Aesthetic Groundwater Quality Impacts from a Continuous Pilot-Scale Release of an Ethanol Blend

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Abstract

A pilot-scale aquifer system (8 m^3 continuous-flow tank packed with fine grain sand) was used to evaluate groundwater quality impacts from a continuous release of 10% v:v ethanol solution in water mixed with benzene and toluene (50 mg/L each). The geochemical footprint (methane [CH_4], volatile fatty acids [VFAs], pH, oxidation reduction potential [ORP], dissolved oxygen [DO], and temperature) was monitored more than 11 months. A rapid depletion of DO (from 5.3 to less than 0.1 mg/L) and a decrease of ORP (from 110 to −310 mV) were observed within 25 d of the release. The high-biochemical oxygen demand exerted by ethanol resulted in strongly anaerobic conditions, indicated by the accumulation of CH_4 (up to 17.9 mg/L) and VFAs (up to 226 mg/L acetic acid and 280 mg/L n-butyric acid). Measurements at the sand surface (40 cm from the water table) using a portable combustible gas detector did not detect CH_4. However, accumulation of VFAs (particularly n-butyric acid) during the summer exceeded the secondary maximum contaminant level value for odor (odor levels extrapolated from aqueous concentrations), which represents a previously unreported aesthetic impact. Temperature variations (3.9 to 30.0 °C) significantly affected microbial activities, and a strong correlation was observed between groundwater temperature and CH_4/VFAs generation (p less than 0.05). Overall, these results suggest that seasonal variation of odor generation and CH_4 concentration should be considered at sites contaminated with fuel ethanol blends.

Introduction

Ethanol is increasingly being used as a blending agent for gasoline, which increases the likelihood of ethanol blend releases during transportation and from underground storage. Thus, it is important to investigate the potential groundwater quality impacts of such releases. Previous research has studied the migration characteristics of ethanol in the subsurface (Dakhel et al. 2003; McDowell et al. 2003a; McDowell and Powers 2003b; Corseuil et al. 2004; Capiro et al. 2007; Stafford et al. 2009), its impact on indigenous microorganisms (Capiro et al. 2008; Feris et al. 2008; Nelson et al. 2010), and its influence on the concentration and persistence of petroleum hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX; Corseuil et al. 1998; Lovanh et al. 2002; Ruiz-Aguilar et al. 2003; Mackay et al. 2006; Beller et al. 2008). However, less attention has been directed toward potential groundwater quality

impacts of intermediate ethanol biodegradation products, and how these impacts may change with seasonal variations in temperature.

In groundwater, ethanol biodegradation rapidly consumes oxygen and other electron acceptors creating an anaerobic environment. Under these anaerobic conditions, ethanol can be fermented to volatile fatty acids (VFAs) such as acetic, propionic, n-butyric, and isobutyric acids, which can be further syntrophically transformed to hydrogen (H_2) and methane (CH_4) (Powers et al. 2001). The intermediate degradation products are ultimately mineralized (to H_2O and CO_2) under oxidizing conditions. Transient presence of VFAs, however, may cause aesthetic impacts to potable groundwater because of their odor and taste. In the United States, the Environmental Protection Agency (US EPA) includes odor as 1 of 15 contaminants in National Secondary Drinking Water Regulations. Furthermore, CH_4 could accumulate in shallow aquifers and subsurface soils and pose hazards at sites with subsurface confined spaces and conditions conducive to ignition (Freitas et al. 2010; Nelson et al. 2010).

Groundwater temperature is an important factor that affects indigenous microbial activities (Alvarez and Illman 2005). Therefore, variations in groundwater temperature

with seasonal changes should be considered when assessing an aquifer's capacity for natural attenuation of ethanol blends releases and characterizing impacts from by-products of ethanol biodegradation. In this study, a pilot-scale aquifer system was used to assess the groundwater quality impacts from a continuous release of a simulated fuel ethanol blend (ethanol, benzene, and toluene). The information gained by monitoring this release over various seasons improves the understanding of VFAs-induced odor and CH_4 generation and accumulation, and the influence of temperature on these interrelated processes.

