of the ground water with either those objectionable substances or their metabolites.

Indeed, the environmental engineering professions have not yet developed a reliable, reasonably inexpensive, technology that could be fast for the complete remediation and rehabilitation of contaminated soil. The main objective of this paper was to develop and test an innovative *in situ* soil washing system that could extract contaminants from the soil, quickly and cost-effectively, without causing any threat to water resources. More specifically, the objectives were:

1) To use the proposed two-tier system to “wash” diesel hydrocarbons out from an old diesel-contaminated soil using hexane, a light organic solvent that is immiscible with water,

2) To use the proposed system to “wash” diesel hydrocarbons out from a fresh diesel-contaminated soil, using hexane,

3) To determine the number of flushing cycles required bringing diesel TPH (Total Petroleum Hydrocarbon) levels to less than 40 mg/kg of soil, which is the maximum allowable level in the soils.

MATERIALS AND METHODS

Experimental Setup

Two diesel contaminated soils were used in this study-an old contaminated soil (OCS) which was contaminated by fuel diesel for more than 20 years, and was excavated from a site in Quebec, and a fresh contaminated soil (FCS) simulated by spraying 0.1% diesel on a sand soil. The old contaminated soil had a 98% sand and 2% silt content with a saturated hydraulic conductivity of 3.5 m/day. The fresh contaminated soil had 94.5% sand and 5.5% silt content with a saturated hydraulic conductivity of 2.9 m/day. Both soils were homogenised with an electric driven rotary cement mixer and kept in a closed container for a week. Each soil was then packed into a stainless steel column, 1 m long x 0.2 m diameter, with the bulk density of the soil in the columns simulated to be at field conditions (1,400 kg/m^3). Cast iron perforated pipe, 250 mm long x 12.5 mm diameter, was inserted into each column at a height of 30 mm from the bottom and welded. Each column had soil-sampling ports drilled at 150, 450, and 750 mm depths from the soil surface and an overflow port drilled close to the soil surface in order to collect the contaminated-solvent mixture into a 4-litre bottle as shown in Figure 1. A wide bore syringe was used to collect about 5 g of soil samples from the columns, via the sampling ports. Initial soil samples were collected and stored in amber bottles at 4 ^{o}C for analysis. All the sampling ports were then stoppered with suba recess

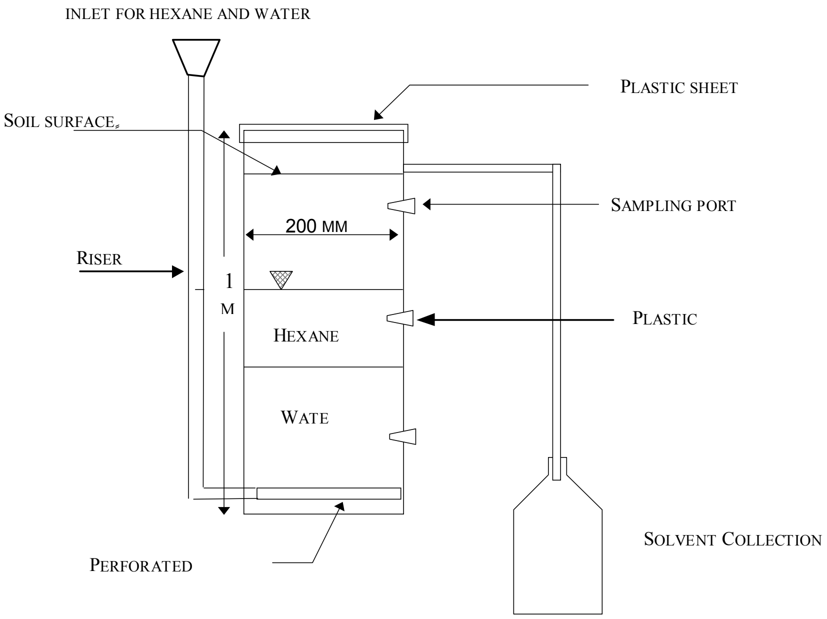


Figure 1. Schema of a soil column.

plastic plugs. The treatment soil columns were covered with plastic to prevent evaporation of hexane/contaminant mixtures from the columns.

