Is Methane Produced from a Fuel-Ethanol Spill Predictable?

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Abstract

With an increase in the use, production, and transportation of fuel-ethanol, the likelihood of a release increases. Under anaerobic conditions, ethanol biodegrades to acetate, which then biodegrades to methane. This methane has been shown to get to explosive levels. The purpose of this study was to examine the predictability of methane produced from fuel-ethanol spills. A conceptual mass budget model was constructed and compared to measured data collected from two E95 fuel-ethanol spill sites. The model consistently predicted higher concentrations of dissolved methane than what was measured and consistently predicted lower concentrations of soil gas methane than what was measured. This difference is likely due to the many assumptions of the model. Based on chi square analyses, there was no significant agreement between the models and the measured data. Calculated ethanol decay rates fell within the range of findings from other studies. In order to further inspect the measured data, correlation coefficients were calculated. Correlation analysis showed a significant, positive correlation between acetate and dissolved methane for both sites and significant, positive correlation between dissolved methane and soil gas methane for one site. Overall, the model contains useful concepts and is a starting point for understanding the complex degradation process. The results demonstrate how site physical characteristics play a role in contaminant fate and transport. The model is useful in that it gives us an idea of the sensitivity of the resulting concentrations to the inputted rate constants and coefficients. The correlation calculations are useful, in that there is a significant pattern in constituent increase. Finally, because the model only encompasses biological decay and spreading from groundwater flow, the results show the environmental process is not that simple.

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Introduction

Importance

Ethanol Use, Production, and Transportation

In an effort to reduce American dependence on foreign resources and to encourage the use of renewable, cleaner energy, Congress passed The Energy Independence and Security Act was passed in 2007. The Act increased the volume of renewable fuel required to be mixed into transportation fuel in the United States from 9 billion gallons in 2008 to 36 billion gallons by 2022 (EPA, 2013). Many states also passed legislation to increase the volume of renewable fuel used. In Minnesota, Statute §239.791, subdivision 1a was passed in 2005 mandating that all gasoline sold in Minnesota must contain 20 percent ethanol by August 30, 2013 (Connelly, 2011). This statute was revised in 2012 and the date changed to August 30, 2015.

As a result of these mandates, ethanol production in the United States has more than doubled in the past 6 years to 14 billion gallons (EIA, 2012). With 21 ethanol plants, production in Minnesota has more than doubled in the past 10 years to 1.1 billion gallons produced per year with 80 percent of the production being exported (Ye, 2012).

Increased use and production leads to increased transportation of ethanol. Ethanol cannot be produced in the same facilities as petroleum due to its hygroscopic properties (McDowell, 2003). Therefore, it is transported mainly by tanker truck, railcar, and tank barges, rather than by pipeline networks like most petroleum (McDowell, 2003; ITRC, 2011; Shaw, 2011). This variable and less direct route increases the likelihood of a release. Also, releases can occur from material incompatibility within the supply chain, such as storage tanks, hosing, piping, dispensers, and leak detectors (ITRC, 2011). Thus, an increase in the use, production, and transportation of ethanol results in a higher likelihood of ethanol releases.

Hazards

Although ethanol is well known to be easily biodegradable in soil, less is known about ethanol's degradation products. Ethanol spills have been shown to produce large amounts of methane, sometimes exceeding explosive limits. Methane is able to diffuse out of soil and into the atmosphere or intrude into buildings or basements. In cases like these, methane gas could pose an explosion risk or fire hazard where oxygen levels are higher. Methane combustion occurs by the following equation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (1)$$

The equation shows methane requires a certain mixture with oxygen in order to be a fire risk. This is also evidenced by Coward's Diagram as seen in Figure 1. Methane needs to be between 5-14% by volume at the same time oxygen needs to be between 11-20% by volume to be spontaneously explosive.

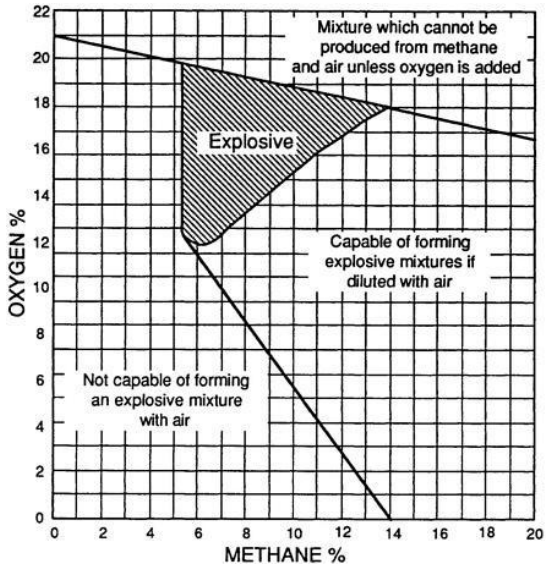


Figure 1: Coward's Diagram of methane flammability (1931). Adapted by Garcia, H.D.; James, J.T., 2004.

At high levels, methane can cause human health risks. Methane is a simple asphyxiant that displaces oxygen in a confined space. In this way, methane can cause suffocation, headache, dizziness, vomiting, or loss of consciousness (Brown, 2013). There is no enforceable Permissible Exposure Limit (PEL) set by OSHA for methane, but the

American Conference of Governmental Industrial Hygienists (ACGIH) recommends a Threshold Limit Value (TLV) of 1000 ppm (*Material safety data sheet: Methane*, 2010).

Overview

Requirements for Biodegradation

Bacteria are the drivers of contaminant biodegradation. In order for a contaminant to biodegrade, bacteria need to reside in the soil. Bacteria use certain contaminants as energy and carbon sources and can also catalyze contaminant conversion to products useful to other bacteria. Bacteria can only exist in certain environmental conditions that sustain life functions. They need favorable nutrients, pH, temperature, and moisture. Bacteria require carbon, nitrogen, phosphorus, and some trace metals to grow and reproduce, but not amounts high enough to be toxic. They function best in neutral pH (6-8) environments, and at temperatures ranging from 20ºC-40ºC (Alvarez & Hunt, 1999). Moisture levels below 40 percent of field capacity will negatively affect the amount of nutrients bacteria can use. Moisture content around 80 percent is optimal for vadose zone bacteria. Aquifers typically meet most if not all of the environmental requirements for bacteria, and therefore, a variety of bacteria are able to flourish.

Extracellular enzymes that mediate biodegradation need to come into contact with contamination in order to degrade it. This means the bonds requiring cleavage must be exposed and not sterically blocked. There are many mechanisms that could reduce the ability of bacteria to meet with a contaminant; the contaminant could be adsorbed or complexed onto a solid surface, it could be sequestered in soil pores, or it could partition into non aqueous phase liquids (Alvarez & Hunt, 1999). Intracelluar enzymes require the ability of the contaminant to pass through the cell membrane to be degraded.

Due to ethanol's chemical properties, it is considered highly bioavailable. Ethanol is completely miscible with water, and therefore very accessible for bacterial degradation. Thus, many species of bacteria can degrade ethanol.

Natural Ethanol Production and Degradation

In nature, ethanol is produced from bacterial fermentation of starches and sugars within organic matter. This can be represented by glucose breaking down to form ethanol and carbon dioxide in anaerobic conditions:

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \quad (2)$$

From here, ethanol can be degraded aerobically or anaerobically. In the presence of oxygen, ethanol is reduced to carbon dioxide via the tricarboxylic acid cycle. This process does not produce any concerning byproducts and takes place intracellularly. Ethanol can also be degraded anaerobically by the combined action of several different types of bacteria (White, 1995). Of course, this anaerobic degradation follows the sequential utilization of nitrate, manganese IV, ferric iron, and sulfate as electron acceptors before getting to carbon dioxide which has the metabolic by-product of methane (Alvarez & Hunt, 1999; Karvonen, 2002; Railsback, 2006). In the first step of ethanol degradation, bacteria degrade ethanol to acetate and hydrogen (Alvarez & Hunt, 1999; Wilson, 2013).

$$2CH_3CH_2OH + 2H_2O \rightarrow 2CH_3COO^- + 2H^+ + 4H_2 \quad (3)$$

In the second step, assuming a highly-reduced environment where all other more favorable electron acceptors have been used, a group of methanogenic bacteria metabolize acetate and hydrogen to methane.

$$2CH_3COO^- + 2H_2O \rightarrow 2CH_4 + 2HCO_3^- \quad (4)$$

To complicate matters, some bacteria can directly form methane from surrounding hydrogen and bicarbonate.

$$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O \quad (5)$$

Also, some bacteria can directly form acetate from surrounding hydrogen and bicarbonate.

$$4H_2 + 2HCO_3^- + H^+ \rightarrow CH_3COO^- + 4H_2O \quad (6)$$

This acetate can be used to by methanogenic bacteria to produce more methane under anaerobic conditions. Bicarbonate can combine with hydrogen again to make carbon dioxide and water.

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \quad (7)$$

The degradation process can be much more complex depending on the available microorganisms and the redox conditions. There are also sulfate-reducing bacteria which use hydrogen and sulfate to produce sulfide. These sulfate-reducing bacteria can decrease the amount of hydrogen available for the methanogenic bacteria to use in the production of methane. The addition of equations 3, 4, 5, and 7 results in the overall equation for methanogenesis from ethanol:

$$CH_3CH_2OH \rightarrow 1.5\ CH_4 + 0.5\ CO_2 \quad (8)$$

Therefore, for every mole of ethanol, 1.5 moles of methane are produced under anaerobic and highly-reduced conditions.

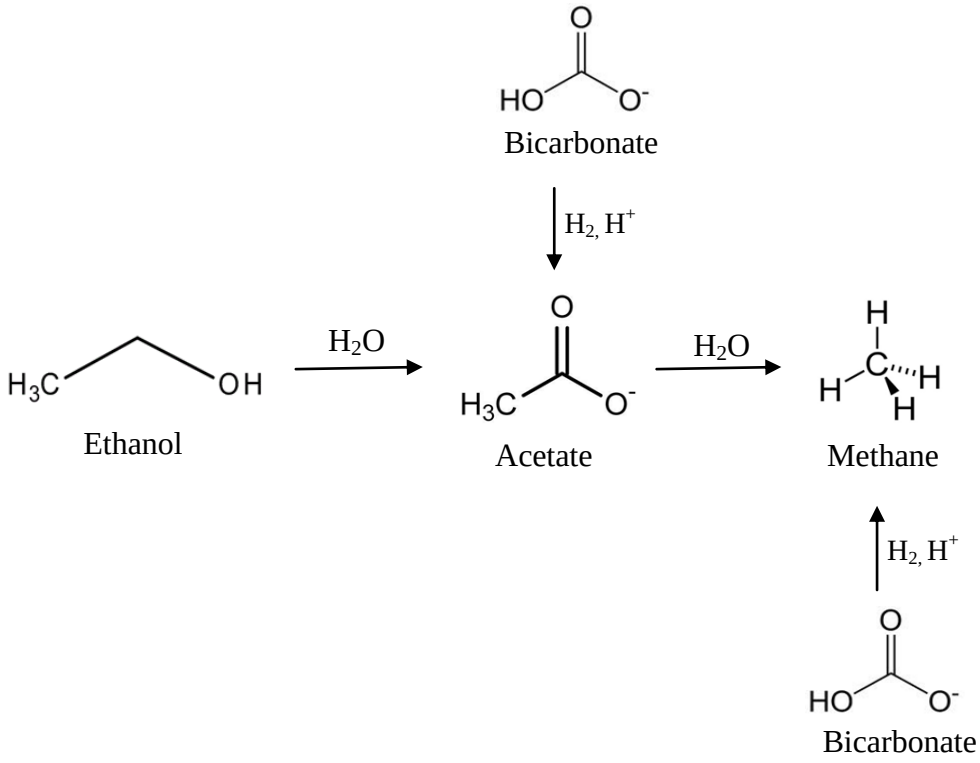


Figure 2: Anaerobic biodegradation of ethanol.

Pathways of Methane in Soil

Methane can be removed by oxidation under aerobic conditions and there is growing evidence that oxidation of methane can also occur under anaerobic conditions. Under aerobic conditions, proteobacteria oxidize methane to carbon dioxide typically at the border between the oxic and the anoxic layers, or just above the water table (O'Connor, 2009). Under anaerobic conditions, sulfate is the terminal electron acceptor and hydrogen sulfide is produced (Boetius et al., 2000). The mechanism for anaerobic oxidation is still unknown and the degree to which the process occurs in soils is not completely understood. However, both of these processes decrease the amount of methane that could move out of the ground or into basements.

There are four pathways of transport for methane that can be combined in any way; diffusion, advection, ebullition, and plant-mediated. Diffusion is the random movement of methane molecules moving from high to low concentration. Advection is mass transport with the mean fluid flow. This movement is due to a pressure differential between two areas. Ebullition is the bubbling of gas from the sediment to the atmosphere. At high levels, methane can form bubbles and escape from soil or water. Finally, plants can mediate methane transport via intercellular spaces, allowing methane to travel through oxic layers without contacting oxidizing bacteria.

Degradation Rates

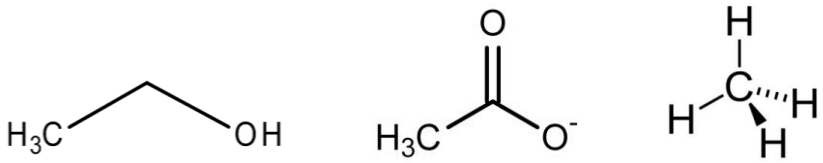
The rate of degradation of ethanol depends on the amount and healthiness of the bacteria, pH, temperature, and nutrient conditions as previously mentioned. Most bacteria will not survive ethanol concentrations higher than 100,000 mg/L (Alvarez & Hunt, 1999), and more recent research indicates concentrations over 60,000 mg/L are toxic (Nelson et al., 2010). It is possible that near source areas, the ethanol will not be degraded if all of the bacteria have died. There have been limited field studies of ethanol biodegradation rates with various results. Field studies have found ethanol half-lives ranging from 2.2 days to 2.1 years (Zhang et al., 2006; Corseuil et al., 2011; Mravik et al., 2003). There has been one field study which used methanol and found a half-life of 40 days (Butler et al., 1992).

There have been a few laboratory studies which have shown ethanol anaerobically degrading in 12-25 days (Kavanaugh, 1999), and aerobically in 0.1-5 days (Davidson, 2001).

Chemical Properties of Ethanol and its Degradates

Substance	Boiling Point (°C)	Melting Point (°C)	Density (g/mL)	Water Solubility (mg/L) at 25°C	Vapor Pressure (mmHg) at 25°C	Octanol-water partition coeff (K_{ow})	Organic carbon-water partition coeff (K_{oc})	Henry's Law constant (atm-m3/mole)
Ethanol	65.1	-87.8	0.789	infinite	59.3	-0.31	1.05	5.0e-6
Acetate	122.3	-21.26	1.05	infinite	17.2	-0.17	1.0	1.0e-7
Methane	-62.4	-152.9	0.66	22.0	5.31e5	1.09	3.98	6.58e-1

Table 1: Substance chemical properties. Values obtained from Environmental Protection Agency's EPI Suite database.