Methods

Pilot-Scale Aquifer System

An 8 m^3 (3.7 × 1.8 × 1.2 m) pilot-scale continuous-flow tank packed with fine grain sand was used in this study. The tank was covered by a canopy to avoid confounding effects from rain water and was open to the atmosphere. Details on the tank construction, gravity-fed hydraulics, media, and packing methods can be found in Stafford (2007). A plan view of the tank is shown in Figure 1. Two parallel channels separated by an acrylic barrier were equipped with independent inlet and outlet lines and instrumented with sampling ports and wells to monitor groundwater. Tap water was injected from the inlet of each channel to obtain a water table elevation of 0.75 m from the bottom of the tank. The vadose zone was 0.35 m high and the total aquifer thickness was 1.1 m. Inlet water characteristics can be found in Table 1. In Channel 1, a municipal water feed amended with 10% (v/v) ethanol, 50 mg/L benzene, 50 mg/L toluene (E/B/T), and 24,000 mg/L sodium bromide (NaBr) was injected at a depth of 22.5 cm below the water table at a rate of 0.4 L/d. The NaBr was added as a conservative tracer, and to maintain a solution density to reach a neutral buoyancy condition with the flowing groundwater. Although high-salt concentrations can be inhibitory to bacteria because of osmotic stress, the added bromide salt was diluted by the tank flow to less than 5000 mg/L, which is within the typical

Table 1	
Inlet Water Characteristics	
Parameter	**Value (± SD, $n = 158$)**
Flow rate (L/d)	170 ± 40 L/d (each channel)
pH	7.5 ± 0.4
DO (mg/L)	5.5
Ionic strength (mM)	6–12

tolerance range of soil bacteria (Atlas and Bartha 1993). The density of the ethanol/NaBr solution injected, relative to water, was measured as 1.002 at 20 °C. Channel 2 served as a control with the same injection depth and injection rate of a water mixture containing 50 mg/L benzene, 50 mg/L toluene (B/T), and 24,000 mg/L NaBr with an estimated density relative to water of 1.019 at 20 °C. The monitoring network was designed to delineate the developed solute (i.e., B/T and ethanol) plumes and characterize solute degradation and accumulation of CH_4 and VFAs. All sampling ports (sample ports were steel tubes screened on the bottom outlet) were at the same depth as the E/B/T mixture injection point. Vertical sampling in Channel 2 was conducted at various depths given the possibility of some downward migration.

CH_4 and VFAs Analysis

Aqueous samples (A1, B1 for Channel 1 and A2, B2 for Channel 2) were collected every 10 d from August 7, 2009 to June 9, 2010 and analyzed for CH_4 and VFAs.

For CH_4 analysis, aqueous samples (50 mL) were injected into glass serum bottles (125 mL) capped with a Teflon-lined septa and aluminum crimps. Bottles were shaken on an Orbit 300 Multipurpose Vortexer (Labnet International Inc., Edison, New Jersey) at 35 revolutions per minute (rpm) for 1.5 h. Headspace samples (100 μL) were injected into a gas chromatograph (GC; HP 5890, Minnesota, equipped with a flame ionization detector [FID]) using a packed column (6 foot × 1/8 in o.d. 60/80 carbopack B/1% SP-1000, Supelco, Bellefonte, Pennsylvania). The detection limit was 0.1 mg/L.

For VFA analysis (acetic, propionic, and n-butyric acid), 2.7 mL aqueous samples were collected and mixed with 0.3 mL of 0.3-M oxalic acid (to acidify the samples and protonate the VFAs; Capiro et al. 2008). Mixtures were then filtered into 1-mL screw-cap vials followed by 1 μL injections into a GC (hp 5890, Minnesota) equipped with a FID and a glass column (2 m × 2 mm inner diameter) containing 80/120 Carbopack B-DA*/4% Carbowax 20 M (Supelco, Bellefonte, Pennsylvania). The GC heating program was 175 °C for 10 min, injection port temperature 200 °C, and FID temperature 200 °C. The method detection limit was 1 mg/L for acetic and propionic acid, and was 2 mg/L for n-butyric acid.

