Removal of petroleum hydrocarbons from the vadose zone during multi-phase extraction at a contaminated industrial site

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Abstract Field trials of multi-phase extraction techniques evaluated the contribution of volatilization and biodegradation to removing petroleum hydrocarbons from a contaminated industrial site. The techniques combined the extraction of soil vapours with the recovery of mobilized non-aqueous phase liquid (NAPL) from wells. Inducing air-flushing of the vadose zone by applying a vacuum to the recovery well promoted both the recovery of mobile NAPL near the water table as well as the volatilization and biodegradation of petroleum hydrocarbons in the vadose zone. Biodegradation and volatilization in the vadose zone were the major processes of removal under high water table conditions where liquid recovery rates were modest. In this case, biodegradation contributed most to removal. Where liquid recovery rates were increased under lowered water table conditions, volatilization and biodegradation still contributed 46% of the total removal rate.

Key words: biodegradation; bioslurping; bioventing; multi-phase extraction; NAPL; oxygen utilization; petroleum hydrocarbons; soil vapour extraction; vacuum-enhanced recovery; volatilization

INTRODUCTION AND BACKGROUND INFORMATION

Multi-phase extraction of non-aqueous phase liquid (NAPL) petroleum hydrocarbons from contaminated aquifers generally focuses on the removal of the liquid phase from recovery wells. While the suction applied to the air phase in the vadose zone is primarily to create hydraulic gradients that enhance liquid flow to a recovery well, it also adds bioventing to the overall removal strategy. The induced air flow through the vadose zone provides oxygen for aerobic biodegradation and volatilized hydrocarbons from the NAPL are extracted by the air stream. The removal rates of a weathered gasoline/kerosene NAPL by these two mechanisms were quantified during multi-phase extraction at an industrial site near Perth, Western Australia.

Johnston et al. (1998) described the general geomorphology, stratigraphy and climate of the area. The water table at the study site varied between 3.1 and 2.6 m below ground during the experiment, in response to rainfall. Aquifer materials were generally fine-sand sized, calcareous sands with coarser layers, notably in the vicinity of the water table. The top one metre of the profile consisted of sand fill. Between 1.5 and 2.5 m, dry bulk density was generally 1.3–1.4 Mg m⁻³ (porosity ~0.5) while dry bulk densities were around 1.2 Mg m⁻³ (porosity ~0.55) at 2.5–4.0 m below ground.
In May 2000 before the start of NAPL recovery and soil vapour extraction, low levels of NAPL petroleum hydrocarbons existed through most of the vadose zone below 1.5 m (\(\sim 3000 \text{ mg kg}^{-1}\) between 1.5 and 2.2 m) with high levels encountered in a sharp peak at 3.0 m in the capillary fringe (Fig. 1). The peak in the NAPL contents moved with varying water table elevations and was observed as high as 2.7 m on 18 July (Fig. 1). Residual NAPL was observed below the water table.

From June to August 2000, NAPL was recovered from a screened well using a variety of techniques that included soil vapour extraction from the NAPL recovery well as part of the testing of multi-phase extraction. Results from two different techniques are presented here—partial vacuum applied to the well casing during recovery of the NAPL (vacuum-enhanced recovery), and combined recovery of air, NAPL and water (bioslurping)—although the vacuum-enhanced recovery was also tested with water table drawdown. Concentrations of petroleum hydrocarbons and major gases in extracted air along with changes in the mass and composition of the NAPL in the aquifer were monitored throughout the trial. Petroleum hydrocarbon concentrations were determined using gas chromatography–mass spectrometry from the abundance of selected ions normalized with an internal standard. Major gases were determined by gas chromatography using a thermal conductivity sensor. Production of CO\(_2\) was used to quantify biodegradation rates. *In situ* measurements of O\(_2\) concentration (Davis *et al.*, 1998) in the aquifer were used to determine oxygen utilization and by inference, biodegradation of NAPL (Davis *et al.*, 1995). Air-filled porosities were monitored with a neutron soil water probe. Removal of petroleum hydrocarbons through volatilization and biodegradation were compared to the rate of recovery of liquid hydrocarbons. In the cases presented here, liquid recovery rates alone were
27 kg day\(^{-1}\) for bioslurping, 31 kg day\(^{-1}\) for vacuum-enhanced recovery and 96 kg day\(^{-1}\) for vacuum-enhanced recovery with water table drawdown. High water table conditions limited the recovery of liquid hydrocarbons.

**AIR FLUXES AND PRESSURES DURING SOIL VAPOUR EXTRACTION**

Air pressures of \(-4\) kPa was applied at the recovery well in the case of vacuum-enhanced recovery while the air pressure in the recovery well for bioslurping varied from \(-1.2\) to \(-1.8\) kPa. An example of the resultant distribution of air pressure in the vadose zone is shown in Fig. 2. Vertical gradients near the recovery well were a result of the top of the screen being located 2.6 m below ground. The flux of air decreased from 15 to 11 l s\(^{-1}\) (measured by an in-line, variable-area gas flow meter) over the period of the first application of vacuum-enhanced recovery. Fluxes during bioslurping were lower and remained around 9.2 l s\(^{-1}\).