Ethanol Acetate Methane

Figure 3: Chemical structures of substances.

Properties of Ethanol

Ethanol is an organic compound containing a hydroxyl group. The structure of ethanol resembles water as seen in Figure 3, with an alkyl group replacing one of the hydrogen atoms. For a similar molecular weight molecule such as propane, ethanol has a boiling point 120°C higher, suggesting very high intermolecular attraction (Wade, 2010). Hydrogen bonding of the hydroxyl hydrogen atom is responsible for this high boiling point.

Based on ethanol's properties as seen in Table 1, ethanol is expected to have high mobility through soil. Ethanol is infinitely soluble in water and will not adsorb to soil

particles. Some volatilization of ethanol will occur. Due to ethanol's low density, it is expected to accumulate in the capillary fringe (Freitas et al., 2011; McDowell et al., 2003). Ethanol is not expected to bioconcentrate.

Properties of Acetate

Acetate is a derivative ion of acetic acid. It is a carboxylic acid that contains a carboxyl group. It is strongly polar, and completely miscible in water.

Like ethanol, acetate is also expected to be highly mobile in soil and is infinitely soluble in water. With a low vapor pressure, acetate is not very volatile. The density of acetate is comparable to water. Acetate has a low potential for bioconcentration.

Properties of Methane

Methane is a one-carbon alkane. It is non-reactive, non-polar, and is odorless (Wade, 2010). It is a gas at room temperature and pressure.

As seen in Table 1, methane is not very soluble in water. It will start to come out of solution at 14.5ºC (MDH, 2013). Groundwater is typically in the range of 5°C-15ºC, so methane will start to be released as it is pulled out of the ground as it becomes warmer. The vapor pressure is high, as methane is a gas at standard temperature and pressure. The lower density of methane indicates it will rise in ambient air. Methane has a low potential for bioconcentration.

Spill Site Backgrounds

Fuel-Grade Ethanol

Ethanol has replaced methyl tert-butyl ether (MTBE) as a fuel oxygenate in many states due to its lessened toxicity and renewability. In Minnesota, essentially all gasoline sold is blended with 10 percent ethanol- also called E10 (Connelly, 2011). Flex fuel vehicles are equipped to use 85 percent ethanol (E85). Ethanol is produced by fermenting large amounts of organic matter- typically corn- then distilled and put through a molecular sieve. This results in anhydrous ethyl alcohol, nearly 200 proof. Fuel ethanol is then

denatured to make unfit for human consumption by adding between 2 percent and 5 percent gasoline, creating E95 (EPA, 2009).

Balaton, Minnesota

On July 28, 2004, a train derailment occurred in Balaton, MN where an estimated 40,000 gallons of E95 denatured ethanol was spilled (Pinnacle Engineering, 2007). The site is located in Western Minnesota south of Lake Yankton. Remediation of the site consisted of constructing a holding pond from clay berms to collect free product which was then pumped off and sent to a treatment plant. In addition, the spill area was excavated to a depth of 18 inches for a total of 2100 cubic yards of soil removed. It is estimated that 10,000 gallons of the contamination remained (Spalding et al., 2011). The source area was estimated to be limited to a 6075 square foot area just northwest of a grain elevator. Monitoring wells and vapor points have been installed at this site and data has been collected since 2005. See Appendix A for a site map.

The groundwater province in this area of Minnesota is characterized by clayey glacial drift overlying bedrock (DNR, 2013). Soil borings from unpublished MPCA data show poorly sorted silty sands over top of variable silty/sandy/clay layers.

Surface elevation at the Balaton site ranges between 1515-1523 feet above mean sea level. Well depths are between 8-23 feet with screen lengths between 5-10 feet. See Appendix C for a cross section with projected wells.

Cambria, Minnesota

On November 22, 2006 a train derailment occurred in Cambria, MN where an estimated 25,000 gallons of E95 denatured ethanol was spilled. The site is located in south central Minnesota on the floodplains of the Minnesota River next to the Little Cottonwood River. Remediation of the site consisted of removing 11,500 gallons of pooled liquid. It is estimated that 13,000 gallons of the contamination remained (Spalding et al., 2011). Source areas were estimated to be limited to a 10,000 square foot area south of the tracks

and a 3600 square foot area at the trestle. Monitoring wells and vapor points have been installed at this site and data has been collected since 2007. See Appendix B for site map.

The groundwater province in this area of Minnesota is characterized by thick clayey glacial drift overlying sandstone, limestone, and dolostone aquifers (DNR, 2013). As this site is in a floodplain, soil borings from unpublished MPCA data show poorly sorted silty-sand and loam.

Surface elevation at the Cambria site ranges between 790-803 feet above mean sea level. The total well depths are between 7-40 feet with 5 foot length screens. See Appendix D for a cross section with projected wells.

Project Statement

With increasing production, use, and transportation of fuel-grade ethanol, likelihood of a release increases. Although ethanol is known to be readily biodegradable in soil, the degradation product of methane has concerning hazards. The objective of this paper was to assess the predictability of methane produced from an ethanol spill. A conceptual mass budget model of parameters was constructed and compared to measured data collected from two E95 spill sites. As part of the model, decay rates for ethanol and acetate were calculated. In order to further inspect measured data, correlations between ethanol and its breakdown products and dissolved versus soil gas phases were calculated to assess methane's predictability.

Methods

Sampling and Labs

Samples were collected from the Balaton spill site since 2005 and from the Cambria spill site since 2007 between two and three times a year. The analytes used in the analyses

were dissolved ethanol, dissolved acetate, dissolved methane, and soil gas methane. Monitoring well water was analyzed at the Minnesota Department of Health laboratory (MDH) for concentrations of dissolved ethanol and dissolved acetate and using EPA method 8260 and EPA method 300.1, respectively. Method 8260 uses gas chromatography-mass spectrometry while method 300.1 uses ion chromatography. Monitoring well water was also analyzed for dissolved methane at Interpoll Laboratory using method RSK- 175, also known as EPA modified method Headspace gas chromatography with a flame ionization detector. Vapor points were analyzed for soil gas methane at Pace Analytical using Method 3C Air for Fixed Gases which uses gas chromatography. Measurements of soil gas were also taken in the field using a Landtec GEM gas meter.

For more detailed information describing sampling methods and analyses, refer to MPCA guidance document on investigation requirements for ethanol blended fuel- releases: Appendix E.

Conceptual Mass Budget Model

It would be expected based on anaerobic biodegradation of ethanol, Equations 3-8, that as ethanol degrades, there would be an increasing concentration of acetate, followed shortly thereafter by an increase in dissolved methane. Presumably the primary methane would be dissolved as the bacteria that produce methane are in the anaerobic zone which is beneath the water table. Ethanol is being biologically biodegraded to acetate at the same time it is advected downgradient from the source area by groundwater flow and dispersed leading to reduced concentration. Acetate is also being biologically biodegraded to methane at the same time it is being advected downgradient with flowing groundwater away from its source zone and being dispersed. Dissolved methane will also be advected downgradient and dispersed from groundwater flow, while it is also partitioned into the gas phase. A mass budget model encompassing these concepts of ethanol biodegradation and spreading was constructed in MATLAB R2013b and the ordinary differential

equations were solved using the ode45 function. See Appendix F for the MATLAB code. The mass budget equation for ethanol is given by

$$\frac{dC_1}{dt} = \{-k_1 C_1\} - \{RC_1\} \quad (9)$$

where C_1 is ethanol concentration in g/m^3, k_1 is the biological ethanol decay rate in 1/days, and R is the spreading rate constant in 1/days. This equation accounts for the first-order biological decay of ethanol and the spreading of ethanol due to advection produced from flowing groundwater. The mass budget equation for acetate is given by

$$\frac{dC_2}{dt} = \{1.0 * k_1 C_1\} - \{k_2 C_2\} - \{RC_2\} \quad (10)$$

where C_2 is the concentration of acetate in g/m^3, 1.0 is the stoichiometric coefficient for the conversion of ethanol to acetate, k_2 is the biological acetate decay rate in 1/days. This equation accounts for the conversion of ethanol to acetate and the spreading of the acetate plume due to dispersion produced by flowing groundwater. The mass balance equation for dissolved methane is given by

$$\frac{dC_3}{dt} = \{1.5 * k_2 C_2\} - \left\{\frac{D_{aqgas}^{**}}{T\_sat} * \left[C_3 - \frac{C_4}{H}\right]\right\} - \{RC_3\} \quad (11)$$

where C_3 is the dissolved methane concentration in g/m^3, 1.5 is the stoichiometric coefficient for the conversion of acetate to methane, D_{aqgas}^{**} is the diffusion conductance coefficient for methane between water and soil gas air in meters/day, T_sat is the thickness of the saturated layer in meters, C_4 is the gaseous methane concentration in g/m^3, and H is the unitless Henry's Law Constant for methane. This equation accounts for the conversion of acetate to dissolved methane and the dispersion of the dissolved methane plume. The changing concentration of gaseous methane over time is given by

$$\frac{dC_4}{dt} = \left\{\frac{D_{aqgas}^{**}}{T\_unsat} * \left[C_3 - \frac{C_4}{H}\right]\right\} - \left\{\frac{D_{gas}^{**}}{T\_unsat} * C_4\right\} \quad (12)$$

where C_4 is the gaseous methane concentration in g/m^3, T_unsat is the thickness of the unsaturated layer in meters, and D_{gas}^{**} is the diffusion conductance coefficient for methane between soil gas air and the atmospheric air in meters/day. This equation accounts for the conversion of dissolved methane to gaseous methane and the loss of methane gas to the atmosphere.

Determination of Rate Constants and Coefficients

Spreading Rate Constant

The spreading rate constant, R, in Equations 9-11 accounts for the loss in concentration of the constituent away from the source zone due to advection and dispersion from groundwater flow. This term was obtained by calculating a Darcy velocity in meters/day using a calculated hydraulic conductivity based on properties of water and soil type. Darcy's Law for one-dimensional laminar flow is described by the equation:

$$q = -K \frac{\Delta h}{\Delta L} \tag{13}$$

where q is specific discharge or Darcy velocity, K is hydraulic conductivity, h is hydraulic head, and L is distance. Within this equation, hydraulic conductivity is described by

$$K = \frac{\rho g k}{\mu} \tag{14}$$

where K is hydraulic conductivity, ρ is the density of the fluid, g is gravitational acceleration, k is the permeability of the porous material, and μ is the dynamic viscosity of the fluid. Therefore, hydraulic conductivity describes how easily a porous material transmits fluid which includes properties of the solid matrix and properties of the fluid. The intrinsic permeability, k, of the spill site soil textures were estimated based on Figure 4. This flow rate is divided by the thickness of the layer though which the contamination is located. The end result is essentially a rate constant describing how the particular material flows through a particular porous matrix in 1/days. In this case, it describes the rate that water with dissolved ethanol, acetate, or methane flows through the soil type of the Balaton or Cambria site and away from the source zone.

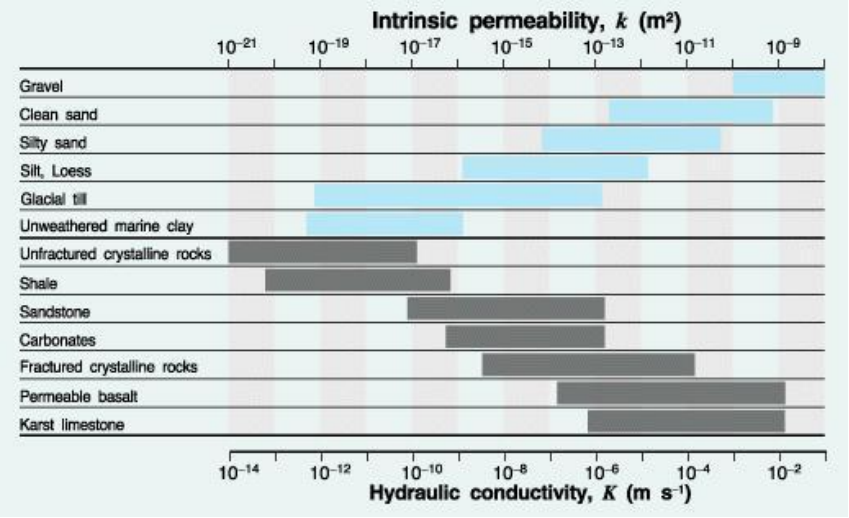


Figure 4: Ranges of hydraulic conductivities and permeabilities. From Humphrey, N.F., 2006.

Biological Rate Constants

The biological rate constant, k_1, for ethanol was determined using measured data. Surfer Version 7 software was used to estimate the total mass of ethanol on each sampling date by Simpson's Rule. This rule uses a formula to approximate the integral of a function or set of functions using parabolic arcs rather than straight line segments. The resulting mass of ethanol was plotted against days post-spill to obtain a first-order exponential biological decay rate. See Figures 5 and 6 for graphs of ethanol decay for the Balaton and Cambria spill sites, respectively. The half-life of the ethanol can be determined using the equation for first-order reaction coefficients:

$$T_{1/2} = \frac{0.693}{K} \tag{15}$$

where $T_{1/2}$ is the half-life and K is the rate constant. The half-lives of ethanol in these site conditions can be compared to other literature values.

The calculation of biological rate constant, k_2, for acetate was more complex because the rate must account for the generation of acetate from ethanol. Therefore, k_2 was solved for its best fit using the Solver function in Microsoft Excel. The solver found the value of k_2

that minimized the difference between theoretical concentrations of acetate and the measured concentrations of acetate. See Appendix G for additional explanation.

Diffusion Coefficients

Methane diffusion coefficients in m^2/day were taken from Schwarzenbach et al. (1993). Since these values represent diffusion in free space, soil porosity and tortuosity needed to be taken into account using the effective diffusion coefficient. The effective diffusion coefficient as described by Ho and Webb (2006) when the gas saturation is assumed to be one is given by

$$D^* = \emptyset * \tau * D \tag{16}$$

where $\emptyset$ is total porosity, τ is tortuosity, and D is the diffusion coefficient in free space. Tortuosity is given by

$$\tau = \emptyset^{1/3} \tag{17}$$

The resulting effective diffusion coefficient D* is then divided by the thickness over which the concentration difference occurs to obtain D** in m/day. See Appendix H for more details.

Stoichiometric Coefficients

The stoichiometric coefficient between ethanol and acetate of 1.0 is obtained by dividing Equation 3 through by two. The stoichiometric coefficient of 1.5 between acetate and methane is obtained by adding Equations 4 and 5 and dividing through by two.

Thickness of Layers

The thickness of the unsaturated layer was calculated by the average distance to the water table. The thickness of the impacted saturated layer is assumed to be one meter. This assumption tries to incorporate the low density of ethanol, which points to ethanol tending to accumulate near the top of the water table and within the capillary fringe.