Ethanol, Benzene, Toluene, and Bromide Tracer Analysis

Aqueous samples were collected every 2 d from August 7, 2009 to June 9, 2010 and analyzed for ethanol, benzene, and toluene. The samples withdrawn from the tank were injected into gastight 20-mL glass vials without headspace
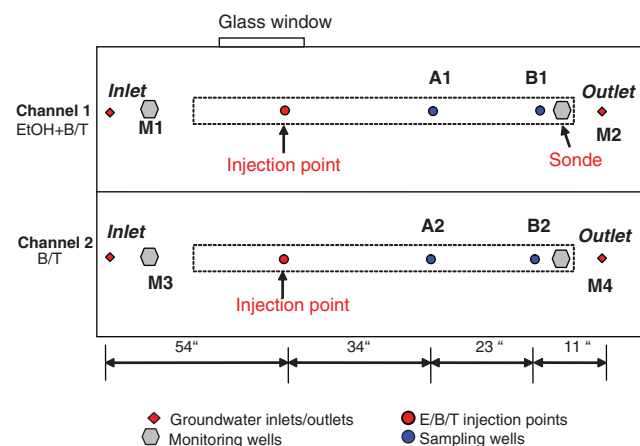

Figure 1. Plan view of the experimental release system. The water table elevation was 0.75 m from the tank bottom and the vadose zone thickness was 0.35 m. Sampling ports and injection points are located 22.5 cm below the water table.

and stored at 4 °C until further analysis. The vials were centrifuged at 2000 rpm for 5 min during sample preparation. For ethanol analysis, supernatants were collected in 2-mL gastight glass vials with polypropylene caps and PTFE septa (Sun SRI, Rockwood, Tennessee) and were injected directly into a GC (hp 6890, Santa Clara, California) equipped with a capillary column (Supelco, model SPB-5, 30 m length, 0.53 mm diameter, 5 m film thickness, St. Louis, Missouri) and a FID (OI Analytical, College Station, Texas). The detection limit was 1 mg/L. For benzene and toluene analysis, supernatants (5 mL) were placed into a Tekmar P&T Autosampler (model no. 2016, Mason, Ohio) and measured by GC (Agilent 6890N, Santa Clara, California) equipped with a 5973N Mass Selective Detector (J&W Scientific, model DB-624, 20 m length, 0.130 mm diameter, Santa Clara, California). The detection limit was 1.0 mg/L for both benzene and toluene. Bromide samples were collected separately in 125 mL field sampling bottles (Fisher Scientific, Pittsburgh, Pennsylvania) and analyzed using a bromide ion selective electrode (Cole-Parmer, Vernon Hills, Illinois) as described by Capiro et al. (2007). The detection limit was 1 mg/L.

Groundwater Geochemical Parameters Analysis

Temperature, pH, oxidation reduction potential (ORP), dissolved oxygen (DO), and conductivity of groundwater were monitored in Channel 1 by a Water Quality Sonde (YSI 600XLM, YSI Inc., Yellow Springs, Ohio) installed at M2 (Figure 1). The Sonde was programmed to take readings at 0:00 am and 12:00 pm daily from April 27, 2009 to June 9, 2010. Sensors were calibrated per manufacturer protocols.

Results and Discussion

Effect of Temperature on CH4 Production

Within the channel exposed to the ethanol, dissolved CH_4 in A1 (Figure 2) increased from less than 0.1 (August 7th, 29.9 °C) to 6.8 mg/L (December 18th, 10.8 °C) and
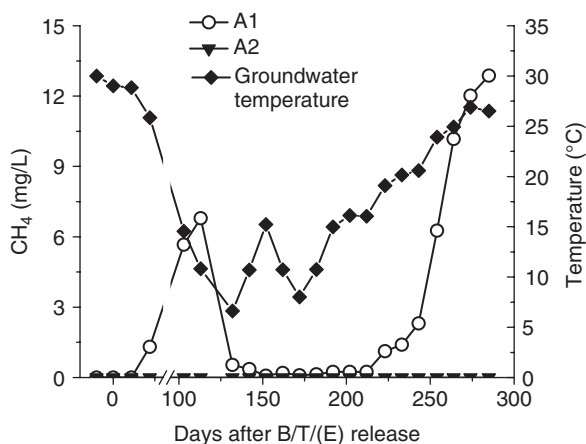

