Volatilization and biodegradation during air sparging of a petroleum hydrocarbon-contaminated sand aquifer

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Abstract Mass removals due to volatilization and biodegradation were quantified during air sparging trials in a sand aquifer contaminated by dissolved petroleum hydrocarbons (mostly BTEX—benzene, toluene, ethylbenzene and xylene). Volatilization was determined from measurements of volatile organic compounds in extracted soil gas and biodegradation was evaluated from oxygen utilization in the aquifer. The removal of the dissolved petroleum hydrocarbons from the aquifer was also determined in relation to the distribution of sparged air and dissolved oxygen in the aquifer. Volatilization was the dominant mechanism and petroleum hydrocarbons were removed from the air contact zone within 1–2 days. An evaluation of the rates of biodegradation was complicated by trapped air in the aquifer and other sinks of oxygen. However, biodegradation rates were at least an order of magnitude less than volatilization rates when most dissolved petroleum hydrocarbons were being removed.

INTRODUCTION

In situ air sparging has become accepted as a successful tool for the remediation of dissolved volatile organic compounds (VOCs) contaminating groundwater. However, its acceptance has largely preceded a clear understanding of the processes involved (Johnson et al., 1997) and there is still scope for optimizing this remediation technology. It has long been postulated that air sparging attenuates organic compounds dissolved in groundwater through physical stripping (volatilization) as air moves through the aquifer and through aerobic biodegradation of the dissolved organics from the increased supply of oxygen to groundwater (Johnson et al., 1993). Although postulated, there is relatively little experimental evidence of the relative contributions of these two mechanisms at the field scale. In particular, there is a dearth of information on the extent of biodegradation in groundwater during air sparging. Most efforts so far have focussed on determining the volume of the aquifer in which air from a sparging well is found and otherwise determining the so-called radius of influence (e.g. Lundegard & La Brecque, 1995). There have also been recent laboratory studies to determine mass transfer limitations both on the partitioning of the VOCs from the aqueous to the gas phase as well as the partitioning of O₂ from the gas to aqueous phase (e.g. Rutherford & Johnson, 1996).

This paper presents results from two short-term (up to 10 days duration) field
trials (Johnston et al., 1997, 1998) of air sparging that were monitored to determine the contribution of both volatilization and biodegradation to the remediation of contaminated groundwater. The groundwater at the site of the trials was highly contaminated with dissolved petroleum hydrocarbons from spills of gasoline but there was no non-aqueous phase liquid gasoline at the test site. The total concentration of BTEX (benzene, toluene, ethylbenzene and xylene) in groundwater was typically around 20 000 µg l\(^{-1}\) with benzene accounting for 75% of the total. There was no dissolved oxygen in the groundwater before the start of sparging. The aquifer materials were high porosity (around 0.51 m\(^3\) m\(^{-3}\)), fine-medium calcareous sands. At the time of the trials, the water table was 3.0–3.3 m below ground. The field trials were conducted in December 1996 and April 1997. Air distribution in the December 1996 trial was relatively limited and the April 1997 trial was run at higher capillary pressures to produce a more extensive distribution of air in the aquifer. For brevity, results are presented only for the more extensively monitored April trial.

METHODS

Details on the methods used for the air sparging trials are given by Johnston et al. (1997, 1998) and only a summary is given here.

The sparging well was screened across the interval 6.2–7.2 m below ground and air was injected at 35 kPa from 12:14 h 14 April until 13:30 h 23 April. At the time, the water table was 3.3 m below ground. Air flow rates increased to something greater than 8.3 l s\(^{-1}\), the capacity of the flow meter used, after one day of sparging. Sparging was turned off on occasions for a period of 4–5 h during the course of air sparging to sample groundwater and determine oxygen utilization. Soil gas was extracted through five wells screened in the vadose zone. The total air extraction rate was 18 l s\(^{-1}\) with the highest rate, 10 l s\(^{-1}\), from a well adjacent to the sparging well.

Multi-depth sampling bores (multiports), in situ oxygen probes and neutron access tubes were used to determine changes in groundwater chemistry, oxygen utilization and the fate of injected air in the aquifer. Biodegradation was determined from oxygen utilization, and the quantity of VOCs that partitioned from the aqueous phase into the gas phase was measured in the extracted soil gas. Sampling and analytical techniques are given in Johnston et al. (1997).

