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Key Factors Affecting Subsurface Contamination of Natural Waters near Sour-gas Plants*

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Abstract: *Hydrocarbon contamination of lakes and rivers from subsurface discharge of groundwater is a common environmental problem in many countries. This source of contamination, particularly dissolved phase hydrocarbons, can significantly reduce the quality of natural waters. Laboratory results show that the aqueous solubility of benzene can be predicted by Raoul's Law for BTEX mixtures and for gas condensate. In contrast, the solubility of total xylenes was up to three times higher than the calculated results using Raoul's Law. A comparison of these finding with the composition of BTEX in groundwater at a sour-gas plant, indicated that the mole fraction and groundwater flow velocity were two principle factors affecting the discharge concentration of benzene and xylenes to natural waters.*

Keywords: *Natural waters contamination, groundwater contamination*

1. Introduction

Hydrocarbon contaminants to rivers and lakes can occur through subsurface discharge of groundwater (Borden and Piwoni 1992; Hadley and Armstrong 1991; Fetter 1992). This problem was believed to be widespread in Western Canada (Sorensen *et al.* 1994) and therefore studies were conducted at gas plants in Southern Alberta to determine the factors controlling the concentration of benzene, toluene, ethylbenzene, and xylenes (BTEX) in groundwater. These factors included the (a) salinity of the water, (b) pH, (c) gas condensate composition, (d) cosolvency, (e) the volume ratio of groundwater to discharged hydrocarbon, and (f) temperature of the groundwater. This paper discusses the results obtained for an investigation of primarily two of these factors (c) and (e), with reference to preliminary results obtained for effects arising from the salinity of groundwater.

Gas condensate, a thick brown liquid, is composed of aliphatic and cyclic hydrocarbons with carbon numbers of C_5 to C_{30}. It contains 10 to 20% of aromatic compounds (by mass) such as BTEX (Hardisty 1995). The latter components are of concern because they have relatively high toxicity and solubility in natural waters (Lide 1996).

Extensive research on the solubility of these and other aromatic contaminants has been reported (Cambell *et al.* 1983; Dickhut *et al.* 1991; Lee *et al.* 1992; Poulsen *et al.* 1992; Wise *et al.* 1992), reflecting the growing concern of the effects of petroleum contaminants on water quality. For example, early work has been reported by Banerjee (1984) and Burris and MacIntyer (1985,

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1986a, 1986b) on the aqueous solubility of components in hydrophobic hydrocarbon mixtures. They found that a mixed organic phase of similarly structured molecules displayed near ideal behavior. The solubility of a component from such mixtures could be defined by an equation known as Raoul's Law:

$$C_i = x_i S_i \tag{1}$$

where C_i is the equilibrium concentration of the *i*th component in the aqueous phase from the mixture; S_i is the solubility of the *i*th compound in its pure form; and x_i is the mole fraction of the *i*th component in the organic phase.

For studies of chlorobenzenes and other mixtures of organic compounds, the difference between the calculated and the experimental results was approximately 10 to 20%. Burris *et al* (1986a,b) also studied the solubility of components in a liquid containing seven medium molecular weight substances such as methylcyclohexanes. The results showed that the ratio of the hydrocarbon concentration in the organic phase to that in the water phase appeared to be independent of the degree of saturation in the aqueous phase. These studies indicated that some hydrocarbon mixtures can be assumed to behave as ideal solutions.

Partition coefficient P_t have also been used in evaluating the concentration of a contaminant in a given aqueous phase:

$$P_t = \frac{C^h}{C^w} \tag{2}$$

where C^h and C^w are the concentration of *i*th component in the organic phase and water phase respectively. The greater the P_t value, the greater the tendency of the *i*th component to be in the organic phase. However, as demonstrated by Cline *et al* (1991), partition coefficients of BTEX in gasoline and water vary by less than 30% for corresponding changes in BTEX concentrations of over one order of magnitude.

