Natural attenuation of remnant coking liquor contamination from a deep unsaturated zone

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Abstract A 21-m deep sandstone unsaturated zone continues to produce groundwater contamination 28 years after disposal of ammoniacal coking liquors ceased. The contamination consists of ammonium, nitrate and (total) organic carbon (TOC), with concentrations in groundwater up to 300 mg l\(^{-1}\), 500 mg l\(^{-1}\) and 50 mg l\(^{-1}\), respectively. High groundwater concentrations of HCO\(_3\)\(^-\) and nitrate suggest that the deep unsaturated zone plays an important part in enhancing biodegradation of organic carbon and ammonium, reducing the impact of both to groundwater. Nitrate, however, is itself an important groundwater contaminant, and being unretarded can pose a greater risk to groundwater receptors than either ammonium or TOC. Data from multilevel samplers downgradient of the source, indicate denitrification combined with the oxidation of TOC, reducing concentrations of both nitrate and TOC. This field example demonstrates how nitrification in the unsaturated zone enhances the removal of both ammonium and organic carbon, the principal contaminants in coking liquors.

Key words ammonium; coking liquors; groundwater contamination; natural attenuation; nitrate; Sherwood Sandstone (UK)

INTRODUCTION

Ammonium is often overlooked as a significant groundwater contaminant, overshadowed by more prominent pollutants such as petroleum hydrocarbons, heavy metals, chlorinated solvents, etc. This fact was highlighted by Erskine (2000) and Christensen et al. (2000) who both stated that by mass, ammonium is the most significant and persistent groundwater contaminant in landfill leachate. Neither study, however, mentioned the huge legacy (3000 to 5000 sites in the UK alone; Petts et al., 1997) of contamination from coking plants of the early to mid 1900s, of which ammonium is likely to be the most significant persistent contaminant; this paper highlights one such example.

Ammonium is retarded by cation exchange (CIX), and often undergoes slow transport, therefore, it is likely that some ammonium plumes remain undiscovered and may impact groundwater receptors in the future. In groundwater, ammonium is only oxidized by dissolved oxygen (DO) to produce nitrate, itself a groundwater contaminant:

\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ \quad (\Delta G^\circ_f = -301.8 \text{ kJ mol}^{-1} \text{NH}_4^+) \quad (1)
\]

Because of the low solubility of DO (8.5 mg l\(^{-1}\) at 12°C and 1 atmosphere), ammonium plumes are slow to biodegrade and can persist for long periods, providing ammonium and nitrate for years. In the unsaturated zone, oxidation of ammonium by both dissolved and gaseous oxygen can produce significant loads of nitrate to groundwater for many years.
SITE DESCRIPTION

The Rexco coking plant, near Mansfield in the English East Midlands, is estimated to have disposed of 70,000 tonnes of ammoniacal liquor into a settling lagoon via a drainage ditch (Fig. 1) between 1956 and 1969. The liquor contained between 10,000 and 20,000 mg l\(^{-1}\) ammoniacal nitrogen (\(\text{NH}_4^+\) and \(\text{NH}_3\)) and 5000 to 15,000 mg l\(^{-1}\) phenols (Barker & Hollingworth, 1958; Christopher & Byrom, 1952; Owen, 1979; Broholm et al., 1998). Between 1994 and 1997 a large field investigation was undertaken to study the natural attenuation of the contamination in the underlying Sherwood Sandstone aquifer (Broholm et al., 1998; Jones et al., 1998, 1999). As part of the investigation, the aquifer was hydraulically and mineralogically characterized and groundwater samples were collected from multilevel samplers and monitoring wells near the location of the former drainage ditch (Fig. 1). This paper discusses groundwater contamination entering the aquifer from the vadose zone under the location of the drainage ditch source, 28 years after disposal of liquor into the ditch ceased.

Figure 2 is a schematic cross-section along a groundwater flow line from borehole (BH) 31 to BH30. The vadose zone under the location of the former drainage ditch is approximately 21 m deep and comprises permeable weathered Pebble Beds of the Sherwood Sandstone Group. The Pebble Beds end where the less permeable Mottled Sandstones begin at approximately 40 m b.g.l. (metres below ground level). The aquifer is contaminated with retarded and recent ammonium to approximately 15 m...
b.w.t. (metres below water table) just downgradient of the drain source. Current contaminated recharge only penetrates to 2 to 4 m b.w.t. in the area shown on Fig. 1.

**GROUNDWATER CHEMISTRY**

Selected representative groundwater chemistry data from the top 6 m of the saturated aquifer are given in Table 1 and Fig. 3. Groundwater data collected from 1995 to 1997 indicate that source input varies with time, probably due to variations in surface recharge. Interpretation of groundwater chemistry data taken from near the water table and close to the contaminant source is difficult because contaminant concentrations are significantly diluted over short distances and sampled concentrations vary due to effects of the fluctuating water table and different well screen lengths and depths. However, the overall trends in chemistry are interesting. Background groundwater is represented by well 23, which lies 250 m upgradient of BH31. BH31 is located on the upgradient side of the drain source, whilst the screen of BH8 is more or less under the drain. BHs 6, 17, 36 and 16 all lie between 14 and 22 m downgradient from the source. A good indication of the chemistry and processes ongoing in the unsaturated zone under the drain can be gained by looking at the chemistry in these shallow wells just downgradient of the source.

