

Bioventing of Gasoline-Contaminated Soil: Some Aspects for Optimization.

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ABSTRACT

Underground storage tank leakage is a concern in North America because gasoline contaminated soil can cause significant groundwater contamination. São Paulo (Brazil) has leakage rates similar to North America. The typical in-situ remediation process is soil vapour extraction (SVE), but experience shows that tailing usually occurs. Bioventing is an innovative technology to address tailing in the remediation of contaminated sites, where natural occurring hydrocarbon degrading microorganisms are stimulated. The drawback is the prediction of time needed for bioventing to reach site closure. Encouraging laboratory results have not always translated into similar outcomes in the field. One reason for this inconsistency is the scale-dependent phenomenon that influences the process. Research is being conducted to develop correlations that incorporate a variety of factors including soil type, contaminant composition, and nutrient composition. These correlations will assist in better predicting the necessary time to reach site closure.

INTRODUCTION

Gasoline contaminated soils are one example of hazardous waste requiring extensive cleanup around the world. The typical in situ remediation technology used to remediate gasoline-contaminated soil is soil vapor extraction (SVE), but once tailing occurs, where the residual gasoline levels still exceed cleanup levels, SVE is ineffective (1; 2). Bioventing is a source control treatment that has emerged as one of the most cost-effective in situ technologies currently available to address this issue of tailing in the remediation of gasoline contaminated sites. The operation and maintenance duration for bioventing varies from a few months to years, depending on specific site conditions (3). Sub-optimal operation of bioventing translates into higher residual concentrations in the soil and longer cleanup times and consequently higher costs. Improving an understanding of bioventing will result in better performance, lower costs, and better prediction time for reaching site closure.

The main objective of this research is to develop correlations that can be used to predict the effectiveness of bioventing under different conditions. This will improve soil conditions, thus helping to protect human health and the environment. The scenario involves gasoline and gasohol contaminated sites where soil vapor extraction (SVE) was initially applied to remove the bulk of the contaminant. This paper begins with a brief review of the literature followed by a description of the laboratory experiments being conducted to collect the data and a discussion of the relevant factors that should be considered in the development of correlations.

OVERVIEW

Gasoline contaminated soil has been identified as one of the largest potential risks to water quality as the various gasoline phases (free product, dissolved and sorbed) act as feedstock for groundwater contamination (4). Also, the hydrocarbon vapour phase poses an explosion threat in subsurface buildings (basements) or other structures. One source of gasoline contamination comes from gasoline underground storage tank (UST) leakage. This is a big concern in Canada and the United States as about 35% of UST systems are leaking (5). Some of these are minor, while others require large remediation projects. This threat is not confined to North America as locations like São Paulo (Brazil) have leakage in approximately 25% of their USTs (6).

It is important to remember that avoiding the problem in the first place is far better than cleaning it up after a spill has occurred. Attempts to avoid leakage and/or to better monitor the potential leakages are always the best action in such a situation. The primary goal has to be the reduction of contamination sources.

All remediation technologies for contaminated sites have their limitations. As a result, the use of a combination approach to integrate different processes, has received increasing attention because it enhances the final performance or increases the speed of treatment to achieve site closure. This has been named “bundled technologies” or “treatment trains” (1, 7).

Soil vapor extraction (SVE) is the common approach for remediation of gasoline-contaminated sites. Under SVE a vacuum is applied to the soil to induce the flow of air and remove volatile and semi-volatile organic contaminants from the soil. Off-gas treatment is required. The contaminant level left in the soil typically does not reach the closure criteria because of tailing due to mass transfer limitations (8; 9). Bioventing is a technology whereby indigenous microorganisms present in the soil degrade the

contaminant once sufficient oxygen, nutrients and moisture are supplied to stimulate the microorganisms. The degraded hydrocarbons are then converted into less harmful compounds. Due to the theoretically simple process of converting from SVE, bioventing is getting increased attention as a cost-effective bioremediation process to attain clean-up goals. The main objective of this conversion is the optimization of biodegradation while minimizing volatilization. There is evidence that bioventing can effectively mitigate several limitations of traditional SVE systems (8). In the USA, bioventing has been approved in 38 states and in all 10 Environmental Protection Agency (EPA) regions (10; 11).