In an innovative approach, Mackay *et al* (1991) used first order kinetics to study the dissolution process for BTEX (from a synthetic oil) to groundwater, flowing at a specific velocity in a column. They concluded that the chemicals present in the light non-aqueous phase liquid (LNAPL) and dissolved in water can be estimated by the partition coefficient P_t:

$$x^h = \exp(-\frac{Q_v}{P_t}) \tag{3}$$

where Q_v is the volume ratio of water to LNAPL, and x^h is the residual concentration of a component in the LNAPL This model can be used to estimate the concentrations of a contaminant in an organic phase at various distances from a source.

2. Experiments

Sour gas condensate and LNAPL samples were stored in a –4 °C cold room prior to laboratory measurements. For simplicity, the solubility of BTEX from condensate was studied using two steps: (a) measurement of BTEX concentration in a sour-gas condensate, gasoline, and diesel samples, and (b) calculation of partition coefficients of BTEX for the condensate and aqueous phases.

A benzene-condensate mixture (1:1 in volume) was prepared, using a gas condensate with density of 0.86, and average molecular weight assumed to be 100, based on the composition of the condensate. The molecular weight of the benzene-condensate mixture was calculated as 89.

Saturated aqueous solutions were prepared at room temperature (24±1 ℃℃). A volume of 50 ml of aqueous solution and 10 ml organic phase were placed in a 100 ml bottle and capped using a Teflon septum. The bottle was then shaken using a rotating disk apparatus for 14 hours at 120 cycles/min, and inverted and allowed to sit undisturbed for 2 hours. The separated aqueous phase (0.5 ml) was removed via the septum using a 0.5 ml syringe, extracted using 10 ml of Dichloromethane (DCM) and the DCM extracts analyzed using a gas chromatography/flame-ionization detection employing a Hewlett-Packard 5890 GC equipped with a 30 m DB-5 column (Headley and Rae 1992).

The BTEX composition in the condensate was measured using DCM dilutions of 500, 1 250, and 2 500. The solubility of each BTEX compound was studied using NaCl solutions of 0 to 2 $\mathrm{Mol{\cdot}L^{-1}}$. These aromatic compounds were mixed well prior to dissolving the benzene in the aqueous phases. The two ratios of B:T:E:*o*-X:*m*-X:*p*-X were: 40:5:2:2:2:2 and 20:5:2:2:2:2. The mole fractions of benzene and total xylenes in the two mixtures were: benzene 0.80 and 0.67 respectively, total xylenes 0.145 and 0.087 respectively.

3. Results and discussion

3.1 Solubility of BTEX Mixtures

Up to a twofold decrease in the solubility of BTEX was observed for increasing NaCl concentrations for the two BTEX mixtures investigated. Similar effects were also observed for effects of TEX on the solubility of benzene. In agreement with Raoul's Law, the lower the mass fraction of benzene, the lower was the measured solubility of benzene. However, for toluene, ethylbenzene and xylenes, the measured results were 1.1 to 3.4 times higher than the calculated results based on Raoul's Law. The lower the mole fraction of T, E, X in the BTEX mixture, the higher was the ratio of the measured to the calculated results. This indicates that the Raoul's Law is not applicable for the effects of benzene (10 times higher solubility than TEX) on the solubility of T, E, and X.

If the results are interpreted as partition coefficients, it is found that the partitioning coefficients of BTEX are in the order of m,p-xylene > ethylbenzene > o-xylenes > toluene > benzene, which is in the opposite order to that of their solubility. The partition coefficients of all BTEX components increase as the NaCl concentration increase. As illustrated in Figure 1, this tendency for the partition coefficient to increase for both benzene and total xylenes in NaCl solution matches the exponential curves:

Benzene $$x_b = 0.8,\ 0.67:\quad P_b^s = P_b^w \exp(0.440I) \tag{4}$$

Total xylenes

$$x_x = 0.145:\quad P_x^s = P_{x(0.145)}^w \exp(0.0.410I) \tag{5}$$

$$x_x = 0.087:\quad P_x^s = P_{x(0.087)}^w \exp(0.0.508I) \tag{6}$$

where P_b^w and P_x^w are the partition coefficients of benzene and total xylenes in pure water respectively, and the P_b^s and P_x^s are the partition coefficient of benzene and total xylenes in salt solution respectively. In this experiment, P_b^w was measured as 502, which is higher than the value of 350 reported earlier for gasoline by Cline *et al* (1991).