The experimental procedures were adopted to simulate the introduction of 2 L of hexane in each column (200 mm hexane front in the column), followed by a slow and steady raising of the front with water. The flow rate of water was 2.5 litres per hour and the front was raised in a stepwise manner over a 4-hour period. The mixture of hexane and contaminants were collected from the soil surface, via the overflow port at the top, and the columns were drained once hexane had come out of the columns. At the completion of each cycle, additional soil samples were collected via the sampling ports once the soil had reached field capacity. The hexane/contaminant mixture was also sampled and analyzed for diesel TPH levels. This process was repeated five times.

Extraction and Analysis

A 3.0 g sample of soil was weighed and 1.5 g of magnesium sulfate was added to it to adsorb the remaining moisture in the soil. Ten mL hexane was added to the mixture and sonicated for 20 minutes. After sonication, 1.5 g of silica gel was added to the mixture and shacked for a further 20 minutes. Then, a sample of the liquid phase of the mixture was taken and filtered through a barrel of a 5-mL syringe with its needle end capped by a 0.2 μm nylon filter. The filtered extract was collected directly into autosampler vials for analysis using a gas chromatography/flame ionization detector. A calibration curve was prepared with a diesel standard supplied by Imperial Oil Company. The standards were spiked on garden soil and extracted and dried; the soil samples were similarly treated before injection.

Gas chromatography of extracts was carried out on a 30 m long DB-5 megabore fused silica column, installed in a GC Varian 3400 model, equipped with an FID detector and an integrator. The flow rate of the carrier gas (helium) was 6 mL/min. The FID air and hydrogen flow rates were 300 and 30

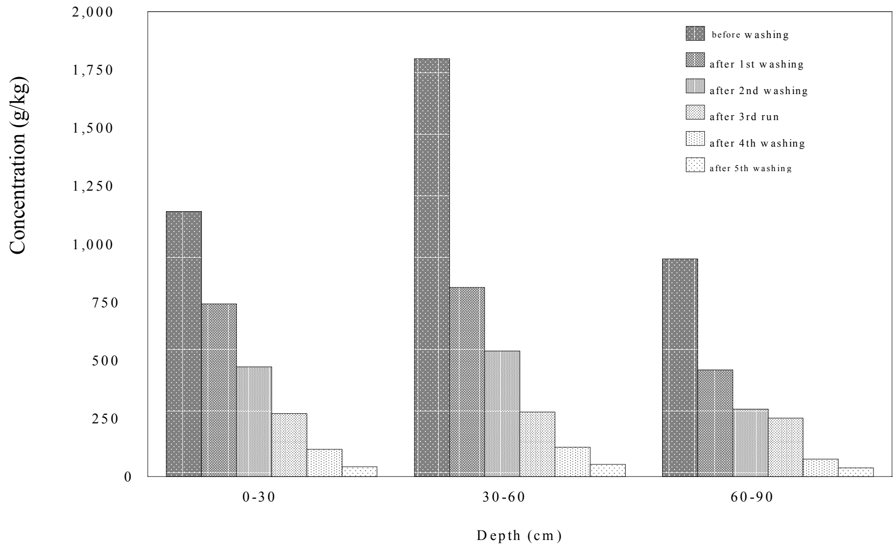


Figure 2. Diesel TPH levels in the freshly contaminated soil.

mL/min, respectively, while that of the make-up gas (nitrogen) was 30 mL/min. The injector and detector temperatures were 280 and 310 °C, respectively. Oven temperature programming was as follows: initial oven temperature at 40 °C with a holding time of 2 minutes, increased at a rate of 10 °C per minute to 270 °C and held for 5 minutes. This was further increased to 300 °C, at a rate of 12 °C per minute and held for 20 minutes (Suros, 1994; Ugwuegbu, 1996). Data acquisition was done on a Varian electronic integrator, using its valley to valley baseline function. Hydrocarbon quantification was effected by an external calibration curve drawn from the total peak heights of a diesel standard.