Figure 2. CH_4 concentration at sampling well A1 (in Channel 1, exposed to ethanol and B/T) and A2 (in Channel 2, exposed to B/T alone). Sampling wells are depicted in Figure 1. Day 0 corresponds to August 17, 2009.

then decreased to less than 0.5 mg/L concomitantly with the lower temperatures in January and February (less than 10 °C). CH_4 concentration then increased 0.2 (March 29th) to 12.9 mg/L (June 9th) with the increasing temperatures (from 16.0 to 30.0 °C). A similar trend was observed at the B1 sampling well. The maximum CH_4 concentration was 17.9 mg/L (B1, May 29th, 26.9 °C), representing 81% of the solubility limit at the corresponding temperature (Yamamoto et al. 1976). CH_4 was not detected in the control channel amended with only benzene and toluene (Channel 2) during the 11-month period. The lack of CH_4 detection in the control channel may be because of (1) much longer acclimation periods required for BTEX than for ethanol degradation under methanogenic conditions, often requiring years (Da Silva and Alvarez 2004) and (2) the control channel was exposed to a much lower concentration of organic compounds (92 vs. 1.3×10^4 mg/L as total organic carbon) that are potential sources of reducing equivalents for CH_4 formation.

A BX 168 portable combustible gas detector (Henan Hanwei Electronics Co. Ltd, China; detection limit: 1% of CH_4 lower explosive limit, or 400 ppm_v CH_4) was used to analyze for CH_4 concentrations in the air just above the sand surface of the ethanol-amended channel. No CH_4 was detected, probably because of dilution by air movement as CH_4 reaches the surface, as well as to some possible CH_4 biodegradation by methanotrophs in the vadose zone (King 1997; Bull et al. 2000). However, migration of CH_4 from near-source ethanol impacted groundwater and subsequent accumulation in subsurface enclosed spaces could lead to potential explosion risks where ignitable conditions exist. Thus, further research is needed to delineate conditions that are conducive to CH_4 accumulation to inform the need for periodic monitoring.

A strong correlation existed between CH_4 production (A1) and water temperature ($p = 0.00075$; Figure 5a), which indicates that CH_4 generation from the fuel ethanol blends were significantly influenced by the variation of temperature. The annual average temperature of shallow groundwater (10 to 25 m depth) in the United States ranges from 4 °C in the north central areas to approximately 25 °C in southern Florida. The seasonal variation in groundwater temperature is greatest near the surface, amounting 5 to 10 °C (Heath 1983). Methanogenesis is known to be enhanced at higher temperatures and inhibited by low temperatures (Cullimore et al. 1985; Conrad et al. 1987; Westermann 1993).