3.2 The Solubility of BTEX from Sour-gas Condensate

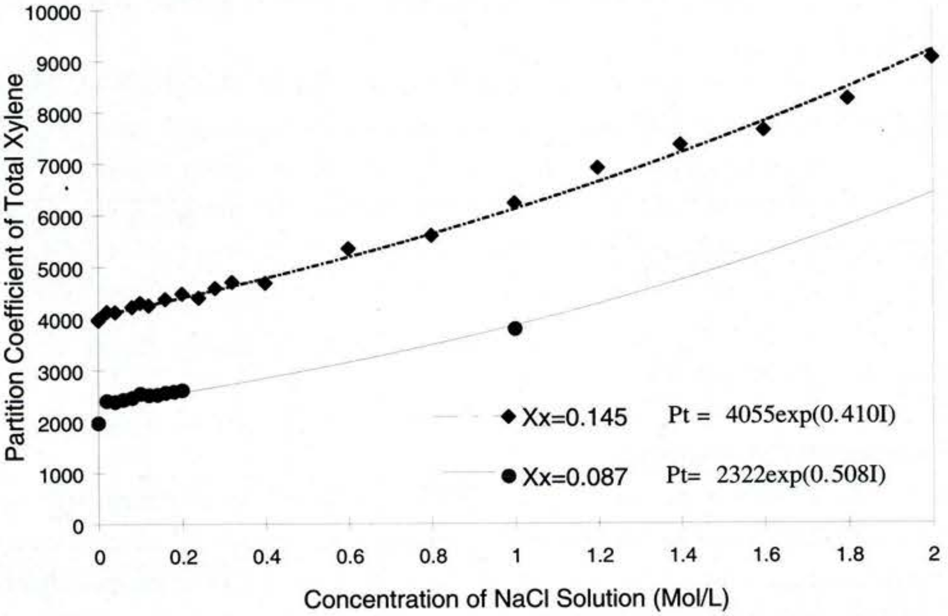

Fig. 1 Partition Coefficients of Total Xylenes from BTEX Mixtures versus Concentration of NaCl Solutions

The composition of BTEX in a condensate sample from a sour-gas plant in Alberta (product in storage tank) was measured as 111.7 $g \cdot l^{-1}$, corresponding to a mass faction of 12.99 %. The concentration of the BTEX components were: benzene 42.51 $g \cdot l^{-1}$, toluene 41.59 $g \cdot l^{-1}$, ethylbenzene 2.71 $g \cdot l^{-1}$, and total xylenes 25.78 $g \cdot l^{-1}$. The density of the condensate sample was measured to be 0.86 $g \cdot ml^{-1}$. The total concentration of BTEX from the LNAPL under this site was much lower (1.86 % by mass) than that from the sample of the condensate storage tank (13 % by mass). This difference may reflect losses due to dissolution, volatility, and biodegradation of BTEX since the gas plant in question was built 20 years ago, and LNAPL in the groundwater table has been reported since 1985 (Komex International, 1992).

A comparison of the results show that the measured values of solubility of benzene from either the gas condensate or benzene-condensate mixtures were within 7 % of the calculated results using Raoul's Law. However, the measured values of T, E, and X were 2 to 5 times higher than the calculated results. Based on this comparison, the gas condensate can only be considered as an ideal liquid for benzene. Raoul's Law does not predict the behavior of T, E, X reflecting possible interference from the complex gas condensate mixture.

The partition coefficients for benzene and total xylenes calculated for the gas condensate ($x_b = 0.063$) and benzene-condensate mixture ($x_b = 0.61$); based on the experimental results, were 398 and 450 respectively. These values are lower but comparable to that the partition coefficient of benzene obtained from BTEX mixtures (502 when $x_b = 0.80$ and 0.67). In contrast, the measured partition coefficient of total xylenes were observed to increase significantly with xylene mole fraction.