RESULTS AND DISCUSSION

Air movement in the aquifer

Neutron probe measurements below the initial water table elevation showed lateral movement of air from the sparging well was limited to about 2 m. At this radial distance, air contents increased by around 0.03 m\(^3\) m\(^{-3}\). Air contents of as much as 0.28 m\(^3\) m\(^{-3}\) were observed 0.5 m from the sparging well with air detected to 7.0 m below ground. At 1.0 m from the sparging well, air was detected to 6.5 m below ground with maximum contents of 0.20 m\(^3\) m\(^{-3}\). The effect of layering of the aquifer materials was evidenced by small and delayed increases in air content around 4.0–
4.25 m below ground as well as at 5.75 m. The distribution of air was not radially symmetric with more air seen to the west of the sparging well and no evidence of air below the water table 2 m north of the sparging well.

The \textit{in situ} oxygen sensors confirmed the extent of air movement indicated from neutron probe measurements. At 0.5 m from the sparging well O$_2$ partial pressures were the same as atmospheric air (0.21 atm) to a depth of at least 6.5 m below ground during sparging. One metre from the sparging well, full oxygenation was observed to at least 5.5 m but not at 6.5 m where, other than immediately after sparging first started, partial pressures of O$_2$ were only occasionally above zero (Fig. 1). Figure 1 also shows it took 2 days for fully oxygenated conditions to be established at 4.5 m and that O$_2$ partial pressures reduced noticeably during the periods that sparging was turned off. O$_2$ partial pressures at 1.5 m from the sparging well showed aeration at 3.5 and 4.5 m depths during sparging and for a couple of hours after sparging was restarted at 5.5 m.

\textbf{Dissolved oxygen in groundwater}

Dissolved oxygen (DO) was not seen at distances greater than 2 m from the sparging well and indeed DO was only seen at 2 m while sparging was in progress. The depth at which DO was observed decreased with distance away from the sparging well: to at least 6.5 m at a distance of 0.5 m from the sparging well; to at least 6 m and occasionally 6.5 m, 1 m from the sparging well and; to no more than 5 m at 1.5 and 2 m from the sparging well. DO concentrations were as much as 7 mg l$^{-1}$ at 0.5 m and 1.0 m from the sparging well immediately after sparging was turned off (Fig. 1). At 1.5 m from the sparging well DO concentrations did not exceed 3.5 mg l$^{-1}$. Decreases in DO concentration during the period sparging was turned off (Fig. 1) showed utilization of O$_2$ in the aquifer. DO concentrations reduced at a greater rate than O$_2$ partial pressures suggesting a mass transfer limitation between residual trapped air in the aquifer and the groundwater.

\begin{center}
\includegraphics[width=\textwidth]{fig1.png}
\end{center}

\textit{Fig. 1} O$_2$ partial pressures and DO at different depths 1 m from the sparging well.
Changes to dissolved petroleum hydrocarbons

Dissolved BTEX and polycyclic aromatic hydrocarbons (PAHs) were very rapidly removed from groundwater from that part of the aquifer in contact with the sparged air. Differences were seen between compounds, with ethylbenzene the most rapidly removed and naphthalene, 2-methylnaphthalene and 1-methylnaphthalene more slowly removed than the BTEX. Time series of benzene concentrations at a depth of 5.5 m at distances of 0.5-1.5 m illustrate the rapid removal, the decreasing depth of removal away from the sparging well and the rebound in concentrations at the periphery of the air contact zone (Fig. 2). Complete or almost complete removal to below detection limits (5 μg l⁻¹) occurred to a depth of 6.5 m, 0.5 m from the sparging well and to 5.0 m at distances of 1.0, 1.5 and 2.0 m. There was also some evidence of reduced BTEX concentrations 3 m from the sparging well. At a lateral distance of 1.0 m, large decreases in concentrations were seen to a depth of 6.0 m and significant decreases at 6.5 m. The incomplete removal at these depths appeared to be a result of a rebound in concentrations at the periphery of the air contact zone as contaminated groundwater displaced air in the aquifer after sparging ceased. Importantly, the great majority of the loss of dissolved BTEX occurred in the initial 2.5 h of sparging and there was very little further removal after 1 day of sparging. Figure 2 shows the mass of benzene between 3.5 and 6.5 m in the profile integrated radially to 1.5 m from the sparging well. For the PAHs, most of the losses occurred within the first day with some evidence of a very slow removal over the rest of the trial.

