



Attenuation of dissolved aromatic hydrocarbons from residual gasoline: source depletion and bioattenuation controls

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ABSTRACT

About 50L each of normal gasoline and gasoline with 10% ethanol (E10) were emplaced side-by-side below the water table in the shallow sand aquifer at CFB Borden. Approximately two years of monitoring at downgradient fences demonstrates similar natural bioattenuation of aromatic hydrocarbons (benzene through trimethylbenzenes and naphthalene) in both plumes. Core analysis and simple interpretations were not sufficient to predict the rate of mass depletion in gasoline sources, but captured the biodegradation rate well. However, the extent of bioattenuation appears to exceed that predicted by models considering electron acceptor availability.

RÉSUMÉ

Approximativement 50L d'essence régulière et 50L d'essence contenant 10% de l'éthanol (E10) furent injectés, l'un à proximité de l'autre, sous la nappe phréatique dans l'aquifère peu profond de sable à BFC Borden, Ontario. Deux ans de surveillance de plusieurs puits d'observations situés en aval, ont démontré la bioatténuation des hydrocarbures aromatiques (benzène, triméthylbenzènes et naphthalène) dans les deux panaches. L'analyse des échantillons prélevés à la source et des techniques d'interprétation simples n'ont cependant pas permis de prévoir le taux d'épuisement de masse dans les sources d'essence, mais ont bien capturé le taux de biodégradation. Cependant, ce dernier semble supérieur à la valeur estimée par des modèles numériques en prenant compte de la disponibilité des accepteurs d'électrons.

1 INTRODUCTION

Ethanol is increasingly being blended into gasoline in Canada and the US. For example, Ontario now requires an average of 5% ethanol in gasoline and hopes to move to 10%. Ethanol is termed an oxygenate as it provides oxygen to gasoline. This aims to reduce greenhouse gas emissions, improve air quality, and reduce dependence on non-renewable fossil fuels. In this paper, gasoline with ethanol will be labelled as the % by volume ethanol (e.g., E10 is 10% v/v ethanol). Ethanol has been used in Brazilian gasoline for more than 30 years. As elsewhere, gasoline contamination of the subsurface is common: the Environmental Agency of Sao Paulo State, Brazil (CETESB) had registered 1822 contaminated sites in the State in November of 2006, and 74% are fuel dispensing sites.

The overall benefits of ethanol replacing some conventional gasoline are not fully quantified. Claims of enhanced security of supply, support for the agricultural community, and reduced CO₂ emissions are touted. However, Scharlemann and Laurance (2008) discuss the most advanced comparison of the greenhouse gas emission benefits versus the environmental and natural resource costs. Compared to conventionally refined gasoline, ethanol has some reduction in overall CO₂ emissions, but increased environmental and natural resource cost. For ethanol produced from sugar cane, as in Brazil, the CO₂ benefits appear significant; for ethanol produced from corn, as current in North America, the CO₂

benefits are minor and the overall environmental and natural resource costs are much higher. Clearly, deriving increased volumes of ethanol from corn is not sustainable, but may be a step to ethanol production from cellulosic material, which is likely more sustainable.

From a groundwater quality perspective, substitution of ethanol for soluble, toxic and mobile monoaromatics such as benzene, toluene, ethylbenzene and xylenes (termed BTEX) is advantageous. Ethanol itself poses minimal direct environmental risk, other than the high biological oxygen demand (BOD) imposed on receiving waters. A common misperception is that fermentation of ethanol to acetate, methane, etc. removes this BOD and so eliminates ethanol as a competitor with BTEX for electron acceptors. Actually, ethanol fermentation, even to methane and CO₂, does not change the biological oxygen demand. So, when we refer to "ethanol" competing as an electron acceptor (EA) in groundwater, we are really considering ethanol and its fermentation products.