Concentration Change over Time

Since samples were taken from various monitoring wells with various measurements of non-detection towards the edge of the plume on each sampling date, kriging using Simpson's Rule was used in Surfer Version 7 software to estimate a total mass of each constituent and the total volume of impacted soil. The total mass was divided by the total volume of soil, multiplied by the porosity of the soil to obtain an estimated concentration for each sampling date. This calculation provides for a more accurate picture of concentration change over time in the field that can be compared to the model, rather than using averaged concentrations for each sampling date. See the results of the kriged field concentrations over time in Figures 7 and 8 for the Balaton and Cambria spill sites, respectively.

Correlations

Besides conceptual modeling using calculated coefficients, correlation coefficients between dissolved ethanol and acetate, dissolved acetate and methane, dissolved methane and ethanol, and dissolved methane and soil gas methane of the measured data were calculated in order to determine if measured data contains patterns of parameter increase or decrease.

To review, a correlation is a measure of the degree of linear relationship between two variables. The Pearson product-moment correlation coefficient, r, is a description of the relationship and is between -1 and +1. Negative values of r indicate negative correlation, positive values of r indicate positive correlation, and an r value of 0 indicates no correlation. Correlation is calculated by the following equation:

$$r = \frac{\Sigma\left(x-\bar{x}\right)(y-\bar{y})}{\sqrt{\Sigma(x-\bar{x})^2\,\Sigma(y-\bar{y})^2}} \tag{18}$$

where x and y are observations. The statistical significance of the Pearson product-moment correlation coefficient is determined using a critical value table, which depends on the sample size (Siegle, 2009).

Theoretically, it would be expected that ethanol would be negatively correlated with acetate and methane, since acetate and methane are produced as ethanol degrades. It becomes less clear from here as acetate and methane can have sources other than ethanol. Recall the complexity of ethanol biodegradation in Figure 2. Depending upon the buildup of acetate, acetate and methane could be positively or negatively correlated. Acetate could still be produced during breakdown of persistent ethanol while methane begins to be produced. This would be indicated by a positive correlation of acetate and methane. If ethanol has been completely degraded, acetate concentrations may begin to decrease as methane is beginning to be produced, indicated by a negative correlation.

Results

Biological Decay

Rates of biological decay for ethanol and acetate for Balaton and Cambria ethanol spill sites were calculated as described on Page 14. Half-lives were calculated according to Equation 15 and are shown in Table 2. The ethanol half-lives fall within the literature values for other field studies ranging from 2.2 days to 2.1 years (Zhang et al., 2006; Corseuil et al., 2011; Mravik et al., 2003). The ethanol and acetate decay rates are faster at the Balaton spill site than at Cambria.

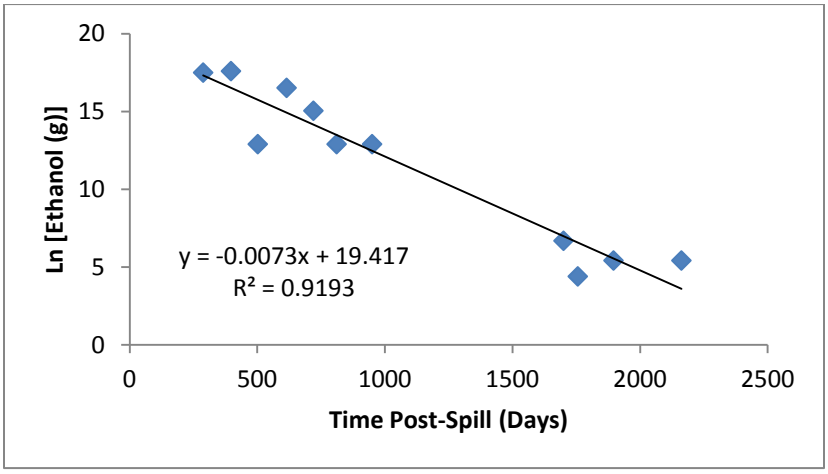


Figure 5: Balaton spill site ethanol decay. Diamonds represent estimated mass of ethanol calculated from Surfer kriging. The solid line represents the estimated decay trendline.

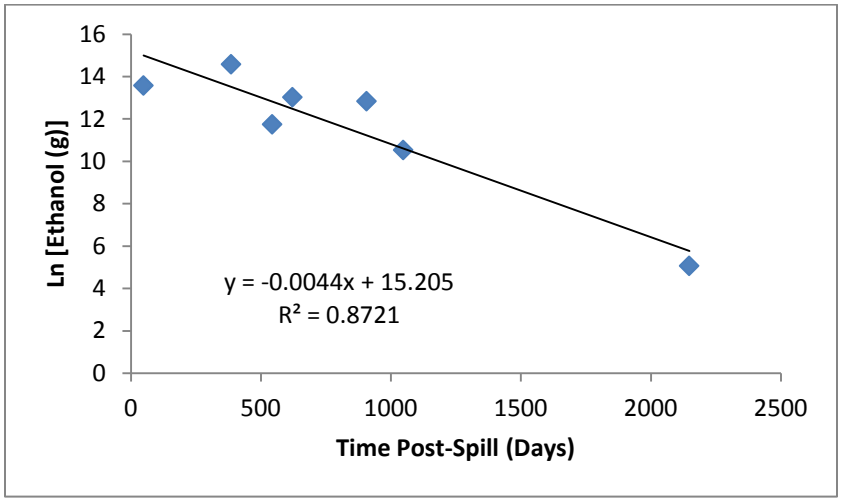


Figure 6: Cambria spill site ethanol decay. Diamonds represent estimated mass of ethanol calculated from Surfer kriging. The solid line represents the estimated decay trendline.

Site	Parameter	Estimated Rate Constant (1/day)	Estimated Half-life (days)
Balaton	Ethanol	-0.0073	94.9
	Acetate	-0.00452	153
Cambria	Ethanol	-0.0044	158
	Acetate	-0.0022	315

Table 2: Site rate constants and calculated half-lives. Acetate rate constants based on best fit using Microsoft Excel solver function.

Conceptual Model

The conceptual models for ethanol biodegradation encompassing differential Equations 9-12 as modeled in MATLAB are displayed in Figures 9-12. For reference, Figures 7 and 8 show only the measured data over time as calculated using Surfer kriging. It is seen that the Balaton acetate model overpredicts the rate of decay of acetate, overpredicts the concentrations of dissolved methane, and underpredicts the concentrations of soil gas methane. There was no significant agreement between the Balaton site ethanol, acetate, dissolved methane, or soil gas methane model and the respective measured data based on chi square analyses, $\chi^2(8, N = 9) = 5.78E+04$, $p = 0.05$, $\chi^2(11, N = 12) = 9.72E+04$, $p = 0.05$, $\chi^2(13, N = 14) = 2.98E+08$, $p = 0.05$, $\chi^2(10, N = 11) = 1.85E+06$, $p = 0.05$. It is seen that the Cambria model overpredicts concentrations of

dissolved methane and underpredicts concentrations of soil gas methane. Also, there was no significant agreement between the Cambria site ethanol, acetate, dissolved methane, or soil gas methane model and respective measured data based on chi square analyses, $\chi^2(6, N = 7) = 3.72E+03$, $p = 0.05$, $\chi^2(12, N = 13) = 1.03E+04$, $p = 0.05$, $\chi^2(12, N = 13) = 2.10E+05$, $p = 0.05$, $\chi^2(4, N = 5) = 9.95E+05$, $p = 0.05$.

Sensitivity of Model

Plausible minimum and maximum values for rate constants and coefficients were inputted into the model to test its sensitivity. The diffusion conductance coefficients D_{aqgas}** and D_{gas}** are sensitive. A high D_{aqgas}** results in very low projected concentrations of dissolved methane. A high D_{gas}** results in very low projected concentrations of soil gas methane. The model is also particularly sensitive to k_2. A high k_2 results in very low projected concentrations of acetate. See Appendix I for the tested ranges.

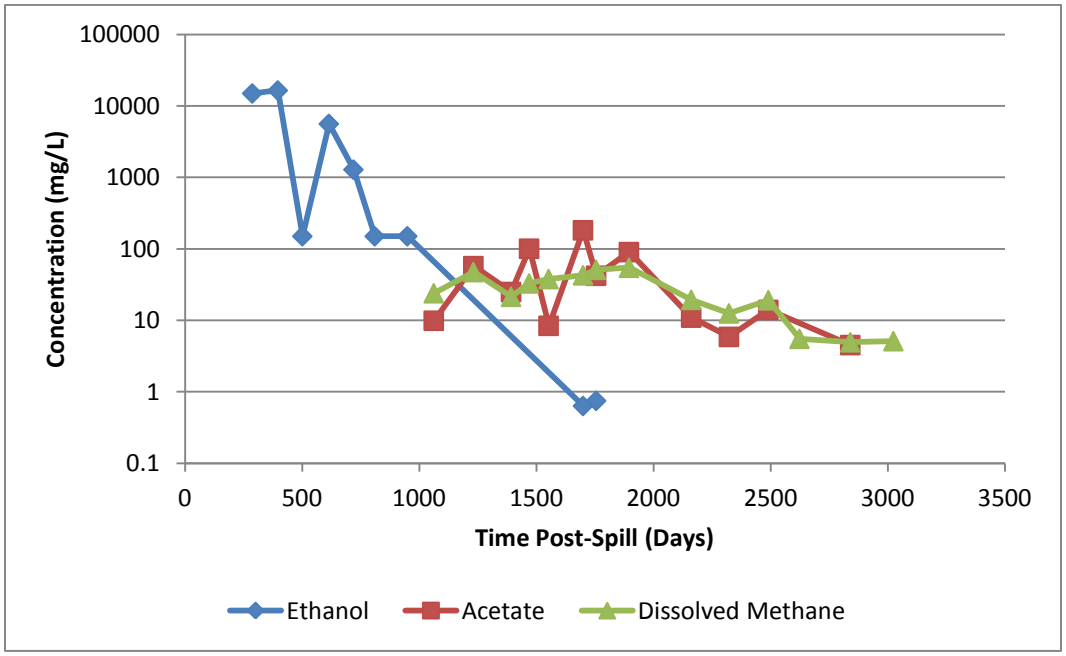


Figure 7: Balaton spill site constituent concentrations over time using total mass divided by total volume as kriged in Surfer.

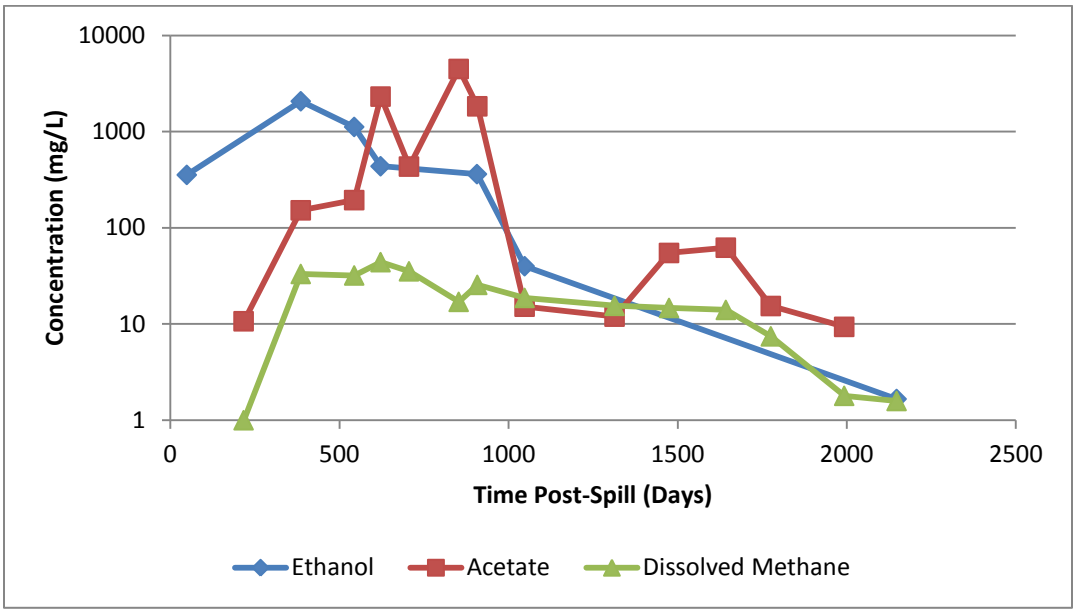


Figure 8: Cambria spill site constituent concentrations over time using total mass divided by total volume as kriged in Surfer.

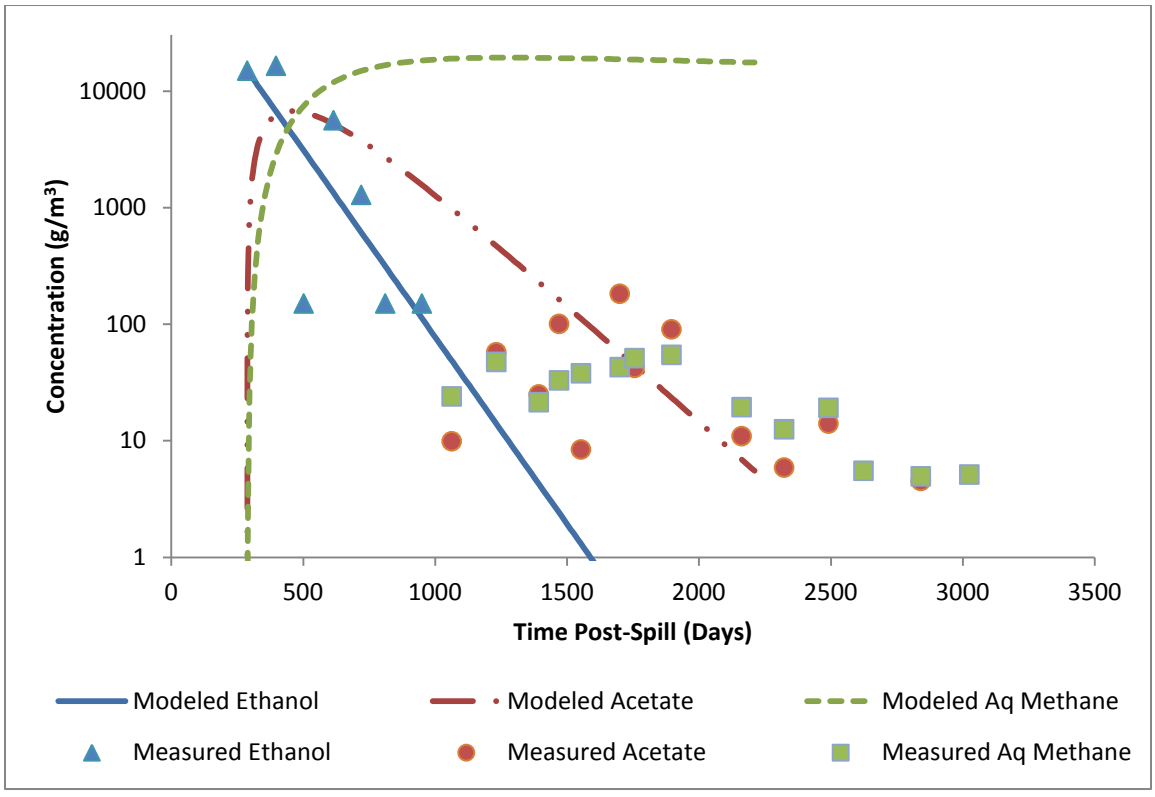


Figure 9: Balaton site model with overlaid measured data.