Groundwater from sample points (SP) 8, 6, 17-pz, 36-1 and 16-pz has a pH of approximately 1 pH unit < background (BH23) with high concentrations of $\text{HCO}_3^-$, resulting in very high $\text{CO}_2$ partial pressures ($p\text{CO}_2$), indicating acidification and carbon dioxide
Table 1 Representative groundwater chemistry data for selected wells shown on Fig. 1.

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<th>Screen bottom mbwt</th>
<th>Fe(II)</th>
<th>Mn</th>
<th>NO₃⁻</th>
<th>NO₂⁻</th>
<th>TOC</th>
<th>Alk as HCO₃⁻</th>
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<th>log pCO₂</th>
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All data in µmol l⁻¹ groundwater, unless stated; SP: sample point; mbwt: metres below water table; TOC: total organic carbon as carbon; pCO₂: partial pressure of carbon dioxide.

Fig. 3 Graph illustrating ammonium and nitrate input at the drainage ditch and subsequent down gradient dilution and denitrification.

production upgradient in the unsaturated zone. BHs 8 and 17-pz have high nitrate concentrations confirming ongoing nitrification in the vadose zone (equation (1)), producing acidity which promotes the dissolution of calcite and dolomite in the aquifer (equations (2) and (3)). By comparing the total mol l⁻¹ of calcium and magnesium with bicarbonate (Table 1), further information can be gained. HCO₃⁻: [Ca²⁺ + Mg²⁺] ratios
close to 1:1 indicate H\(^+\)-driven dissolution of carbonates (equations (2) and (3)), whereas ratios of 1:2 or more indicate the production of CO\(_2\) from the biodegradation of organic carbon and CO\(_2\)-driven carbonate dissolution (equations (4) and (5)).

\[
\begin{align*}
\text{CaCO}_3 + \text{H}^+ &\rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \tag{2} \\
\text{CaMg(}\text{CO}_3\text{)}_2 + 2\text{H}^+ &\rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{HCO}_3^- \tag{3} \\
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} &\rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \tag{4} \\
\text{CaMg(}\text{CO}_3\text{)}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} &\rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- \tag{5}
\end{align*}
\]

Iron(II) (Fe\(^{2+}\)) is generally low in the groundwater, as expected by the presence of nitrate at near-neutral pH. The occurrence of Mn\(^{2+}\) also indicates that Mn(IV) is available in the aquifer and is possibly being abiotically reduced by available Fe\(^{2+}\) (Postma, 1985; Lovely, 1991):

\[
\text{MnO}_2 + 2\text{Fe}^{2+} + 4\text{H}_2\text{O} = 2\text{Fe(OH)}_3 + \text{Mn}^{2+} + 2\text{H}^+ \tag{6}
\]

Mn\(^{2+}\) is particularly high in BH8 and 17-pz indicating that the conditions in the vadose zone and/or up gradient of these wells are suited to the reduction of Mn (IV) minerals.

Figure 4 and equation (7) illustrate the use of field data to make conservative estimates of the concentrations of ammonium, nitrate and TOC in the recharge under the drain based on concentrations measured in 17-pz (minus background concentrations). Equation (7) gives a conservative dilution of factor of 48, meaning that ammonium, nitrate and TOC (based on a 1975 value of 15.6 mg l\(^{-1}\)) in the recharge water are at least 809, 331 and 57 meq l\(^{-1}\), respectively. This crude estimate is supported by detailed MT3D\(^{99}\) modelling of the flow line (data not shown) and indicates that 28 years after the cessation of liquor disposal, contaminant concentrations in the recharge water in the vadose zone under the drain remain extremely high.

\[
C_r = (f_{GW} \times D / [r \times L]) \times (C_{17-pz} - C_{rev}) = (0.105/[0.00055 \times 4]) \times (C_{17-pz} - C_{rev}) \tag{7}
\]

*Fig. 4* Simplified cross-section from contaminant source to BH17-pz, illustrating parameters used in equation (7).
Downgradient of 17-pz, measured contaminant concentrations are reduced by dilution and sampling effects, however, what is shown by the field data and illustrated in Fig. 4 is that denitrification is taking place. Nitrate concentrations fall well below background levels with increased nitrite concentrations confirming rapid denitrification. The most likely reductant is the TOC, with some Fe(II) minerals in aquifer sediment produced by high pollutant load during active liquor disposal (confirmed by sediment oxidation/reduction data from core taken from BH36).

CONCLUSIONS

Whilst the deep unsaturated zone continues to provide high concentrations of contaminants to groundwater 28 years after Rexco closed, it also acts as a large bioreactor increasing the removal rate of retarded ammonium and organic carbon by nitrification and mineralization, respectively. Once in the groundwater nitrate then undergoes denitrification to nitrogen gas and in doing so helps to re-oxidize reduced sediments and biodegrade TOC. This field example illustrates the persistence of ammoniacal coking liquors within the subsurface, and their potential for contaminating aquifers for many years to come.

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REFERENCES