Effect of Temperature on VFAs Production

Acetic acid concentrations remained below 5 mg/L in the control channel throughout the monitoring period. However, in the channel exposed to the ethanol, acetic acid concentrations (A1) (Figure 3) increased from less than 1 mg/L (August 7th, 29.9 °C) to 95.7 mg/L (December 8th, 14.6 °C), followed by a concentration decrease to below 40 mg/L in January (less than 10 °C). From February to June, with the subsequent increase in temperature (from 8.0 to 30.0 °C), the acetic acid concentration increased again to 131 mg/L (April 29th). A similar trend was observed at the sampling well B1. The maximum concentration measured was 226 mg/L (B1, May 10th, 23.9 °C). This indicates that acetic acid production was significantly influenced by temperature variations.
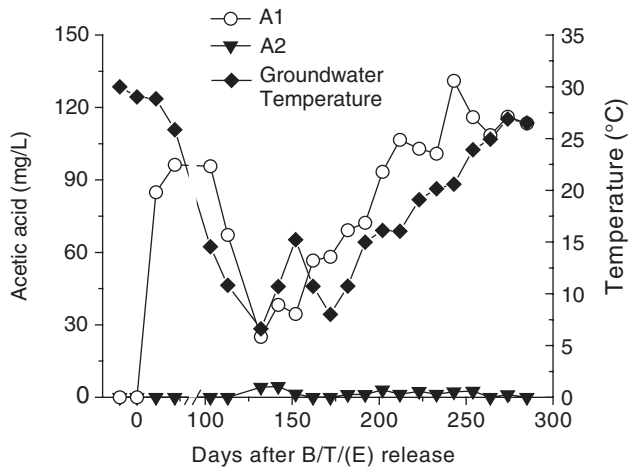
Figure 3. Acetic acid concentrations at sampling wells A1 (in Channel 1, exposed to ethanol and B/T) and A2 (in Channel 2, exposed to B/T alone). Sampling wells are depicted in Figure 1. Day 0 corresponds to August 17, 2009.
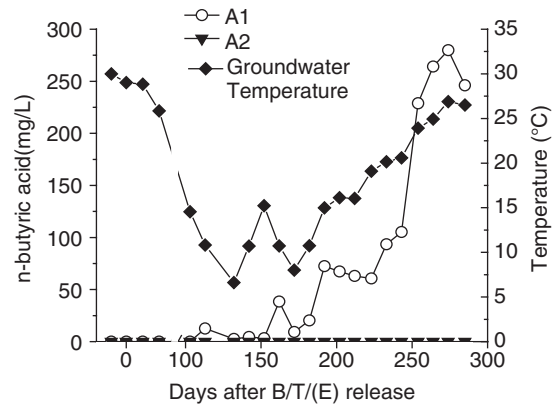

Figure 4. Butyric acid concentrations at sampling wells A1 (in Channel 1, exposed to ethanol and B/T) and A2 (in Channel 2, exposed to B/T alone). Sampling wells are depicted in Figure 1. Day 0 corresponds to August 17, 2009.

Similar to CH_4, a significant correlation was found between acetic acid production (A1) and temperature ($p = 0.000024$; Figure 5b). Apparently, higher temperatures are conducive to faster ethanol biotransformation to VFAs (mainly acetic acid) and H_2, which in turn result in higher CH_4 production. Accordingly, higher availability of acetic acid (or its conjugate base acetate, which is the main substrate for aceticlastic methanogens) was significantly correlated ($p = 0.027$) to CH_4 concentrations (Figure 6a).

Unlike acetic acid, butyric acid remained at a relatively low level (less than 20 mg/L) from August 7th until late February, and then increased steadily to 280 mg/L (A1, May