Volatilization of petroleum hydrocarbons

Benzene and TPH showed an initial flush in the extracted soil gas during the first 24 h of sparging (Fig. 3). Benzene concentrations were as high as 160 μg l⁻¹ while TPH was as much as 3800 μg l⁻¹. All BTEX were reduced to below detection limits
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(5 \, \mu g \, l^{-1}) after 36 h of sparging while low concentrations (20–50 \, \mu g \, l^{-1}) of TPH continued for the remainder of the trial. Much of the TPH in the first hours of sparging consisted of unidentified short chain aliphatics. The timing of the volatilization is largely consistent with the observed decreases in dissolved concentrations (Figs 2 and 3). The slightly extended time for the appearance of VOCs in the extracted soil gas may be a result of a flux of contaminated groundwater into the air contact zone that would not necessarily be apparent in groundwater concentrations.

Evidence for biodegradation of petroleum hydrocarbons

The primary evidence for biodegradation of the petroleum hydrocarbons was the O\textsubscript{2} utilization deduced from the decreases in DO concentrations following the cessation of sparging (Fig. 1). The decreases in DO concentration were approximately linear
over time and the rates of decrease were estimated from linear regressions. The estimates for the 4.5 and 5.5 m depths at 1 m from the sparging well are shown in Fig. 4. The rates of change in DO concentrations were as much as 45 mg l\(^{-1}\) day\(^{-1}\) and differed between locations and depths. Greatest rates of change were seen 1 m from the sparging well. Also, the rate of change in DO concentration decreased over the time of the trial (Fig. 4) and approached zero for two of the depths 0.5 m from the sparging well.

Care needs to be exercised in inferring biodegradation rates of petroleum hydrocarbons from the decrease in DO. Other organic carbon in the aquifer and abiotic processes are also expected to contribute to O\(_2\) utilization. The high rates of DO decrease observed after the first day of sparging following the essentially complete removal of petroleum hydrocarbons, suggest the biodegradation of petroleum hydrocarbons only accounts for a small proportion of the apparent O\(_2\) utilization. On the other hand, the transfer of O\(_2\) from trapped air in the aquifer to the groundwater would mean that O\(_2\) utilization is underestimated. Nevertheless, biodegradation rates were calculated for comparison with the rates of volatilization estimated from removal in extracted soil gas (Table 1). In this it was assumed that 3.53 g of O\(_2\) is required to mineralize 1 g of petroleum hydrocarbon (hexane was used as an average composition). The total biodegradation rate was calculated for the depth interval 3.5-6.5 m and radially integrated to a distance of 1.5 m. In the first day of sparging, before dissolved petroleum hydrocarbons were depleted in the groundwater, the rate of volatilization was as much as 40 times faster than biodegradation. The changes in mass of individual compounds also suggested volatilization was the dominant mechanism. For instance, 80 g of benzene was removed in the extracted air compared to a computed difference of 130 g in groundwater within 2.0 m of the sparging well. These are relatively close given that the air extraction system was probably less than 100% efficient in capturing VOCs and given the relative paucity of data to calculate changes of mass in groundwater.

### Table 1

<table>
<thead>
<tr>
<th>TPH extracted in soil gas</th>
<th>Rate (g day(^{-1}))</th>
<th>Total biodegradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period</td>
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<td>Period</td>
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<tr>
<td></td>
<td></td>
<td>Rate (g day(^{-1}))</td>
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<td>2500</td>
<td>14:49 14 April-19:08 14 April</td>
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<tr>
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<td>400</td>
<td>11:08 15 April-16:08 15 April</td>
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<td>40</td>
<td>10:31 16 April-15:03 16 April</td>
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<td>80</td>
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<tr>
<td>15:20 18 April-13:40 22 April</td>
<td>110</td>
<td>10:35 22 April-17:05 22 April</td>
</tr>
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</table>

### CONCLUSIONS

Further understanding of the transfer of O\(_2\) from entrapped residual air to the groundwater, the degradation of soil organic matter and abiotic sinks for oxygen will enable better estimates of biodegradation rates of the dissolved petroleum hydrocarbons. However, volatilization was the dominant process during these air sparging trials. Biodegradation rates were at least an order of magnitude less than
Volatilization rates during the period of greatest loss of dissolved petroleum hydrocarbons. The sparged air only moved 2 m or less from the sparging well and DO was not observed in the aquifer outside the air contact zone. The reasons for decreases in concentrations of dissolved petroleum hydrocarbons 2–3 m from the sparging well require further investigation.

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REFERENCES