Research has been undertaken in the School of Engineering, University of Guelph, ON, Canada, since 1996 to evaluate the optimum conditions for achieving site closure standards when working with a treatment train: soil vapor extraction followed by bioventing (12; 13; 14; 15 and 16). Respirometers were constructed to measure soil microbial respiration and biodegradation for *m*-xylene, diesel fuel, and gasoline contaminated soil. The experiments with *m*-xylene contaminated soil (silt loam) demonstrated that the microbial population was stimulated by the increase in the contaminant concentration. However, above 1000 mg/kg of *m*-xylene in the soil the microbial activity decreased compared to lower concentrations (12). The experiments with diesel fuel contaminated soil (silt clay) demonstrated that temperature has a positive influence on the degradation rates. The rates increased with increasing temperature between the study range of 2°C to 25°C. Oxygen levels up to 21% were analyzed and they affected the degradation rates in a similar way as temperature.

Equation 1 was developed to integrate the degradation rate constants based on a combination of a Monod type expression to account for O₂ dependencies and a modified form of van't Hoff-Arrhenius relationship to account for the temperature dependencies (13; 14, and 17).

$$k = k_{\max} \left(\frac{O_2}{K_{O_2} + O_2} \right) \theta^{T-T^*} \quad (1)$$

where k = first order rate constant (1/d); k_{\max} = maximum first order constant at T^* (1/d); O_2 = oxygen content in soil (v%); K_{O_2} = oxygen content at $(1/2)k_{\max}$ (v%); θ = temperature correction coefficient; T = temperature (°C); and T^* = reference temperature 0°C.

Using SYSTAT (18) and all the first order rate constants determined in the laboratory, with k_{\max} , K_{O_2} , and θ as variables, Equation 2 was developed to include temperature and O₂.

$$k = 0.0040 \left(\frac{O_2}{0.347 + O_2} \right) (1.051)^T \quad r^2 = 0.918 \quad (2)$$

Equation 2 was successful in capturing the overall trend in the data and does fit the data with an acceptable r-squared value (17). In addition, the decay rates also compared favorably to field data that was measured as part of the study.

A subsequent study on nutrient form/composition showed that for the carbon-to-nitrogen (C:N) ratios tested on diesel fuel contaminated soil (silt clay), the hydrocarbon degradation rates were the highest for the ammonium sulfate (20:1 at 0.032d⁻¹; 40:1 at 0.019d⁻¹) and urea treatments (20:1 at 0.025d⁻¹; 40:1 at 0.011d⁻¹) (19). Correlating the results produced Equation 3.

$$k = 0.032[NH_3] - 0.003[NO_3^-] + 0.004 \quad r^2 = 0.80 \quad (3)$$

where k = TPH degradation rate (1/d); NH_3 = ammonia concentration in soil (mg/g); and NO_3^- = nitrate concentration in soil (mg/g)

Equation 3 shows that the degradation rate is a function of nitrate and ammonia concentrations. The correlation suggests the occurrence of nitrate inhibition at elevated nitrate concentrations.

Other completed laboratory tests with gasoline contaminated soil (sand loam), showed that the optimum soil water content was found to be 18%wt, or approximately 50% of the soil's field capacity. For this soil, the biodegradation rate was severely limited by nitrogen deficiency. It was found that the optimum form of nitrogen for enhanced biodegradation was ammonium under a C:N ratio of 10:1. This study also showed that fungi did not contribute significantly to biodegradation under the completed experiments (20).

Many other universities have research groups working on the development of kinetic models to predict bioremediation. Examples include studies on the substrate inhibition kinetics for toluene and benzene degrading pure cultures. In that case, the results show that three cultures degraded toluene following a pattern consistent with the kinetic model of "Wayman and Tseng" while the other two followed a modification of this model. The pattern followed by benzene degradation was, for all four capable pure cultures, consistent with that described by the model of Luong (21). Monod's equation has also been used to describe the biodegradation rate in other research and Henry's law constants have been used to describe the partitioning of a volatile substrate between the gas and liquid phases. Thus far, attempts have been made to model bioremediation but their efficiency is still limited.