In general, current laboratory and field evidence shows that ethanol is rapidly degraded in the subsurface (Mackay et al., 2006; Zhang et al. 2006). However, ethanol can decrease the biodegradation of other gasoline hydrocarbons, such as benzene, toluene, ethylbenzene and xylenes (BTEX), through substrate competition and through depletion of nutrients, oxygen and other electron acceptors (EAs) that would otherwise be available for BTEX degradation. Also, high concentrations of ethanol that may be present close to

the source of contamination may be toxic to subsurface microorganisms capable of degrading BTEX. However, Williams (2007) demonstrated that this is likely a very minor effect. While microbial activity and survival was significantly diminished upon exposure to groundwater with 25% (v/v) ethanol, column experiments indicated that a viable population quickly recovered after a short exposure to this level. The mechanism for recovery is unclear: migration of microbes in groundwater or survival in the sand column were both possible. Possible implications of these impacts are reduced natural attenuation of gasoline contamination and longer BTEX plumes (Molson et al. 2002). These effects have been observed in the field for benzene (Hubbard et al. 1994; Mackay et al. 2006; Ruiz-Aguilar et al. 2003).

A controlled field experiment was conducted in the shallow sand research aquifer at CFB Borden, ON. The dissolution of oxygenates and aromatic hydrocarbons was followed and the fate during near-source transport was assessed. Ethanol and benzene are the focus of this paper.

2 EXPERIMENTAL DESIGN

In October, 2004 three residual sources of different gasoline were created in a section of the Borden aquifer not previously used for experimentation (Mocanu 2007). Three 50 ± 2 L sources of oxygenated gasoline were emplaced well below the water table. Sources were separated by sheet piling installed parallel to the groundwater flow direction (Figure 1). One source contained 90% gasoline (API 94-1) with 9.8% methyl-*tert*-butyl ether (MTBE) and 0.2% *tert*-butyl alcohol (TBA). This is termed the GMT source. Previous research at Borden demonstrated that MTBE and TBA are unlikely to be biotransformed within the two years it will take for these oxygenates to be leached from the source and transported through the network, given the Borden groundwater velocity of 9 cm d^{-1} . Another source contained 10% ethanol and 90% gasoline (E10). A third source contained 95% ethanol and 5% gasoline (E95), but this source will not be discussed here. The emplacement of each source occurred concurrently with the injection of 2200L groundwater. This likely dissolved essentially all the ethanol, MTBE and TBA, creating a complex dissolved distribution, with gasoline residuals in place. The residual gasoline suffered minimal buoyant rise (Molson et al., in press).

The mass fluxes (mass discharges) of ethanol, MTBE, TBA, BTEX, TMBs and naphthalene were estimated by monitoring three downgradient multilevel sampling fences periodically over almost 600 days. The fences (labelled rows 2, 3 and 4) are perpendicular to groundwater flow and are about 3.5, 9.5 and 15.5 m downgradient of each source. Row 1 is upgradient of the sources.

The "no degradation" mass flux was predicted using the BIONAPL model (Molson, 2005) to estimate dissolution and migration rates without considering biodegradation. The model assumed a homogeneous aquifer with the average properties well defined for the Borden sand aquifer (Sudicky, 1986). Dissolution of oxygenates and aromatics was assumed to approach

equilibrium partitioning between NAPL and passing groundwater. Then, the biodegradation capability of the BIONAPL model was used to estimate the downgradient distribution of hydrocarbons. First biodegradation was considered to proceed at a first-order rate, and secondly, biodegradation was considered to follow Monod kinetics established for the Borden aquifer (Schirmer et al., 2000) with oxygen as the only electron acceptor.