![Fig. 2 Air pressure, \(P_a\), in the vadose zone at different depths and distances, \(x\), from the recovery well for the period 28 June to 5 July during vacuum-enhanced recovery.](image)

**REMOVAL OF NAPL BY VOLATILIZATION**

Estimates of the mass of petroleum hydrocarbons removed in the extracted air during the two seven-day periods of vacuum-enhanced recovery are presented in Table 1. Similar estimates were not attempted for bioslurping. A total of around 450 kg of petroleum hydrocarbons were removed from the vadose zone by the extracted soil vapour during these two periods. Average rates of removal were 37 and 31 kg day\(^{-1}\) for the two periods. Table 1 also shows the dominance of benzene and isomers of trimethylbenzene in the aromatic fraction of the volatilized hydrocarbons. In all but the case of m,p-xylene, smaller masses were extracted in the second period. Changes in the relative proportions (e.g. m,p-xylene and ethylbenzene) indicate a change in composition of the NAPL. The smaller proportion of the measured aromatics relative to TPH in the second period also points to preferential removal of these compounds.
Table 1: Estimated mass of petroleum hydrocarbons in the air extracted from the NAPL recovery well during the two periods of vacuum-enhanced recovery.

<table>
<thead>
<tr>
<th>Compound</th>
<th>28 June–5 July 2000 Mass (kg)</th>
<th>1 August–8 August 2000 Mass (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,3-trimethylbenzene</td>
<td>0.50</td>
<td>0.37</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>2.2</td>
<td>0.94</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>0.34</td>
<td>0.31</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.60</td>
<td>0.59</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.49</td>
<td>0.16</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>0.23</td>
<td>0.33</td>
</tr>
<tr>
<td>o-xylene</td>
<td>0.024</td>
<td>0.015</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.010</td>
<td>0.004</td>
</tr>
<tr>
<td>TPH</td>
<td>247</td>
<td>209</td>
</tr>
</tbody>
</table>

AEROBIC BIODEGRADATION OF NAPL

Aerobic biodegradation of the NAPL in the vadose zone under static conditions was indicated by low (1–7% vol.) $O_2$ concentrations and high (17–26% vol.) $CO_2$ concentrations. By comparison, during periods that air was being extracted, $O_2$ concentrations increased to as much as 18% by volume in the NAPL-contaminated vadose zone. Estimates of $O_2$ utilization rates were obtained at times that aeration ceased using in situ oxygen sensors at depths of 2.0 and 2.25 m at distances of 1 and 3 m from the recovery well. An example of these data is shown in Fig. 3.

Most data show first-order $O_2$ utilization (Fig. 3) especially at lower concentrations. Fitted first-order rate coefficients were used to estimate $O_2$ utilization rates at the $O_2$ concentration at the time aeration ceased. $O_2$ utilization rates were used to calculate equivalent hexane (model hydrocarbon) biodegradation rates (Davis et al., 1998).

Biodegradation rates were variable, generally between 40 and 140 mg kg$^{-1}$ day$^{-1}$ and had a mean value of 95 mg kg$^{-1}$ day$^{-1}$. There were no conclusive trends in biodegradation rate over time nor was there any evidence of dependence on initial $O_2$...

![Fig. 3 Time series of $O_2$ concentration in soil gas, $C_{O_2}$, at 2.0 m and 2.25 m below ground, 1 m from the recovery well.](image-url)
Removal of petroleum hydrocarbons from the vadose zone

concentration. This mean biodegradation rate gives an estimate for the areal degradation rate for a 2.8-m deep vadose zone of the order 0.35 kg m$^{-2}$ day$^{-1}$. The degradation rate of the petroleum hydrocarbons can also be estimated from the volume of CO$_2$ extracted from the vadose zone. Again using hexane as the model hydrocarbon, the stoichiometry of the reaction for complete mineralization:

$$C_6H_{14} + 9.5O_2 \rightarrow 6CO_2 + 7H_2O$$

(1)

dictates that 1 mole of hexane would produce 6 moles of CO$_2$ (Hinchee & Ong, 1992). From this, measured average CO$_2$ flux rates gave estimates of 62 and 50 kg day$^{-1}$ for hexane mineralization rates for the two periods of vacuum-enhanced recovery. These average rates excluded the first 24 h of air extraction to avoid inclusion of resident soil vapour with CO$_2$ produced before aeration of the vadose zone, and any flux of CO$_2$ from its partitioning between the soil water and air under conditions of changed partial pressures. Degradation rates would be expected to be greater than the mineralization rates which do not include incorporation of carbon into the soil biomass. Hinchee & Ong (1992) for instance, suggested that 25% of the carbon goes into biomass during degradation. CO$_2$ production has other limitations as a means of estimating mineralization rates of petroleum hydrocarbons. Involvement of the CO$_2$ in the carbonate chemistry of the soil materials and soil water cause it to be non-conservative. Evolution of CO$_2$ as the soil water equilibrates to lower partial pressures should be shorter lived that that seen for air sparging (Johnston et al., 1998) which has a much lower air:water ratio, and should have been confined to the initial 24 h excluded from analysis. However, Hinchee & Ong (1992) concluded that conversion of CO$_2$ to carbonate in alkaline soils also leads to underestimates of biodegradation rates as does incomplete mineralization of the compounds. While any unquantified production of CO$_2$ from the degradation of other carbon sources, such as soil organic matter, will cause petroleum hydrocarbon mineralization rates to be overestimated, this will also be the case for O$_2$ utilization.