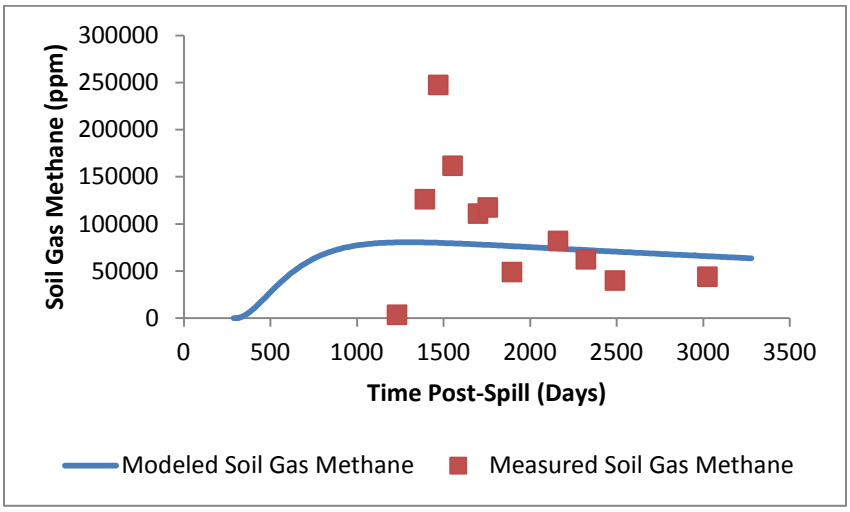


Figure 10: Balaton site measured and modeled soil gas methane over time.

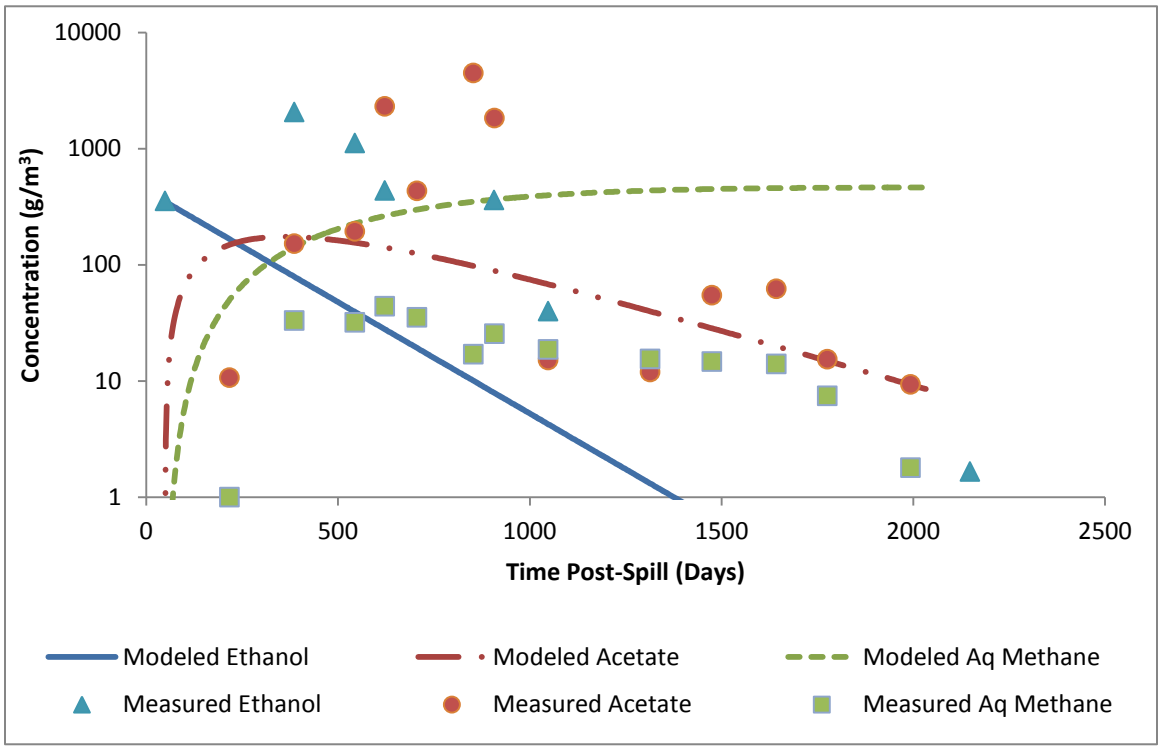


Figure 11: Cambria site model with overlaid measured data.

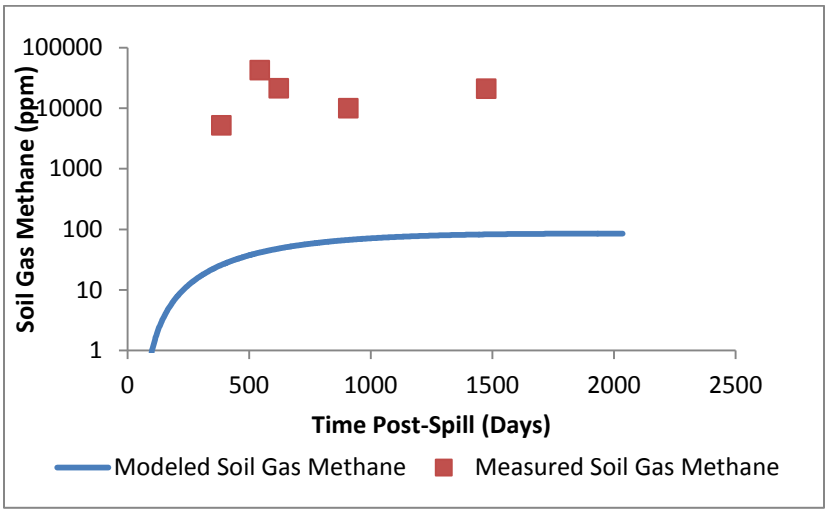


Figure 12: Cambria site measured and modeled soil gas methane over time.

Correlations

Correlations for dissolved phase parameters were calculated for each monitoring well separately, as well as averaged parameters for each sampling date. Data for dissolved acetate and methane were not collected at the Balaton spill site when levels of ethanol were above detection, so correlations between ethanol and acetate, and ethanol and methane were not calculated at this site. Also due to limited data, correlations including soil gas phase on a well-by-well basis could not be calculated. Therefore, correlations between dissolved methane and soil gas methane were calculated using all samples. Field and lab soil gas data were averaged in order to increase the usable data for each sampling date as there was only a 4% average difference found between gas meter percentages measured in the field versus soil gas taken by summa canister analyzed in the lab.

At the Balaton site, monitoring well number 1 had a significant positive correlation between acetate and methane (0.64 at $p<0.05$). When concentrations were averaged for each sampling date, acetate and methane had a significant positive correlation of 0.36 ($p<0.01$). Dissolved methane and soil gas methane had a significant positive correlation of 0.66 ($p<0.05$)(Figure 13).

At the Cambria site, two wells had significant correlations between ethanol and acetate: well 7 at -1.00 and well 11 at 0.65 ($p<0.05$). There were three wells that had significant correlations between acetate and methane, well 9 at 0.64, well 13 at -0.72, and well 1D at 0.67 ($p<0.05$). There was one well that had a significant positive correlation between methane and ethanol at 0.62 ($p<0.05$). When concentrations are averaged for each sampling date, there are significant, positive correlations between every parameter; ethanol and acetate at 0.32, acetate and methane at 0.33, methane and ethanol at 0.30 ($p<0.01$). The correlation between dissolved and soil gas methane was not significant at this site.

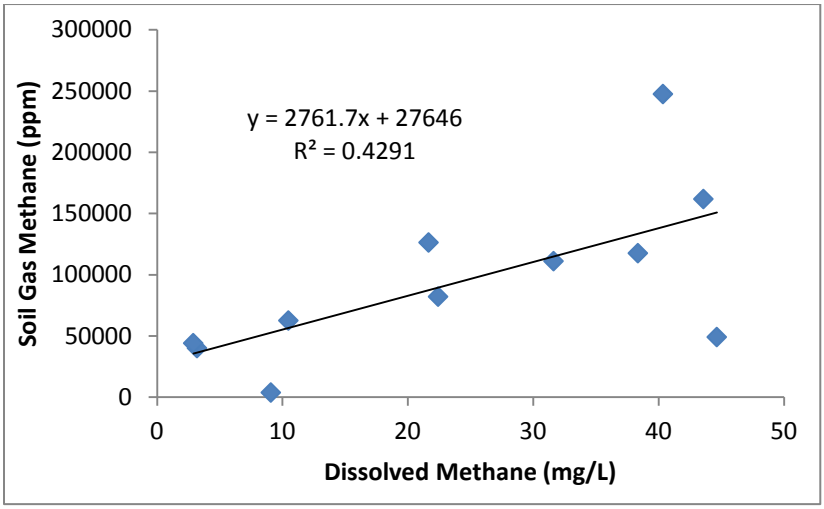


Figure 13: Balaton dissolved methane versus soil gas methane.

Discussion

The purpose of this study was to assess the predictability of methane produced from a fuel-ethanol spill. This was done by constructing a simple, conceptual model that was compared to measured data from two E95 spills. As part of the model, decay rates were determined. To further investigate measured data, correlation coefficients were calculated.

As with any model, the conceptual model has limitations. First, the model assumes completely anaerobic and highly reduced conditions beneath the water table. Generally, beneath the water table there will be a great lack of oxygen. However, this also depends on the soil type, porosity, and connectivity of the pore spaces. In pure sand, for instance, more oxygen could penetrate to the water table and the conditions would not be so reduced. In this case, it is unlikely methane would be produced at all. The spill sites in this study each had poorly sorted soils which allowed for highly reduced conditions. Along similar lines, the model assumes that acetogenic bacteria have unrestricted access to biodegrade ethanol and methanogenic bacteria have unrestricted access to biodegrade acetate. Again, this depends on porosity and connectivity of pore spaces, but because ethanol and acetate are completely miscible in water and do not adsorb to soil particles, it is likely bacteria will be able to contact them and degrade them.

The model assumes no seasonality. Although groundwater temperatures typically only fluctuate from 5ºC-15ºC over long time periods, changing temperatures could affect bacterial count and will affect air-water exchange of methane. In general, the colder it is, the less biodegradation and more dissolved methane. The model also assumes acetate is only being produced by degradation of ethanol and methane is only being produced by degradation of acetate. As explained on Page 4 and Figure 2, acetate and methane could have sources other than ethanol. Certain types of bacteria are able to produce acetate and methane from surrounding bicarbonate and hydrogen.

The model does not take into account the possible oxidation of ethanol, acetate, or methane or loss of methane due to ebullition or plant-transport. Oxidation could very much reduce the concentrations of any parameter. The model assumes the saturated layer is well-mixed with ethanol, acetate, and dissolved methane. In reality, soil is known to be heterogeneous and there could be confining layers. Confining layers could allow contaminants to build in certain areas. The distribution of the contamination will then affect the distribution of the bacteria.

Even after taking into account porosity and tortuosity, the methane gas diffusion coefficient put into the model is high. This means that as soon as dissolved methane partitions into the gas phase, it flows straight up and out into the atmosphere. This explains the very low predicted concentrations seen in the modeled soil gas methane. In reality, methane gas can move horizontally in the unsaturated zone, as evidenced by the site soil gas measurements. All of these assumptions could be large factors for differences seen between the model and measured data.

When comparing spill site rate constants, it is seen that Balaton has a higher spreading rate constant, higher ethanol decay rate, and higher acetate decay rate than Cambria. These differences in the constants and the resulting model can be explained by differences in the spill sites' physical characteristics. Although both sites have rather poorly-sorted soils, the Balaton site is composed of mostly silty-sands, which have higher permeability than the silty-loams at Cambria. This explains the higher spreading rate and the higher rates of ethanol and acetate decay at Balaton. A higher permeability results in easier spreading and easier access for bacteria to biodegrade contaminants.

Slower rates of ethanol and acetate degradation at the Cambria site could also be due to prolonged toxic conditions because of a lower permeability. Recall that bacteria are killed at high concentrations of ethanol; concentrations greater than 60,000 mg/L are toxic (Nelson et al., 2010). Concentrations were over this limit at the time of the spill. At the Balaton site, 41,000 mg/L of ethanol was measured in one well over a year after the spill. Lack of bacteria means lack of biodegradation. In addition, there have been other hypotheses for the persistence of ethanol at some sites. Spalding et al. (2011) observed bacterial slimes in source zones and discusses the possibility of the slime enveloping the ethanol, preventing its decay. It is possible that some of this slime consists of denatured cell components from the toxicity of the ethanol in the source zone. These components could block soil pores, slowing ethanol's decay from spreading and access to living bacteria.

As seen in Figures 9-12, the model overpredicted dissolved methane and underpredicted soil gas methane at each spill site. Again, oxidation could be a large factor bringing down the amount of dissolved methane in the field, especially at the Balaton site since Balaton has a thick unsaturated zone with higher permeability soils that allow for oxygen to penetrate and oxidizing bacteria to proliferate. Bacteria that oxidize methane are typically located right at the interface of the saturated and unsaturated zone and within the capillary fringe, in order to have the minimum amount of oxygen to survive and still be able to contact methane. These bacteria could be taking the methane out of the dissolved phase. Another idea is that plant transport of the dissolved methane is occurring. This process would dominate at the Cambria site since it is more heavily vegetated and has a shallow water table. Finally, the model may overpredict dissolved methane because sampling for dissolved methane is difficult. Methane will be released from solution as it is pulled out of the ground if the ambient temperature is greater than 55ºF. Again, the model's underprediction of soil gas methane at both sites is likely due to the high methane gas diffusion coefficient.

Correlation coefficient analysis of measured data showed there is a significant, positive correlation between acetate and dissolved methane at both sites. This means when acetate concentration increases, dissolved methane concentration increases. This is not to say acetate increase *causes* methane increase or vice versa, as is one of the non-assumptions of correlation. Also, there was a significant, positive correlation between dissolved methane and soil gas methane. At the same time, significance and the direction of correlation varied when looking at individual monitoring wells for every parameter.

Overall, environmental fuel-ethanol biodegradation and methane production is a complex process. The model contains useful concepts and is a starting point for understanding. The results demonstrate how site physical characteristics play a big role in contaminant fate and transport. The model is useful in that it gives us an idea of the sensitivity of the resulting concentrations to the inputted rate constants and coefficients. The correlation calculations are useful, in that there is a significant pattern in constituent increase.