The literature reports the dependence between the microorganism's kinetic parameters and the concentration and type of the substrate under different bioremediation projects. This is an important area that needs to be addressed in any correlation being developed, but this is strongly affected by the variability in site conditions. An important factor to also be considered is scale-up as the literature shows limited success in translating lab results to the field. Doing so will help to determine the optimized operating conditions that need to be induced at a bioventing site to attain the clean up criteria and permit site closure.

METHODOLOGY

In order to develop the required correlations between site conditions and bioventing performance, data from previous studies are being reviewed and supplemented with additional data as needed. The additional experiments include the following:

- Correlation of three types of soil with bioventing performance at the laboratory scale.
- Correlation of two distinct gasoline compositions with bioventing performance at laboratory scale.
- Correlation of two types of nutrients with bioventing performance at laboratory scale.
- Evaluation of bioventing performance tests from three different laboratory scales, i.e., formulation of scale-up factors as shown in Table 1.

The soil being used in the additional tests consists of clean soil with 18% of water content by weight and spiked with the contaminant formulated in the laboratory (Table 2) to reach 2g of contaminant per kg of soil. The sample is aged for 45 days. After this period a nutrient source is added to reach a ratio of C:N of 10:1, assuming the carbon content is the contaminant concentration. Two nutrient sources are used for nitrogen: ammonium chloride (NH_4Cl) and anhydrous ammonia (AA).

The respirometers, micro-scale reactors, were developed with the objective of having an ideal system to mimic field conditions (12). The reactors have since been modified and optimized (13; 14; 15 and 16) with the most recent change allowing for a larger number of experiments to be performed. These respirometers take soil samples instead of slurry, which produces a more realistic result when translated into the field. The respirometer apparatus consists of 1 liter glass respirometers equipped with pressure measurement devices. The respirometers are used to determine oxygen consumption and carbon dioxide production by aerobic microorganisms in contaminated soil samples. The carbon dioxide evolved by microbial respiration is trapped in a potassium hydroxide (KOH) solution, and oxygen consumption is measured using the overall pressure decrease within the reactor. Sampling techniques allow the measurement of the different microbial populations to determine their response to the treatment.

For the first step of the soil reactor tests, the meso-scale reactors were devised and constructed, to allow for approximately 4kg of contaminated soil to be tested in each reactor (16). The reactor consists of a plastic bucket with multiple perforations on the sides. A vacuum pump induces a negative pressure in the reactors, allowing for atmospheric air to be drawn in towards a slotted extraction well (1/4" polytetrafluoroethylene tubing) in the centre. Stainless steel needle valves, union elbows, tees and crosses are used for the manifold assembly, in conjunction with the PTFE tubing. Four soil sampling ports are located on top of each reactor, in order to obtain soil core samples from varied locations in the reactor. A soil coring tool is utilized to extract soil from the reactors. Sampling techniques similar to that for the microscale reactors is also used.

For the second step of the soil reactor tests, the macro-scale experimental apparatus is being devised and constructed by T. Patros, a M.Sc. student. This reactor consists of a perforated cylindrical stainless steel vessel (diameter = 40cm, height = 40cm) that holds approximately 90 kg of soil. The top and bottom are sealed to induce radial flow, typically what happens in the field. The well in the center of the reactor is about 3cm in diameter with a sealed bottom and its head is connected to a vacuum pump to induce low airflow. Temperature sensors are connected to the reactor in order to monitor the temperature continuously to correct the decay rate for temperature changes. Also, moisture sensors are connected to the reactor to monitor the moisture level in order to add water continuously to keep it constant.

RESULTS

Ideally when all the data is compiled a correlation will be found that relates decay rates, various factors that are discussed below and obviously scale effects. Based on the experimental data available so far and based on literature readings, factors to be considered include gasoline composition, soil type and nutrient form/concentration.