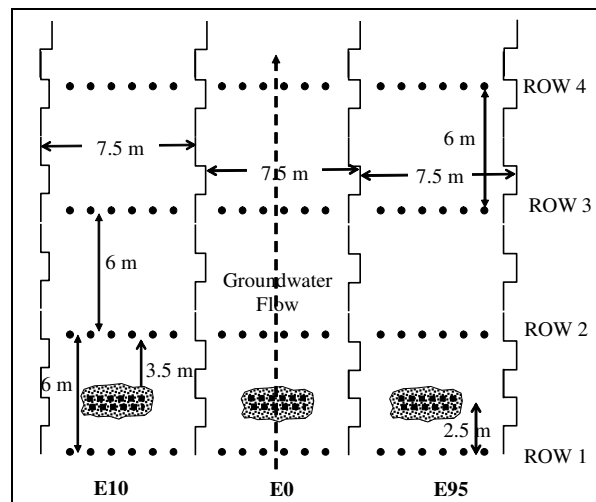


Figure 1. Layout (plan view) of the Borden field experiment. The shading shows the areas of residual saturation created by injection below the water table with 15 wells per source. The 4 vertical notched lines represent the sheet piling installed to isolate sources and their groundwater plumes. The E95 source will not be discussed here.

Two cores were collected in June, 2007 (about day 970) from each source zone: one in the centre of the gasoline injection area and one 30 cm upgradient of the centre of the source. Core was recovered from 1.5 to 4.5 m bgs, covering the depth range of gasoline injection. Core was subsampled and analyzed for the aromatics (Yang, 2008).

3 FINDINGS

3.1 Ethanol

The estimate of ethanol mass passing rows 2 to 4 in the E10 gate over 600 days is shown in Figure 2 with the "no-degradation" mass flux estimate derived from the BIONAPL simulation. The ethanol from the E10 source passed Row 4 within 300 days, consistent with a soluble chemical dissolving into the groundwater and being transported without retardation. In Row 2, the day 50 sampling produced a much higher than expected ethanol mass flux and this suggests the actual flux likely arrived as a shorter "slug" in a shorter time period than predicted by equilibrium dissolution and advection and dispersion modeling. This is consistent with essentially all the

ethanol dissolving in the groundwater co-injected with the E10.

Little mass of injected ethanol passed Row 4. Ethanol mass was lost due to biodegradation, but little product (acetate, methane) was found (Mocanu, 2007). The effect of ethanol biotransformation on benzene bioattenuation is examined next.

3.2 Benzene

Figures 3 and 4 show similar information for benzene in the GMT plume and in the E10 plume, respectively. Note that benzene was expected to have been swept through the fences by day 600 as it is quite soluble and essentially unretarded. Less soluble, more retarded aromatics (xylenes, trimethylbenzenes, and naphthalene) still remain in both the sources and dissolved plumes (see section 3.3).

Benzene flux decline in the GMT gate is consistent with biotransformation at an apparent first order rate of about 0.004 d^{-1} (Figure 3). This is similar to the apparent rate found for benzene from a dissolved gasoline source in a previous experiment at Borden (Hubbard et al., 1994). On the other hand, Hubbard et al. found that the presence of up to 6000 mg/L methanol (an alcohol with similar properties to ethanol) slowed the apparent benzene biotransformation rate to 0.001 d^{-1} . Ethanol concentrations in the E10 gate were up to 2400 mg/L, somewhat lower than the initial concentrations of methanol in the Hubbard et al. experiment. In any event, that slower rate was used in the BIONAPL model, but it did not produce a useful match with the E10 field data (Figure 4). Rather, an apparent biotransformation of 0.004 d^{-1} again produce a good fit with the field data. So, the presence of 10% ethanol in the gasoline source appears to have little adverse impact on the biotransformation rate of benzene, the most mobile and toxic of the aromatics.