Finally, because the model only encompasses biological decay and spreading from groundwater flow, the results show the environmental process is not that simple.

There are many options for future work that would increase our understanding of these processes. Gas phase methane is the most concerning by-product due to its explosion hazard and potential human health effects, so it would be beneficial to continue the conceptual model and include terms for soil gas methane to expand horizontally in the unsaturated zone. Also, terms for the removal of constituents by oxidation could be included in the model. Other future work may consist of collection of more usable data for correlation calculations for soil gas and other parameters. It would be ideal to be able to observe background measurements of constituents before a spill occurs in order to see a complete picture of change over time which could be accomplished with a controlled-release ethanol study. Multi-phase, multi-density, three-dimensional fluid flow modeling of ethanol spill sites could be a next step after more simple conceptual models are fully understood. With current and proposed mandates, it appears that ethanol is going to be an almost constant presence for every American for years to come. As such, it is in our best interest to investigate its potential hazards.

References

Alvarez, P.J.J.; Hunt, C.S.,1999. The effect of ethanol on BTEX biodegradation and natural attenuation. Lawrence Livermore National Laboratory: Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate Vol 4, Ch 3.

Atkins, P.W., Paula, J., 2006. Atkins' Physical Chemistry. New York, NY: W.H. Freeman Company.

Boetius, A.; Ravenschlag, K.; Schuber C.J.; Rickert, D.; Widde, F.; Gieseke, A.; Amann, R.; Jùrgensen, B.B.; Witte, U.; Pfannkuche, O., 2000. A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature 407, 623-626. Accessed online at http://alrlab.pdx.edu/courses/marinemicro/boetius.pdf

Brown, J.A., 2013. United States National Library of Medicine. Haz-Map Database, Simple Asphyxiant. Accessed online May 13, 2013 athttp://hazmap.nlm.nih.gov/category-details?id=350&table=tbldiseases

Butler, B.J.; VanderGriendt, M.; Barker, J.F.,1992. Impact of methanol on the biodegradative activity of aquifer microorganisms. Paper presented at the 13th Annual Meeting of the Society of Environmental Toxicology and Chemistry, Nov 8-12. Cincinnati, OH.

Connelly, C.; Groschen, R., 2011. Minnesota Department of Agriculture: Legislative report on ethanol. Accessed online March 9, 2013 athttp://www.mda.state.mn.us/~/media/Files/news/govrelations/legrpt-e20-2010.ashx

Corseuil, H.X.; Monier, A.L.; Fernandes, M.; Schneider, M.R.; Nunes, C.C.; do Rosario, M.; Alvarez, P.J.J., 2011. BTEX plume dynamics following an ethanol blend release: Geochemical footprint and thermodynamic constraints on natural attenuation. *Environmental Science Technology, 45* (8), 3422. doi:10.1021/es104055q

Davidson, J., 2001. Key environmental cleanup considerations for ethanol and alkylates. Alpine Environmental, Inc. Accessed online at http://www-erd.llnl.gov/ethanol/proceed/cleanup.pdf

Environmental Protection Agency (EPA), 2013. Renewable Fuel Standard (RFS). Accessed online February 25, 2013 at http://www.epa.gov/OTAQ/fuels/renewablefuels/

Freitas, J. G.; Doulatyari, B.; Molson, J. W.; Barker, J. F., 2011. Oxygenated gasoline release in the unsaturated zone, part 2: Downgradient transport of ethanol and hydrocarbons. *Journal of Contaminant Hydrology, 125*(1-4), 70-85. doi:10.1016/j.jconhyd.2011.05.002

Garcia, H.D.; James, J.T., 2004. B7 Methane. Spacecraft maximum allowable concentrations for selected airborne contaminants. National Academy Press 1, 143-148. Accessed online at http://www.nap.edu/openbook.php?record_id=9062&page=147

Ho, C. K.; Webb, S. W., 2006. Theory and Applications of Transport in Porous Media, Vol. 20. 446 p.

ITRC (Interstate Technology & Regulatory Council). 2011.*Biofuels: Release Prevention,Environmental Behavior, and Remediation.*BIOFUELS-1. Washington, D.C.: InterstateTechnology & Regulatory Council, Biofuels Team.www.itrcweb.org.

Karvonen, T., 2002. Biodegradation/Biotransformation. Department of Civil and Environmental Engineering, Helsinki University of Technology. Accessed online November 1, 2013 at http://civil.aalto.fi/fi/tutkimus/vesi/www_oppikirjat/yhd_123110/7_biodegradation.pdf

Kavanaugh, M.C., Stocking, A., 1999. Fate and transport of ethanol in the environment. Accesssed online at http://www.epa.gov/air/caaac/mtbe/mtbeethan.pdf

Material safety data sheet: Methane (2010). . Radnor, PA: Airgas INC. Accessed online at http://www.airgas.com/documents/pdf/001033.pdf

McDowell, C. J.; Buscheck, T.; Powers, S. E., 2003. Behavior of gasoline pools following a denatured ethanol spill. *Ground Water, 41*(6), 746. Accessed online at http://search.ebscohost.com.ezp2.lib.umn.edu/login.aspx?direct=true&db=aph&AN=11720450&site=ehost-live

Minnesota Department of Health (MDH), 2013. Methane in Minnesota Well Water. Accessed online July 5, 2013 at http://www.health.state.mn.us/divs/eh/wells/waterquality/methanemn.html#top

Minnesota Department of Natural Resources (DNR), 2013. Ground water provinces. Accessed online July 5, 2013 at http://www.dnr.state.mn.us/groundwater/provinces/index.html

Mravik, S.C.; Sillan, R.K.; Wood, A.L.; Sewell, G.W., 2003. Field evaluation of the solvent extraction residual biotreatment technology. Environmental Science and Technology, 37 (21), 5040-5049.

Nelson, D.K.; Lapara, T.M.; Novak, P.J., 2010. Effects of ethanol-based fuel contamination: microbial community changes, production of regulated compounds, and methane generation. Environmental Science and Technology 44, no. 12: 4525-4530.

O'Connor, I.; Liebner, S.; Zeyer, J., 2009. The influence of plants on CH4-emissions from permafrost soils. Accessed online at http://www.ibp.ethz.ch/research/aquaticchemistry/teaching/archive_past_lectures/term_paper_08_09/HS08_OConnor_rev_termpaper_ms.pdf

Pinnacle Engineering, Inc., 2011. Annual Monitoring Report, Balaton, Minnesota. Pinnacle Engineering, Inc., Maple Grove, Minnesota.

Pinnacle Engineering, Inc., 2011. Annual Monitoring Report, Cambria, Minnesota. Pinnacle Engineering, Inc., Maple Grove, Minnesota.

Railsback, B.L., 2006. Common redox reactions in the oxidation of organic matter. Department of Geology, University of Georgia. Accessed online November 15, 2013 at http://www.gly.uga.edu/railsback/Fundamentals/RedoxReactions03LS.pdf.

Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M. 1993. Environmental Organic Chemistry. John Wiley & Sons, Inc. p. 238.

Shaw's Environmental and Infrastructure Group (Shaw), 2011. Large volume ethanol spills-environmental impacts and emergency response options. Prepared for the Massachusetts Department of Environmental Protection. Accessed online at http://www.mass.gov/eopss/docs/dfs/emergencyresponse/special-ops/ethanol-spill-impacts-and-response-7-11.pdf

Siegle, D., 2009. Using a critical value table for Pearson's r. University of Connecticut. Accessed online July 22, 2013 at http://www.gifted.uconn.edu/siegle/research/correlation/alphaleve.htm

Spalding, R. F.; Toso, M. A.; Exner, M. E.; Hattan, G.; Higgins, T. M.; Sekely, A. C.; Jensen, S. D., 2011. Long-term groundwater monitoring results at large, sudden denatured ethanol releases. *Ground Water Monitoring & Remediation*, *31*(3), 69-81. doi:10.1111/j.1745-6592.2011.01336.x

United States Department of Energy, Energy Information Administration (EIA), 2012. Annual Energy Review 2011. Accessed online May 5, 2013 athttp://www.eia.gov/totalenergy/data/annual/pdf/aer.pdf

Wade, L.G., 2010. *Organic Chemistry* (7th ed.). Upper Saddle River, New Jersey: Prentice Hall.

Weaver, J.W.; Skaggs, S.A.; Spidle, D.L.; Stone, G. C., 2009. Composition and Behavior of Fuel Ethanol. Environmental Protection Agency (EPA). Accessed online at http://www.epa.gov/athens/publications/reports/Weaver_EPA600R09037_Composition_Fuel_Ethanol.pdf

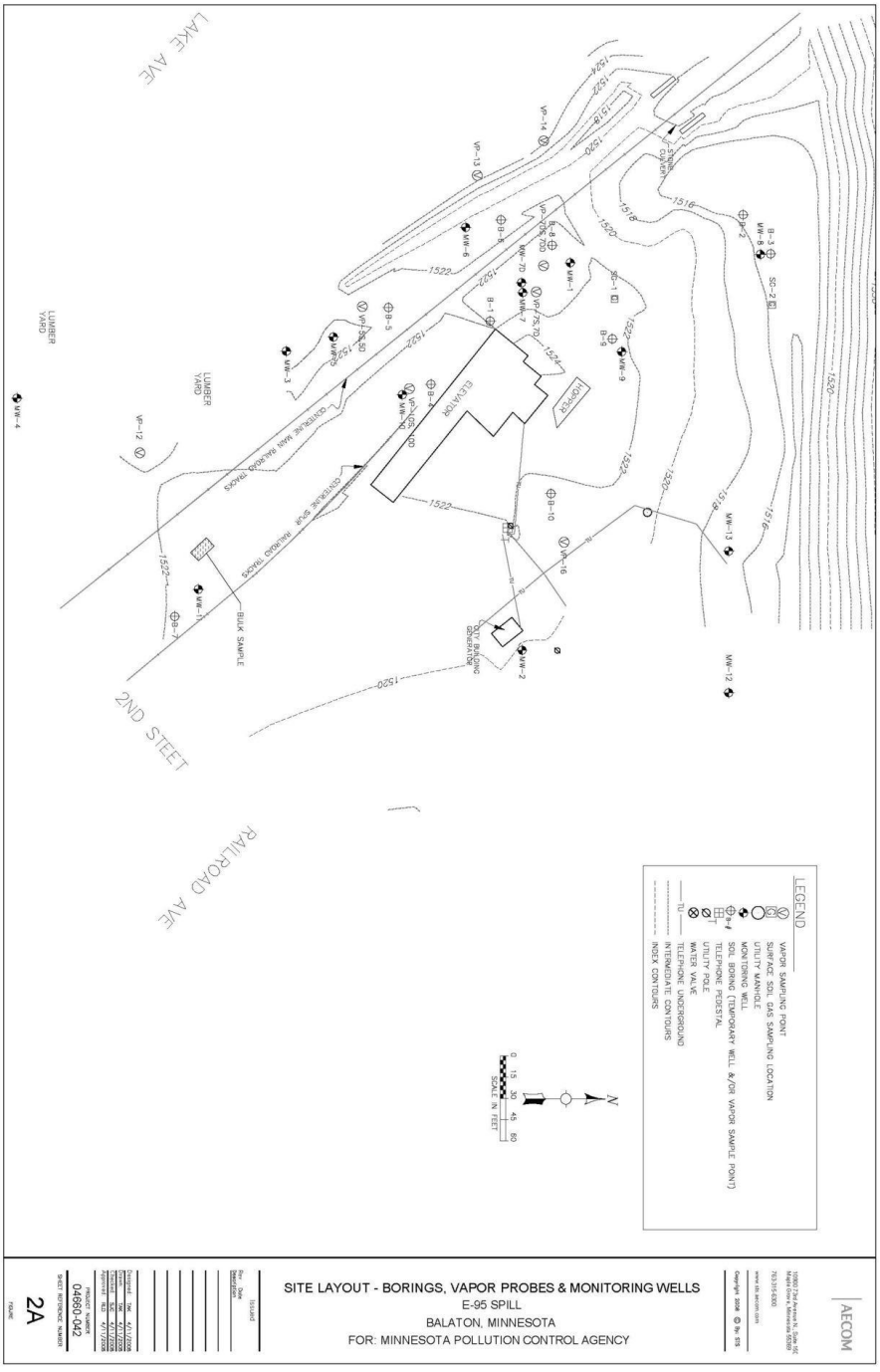
White, D., 1995. The Physiology and Biochemistry of Prokaryotes. Oxford University Press, New York, NY, 101-102.

Wilson, J.T.; Toso, M.; Mackay, D.; de Sieyes, N.; Devaull, G.E., 2013. What's the deal with methane at LUST spill sites? Part 2: Vapor Intrusion. *Lustline*, 72, 5-11, 21-22. Accessed online at http://www.neiwpcc.org/lustline/lustline_pdf/lustline_current.pdf

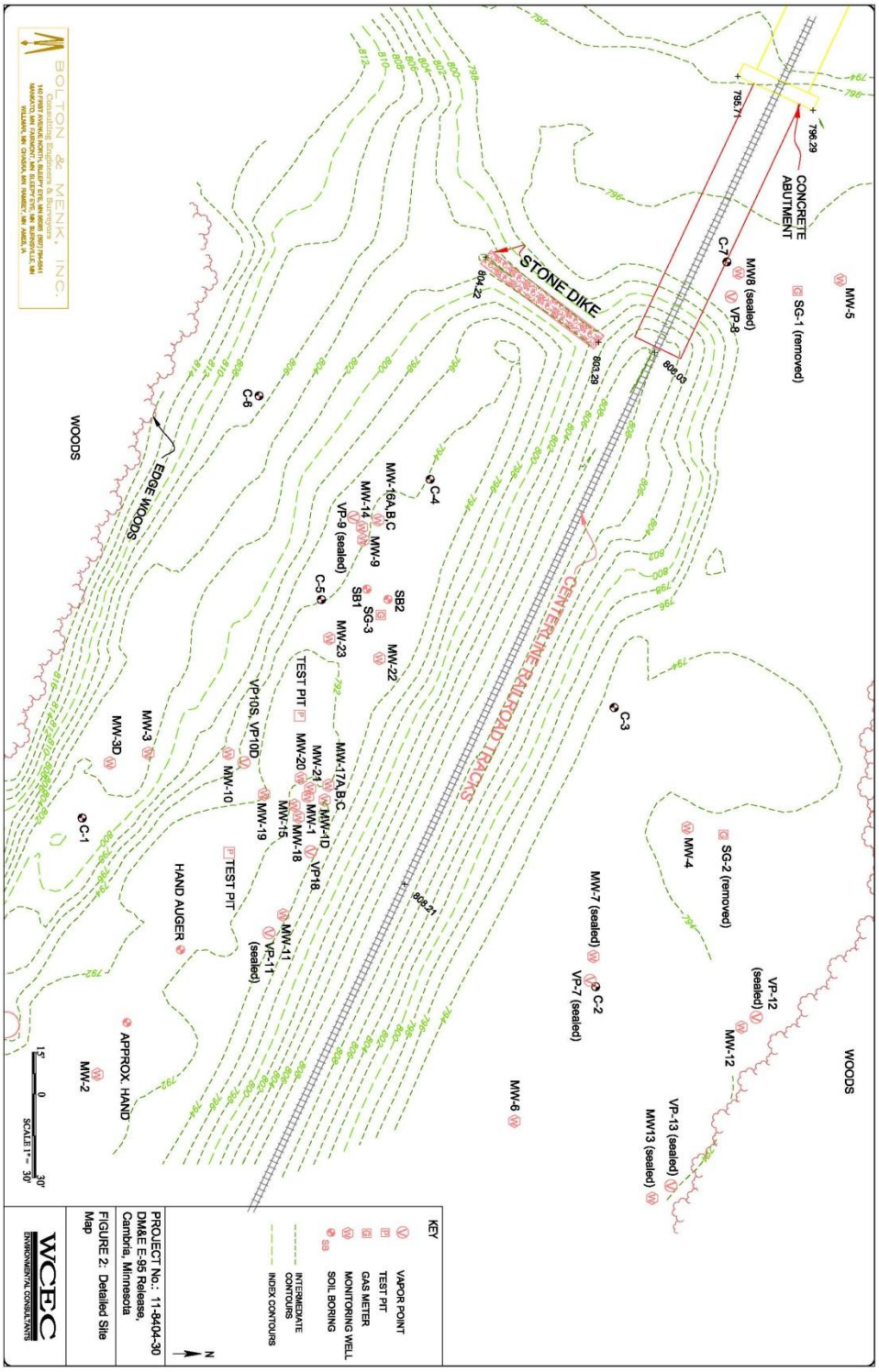
Ye, S., 2012. Minnesota Department of Agriculture: Minnesota Ethanol Industry. Accessed April 5, 2013. Accessed online at http://www.mda.state.mn.us/~/media/Files/food/business/economics/plantsreport.ashx