RESULTS AND DISCUSSION

Hexane solubility of the diesel was measured in the laboratory and estimated to be about 100 g/L. The total mass of diesel in the freshly contaminated soil was 50 g, comprising the mass that was added to the sandy soil to make the freshly contaminated soil. The total mass of diesel in the old contaminated soil was measured and estimated to be about 34 g , and the total volume of hexane, required to dissolve 50 g of diesel, was estimated to be 500 mL (50g/hexane solubility). However, it was decided to apply 2 L of hexane in each column since it was expected that some of the hexane would be volatilized through the system and some would remain in the soil pores. In addition, the recovery rate of diesel from the soil is not 100%. This volume of hexane (2 L) was able to saturate 200 mm tickness of the soil profile in the column because porosity of the soil was about 30%.

The results of soil samples, collected before and after applying the hexane into the soil columns, are given in Figures 2 and 3. These Figures show the diesel TPH level for the freshly contaminated soil and old contaminated soil, respectively. Figure 2 shows that the diesel TPH levels decreased significantly at all the three depths in freshly contaminated soil. The contaminants were being flushed out with this system consistently and effectively, and the diesel TPH levels were reached around 40 µg/g from an initially

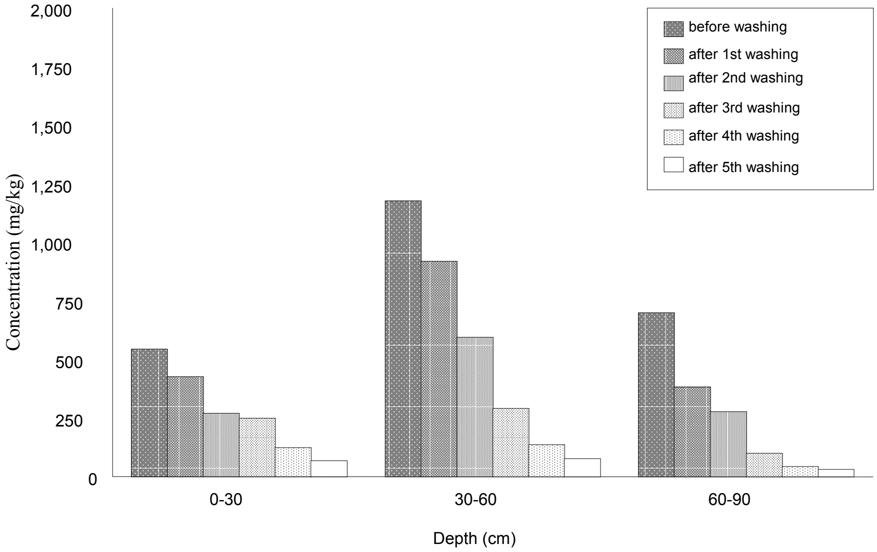


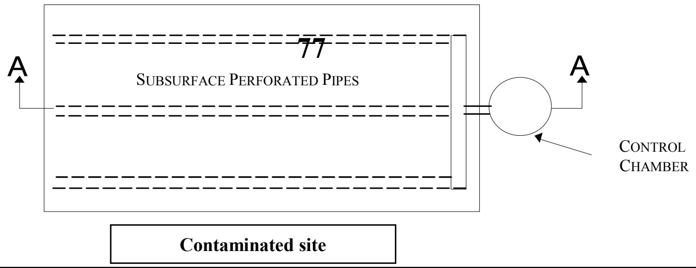
Figure 3. Diesel TPH levels in the old contaminated soil.

high level of 1200 μg/g after five flushing cycles. This means that about 97% of the diesel has been flushed out of the column and only 3% of it has remained in the soil after five flushing cycles. In the old contaminated soil, the results were also promising, but the reduction of the diesel TPH level in the soil samples was not as much as for the freshly contaminated soils. The diesel TPH levels were decreased significantly at all three depths. In five flushing cycles, they were reduced from over 600 μg/g to less than 70 μg/g (Figure 3). This means that about 90% of the diesel has been flushed out of the column and 10 % of it remained in the soil after five flushing cycles. The difference in diesel TPH levels between the cycles determined the rates of the remediation rate of the process. These rates were one-half for the freshly contaminated soil and one-fourth for the old contaminated soil.