29th) (Figure 4). The initial lag in butyric acid production was expected as butyric acid was likely a product of acetic acid biotransformation. Under anaerobic conditions, ethanol is oxidized to acetate followed by a conversion to acetyl coenzyme A (acetyl-CoA). Two acetyl-CoA can form one butyryl-coenzyme A, which can then be converted to butyrate (Barker et al. 1945; Gibson 1965). As acetic acid is a direct precursor for butyric acid formation, its higher abundance is conducive to higher butyrate accumulation, and a significant correlation was found between their concentrations ($p = 0.0012$; Figure 6b). Accordingly, a significant correlation was also found between butyric acid production (A1) and temperature ($p = 0.00000023$; Figure 5c).
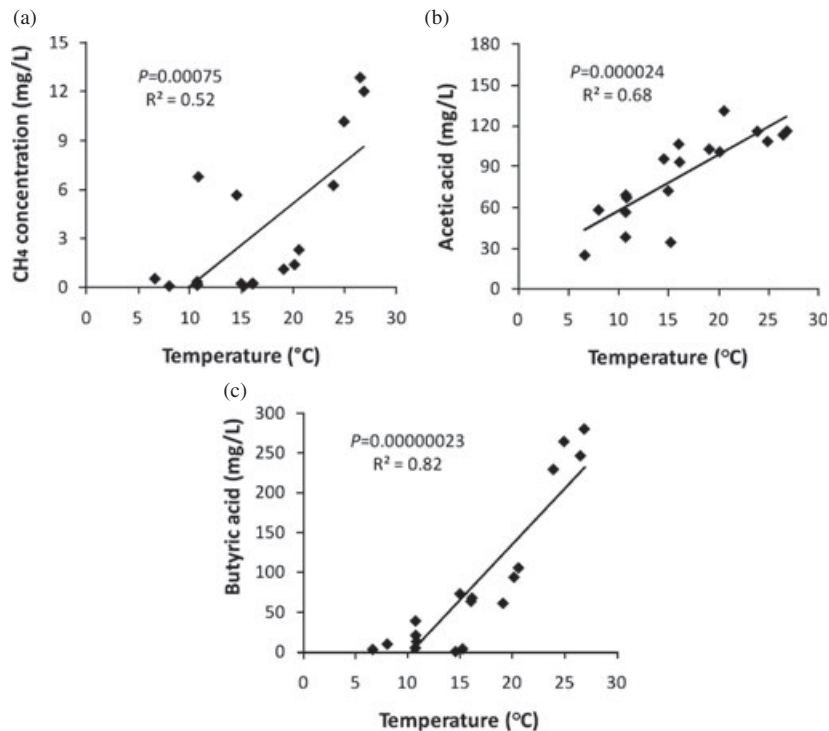

Figure 5. Significant correlations between (a) CH_4, (b) acetic acid, and (c) butyric acid concentrations (measured at A1) vs. groundwater temperature.
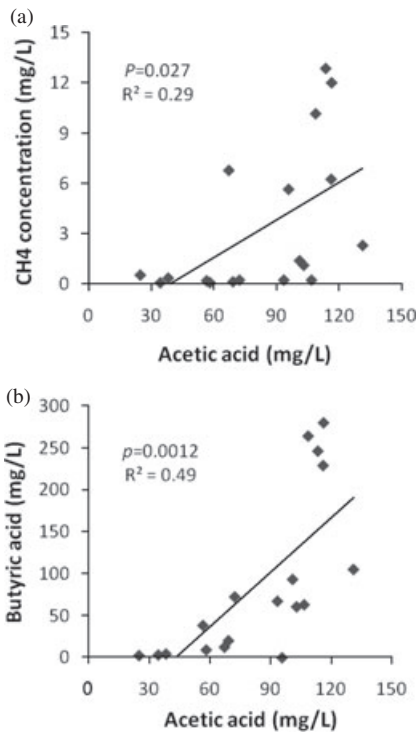
Figure 6. Significant correlations between acetic acid availability and (a) CH_4 and (b) butyric acid concentrations (measured at A1). Acetic acid is a precursor to both CH_4 and butyric acid formation.

Ethanol, Benzene, and Toluene Attenuation

Attenuation of ethanol, benzene, and toluene in Channel 1 was also affected by temperature (Figure 7). The data in Figure 6 are plotted as normalized solute concentrations $(C/C_o)_i$ divided by the normalized bromide concentrations $(C/C_o)_{Br}$. When plotted in this way, attenuation because of dilution is separated from attenuation resulting from biodegradation and volatilization. For ethanol, a short acclimation period with negligible attenuation was followed by
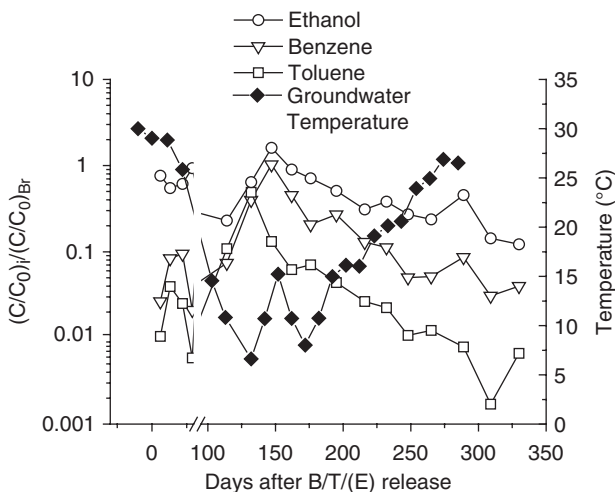