Effects of Gasoline Composition on Bioventing

Gasoline is a complex mixture of hundreds of compounds, some of which are more amenable to volatilization than to dissolution, and vice versa. Also, other components within gasoline are not particularly prone to either and tend to persist in the subsurface (22). The age of contamination will also

have a significant impact on SVE and bioventing removal efficiency because increased residence time translates into decreasing contaminant accessibility (23). In addition, some countries like Brazil promote the addition of ethanol to the gasoline which changes how gasoline behaves in the soil. The Brazilian gasoline contains up to 25% of ethanol and is referred to as gasohol. Currently the fate mechanisms regarding the partition between ethanol from gasoline in the vadose zone is not fully understood (24; 25). The presence of ethanol in gasoline has a significant impact on the infiltration of gasoline through the vadose zone as ethanol and water are infinitely miscible (26, 27). The ethanol partitions from the gasohol into residual water and this phenomenon retards the migration (26). Biodegradation was not evaluated in their research, which is consistent with the lack of information in the literature regarding the performance of bioventing under gasohol-contaminated site.

Effects of Soil on Bioventing

Soils are a complex system formed by a heterogeneous mixture of diversity types, particle size distribution, porosity, permeability, water content, and soil organic matter. These factors do not function in isolation when influencing the biodegradation of gasoline in the soil. In addition, the soil characteristics vary with depth. Soil structural characteristics also vary temporally and changes can occur at scales ranging from hours to decades (28, 29). Soil heterogeneity strongly influences the evaluation of bioventing scale-up factors.

Initially the parameter analyzed was particle size distribution because this influences the flux of water and solubles. This characteristic also helps to determine the availability of oxygen to promote aeration. Another important soil characteristic is soil organic matter as it can provide the home for the microorganisms and it also affects the total porosity. In addition when looking at other biological models, the form of treatment may also be considered. For example, for an attached growth model, the surface area in the soil should also be considered. The smaller the particles, the greater will be the surface area provided for gasoline adsorption on soil particles. This is especially evident with clay in which many binding sites are provided (28). Soil pH and cation exchange capacity affect the gasoline sorption on soil particles and is also an important aspect to be accounted for. Other soil factors will be considered as the research evolves.

Effects of Nutrient Addition and Microorganisms on Bioventing

In using a process in environmental biotechnology like bioventing, there must be sufficient nutrients and electron acceptors in the soil to support biomass growth and energy generation (30). Various authors state that nitrogen and phosphorus are the most important ones. The ratio of C:N:P that have been published have discrepancies between them and it is difficult to extract an average value. It is a challenge to define the right amount and type of nutrient, and how to apply the nutrients to the site. For example, is it better to dissolve the nutrients in water and trickle the solution into the subsurface, or should any gaseous form be injected into the subsurface (31). Anhydrous ammonia was found to be a good nutrient source for soil microorganisms. In its gaseous form, it has the added benefit of being more easily distributed in the soil matrix, provided adequate moisture is present (16; 31).

Directly related to the nutrient level is the microbial population. Due to the sampling protocols developed, sufficient detail on type of microorganism population will be available. How this influences the transportability of results will also be reviewed.

Correlation

Table 3 gives the data matrix available thus far. Using SYSTAT (18) to explore the best fit of the degradation rate obtained from the laboratory tests, Equation 4 was developed.

$$k_{predicted} = 0.0113 \times SAND - 0.0083 \times SILT - 0.0095 \times CLAY - 0.0036 \times N_{AA} + 0.0036 \times N_{NH_4Cl} - 0.83124$$

(4)

Review of Equation 4 shows that sand content in the soil has a positive influence on the degradation rate but silt and clay have a negative impact. This trend agrees with the literature because the higher the sand content is in the soil the greater the porosity and consequently the aeration in the soil. High aeration in the soil helps to provide the microorganisms with enough oxygen to metabolize the contaminant. Of the two nutrients studied the ammonium chloride (NH_4Cl) has a positive influence on the degradation rate. Anhydrous ammonia is still being studied because, in its gaseous form, it makes the nutrient addition into the site easier. This is because the same pipes used to provide oxygen to the soil can be used to inject the nutrient in its gaseous form. More studies are under investigation related to this last aspect.