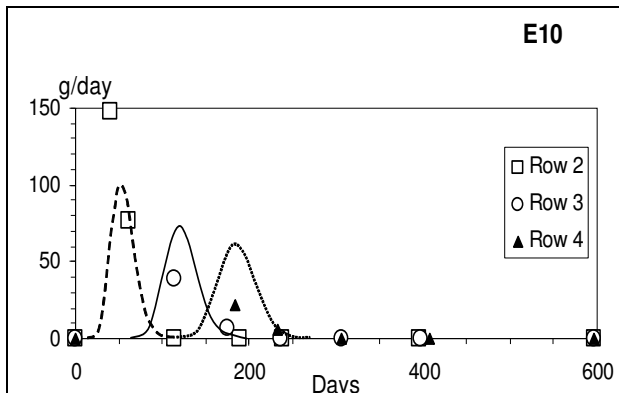


Figure 2. Mass flux of ethanol passing Row 2 and Row 4 from the E10 source. Lines are the estimated mass flux using the BIONAPL model without biodegradation. The dashed line is for Row 2, the solid line for Row 3 and the dotted line for Row 4.

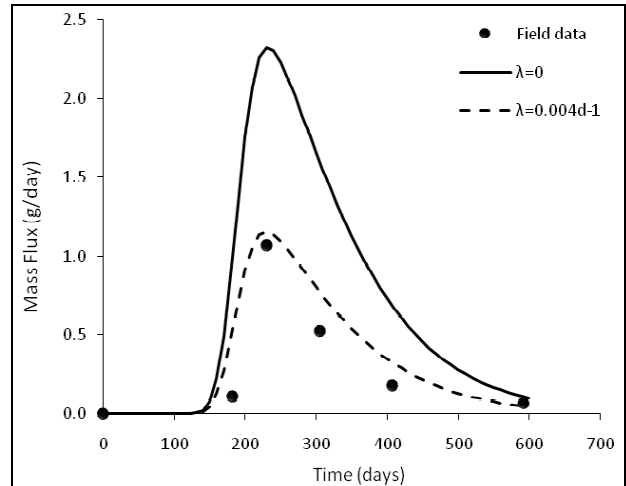


Figure 3. Observed and modeled mass flux of benzene expected at Row 4 of the GMT plume, considering no biodegradation ($\lambda = 0$), and a good fit rate ($\lambda = 0.004 \text{ d}^{-1}$).

3.3 Residual Gasoline in GMT and E10 Sources

Core collected in 2007 from the GMT and E10 sources was subsampled every 10 cm depth, extracted and analyzed for BTEX, trimethylbenzenes, and naphthalene (Yang, 2008). Only 1 core per source was collected. A second core about 30 cm downgradient of that core had no residual detected.

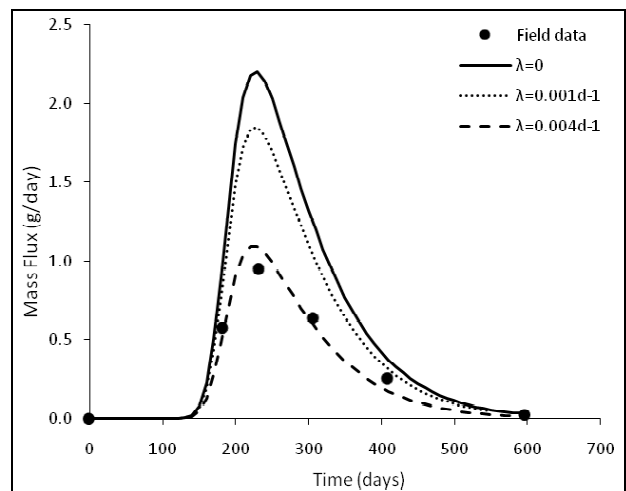


Figure 4. Observed and modeled mass flux of benzene expected at Row 4 of the E10 plume, considering no biodegradation ($\lambda = 0$), slow biodegradation as observed by Hubbard et al. ($\lambda = 0.001 \text{ d}^{-1}$) and a good fit rate ($\lambda = 0.004 \text{ d}^{-1}$).