Figure 7. Ethanol, benzene, and toluene attenuation at sampling well A1 (in Channel 1, exposed to ethanol and B/T). Sampling ports are depicted in Figure 1. Day 0 corresponds to August 17, 2009.

significant removal; then, the low-temperature winter conditions occurred and little ethanol degradation was observed. Benzene and toluene similarly experienced lower attenuation during the winter. Significant attenuation for ethanol, benzene, and toluene returned in the spring as temperatures increased. Attenuation of toluene was generally one order of magnitude greater than that for benzene.

Because the injected mixtures for both channels were the same except for the ethanol concentration, the absence of the lighter ethanol in Channel 2 could have resulted in a denser solute plume. Additional sample points from different depths were collected and analyzed, but a solute plume was not identified in this channel. As monitoring did not identify the location and fate of the B/T plume in Channel 2, a comparison of attenuation of benzene and toluene in the presence vs. the absence of ethanol was not possible.

Effect on ORP, DO, and pH

ORP, pH, and DO data varied seasonally. The decrease in ORP (from 110 to −310 mV), pH (from 7.0 to 5.1), and DO (from 5.3 to 0 mg/L) following the release of the ethanol blend indicated transition to anaerobic conditions. During January and February, microbial activity was inhibited by low temperatures (less than 10 °C), resulting in an increase in ORP (to 80 mV), DO (to 3.6 mg/L), and pH (to 6.7) thereby shifting the aquifer system from anaerobic to aerobic conditions (Hillel 2004). After March, the system reverted back to an anaerobic state indicated by a decrease of ORP (to −400 mV), DO (to less than 0.1 mg/L), and pH (to 4.6) thereby corroborating the relationship in ORP, pH, and DO with temperature.

VFA Odor Generation

The standard odor criteria (secondary maximum contaminant level [SMCL]) for the US EPA National Secondary Drinking Water Regulations is a threshold odor number (TON) = 3. The TON is defined as the greatest dilution of sample with odor-free water yielding a definitely perceptible odor (Greenberg et al. 1992). We determined the TON for each VFAs species according to Equation 1:

$$\text{Threshold odor number} = \frac{\text{Odorant concentration } (C_{gas})}{\text{Odor threshold value for that odorant}}$$

(1)

The "odor threshold value" is the lowest concentration of a specific odorant detectable by human olfaction. The "odorant concentration" is the gas phase concentration (C_{gas}) of a specific odorant (e.g., VFAs), which can be estimated based on the measured aqueous concentration (C_{aq}). Note that C_{aq} is the total concentration comprising both the weak acid (i.e., the protonated form susceptible to volatilization) and its conjugated base (which is charged and not susceptible to volatilization). The concentration of the protonated form that can undergo volatilization (and thus generate odor), C_{HA}, can be calculated based on the measured C_{aq}, the pH of the solution, and the corresponding acid/base equilibrium constant (Ka) and molecular weight (MW) according to Equation 2:

$$C_{HA}(\text{mol}/L) = \frac{C_{aq}\ (\text{mg}/L)\times 10^{-3}\ (\text{g}/\text{mg})}{MW\ (\text{g}/\text{mol})\times(1+K_a/10^{-pH})} \quad (2)$$

C_{gas} can be calculated using Henry's law (Equation 3), where K_H is Henry's law constant:

$$C_{gas}\ (\text{ppm}_v) = \frac{C_{HA}\ (\text{mol}/L)\times 10^3 (L/m^3)\times K_H\ (\text{atm}\cdot m^3/\text{mol})}{1\ \text{atm}}\times 10^6$$

$$(3)$$

Two representative samples of different seasons (A1, Jan 8th and A1, May 29th) were chosen to assess the seasonal variation of odor generation. The groundwater temperature and pH for these two samples were 6.6 °C, pH 6.6 for A1 (Jan 8th) and 26.9 °C, pH 4.6 for A1 (May 29th). Table 2 summarizes the calculated C_{gas} values, and Table 3 depicts the odor threshold value for each VFAs and the TON values for each sample. Specific odor occurrence and impact will vary between direct testing methods and specific use scenarios (drinking, cooking, washing, showering, and so forth).