Even though Figure 1 shows that the correlation is reasonable, there is insufficient detail available to transport the data from condition to condition. More parameters have to be included as independent variables in order to get a more realistic trend. Particle size distribution and nutrient addition influence the rates but also the organic carbon content effects have to be investigated in association with other parameters such as cation exchange capacity and superficial area. These last parameters will affect the way the contaminant is absorbed on the soil particle as well as the way the microorganisms attach on the soil particle to form biofilms. This is because the contaminant must be both susceptible and readily available for biological attack. More tests are being done in order to collect a complete set of data and develop more correlations. Hopefully the final correlations will represent the effect of gasoline composition, soil type, organic carbon content, CEC, surface area and nutrient addition on the biodegradation rate.

CONCLUSIONS

Bioventing has a number of benefits that make it an attractive option for site remediation. However, at present, bioventing actions are based on many assumptions and often incorrect decisions are made, preventing the closure of the site and requiring the client to spend more funds.

More laboratory studies are being done to build an extended database of soils and operating conditions in order to determine the correlations between soil types, contaminant composition and scales. Using the correlations, attempts will be made to use the available data to determine scale-up factors between laboratory experiments and field operations.

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Table 1: Experiment set-up

Micro-scale			Meso-scale			Macro-scale		
Respirometer			Small reactor			Large reactor		
Volume: 1 liter			Volume: 4 liters			Volume: 66.7 liters		
Soil sample: 0.15 kg			Soil sample: 3.5 kg			Soil sample: 94 kg		
Soil A	Soil B	Soil C	Soil A	Soil B	Soil C	Soil A	Soil B	Soil C
Sandy	Silt	Clay	Sandy	Silt	Clay	Sandy	Silt	Clay

Table 2. Simplified gasoline composition

Compound	Percentage (%)
Naphthalene	3.2
Mesitylene	11.9
m-Xylene	23.9
Isooctane	24.9
Toluene	36.1

Table 3. Parameters for preliminary correlations

	Particle Size Distribution (%)			Nutrient*		k (1/d)
	Sand	Silt	Clay	AA	NH ₄ Cl	
Case 1 (Shewfelt, 2002)	90.6	7.4	2.0	0	1	0.12
Case 2 (Hallman, 2003)	87.9	7.6	4.4	0	1	0.027
Case 3 (Hallman, 2003)	86.5	9.4	4.1	1	0	0.021
Case 4	87.7	7.8	4.5	0	1	0.063
Case 5	87.7	7.8	4.5	1	0	0.078

* 0 = that form of nutrient is not added and 1 = that form of nutrient is added, both C:N as 10:1

AA = anhydrous ammonia

NH₄Cl = ammonium chloride

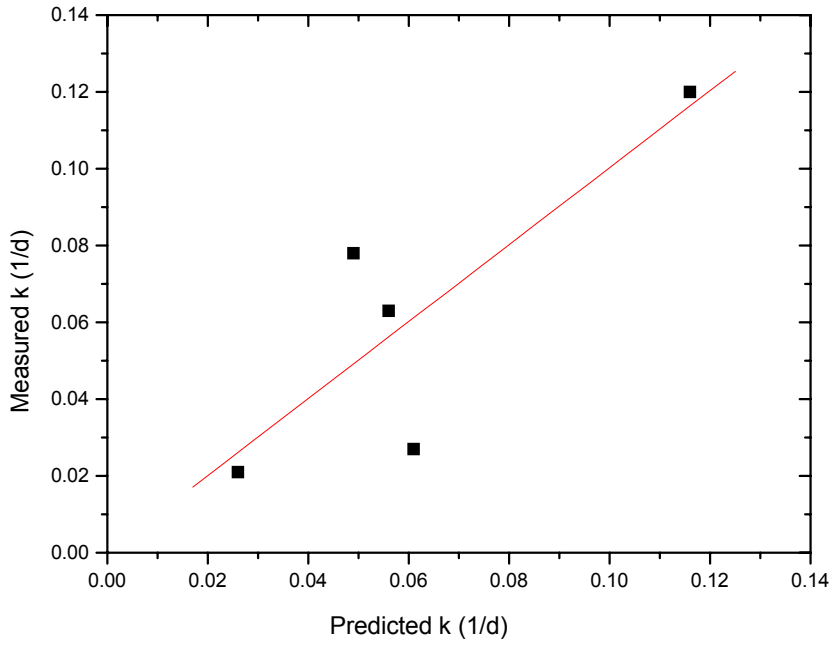


Figure 1. Predicted k