The analyses were subjected to the calculation of Feenstra et al. (1991). Essentially, this calculates the maximum analyte that can be present in the sand core

without there needing to be a residual NAPL phase. For the GMT and E10 sources respectively, about 13 mg aromatics/kg of wet soil and 17 mg/kg was the concentration in core above which a residual NAPL phase was inferred. Figures 5 and 6 show the irregular distribution of aromatics in each source core and the depth at which gasoline had been injected to form each source zone. The highest aromatic concentrations, were found at about the same depths at which gasoline was injected and have apparently still been retained as residual NAPL.

This irregular distribution of residuals suggests the sources have not been emplaced uniformly and so were not likely dissolved uniformly at equilibrium as assume in the BIONAPL modeling and in the application of Raoult's law to describe source dissolution. Table 1 presents the estimated mass in the GMT and E10 sources in June, 2007, assuming the single core from each source is representative and that the surficial area of the source, based on injection well locations, is about 1.4 m². Also, the estimated mass of residual remaining is calculated first using Raoult's law to estimate mass dissolved and subtracting that from the initial mass to obtain residual mass (see Yang, 2008, for details).

Both calculation approaches demonstrate that a large portion of the residuals have been dissolved by day 970. Interestingly, Raoult's law estimates a much smaller mass remaining in the source than does the calculation using core data. There are probably a number of limitations which may produce such an outcome. First, Raoult's law would provide for the maximum dissolution of the NAPL and so would be expected to underestimate the NAPL residual in a heterogeneous system. In addition, groundwater sampling in Row 2 in January, 2008 still found benzene, so the source is clearly not free of benzene as the Raoult's law model suggests. On the other hand, assuming one core in the centre of the source represents the total source likely results in an over estimate of the mass in the source.

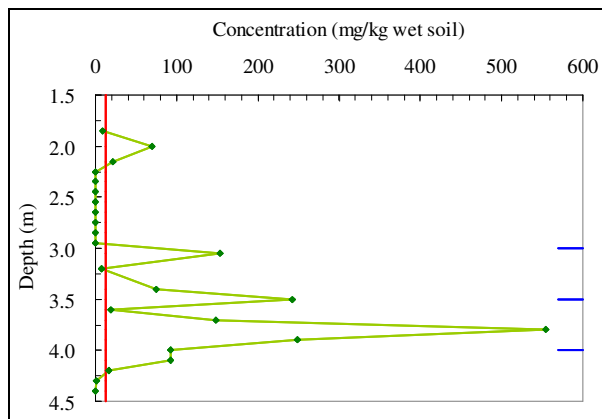


Figure 5. Distribution of BTEX + trimethylbenzenes + naphthalene found in core from the GMT source. The vertical line is the minimum soil concentration at which a residual phase likely persists. The three horizontal lines are depths at which GMT gasoline was injected.

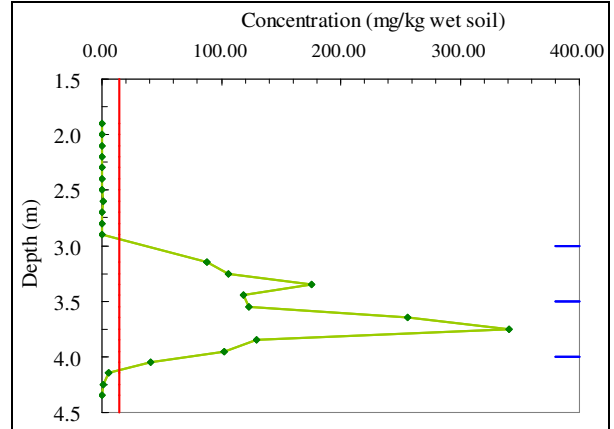


Figure 6. Distribution of BTEX + trimethylbenzenes + naphthalene found in core from the E10 source. The vertical line is the minimum soil concentration at which a residual phase likely persists. The three horizontal lines are depths at which E10 was injected.