The hexane/contaminant mixture was also sampled for diesel TPH levels to ascertain that the contaminants were being flushed out with each cycle. A complete mass balance was carried out for each column (Table 1). The diesel TPH levels in the hexane/contaminant mixtures, obtained from each column and after each cycle, contained very high levels, indicating a fast and effective hydrocarbon removal (see Table 1). The diesel levels in the hexane/contaminant mix-

Table 1. The diesel TPH levels and Mass recovery in hexane/contaminant mixtures.

	Freshly contaminated soil		Old contaminated soil	
Run	Diesel TPH levels (mg/L)	Mass recovery (mg)	Diesel TPH levels (mg/L)	Mass recovery (mg)
1	20,000	14,800	12,000	8,400
2	11,000	12,300	7,500	8,475
3	7,000	9,800	5,000	4,600
4	5,000	5,500	4,500	5,400
5	2,000	3,700	3,000	4,200
Total		46,100		31,075



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tures ran from 2,000 to 20,000 mg/L in the freshly contaminated soil and from 3,000 to 12,000 mg/L in the old contaminated soil. The high efficiency of the system for reducing diesel TPH levels could be explained by the fact that the solvent was introduced from the bottom, which “wet” the soil completely and uniformly and thus removed the contaminant effectively. Moreover, the contact between solvent and contaminants was very good in this system. The recovery or removal masses of diesel are given in Table 1. This Table indicates that the recovery mass tends to reduce from the first cycle to the next cycles. The removal mass from the freshly contaminated column was 14,800 mg in the first cycle. However, it was reduced to 4,700 mg in the fifth cycle. These values in the old contaminated column were 8,400 and 3,800 mg for the first and fifth cycle, respectively.

In this study, hexane was not separated from the contaminants. Therefore, it was not used again in the next cycles. However, it is believed that it can be separated easily and be reused again. The cost of this system for remediation of contaminated soils could be reduced, if an easy way can be found for separating the hexane from contaminants.

It should be noted that the water layer at the bottom acts as a buffer and prevents any downward movement of hexane. The non-solubility of the organic solvent in water is a crucial requirement of this method. It may also be noted that no attempts were made in this initial study to optimise the remediation process. Therefore, this method holds a lot of promise for both fresh and old contaminated sites. Under field conditions, a contaminated site can be isolated with impermeable plastic barriers both on the sides and at the surface. The water table will act as a buffer in the proposed system to prevent downward movement of contaminants. Due to the great solubility of contaminants in organic solvents, the solvent front will act as a sink and will not permit downward leaching (Figure 4).

Economic and Technical Advantages of the Proposed Technique

Although solvent washing method has been tried before, it has not been proven to be very effective due to following reasons: the solvent is applied from the top, therefore solvent flow in the system can not be uniform, and as a consequence contact between the solvent and the contaminants are poor; some of the solvent travels along preferential pathways within the medium which cause low contact between the solvent and contaminants; the soil profile is required to be fully saturated with the solvent that made it very expensive. In our method, we use an underground network of pipes to introduce solvent, and bring it up slowly. This process “wets” the soil more uniformly and water is used to push the solvent front up, thus decreasing the cost of treatment. The risk of further pollution is also minimal due to following reasons: the solvent is immiscible with water and is taken out of the soil profile by rising water, thus the risk of groundwater contamination is minimal; the affinity between hexane and soil is lower than that between water and soil, thus hexane is replaced by water in the soil easily; and since hexane is bio-degradable, the little hexane left in the soil will dissipate or it may be removed quickly by passing air through the soil (the probability of this occurrence is negligible, however).

CONCLUSION

The proposed method is an *in-situ* remediation technique that could remediate a site in a very short time. It can become the method of choice for quick and effective remediation of both old and fresh contaminated sites. Since the application of the solvent and water takes place from the bottom, there is more uniform wetting of the soil and also more uniform contaminant removal. The amount of solvent used in this technique is much less than other solvent washing methods since water is used for the most part to move the solvent up the soil profile. Therefore, it is believed that the method could be very cost-effective, compared to the other remediation methods; the solvent costs can be minimized by finding a way of separating it from the mixture at the end of each run.