For simplicity, we assumed that only acetic acid, propionic acid, and n-butyric acid contribute to the odor in the groundwater sample. The TON of the summer sample (A1, May 29th; 1045 TON) was much larger than the SMCL, and n-butyric acid was the major contributor to odor generation. The TON of the winter sample (A1, Jan 8th; less than 0.4 TON), however, was lower than the SMCL. As discussed previously, lower temperatures decreased microbial activities (including transformation of ethanol into VFAs) that mitigated odor generation. Overall, the results indicate that near a source, ethanol-blend releases to groundwater can generate odor problems that compromise water quality, but the level of impact would likely vary seasonally.

Conclusions

A strong correlation was observed between groundwater temperature and CH_4/VFAs concentrations (p less than 0.05) and associated odor generation within the channel exposed to continuously released ethanol. The main contributor to water odor was n-butyric acid, which accumulated at levels

Table 2
Calculated VFAs C_{gas}

VFAs	Measured C_{aq} (mg/L)	pKa	C_{HA} (mol/L)	Henry's Law Constant (atm m³/mol)[a]	C_{gas} (ppm$_v$)
Summer (sampled at A1, May 29th, 26.9 °C)					
Acetic acid	116	4.75[b]	1.02×10^{-3}	1.08×10^{-7}	1.10×10^{-1}
Propionic acid	7	4.87[b]	5.64×10^{-5}	4.42×10^{-7}	2.49×10^{-2}
Butyric acid	280	4.85[b]	1.86×10^{-3}	5.62×10^{-7}	1.04
Winter (sampled at A1, Jan 8th, 6.6 °C)					
Acetic acid	25	4.75[b]	5.80×10^{-6}	4.58×10^{-8}	2.66×10^{-4}
Propionic acid	4	4.87[b]	9.87×10^{-7}	2.17×10^{-7}	2.15×10^{-4}
Butyric acid	3	4.85[b]	5.95×10^{-7}	3.23×10^{-7}	1.92×10^{-4}

[a]Henry's constants were obtained from (Howard 1990) for acetic acid, and from (Howard 1997) for propionic and butyric acids. These constants were corrected for the corresponding temperature using the Van't Hoff equation, using standard enthalpy values from Haynes (2010).
[b]Source: Schwarzenbach et al. (2002).

Table 3
VFAs TON

VFAs	Odor Threshold Value (ppm$_v$)	C_{gas} (ppm$_v$)	TON
Summer (sampled at A1, May 29th, 26.9 °C)			
Acetic acid	1[a]	1.10×10^{-1}	0.1
Propionic acid	0.0057[b]	2.29×10^{-2}	4.4
n-Butyric acid	0.001[b]	1.04	1045
Winter (sampled at A1, Jan 8th, 6.6 °C)			
Acetic acid	1[a]	2.66×10^{-4}	Less than 0.1
Propionic acid	0.0057[b]	2.15×10^{-4}	Less than 0.1
n-Butyric acid	0.001[b]	1.92×10^{-4}	0.2

[a]Source: Cheremisinoff (1999).
[b]Source: Nagata (2003).

that exceeded the SMCL stipulated by National Secondary Drinking Water Regulations. The production of CH_4 up to C_{aq} of 17.9 mg/L did not result in detectable concentrations at the surface (40 cm above the water table). The potential for transport and accumulation of CH_4 gas from groundwater to subsurface confined spaces without adequate mechanisms for dilution and attenuation needs further evaluation. Overall, these results show that groundwater temperature fluctuations can influence CH_4 and VFAs generation. Therefore, seasonal variation of odor generation and CH_4 accumulation in the subsurface (or subsurface confined spaces) should be considered at sites contaminated with fuel ethanol blends.

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