Zhang, Y.; Khan, I. A.; Chen, X.; Spalding, R. F., 2006. Transport and degradation of ethanol in groundwater. *Journal of Contaminant Hydrology, 82* (3–4), 183-194. doi:10.1016/j.jconhyd.2005.09.007

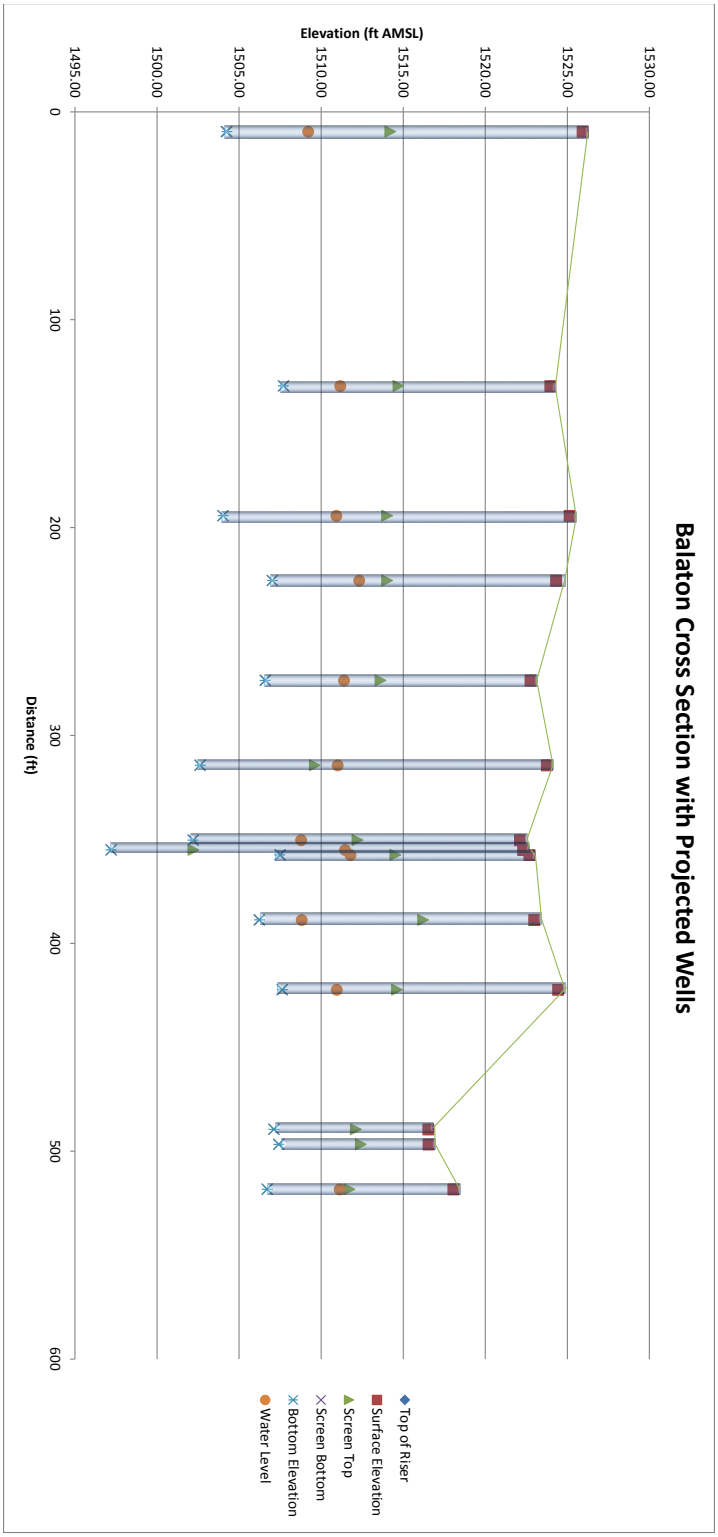
Appendix A


LAKE AVE
2ND STEET
RAILROAD AVE
LUMBER YARD
LUMBER YARD
ELEVATOR
HOPPER
CENTRAL MAIN RAILROAD TRACKS
CENTRAL SPUR RAILROAD TRACKS
BULK SAMPLE
CITY BUILDING GARAGE
LEGEND
VAPOR SAMPLING POINT
SURFACE SOIL GAS SAMPLING LOCATION
UTILITY MANHOLE
MONITORING WELL
SOIL BORING (TEMPORARY WELL &/OR VAPOR SAMPLE POINT)
TELEPHONE PEDESTAL
UTILITY POLE
WATER VALVE
TELEPHONE UNDERGROUND
INTERMEDIATE CONTOURS
INDEX CONTOURS
SCALE IN FEET
0 15 30 45 60
N
SITE LAYOUT - BORINGS, VAPOR PROBES & MONITORING WELLS
E-95 SPILL
BALATON, MINNESOTA
FOR: MINNESOTA POLLUTION CONTROL AGENCY
AECOM
2A
04660-042

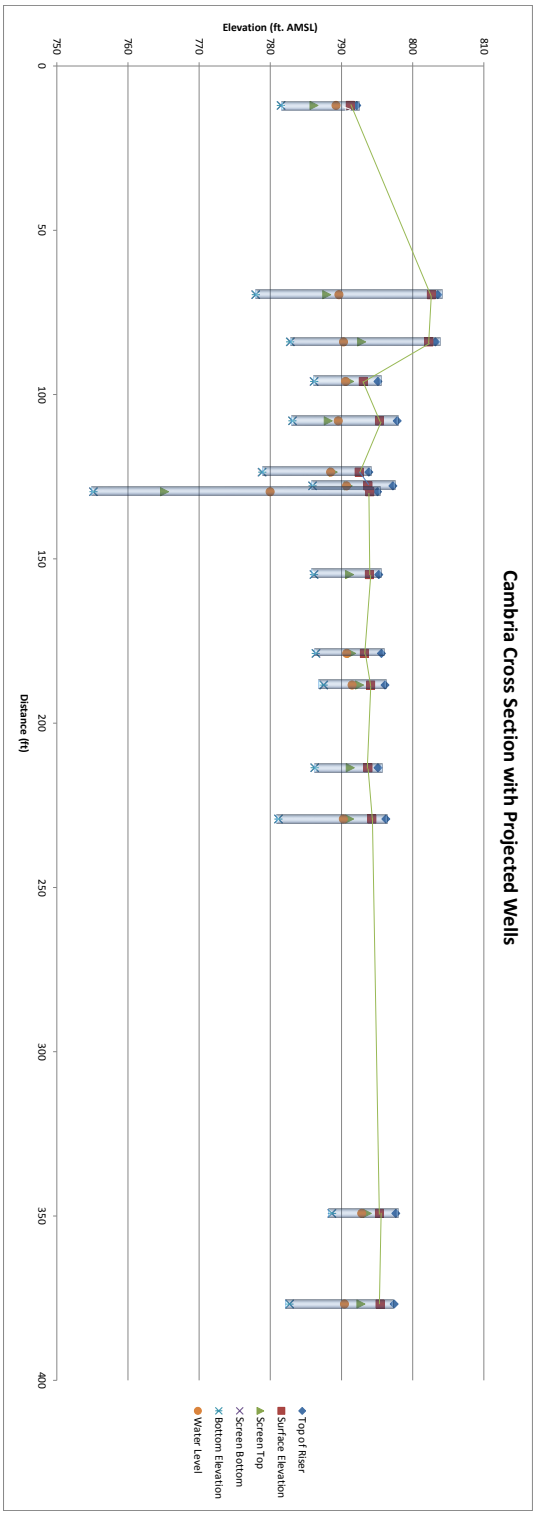
Appendix B


CONCRETE ABUTMENT
796.29
798.71
C-7
MW8 (sealed)
VP-8
SG-1 (removed)
MW-5
STONE DIKE
804.22
808.29
808.03
C-6
WOODS
EDGE WOODS
C-4
MW-16A,B,C
MW-14
MW-9
VP-9 (sealed)
C-5
SB1
SG-3
SB2
MW-23
MW-22
CENTERLINE RAILROAD TRACKS
C-3
TEST PIT
VP-10S, VP10D
MW-3
MW-3D
MW-10
MW-19
MW-20
MW-21
MW-17A,B,C
MW-1
MW-1D
VP18
MW-18
MW-15
MW-11
VP-11 (sealed)
C-1
HAND AUGER
TEST PIT
APPROX. HAND
MW-2
808.21
MW-7 (sealed)
VP-7 (sealed)
C-2
SG-2 (removed)
MW-4
VP-12 (sealed)
MW-12
MW-6
VP-13 (sealed)
MW13 (sealed)
WOODS
KEY
VAPOR POINT
TEST PIT
GAS METER
MONITORING WELL
SOIL BORING
INTERMEDIATE CONTOURS
INDEX CONTOURS
N
SCALE 1" = 30'
BOLTON & MENK, INC.
Consulting Engineers & Surveyors
WCEC
ENVIRONMENTAL CONSULTANTS
PROJECT No.: 11-8404-30
DM&E E-85 Release,
Cambria, Minnesota
FIGURE 2: Detailed Site Map

Appendix C


Balaton Cross Section with Projected Wells
Elevation (ft AMSL)
1530.00
1525.00
1520.00
1515.00
1510.00
1505.00
1500.00
1495.00
Distance (ft)
0
100
200
300
400
500
600
Top of Riser
Surface Elevation
Screen Top
Screen Bottom
Bottom Elevation
Water Level

Appendix D


Cambria Cross Section with Projected Wells
Elevation (ft. AMSL)
750
760
770
780
790
800
810
Distance (ft)
0
50
100
150
200
250
300
350
400
Top of Riser
Surface Elevation
Screen Top
Screen Bottom
Bottom Elevation
Water Level

Appendix E

Minnesota Pollution Control Agency

Investigation Requirements for Ethanol-Blended Fuel Releases

Petroleum Remediation Program
Guidance Document 4-21

This guidance document describes site investigation requirements for ethanol-blended fuel releases for the Minnesota Pollution Control Agency's (MPCA) Petroleum Remediation and Emergency Response programs. An ethanol-blended fuel is defined as a fuel containing greater than 10 percent ethanol by volume (E10). This would include E85, denatured fuel- grade ethanol (E95), and other fuel blends greater than E10 such as E15 or E20. These requirements are for sites that had a confirmed ethanol-blended fuel release and for releases at facilities that store or have stored ethanol-blended fuel where the released product is unknown (potential release).

I. Introduction

Ethanol-blended fuel releases will require investigation beyond that described in Guidance Documents 4-01 *Soil and Ground Water Assessments Performed During Site Investigations*, 4-01a *Vapor Intrusion Assessments Performed During Site Investigations*, 4-02 *Potential Receptor Surveys and Risk Evaluation Procedures at Petroleum Release Sites*, and 4-05 *Ground Water Sample Collection and Analysis Procedures*. The degree of additional investigation may vary depending on if the release is confirmed or potential. Confirmed releases will generally require a Remedial Investigation (RI). For potential releases, ethanol release-specific data collected during the Limited Site Investigation (LSI) will be used to determine the need for additional investigation.

These requirements are necessary due to additional risk factors as well as the influence ethanol has on subsurface fate and transport of petroleum hydrocarbons. Ethanol poses additional environmental risks not typical or inherent with petroleum releases, such as:

- Ethanol degradation in the subsurface has the potential to produce large quantities of methane gas that could lead to explosive conditions. Methane generation may be delayed for months to years after a release and may persist for years after the ethanol is no longer present in groundwater. At some sites, methane might be the primary contaminant of concern and the risk driver for corrective action or long-term monitoring.
- Unlike conventional petroleum fuels, ethanol is miscible in water and, as a result, has implications for the distribution of contamination and occurrence of light non-aqueous phase liquid in the subsurface.
- Releases of ethanol-blended fuels to surface waters present several issues. These include phase separation and extreme dissolved oxygen demand that occurs during ethanol degradation, which could quickly lead to anoxic conditions resulting in

significant fish and wildlife mortality. Extreme dissolved oxygen demand can also be an issue with disposal of recovered liquids.

The effect of ethanol on the fate and transport of petroleum hydrocarbons may affect site investigation and risk evaluation in the following ways:

- Natural attenuation of petroleum hydrocarbons can be delayed due to preferential biodegradation of ethanol. This may result in delayed aqueous phase plume stabilization or longer plumes, which could increase risk to groundwater receptors.
- Elongated petroleum plumes in groundwater may serve as a vapor source and present increased risk for the vapor intrusion pathway.
- The increased production of methane and carbon dioxide may strip petroleum hydrocarbons from groundwater and provide a pressure gradient to move vapor into receptors.
- Ethanol can remobilize preexisting, stable petroleum contamination, thus potentially increasing the risk.