3.3 Comparison of Concentration of BTEX in Groundwater Discharge at Gas Plant

The equilibrium concentration of benzene C_b^{eh} in the groundwater at the gas plant can be calculated using Raoul's Law:

$$C_b^{eh} = C_b^{es} x_b = 1700 \times 0.064 = 108 \text{ mg·l}^{-1}$$

The value of the mole fraction is calculated based on an average conce ntration of benzene in condensate of 5 % by weight or 43 g·l^{-1}, condensate density of 0.86 g·ml^{-1} (and thus average molecular weight of approximately 100). The value of C_b^{es} is based on measurement of the solubility of benzene in groundwater at 0.03 mol·l^{-1} ionic strength NaCl solution. A similar value of 105 mg·l^{-1} can also be calculated for the equilibrium concentration of benzene based on the partition coefficient measured for the gas condensate.

Several factors, such as soil/groundwater interactions, temperature, etc (Wise *et al.*,1992) are expected to effect this equilibrium concentration. One such factor, the effect of groundwater flow, can be evaluated using two methods. Mercer and Cohen (1990) estimated that the equilibrium concentration in groundwater would be below 10 % of the equilibrium concentration measured for static conditions, if the groundwater velocity was in the range of 10 to 100 cm·day^{-1}. The average groundwater flow velocity at the site was 86.3 cm·day^{-1}, thus satisfying the condition for application of the method of Mercer and Cohen (1990). Thus, the actual maximum concentration of benzene in groundwater (C_b^{eg}) can be estimated using:

$$C_b^{eg} = 10\% C_b^{em} = 10\% \times 105 = 10.5 \text{ mg·l}^{-1}$$

The maximum concentration of benzene calculated above were compared with the actual concentration observed for field samples. The results showed that the method of Mercer *et al* gave values somewhat higher than the actual values measured for groundwater at the gas plant.

The effects of groundwater flow can also be considered based on an approach developed by Mackay *et al* (1991). In this approach, the BTEX concentration in groundwater is evaluated using the residual concentration in the LNAPL and assuming ideal-behavior for application of Raoul's Law. In this experimental, the concentration of benzene in the LNAPL of the gas condensate was less than 2500 mg·L^{-1}. Thus, the maximum concentration of benzene in groundwater can be calculated as follows:

$$C_b^{ep} = \frac{C_b^{ep}}{P_b^t} = \frac{2500}{403} = 6.2$$

A similar calculation can also be used for computing the total equilibrium concentration of xylenes. Based on a composition of total xylenes in gas condensate of about 28 g·L^{-1}, the mole fraction of xylenes will be 0.03. The solubility of xylenes is about 180 mg·L^{-1}(Verschueren, 1983), and the partition coefficient in gas condensate/water mixtures was measured to be about 2230. Based on these data, the total equilibrium concentration of xylenes can be calculated as 5.4 mg·l^{-1} using Raoul's Law, and 12.6 mg·l^{-1} using the measured partition coefficient. If the method of Mercer and Cohen (1990) is used to calculate the groundwater flow effect, the concentration of xylenes in groundwater is predicted to be lower than 1.26 mg·l^{-1} (not accounting for salting and cosolvency effects). This is in poor agreement with the measured value of 30 mg·l^{-1}, the concentration of total xylenes in groundwater samples at this gas plant.

These comparisons of the calculated results and actual values measured for field samples confirm that the Raoul's law is not applicable to xylenes in gas condensate. In contrast, the calculated results using measured partition coefficients of xylenes were in good agreement with values obtained for field samples of condensate in groundwater at gas plants and other LNAPLs (gasoline and diesel).

4. Conclusion

The solubility of benzene for gas condensates, BTEX mixtures, and petroleum mixtures such as gasoline and diesel, is given by Raoul's law. However, for TEX, non-ideal behavior is observed for gas condensate mixtures.

Based on the experimental results, the maximum concentration of benzene in groundwater that may discharge to natural waters can be estimated at sour-gas plants. Two key factors effecting the concentration of benzene in groundwater are shown to be: non-polar effects of organic chemicals in the gas condensate, and groundwater flow. These two combined factors alone can lead to more than a 100 fold decrease of the concentration of benzene in groundwater.

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