There is also minimal threat of groundwater pollution from this method since the solvent selection is done on the basis of its immiscibility in water and density. Since the solvent is lighter than water as well as immiscible, a distinct solvent front is established with the proposed method for faster and effective remediation.

Though this method was proposed to remediate a diesel-contaminated soil, it may be equally suited to other contaminant soils as well. Further work is needed to test the proposed method for other contaminant soils. It is also necessary: to compare this method with the effectiveness of other methods; to test this method on actual sites with heterogeneous contaminates in the soil; to investigate the effect of flow rate or the residence time of the solvent on the removal of diesel from soil; to determine optimal soil:solvent ratios for fast and effective removal of diesel from the soil; and to investigate the effect of raising and lowering the solvent/air mixture on the efficiency of diesel removal from soil.

In this study, the hexane front was raised slowly in the soil columns by letting the water in through the delivery pipes. The rate of water entry into the system will govern the rate of rise of hexane front in the soil; different rates of rise will be required to determine the most effective residence time in the columns. For this purpose, the soil columns should be subjected to a certain fixed rate of rise. Once the soil has been remediated with that rate, new soil can be packed and a different rate of rise can be simulated. A total of three different rates of rise can be simulated. This can be carried out for both old and freshly contaminated soils.

Another set of experiments can be carried out on both soils by simulating fluctuating hexane fronts in the columns. This will cause greater "mixing" of the solvent and the contaminants, and thus may prove to be a more effective strategy than a unidirectional raising of the organic front. It can be done easily in the laboratory as well as in the field.

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یک سیستم شستشوی خاک در محل برای خاکهای آلوده

ع.م. لیاقت و اس. پراشر

چکیده

افزایش در تولید و مصرف سوختهای فسیلی احتمال آلودگی منابع خاک بوسیله مواد نفتی و روغنی را افزایش داده است و باعث بروز خطر برای انسان شده است. بیش از ٤۳۰۰۰ محل آلوده در کانادا و آمریکا وجود دارد که از بین آنها ۲۲۰۰ محل بعنوان خطر جدی طبقه‌بندی شده‌اند (اسمیت ۱۹۹۱). در آمریکا، بیش از ۱۰ میلیون دلار سالانه برای تمیز کردن محلهای آلوده صرف می‌شود (بردهوفت ۱۹۹٤) هدف اولیه این تحقیق این بود که یک سیستم جدید شستشو در محل، که بتواند آلودگیهای خاک را به طور سریع و موثر و بدون هیچ خطری برای منابع آب جدا سازد، توسعه دهیم. در این سیستم از یک حلال آلی استفاده شد که نه تنها سبک‌تر از آب بود بلکه با آب نیز مخلوط نمی‌شد. این حلال از پایین ستون خاک از طریق سیستم لوله‌های افقی سوراخ‌دار زیرزمینی به داخل خاک وارد و در سطح خاک جمع‌آوری شد. این حلال چون از پایین به داخل خاک وارد می‌شد خاک را به طور کامل اشباع و آلودگی خاک را بطور موثری درخود حل می‌کرد. برای شناخت و ارزیابی کار این سیستم، یک آزمایش مقدماتی متشکل از ۲ ستون فلزی از جنس استیل (به ابعاد ۱ متر طول و ۰/۲ متر قطر) که با دو نوع خاک آلوده به مواد نفتی (آلودگی جدی و آلودگی قدیم) پر شده بودند تشکیل شد. این تکنیک جدید، بی‌نظر و خیلی سریع می‌باشد و اولین مطالعه در نوع خودش می‌باشد که از یک سیستم آبیاری زیرزمینی برای وارد کردن مواد حلال آلی به داخل خاک و شستشوی خاک در محل استفاده می‌نماید. کاربرد اولیه این سیستم در مورد خاکهای ماسه‌ای آلوده به مواد نفتی موفقیت این سیستم را برای هر دو نوع خاک آلوده (جدید و قدیم) ثابت کرده است. این سیستم می‌تواند برای رفع آلودگیهای دیگر نیز موثر باشد.

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