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II. Investigation Requirements

A. Investigation considerations

1. **General considerations:** For confirmed releases, long-term monitoring of soil gas and groundwater via permanent monitoring points and wells is required because 1) the appearance of methane may be delayed and 2) ethanol degradation can prolong (or inhibit) attenuation and, thus, stability of the aqueous phase petroleum plume. In these cases, an LSI would not be sufficient because long-term monitoring is needed to assess potential methane generation, persistence, and associated risk as well as characterize the stability of the petroleum fraction.
2. **Historical product storage:** Prior to initiating LSI activities, the current and past storage of ethanol-blended fuels should be determined.
3. **Drilling safety:** Due to the potential for elevated methane gas levels, care should be exercised when drilling into areas with potentially high methane concentrations.
4. **Monitoring well installation and sampling:** Research has shown that ethanol-blended fuels will eventually phase separate after contact with soil water, and that the ethanol fraction can move into and disperse within the capillary fringe. In addition, the high degradation rates and associated products will make monitoring well installation and sampling critical. Shorter screen lengths and multi-level wells may be required, and documentation of well installation and sampling methods may be critical to interpret results. Special care in groundwater sampling is critical to avoid volatilization losses, especially for methane.
5. **Soil sample analysis:** The Petroleum Remediation Program does not support the analysis of ethanol from soil samples; therefore, no additional soil analyses are required.
6. **High methane concentrations:** If at any point in the investigation high methane concentrations are detected in groundwater or soil gas, notification is required. Contact the MPCA Project Manager assigned to the release site if either of the following conditions are met.
    a. Groundwater: aqueous methane concentrations exceed 10,000 µg/L.
    b. Soil gas: methane concentrations exceed 10 percent of the lower explosive limit, or 0.5 percent methane by volume (5000 ppmv), within 100 feet of a receptor.
7. **Future requirements:** Acetate is a degradation product of ethanol and can be used to assess the potential long- term generation of methane in groundwater. Acetate and/or dissolved organic carbon analysis may be required upon MPCA request. The MPCA is evaluating if these analytes will become standard requirements.

B. Limited site investigation requirements: These requirements pertain to both confirmed and potential ethanol- blended fuel releases. Samples will typically be collected from soil borings, temporary wells, and preliminary soil gas assessment probes.

1. **Groundwater investigation:** All groundwater samples must be analyzed for ethanol and methane. Quantify ethanol along with volatile organic compounds (VOCs). Quantify methane along with ethane and ethene.

2. **Soil gas investigation:** Soil gas sampling is required regardless if receptors are present. If receptors are present, follow Guidance Document 4-01a *Vapor Intrusion Assessments Performed During Site Investigations* for sample depth and location. If no receptors are present, source-area soil gas samples should be collected two feet above the water table but at least five feet below the surface.

   For confirmed releases, install one permanent soil gas monitoring point in the source area during the LSI. If possible, complete it as a multi-level monitoring point with two individual screened intervals. The deep screen interval should be placed two feet above the water table, and the shallow screen interval should be placed at least five feet below the surface, with a minimum separation distance of eight to ten feet between intervals. See *Vapor Intrusion Assessments Performed During Site Investigations* for more information regarding permanent soil gas monitoring point installation.

   Soil gas samples must be analyzed for the compounds in the Minnesota Soil Gas List (see *Vapor Intrusion Assessments Performed During Site Investigations*) and fixed gases. Ethanol is included in the Minnesota Soil Gas List. Fixed gases include methane, oxygen, carbon dioxide, and carbon monoxide. Fixed gases will require a separate analysis, but a single canister will supply enough sample volume to complete all required analyses.

C. Remedial investigation requirements: These requirements pertain to confirmed releases of ethanol-blended fuel.

1. Groundwater investigation

a. Investigation protocols*:* Groundwater samples will typically be collected from monitoring wells.

Monitoring well construction during the RI should follow guidelines in Guidance Document 4-01 *Soil and Ground Water Assessments Performed During Site Investigations*. Following review of water table elevation conditions, additional monitoring wells with shorter well screens or multi-level wells may be required.

b. Sampling parameters*:* All groundwater samples must be analyzed for ethanol and methane as described herein and for natural attenuation parameters as described in Guidance Document 4-03 *Assessment of Natural Biodegradation at Petroleum Release Sites*. Acetate may be required on a site-specific basis. Specific parameters may be dropped from routine analysis from all or some wells based on investigation results.

2. Soil gas investigation

a. Investigation protocols: Permanent soil gas monitoring points are required as part of the RI regardless if receptors are present. If receptors are present, follow Guidance Document 4-01a *Vapor Intrusion Assessments Performed During Site Investigations* for sample depth and location. If no receptors are present, install one permanent soil gas monitoring point in the source area as described in Section II.B.2 above.

b. Sampling parameters: Samples must be analyzed for compounds in the Minnesota Soil Gas List and fixed gases. Specific parameters may be dropped from routine analysis from all or some monitoring points based on investigation results.

If permanent soil gas monitoring points have been installed for long-term monitoring, a direct reading methane field instrument (e.g., landfill gas meter) may be used in lieu of laboratory analysis for fixed gases if a good correlation between two consecutive laboratory and field measurement events can be demonstrated. It is advised to quantify methane using the required lab analysis and a methane field instrument during the RI.

III. Sample Collection

A. Introduction: Guidance describing equipment decontamination, field procedures, sample collection, sampling event documentation, and required Quality Assurance/Quality Control (QA/QC) sampling should be followed according to Guidance Document 4-05 *Ground Water Sample Collection and Analysis Procedures* unless alternative procedures are specified below.

B. Ethanol in groundwater: Aqueous samples for ethanol analysis should be collected using laboratory-supplied 40-milliliter (ml) HCl-preserved purge-and-trap bottles in a manner that minimizes turbulence, air entrapment and overfilling. Fill the bottle completely, leaving a positive meniscus at the top of the vial and avoid turbulence and aeration by tilting the bottle while filling. After capping, invert the bottle and tap with a finger to check for air bubbles. If bubbles are present, discard the vial and fill a replacement. If the ethanol sample is turbid and effervesces when water comes into contact with the bottle preservative, unpreserved samples should be collected and noted on the chain-of-custody form. Unpreserved samples must be analyzed within a seven day holding time. Samples should be stored at a temperature of 4 degrees Celsius during transport to the analytical laboratory.

Collect multiple bottles according to laboratory instructions to guard against loss by breakage and to allow for laboratory quality assurance. Samples should be submitted for ethanol in groundwater analysis following U.S. Environmental Protection Agency (EPA) method 8260 with modifications. Laboratory QA/QC procedures for ethanol in groundwater samples via EPA 8260 with modifications are described in Section IV below.

C. Methane in groundwater: Aqueous samples for methane, ethane, and ethene analysis should be collected using laboratory-supplied glass serum bottles. Samples should be preserved using a 1:1 hydrochloric or sulfuric acid to a pH less than 2. Preservative should be added to glass bottles using an appropriate dispensing device (e.g., dropper) prior to adding sample water. Fill the bottle completely, leaving a positive meniscus at the top of the vial and avoid

turbulence and aeration by tilting the bottle while filling. Cap the bottle using an appropriate septum and aluminum crimp cap. After capping, invert the bottle and check for air bubbles. If bubbles are present, discard the vial and fill a replacement. Samples should be stored at a temperature of 4 degrees Celsius during transport to the analytical laboratory.

Samples should be collected, at a minimum, in duplicate sets or according to laboratory instructions in order to guard against loss by breakage and to allow for laboratory quality assurance. Samples should be submitted for RSK-175 analysis following the laboratory QA/QC procedures described in Section IV below.

D. Ethanol in soil gas: Soil gas samples for ethanol analysis should be collected using laboratory-supplied evacuated canisters. Samples should be collected according to the appropriate sampling procedures and QA/QC requirements outlined in Sections II and III of Guidance Document 4-01a *Vapor Intrusion Assessments Performed During Site Investigations*. Samples should be submitted for laboratory analysis of compounds on the Minnesota Soil Gas List using EPA method TO-15. Ethanol is included in the Minnesota Soil Gas List. Laboratory QA/QC procedures for TO-15 are described in Guidance Document 4-01a.

E. Fixed gases in soil gas: Soil gas samples for fixed gases (methane, oxygen, carbon dioxide, and carbon monoxide) analysis should be collected using laboratory-supplied evacuated canisters. Samples should be collected according to the appropriate sampling procedures and QA/QC requirements outlined in Sections II and III of Guidance Document 4-01a *Vapor Intrusion Assessments Performed During Site Investigations*. Samples should be submitted for laboratory analysis of fixed gases by EPA method 3C. Laboratory QA/QC procedures for EPA 3C are described in Section IV below.

When using a direct reading methane field instrument such as a landfill gas meter, care must be taken to avoid inference with petroleum VOCs. An in-line activated carbon filter should be used to remove VOCs so the meter is only reading methane.

F. Natural biodegradation parameters: Field parameters and terminal electron acceptors should be collected according to the procedures outlined in Guidance Documents 4-05 *Ground Water Sample Collection and Analysis Procedures* and 4-03 *Assessment of Natural Biodegradation at Petroleum Release Sites*, respectively.

Aqueous samples for acetate analysis may be requested by the MPCA. If requested, samples should be collected using laboratory-supplied 125-ml unpreserved general bottles. Samples should be stored at a temperature of 4 degrees Celsius during transport to the analytical laboratory. Acetate samples can also be frozen allowing for a longer holding time.

IV. Required Laboratory Quality Assurance/Quality Control

A. Ethanol in groundwater: Aqueous samples may be analyzed for ethanol using the most recent version of EPA method 8260. The laboratory may need to modify the method to improve performance and optimize the instrument. Laboratories analyzing samples for aqueous phase ethanol shall follow the method as defined by the EPA in the EPA SW-846 8000 series methods dated December 1996 or later updates and by incorporating the following additional quality control procedures listed below.

1. The laboratory shall incorporate the following procedures for the analysis of ethanol in water by EPA method 8260:

a. Calibration solution standard: Calibration standard used for ethanol must be a water-based standard and not a methanol-based standard. Ethanol water-based standards should be stored at <4 degrees Celsius. Expiration date for stock standard is two years from opening or as stated on the vial, whichever is earlier. Intermediate dilution standards have an expiration date of two months.

b. Initial calibration: The initial calibration curve should contain at least five calibration points. The r^2 for each curve must be greater than or equal to 0.990. The recovery (accuracy) for each point in the curve must be 70 percent to 130 percent except for the lowest point in the curve which must be 60 percent to 140 percent. The lowest calibration point in the curves shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, the sample must be diluted into the calibration range and reanalyzed.

c. Continuing calibration verification: Analyze one low-level ethanol standard at the report level (RL) and one mid-level ethanol calibration verification standard at approximately 500 µg/L prior to the samples. Bracket the batch of samples with a second mid-level calibration verification standard (in each 12 hour period, up to 20 environmental samples can be analyzed between standards). The percent recovery (%R) for ethanol in the low-level standard should be between 60 percent and 140 percent of the true value. The %R for ethanol in the mid-level standards should be between 70 percent and 130 percent of the true value (with a percent difference of less than or equal to 30 percent).

d. Initial demonstration of capability: Analyze 4-7 replicate check standards at a concentration of 500-1000 µg/L. Percent recovery (%R) must be equal to 80-120 percent. The percent relative standard deviation (%RSD) must be less than 20 percent.

e. Method detection limit/report level: Method detection limits (MDLs) and RLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. Analyze a minimum of seven 50-ug/L standards. The RL should be three to five times the MDL. The lowest calibration point in the curves shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60 percent to 140 percent criteria, a new RL standard is chosen and analyzed until the accuracy criteria are met. For Petroleum Remediation Program project sites, the RLs should be at or below 100 µg/L of ethanol.

2. Th e laboratory shall include the following QC procedures in the analysis of ethanol in water:

a. A batch is defined as up to 20 environmental samples. At a minimum, each batch must contain a method blank, a Laboratory Control Sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD) pair. If there is not enough sample to prepare and analyze a MS/MSD pair, a Laboratory Control Sample Duplicate (LCSD) is prepared and analyzed.

b. Method blanks/trip blanks: Analyze one method blank per QC batch of 20 samples or less. The concentration of ethanol in the method blank must be less than the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.

One trip blank should accompany every 20 environmental samples. The concentration of ethanol in the trip blank should be less than the associated report level. If ethanol is present in the trip blank, review the associated method blank. If a comparable level of ethanol is present in the method blank, the source of the contamination may be in the analytical system and measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.

c. Samples: Absolute areas of the quantitation ions for the internal standard and surrogate must not decrease by more than 50 percent from the initial calibration.

d. Accuracy/precision: One MS and MSD is required per batch. The %R for ethanol in the MS/MSD must be between 70 percent and 130 percent with a relative percent difference (RPD) of less than or equal to 30 percent. The %R for ethanol in the LCS and LCSD should be between 70 percent and 130 percent with a RPD of less than or equal to 30 percent.

e. Special notes: The quantitation ion for ethanol is 45 atomic mass units (AMU). Confirmation ions are 46 AMU and 47 AMU. The presence of ethyl ether can cause an interference with the analysis. If ethyl ether is present in the sample, special care must be taken. Ethanol standards must be analyzed separately from the normal 8260 VOC list due to the interference from ethyl ether.

B. Methane in groundwater: Aqueous samples may be analyzed for methane using a headspace gas chromatography/flame ionization detector (GC/FID) technique based on a method developed by the EPA Robert S. Kerr Environmental Research Laboratory (Kerr Labs). The work is detailed in the Standard Operating Procedure from Kerr Labs (RSK-175) and in "Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Chromatographic Technique," Journal of Chromatographic Science, Vol. 36, May 1998. Since this analysis is a performance-based analysis, laboratories analyzing samples for aqueous-phase methane must also incorporate the following additional quality control procedures.

1. **Initial calibration:** An external standard calibration technique is used. The concentration of the target analyte is calculated from the average response factor or from a standard curve.

   The initial calibration curves should contain at least five calibration points. The %RSD for average response factors must be less than or equal to 30 percent or the r^2 value for the curve must be greater than or equal to 0.995. The recovery (accuracy) for each point in the curve must be 70 percent to 130 percent except for the lowest point in the curve which must be 60 percent to 140 percent. The lowest calibration point in the curve shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, the sample must be diluted into the calibration range and reanalyzed. If the instrument calibration results are outside the acceptance criteria, a number of actions can be taken:

   a. Check the instrument operating conditions. Instrument maintenance may be required.

   b. Review the response at each calibration level to insure that the problem is not associated with one standard.

      If the problem appears to be associated with one of the standards, that standard can be re-injected. If the problem persists, remake the standard and reanalyze it.

   c. The last alternative is to delete calibration points from the curve. The MPCA will allow the removal of a calibration point from the curve under the following provisions. If a non-linear calibration model is used in the initial calibration curve, a quadratic (second order) curve will require at least six non-zero standard levels while a polynomial (third order) curve will require at least seven non-zero standard levels. Care must be taken to insure that there are enough remaining calibration points for the initial calibration curve. If the calibration criteria are now met, the analysis can proceed. However, there are ramifications in removing calibration points. If the top point is removed, the need for diluting samples and reanalyzing will occur at a lower concentration level. If the low point in the curve is removed, the sensitivity of the analysis has changed and thus the report level will need to change.