Table 1. Injected mass in GMT and E10 sources and residual mass as of June, 2007, estimated from core data and from calculation based on Raoult's law.

Compound	Injected mass (g)	Residual mass estimate from core (g)	Residual mass Raoult's law (g)
GMT source			
B	390	28	0.0
T	2500	69	700
E	1100	51	420
P,m-X	2400	74	960
o-X	840	39	310
1,3,5-TMB	350	42	200
1,2,4-TMB	1100	110	760
1,2,3-TMB	220	19	140
Naphthalene	170	17	84
E10 Source			
Benzene	330	8.4	0.0
T	2100	41	810
E	910	60	310
P,m-X	2000	110	740
o-X	710	47	230
1,3,5-TMB	290	28	200
1,2,4-TMB	910	76	610
1,2,3-TMB	180	13	120
Naphthalene	140	15	57

The depth of high residual aromatics corresponds well with high dissolved aromatic concentrations in a multilevel well 3.5 m downgradient of the core for both sources/plumes. This is illustrated in Figure 7 for the E10 source and plume. This confirms that the heterogeneities

of contaminant distribution in the plume are largely derived from the heterogeneity of the residual source. This is in a rather homogeneous sand aquifer with essentially horizontal groundwater flow and so may not be found at sites where flow itself is more complex.

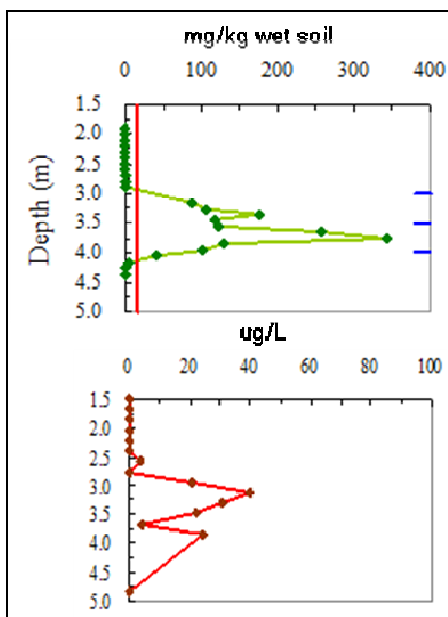


Figure 7. Distribution of total aromatics in core (top) from the centre of the E10 source and in groundwater (bottom) 3.5m downgradient of the core location.

3.4 Electron Acceptor Considerations

In this segment of the Borden aquifer, dissolved oxygen is the dominant electron acceptor. The flux of oxygen entering the source from upgradient, as well as the oxygen available by transverse mixing was calculated using a measured average background oxygen concentration of 4 mg/L and well defined Borden dispersivity values (Sudicky, 1986). In brief, there was simply not enough oxygen available to support complete mineralization of the missing ethanol and aromatic mass to dissolved inorganic carbon. Preliminary modeling was also done using BIONAPL with dual Monod kinetic terms to account for both electron acceptor and organic compound utilization. Again, the calculated rate of mass loss for benzene, for example, was much lower than observed. Evidence for use of other electron acceptors is absent. For example, very little sulfate utilization and methane production was noted. Partial mineralization to organic acids may improve the electron acceptor – electron donor mass balance, but few samples were analyzed to test this hypothesis.

4 SUMMARY

Ethanol biotransformed quickly in the Borden aquifer, but does not seem to impair the biotransformation of benzene

when both are derived from E10 gasoline. Core from within the injected source zones confirms the vertical aspect of source locations and demonstrates a good spatial correlation with downgradient vertical dissolved aromatic distributions. It appears that heterogeneity of sources will be a dominant cause of heterogeneous contaminant distribution in the downgradient plume, at least for rather homogeneous sand aquifers such as Borden. There appears to be insufficient electron acceptors (oxygen) to account for complete mineralization of the unaccounted for mass of ethanol and aromatics apparently biotransformed. Ongoing research will try to resolve this issue.

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