Despite these inherent limitations, degradation rates from the production of CO$_2$ are in accord with estimates from O$_2$ utilization. The rates from CO$_2$ production are equivalent to O$_2$ utilization over an area of at least 160 m$^2$, or a radius of at least 7 m from the recovery well. This appears reasonable given the lateral distribution of air pressures in the vadose zone (Fig. 2).

COMPOSITIONAL CHANGES SHOWING EXTENT OF BIODEGRADATION

The total ion current (TIC) gas chromatograms obtained from the soluble organic material extracted from cores revealed a decreasingly biodegraded signature with increasing depth, to a depth of 2.5 m. Typical features of this signature were the predominance of an unresolved complex mixture of hydrocarbons, manifested as a hump in the chromatogram, and the depletion of $n$-alkanes relative to other alkanes. Aromatic hydrocarbons, in particular alkynaphthalenes, have been shown to display differences in their susceptibilities to biodegradation (Volkman et al., 1984). Furthermore, marked differences in the susceptibility/resistance between isomers of polymethynaphthalenes have been observed and used to assess the extent of
biodegradation of petroleum (Fisher et al., 1998). Therefore, changes in the composition of petroleum hydrocarbons in the residual NAPL due to biodegradation may be differentiated from those caused by evaporation during the period of vacuum-enhanced recovery, because of the similar volatility of aromatic hydrocarbon isomers.

Differences in the extent of biodegradation exhibited by the residual hydrocarbons in each of the cores are apparent in the change in concentration of 2-methylnaphthalene (2-MN) relative to 1-methylnaphthalene (1-MN) with depth, as shown in Fig. 4. Prior to the start of the recovery trial (3 May 2000), there was no apparent depletion in the concentration of 2-MN relative to 1-MN throughout the core, suggesting that the extent of biodegradation, inferred from changes in the TIC chromatograms, was minor (Fisher et al., 1998; Peters & Moldowan, 1993). After completion of the first period of vacuum-enhanced recovery (18 July 2000), the residual petroleum in the upper portion of the core (shallower than approximately 2.25 m) is depleted in 2-MN. This depletion of the isomer relatively susceptible to biodegradation is accentuated in the petroleum extracted from soil sampled approximately one month later (23 August 2000) following further aeration of the vadose zone. Furthermore, hydrocarbon biodegradation is evident approximately 0.1 m deeper in the soil profile than observed in the previous core, as a result of the aeration during localized water table drawdown.

![Graph showing the distribution of the ratio of the gravimetric contents of 2-methylnaphthalene and 1-methylnaphthalene with depth in cores taken before (3 May) and after (18 July) the first period of vacuum-enhanced recovery, and after the subsequent period of bioslurping and vacuum-enhanced recovery accompanied by water table drawdown (23 August).](image-url)

Fig. 4 Distribution of the ratio of the gravimetric contents of 2-methylnaphthalene and 1-methylnaphthalene with depth in cores taken before (3 May) and after (18 July) the first period of vacuum-enhanced recovery, and after the subsequent period of bioslurping and vacuum-enhanced recovery accompanied by water table drawdown (23 August).
SUMMARY AND CONCLUSIONS

Soil vapour extraction during multi-phase extraction of a gasoline/kerosene NAPL greatly enhanced the removal of petroleum hydrocarbons from the aquifer studied. Under high water table conditions where the recovery of liquid hydrocarbons was modest (31 kg day\(^{-1}\)) with vacuum-enhanced recovery, volatilization (37 kg day\(^{-1}\)) and biodegradation (62 kg day\(^{-1}\)) were the dominant mechanisms for removal of petroleum hydrocarbons. Lowered water tables during drawdown increased the liquid recovery rate (96 kg day\(^{-1}\)) while volatilization (31 kg day\(^{-1}\)) and biodegradation (50 kg day\(^{-1}\)) still accounted for 46% of the total removal. Similar results were seen for bioslurping although removal through volatilization was not quantified.

Measurements of biodegradation rates using \textit{in situ} \(\text{O}_2\) measurements were reasonably consistent with those from the production of \(\text{CO}_2\). Compositional analysis of the NAPL in the vadose zone also confirmed biodegradation as a result of aeration.

It is possible that volatilization and biodegradation will not play such an important role in other cases where NAPL is limited to just the capillary fringe and is not so extensively distributed throughout the vadose zone. Also, the trials conducted here were only of relatively short duration and the smaller mass of petroleum hydrocarbons above the capillary fringe means that the contributions of volatilization and biodegradation will inevitably decline. Relative contributions are also expected to change under low water table conditions with larger liquid recovery rates.

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