2. **Continuing calibration:** The initial calibration curves are verified at the beginning and ending of an analytical sequence and every 12 hours by analyzing a mid-level standard. The drift must be within 70 percent to 130 percent. If the instrument calibration results are outside the acceptance criteria, check the instrument operating conditions and/or perform instrument maintenance. Reanalyze the calibration standard. If the calibration criteria are still not met, a new initial calibration must be performed. All samples that were analyzed since the last passing calibration standard must be reanalyzed. There is one exception allowed for this QC criterion. If the recovery of the calibration verification standard is >130 percent of the true value and the environmental samples show no detection of the analyte, the "less than" value can be reported without reanalysis.

3. **Method validation:** The laboratory must perform an initial demonstration of low background for each matrix by analyzing instrument blanks and demonstrating that the analytical system is free of contamination and that the method analytes are not detected above one-half the report levels.

   The laboratory must also perform an initial demonstration of capability for the analysis of each matrix. Four to seven laboratory control samples near the mid-range of the calibration curve must be prepared and analyzed. The samples must be processed through the entire preparation and analysis procedure. The average percent recovery of the replicate analyses must be ≥70 percent and ≤130 percent (with a relative standard deviation of ≤30 percent).

4. **Method detection limit/report level:** Method detection limits (MDLs) and RLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. The RLs should be three to five times the MDLs. The lowest calibration point in the curve shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60 percent to 140 criteria, new RL standards are chosen and analyzed until the accuracy criteria are met. Contact

the MPCA Project Manager for any required report level for each project. RLs depend on program needs. They can change as new information becomes available. RLs are verified after each calibration and at least monthly. For Petroleum Remediation Program project sites, the RLs should be at or below 1,000 µg/L of methane.

5. **Batch QC:** A batch is defined as up to 20 environmental samples. At a minimum, each batch must contain a method blank and a LCS/LCSD pair.

   The concentration of methane in the method blank must be less than one-half of the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.

   Methane is to be spiked into the LCS and LCSD. The spiking levels should be five to ten times the report levels. The LCS is made from reagent-grade water that has been demonstrated to be methane-free. In a water matrix, the percent recovery of methane in the LCS or LCSD must be ≥70 percent and ≤130 percent. The RPD between the LCS/LCSD pairs in water must be ≤30 percent.

   If prepared, the RPD between water sample duplicate pairs must be must be ≤50 percent.

   Any QC failure that is not remedied by reanalysis or re-extraction/reanalysis must be flagged in the final report and corrective actions detailed (along with an explanation of the impact on data quality) in the case narrative.

C. Fixed gases in soil gas: Soil gas samples may be analyzed for methane using a GC/FID. Other fixed gases including oxygen, carbon dioxide, and carbon monoxide may be analyzed using a GC/TCD (Thermal Conductivity Detector) technique based on EPA method 3C. Laboratories analyzing samples for fixed gases in soil gas must also incorporate the following additional quality control procedures.

1. **General considerations:** Helium is used to prepare calibration gases. Use sample collection procedures described in EPA method 3C or 25C. The sample loop must be Teflon or stainless steel tubing of the appropriate diameter. Peak height or peak area can be used for quantitation.

   EPA 3C requires that each sample must be analyzed in duplicate to calculate the average response. For the purposes of the MPCA Petroleum Remediation Program, a single analysis will be adequate.

2. **Initial calibration:** An external standard calibration technique is used. The concentration of the target analyte is calculated from the average response factor or from a standard curve.

   The initial calibration curves should contain at least five calibration points. The % RSD for average response factors must be less than or equal to 30 percent or the r^2 value for the curve must be greater than or equal to 0.995. The recovery (accuracy) for each point in the curve must be 70 percent to 130 percent except for the lowest point in the curve which must be 60 percent to 140 percent. The lowest calibration point in the curve shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, a smaller sample volume is injected into the GC and reanalyzed. If the instrument calibration results are outside the acceptance criteria, a number of actions can be taken:

   a. Check the instrument operating conditions. Instrument maintenance may be required.

   b. Review the response at each calibration level to insure that the problem is not associated with one standard.

      If the problem appears to be associated with one of the standards, that standard can be reinjected. If the problem persists, remake the standard and reanalyze it.

   c. The last alternative is to delete calibration points from the curve. The MPCA will allow the removal of a calibration point from the curve under the following provisions. If a non-linear calibration model is used in the initial calibration curve, a quadratic (second order) curve will require at least six non-zero standard levels while a polynomial (third order) curve will require at least seven non-zero standard levels. Care must be taken to insure that there are enough remaining calibration points for the initial calibration curve. If the calibration criteria are now met, the analysis can proceed. However, there are ramifications in removing

calibration points. If the top point is removed, the need for diluting samples and reanalyzing will occur at a lower concentration level. If the low point in the curve is removed, the sensitivity of the analysis has changed and thus the report level will need to change.

3. **Continuing calibration:** The initial calibration curves are verified at the beginning and ending of an analytical sequence. The drift must be within 70 percent to 130 percent. If the instrument calibration results are outside the acceptance criteria, check the instrument operating conditions and/or perform instrument maintenance. Reanalyze the calibration standard. If the calibration criteria are still not met, a new initial calibration must be performed. All samples that were analyzed since the last passing calibration standard must be reanalyzed. There is one exception allowed for this QC criterion. If the recovery of the calibration verification standard is >130 percent of the true value and the environmental samples show no detection of the analyte, the "less than" value can be reported without reanalysis.

4. **Method validation:** The laboratory must perform an initial demonstration of low background for each matrix by analyzing instrument blanks and demonstrating that the analytical system is free of contamination and that the method analytes are not detected above one-half the report levels.

   The laboratory must also perform an initial demonstration of capability for the analysis of each matrix. Four to seven laboratory control samples near the mid-range of the calibration curve must be prepared and analyzed. The samples must be processed through the entire preparation and analysis procedure. The average percent recovery of the replicate analyses must be ≥70 percent and ≤130 percent (with a relative standard deviation of ≤30 percent).

5. **Method detection limit/report level:** Method detection limits (MDLs) and RLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. The RLs should be three to five times the MDLs. The lowest calibration point in the curve shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60 percent to 140 percent criteria, new RL standards are chosen and analyzed until the accuracy criteria are met.
   Contact the MPCA Project Manager for any required report level for each project. RLs depend on program needs. They can change as new information becomes available. Report levels (RLs) are verified after each calibration and at least monthly. For most analytical work for the MPCA, the RLs should be at or below 1 percent for reported fixed gases. The MPCA requires that final results be reported as a percentage for fixed gases.

6. **Batch QC:** A batch is defined as up to 20 environmental samples. At a minimum, each batch must contain a method blank and a LCS/LCSD pair.

   The concentration of methane in the method blank must be less than the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem.
   All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not
   need to be qualified.

   Methane is to be spiked into the LCS and LCSD. The spiking levels should be five to ten times the report levels. The LCS is made from reagent-grade helium that has been demonstrated to be methane-free. In a soil gas matrix, the percent recovery of methane in the LCS or LCSD must be ≥70 percent and ≤130 percent. The RPD between the LCS/LCSD pairs in water must be ≤30 percent.

   Any QC failure that is not remedied by reanalysis or re-extraction/reanalysis must be flagged in the final report and corrective actions detailed (along with an explanation of the impact on data quality) in the case narrative.

V. Who to Contact

Minnesota statute requires that spills and releases of all grades and types of fuel greater than five gallons be reported to the Minnesota State Duty Officer (800-422-0798 or 651-649-5451) upon discovery. Releases that are not reported immediately may result in penalties or a reduction in Petrofund reimbursement if applicable. See Guidance Document 2-01 *Reporting of Petroleum Releases* for more information regarding when and how to report a release.

When reporting releases of ethanol-blended fuels to the State Duty Officer, the caller should specifically identify the fuel ethanol concentration. When reporting a release of any fuel type at facilities storing ethanol-blended fuel, the caller should specifically indicate the presence of these storage tanks on site. Depending on the nature of the release, the caller may be immediately contacted by the MPCA, or a written response may be issued.

Any questions regarding investigation of ethanol-blended fuel releases from storage tank systems may be directed to MPCA Petroleum Remediation Program staff. Any questions regarding spills and emergency response-related issues may be directed to MPCA Emergency Response Program staff. Please call the MPCA at 800-657-3864 or 651-296-6300 and request the appropriate staff.

Web pages and phone numbers

MPCA staff	http://www.pca.state.mn.us/pca/staff/index.cfm
MPCA phone	**651-296-6300 or 1-800-657-3864**
Petroleum Remediation Program web page	http://www.pca.state.mn.us/programs/lust_p.html
MPCA information request	http://www.pca.state.mn.us/about/inforequest.html
MPCA VIC Program	http://www.pca.state.mn.us/cleanup/vic.html
MPCA Petroleum Brownfields Program	http://www.pca.state.mn.us/programs/vpic_p.html
Petrofund web page	http://www.state.mn.us/cgi-bin/portal/mn/jsp/content.do?id=-
Petrofund phone	**651-215-1775 or 1-800-638-0418**
State Duty Officer	**651-649-5451 or 1-800-422-0798**

Appendix F

Balaton Spill Site MATLAB Model Code

```
function dc=Balaton(t,c)
dc=zeros(4,1);
k1=0.0073;        %Ethanol decay rate (1/day)
k2=0.00452;       %Acetate decay rate (1/day)
T_sat=1.0;        %Thickness of the saturated zone layer (m)
T_unsat=2.66;     %Thickness of the unsaturated zone layer (m)
D_aq_g=0.000043; %Aq.methane diffusive conductance in saturated zone (m/day)
D_gas=0.15;       %Methane gas diffusive conductance in soil air (m/day)
H_part=27;        %Partition of methane between water and air (unitless)
R=0.000092;       %Water flow rate through silty sand at specific site(1/day)

dc(1)= -k1*c(1)- R*c(1)/T_sat;
%Mass budget of the ethanol in the saturated zone
dc(2)=1.0*k1*c(1)-k2*c(2)- R*c(2)/T_sat;
%Mass budget of acetate in saturated zone
dc(3)=(1.5*k2*c(2)) - (D_aq_g*(c(3)-c(4)/H_part))/T_sat - R*c(3)/T_sat;
%Mass budget of methane in the saturated zone
dc(4)=((D_aq_g*(c(3)-c(4)/H_part))/T_unsat) - (D_gas*c(4)/T_unsat);
%Mass budget of methane in the unsaturated zone



clear all;
[t,c]=ode45(@Balaton, [0 3000], [15000 0 0 0]);
plot(t,c(:,1),t,c(:,2),t,c(:,3),t,c(:,4))

%blue line is ethanol, green is acetate and red is
% dissolved methane, and light blue is gaseous methane
```

Cambria Spill Site MATLAB Model Code

```
function dc=Cambria(t,c)
dc=zeros(4,1);
k1=0.0044;        %Ethanol decay rate (1/day)
k2=0.0022;       %Acetate decay rate (1/day)
T_sat=1.0;        %Thickness of the saturated zone layer (m)
T_unsat=1.2;      %Thickness of the unsaturated zone layer (m)
D_aq_g=0.000052; %Aq.methane diffusive conductance in saturated zone (m/day)
D_gas=0.41;       %Methane gas diffusive conductance in soil air (m/day)
H_part=27;        %Partition of methane between water and air (unitless)
R=0.000016;       %Water flow rate through silty sand at specific site(1/day)

dc(1)= -k1*c(1)- R*c(1)/T_sat;
%Mass budget of the ethanol in the saturated zone
dc(2)=1.0*k1*c(1)-k2*c(2)- R*c(2)/T_sat;
%Mass budget of acetate in saturated zone
dc(3)=(1.5*k2*c(2)) - (D_aq_g*(c(3)-c(4)/H_part))/T_sat - R*c(3)/T_sat;
%Mass budget of methane in the saturated zone
dc(4)=((D_aq_g*(c(3)-c(4)/H_part))/T_unsat) - (D_gas*c(4)/T_unsat);
%Mass budget of methane in the unsaturated zone
```

```
clear all;
[t,c]=ode45(@Cambria, [0 2000], [350 0 0 0]);
plot(t,c(:,1),t,c(:,2),t,c(:,3),t,c(:,4))

%blue line is ethanol, green is acetate and red is
% dissolved methane, and light blue is gaseous methane
```

Appendix G

Additional Explanation of k_2 Calculation

According to P.W. Atkins (2006):

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

For species A: $\frac{d[A]}{dt} = -k_1[A]$

For species B: $\frac{d[B]}{dt} = k_1[A] - k_2[B]$

For species C: $\frac{d[C]}{dt} = k_2[B]$

Solutions, assuming initial concentrations of B and C are zero and A is non-zero:

$$[A] = [A]_o e^{-k_1 t} \quad \text{(G1)}$$

$$[B] = [A]_o \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad \text{(G2)}$$

$$[C] = [A]_o \left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right) \quad \text{(G3)}$$

Since ethanol degrades to acetate, which degrades to methane, the solution to Equation G2 was assumed to be equal to the theoretical concentration of acetate. The rate of acetate decay, k2, was solved for its best fit in Microsoft Excel Solver by finding the value of k2 that minimized the difference between this theoretical concentration of acetate by Equation G2 and the measured concentrations of acetate.

Appendix H

Calculation of Diffusion Coefficients

From Schwarzenbach et al. (1993):

Methane diffusion in free space air = D_{gas} = 2.42 m^2/day

Methane diffusion in free space water = D_{aqgas} = 0.00026 m^2/day

From unpublished MPCA data:

Site	Porosity (∅)	Thickness of Saturated Layer (T_sat), meters	Thickness of Unsaturated Layer (T_unsat), meters
Balaton	0.26	1.0	2.66
Cambria	0.30	1.0	1.2

The effective diffusion coefficient as described by Ho and Webb (2006) when the gas saturation is assumed to be one is given by

$$D^* = \emptyset * \tau * D \quad \text{(H1)}$$

where ∅ is total porosity, τ is tortuosity, and D is the diffusion coefficient in free space. Tortuosity is given by

$$\tau = \emptyset^{1/3} \quad \text{(H2)}$$

The resulting effective diffusion coefficient D* is then divided by the thickness over which the concentration difference occurs to obtain D** in m/day.

As an example for the Balaton spill site,

$D^{**}_{gas} = \frac{0.26*0.26^{1/3}*2.42\ m^2/day}{2.66\ m}$ = 0.15 m/day

$D^{**}_{aqgas} = \frac{0.26*0.26^{1/3}*0.00026\ m^2/day}{1\ m}$ = 0.000043 m/day

Appendix I

Ranges of Values for Model Sensitivity Test

Rate Constant or Coefficient	Range
k_1	0.001-0.01 /day
k_2	0.001-0.01 /day
T_sat	1-20 meters
T_unsat	1-20 meters
D_{aqgas}**	0.000012-0.06 meters/day
D_{gas}**	0.112-1.22 meters/day
R	0-10 /day