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International Journal of Phytoremediation

Publication details, including instructions for authors and subscription information:
<http://www.informaworld.com/smpp/title~content=t713610150>

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Online Publication Date: 01 January 2007

To cite this Article: Arnold, C. W., Parfitt, D. G. and Kaltreider, M. , (2007)

'Phytovolatilization of Oxygenated Gasoline-Impacted Groundwater at an Underground Storage Tank Site Via Conifers', International Journal of Phytoremediation, 9:1, 53 - 69

To link to this article: DOI: 10.1080/15226510601139409

URL: <http://dx.doi.org/10.1080/15226510601139409>

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FIELD NOTE

PHYTOVOLATILIZATION OF OXYGENATED GASOLINE-IMPACTED GROUNDWATER AT AN UNDERGROUND STORAGE TANK SITE VIA CONIFERS

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A stand of five conifers (Pinus sp.) bordering a gasoline service station was studied to estimate the methyl tert-butyl ether (MTBE) emission rate from gasoline-impacted groundwater. Groundwater was impacted with gasoline oxygenates MTBE and tert-butyl alcohol (TBA) at combined concentrations exceeding 200000 µg/L. Condensate from trees was collected in sealed environmental chambers and analyzed. Concentrations of MTBE in condensate ranged from 0.51 to 460 µg/L; TBA ranged from 12 to 4100 µg/L (n = 19). Transpire concentrations were derived from MTBE air-liquid partitioning data exhibited in controls spiked with known concentrations of analyte. Tree emissions were estimated by multiplying average transpire concentrations by transpiration rates derived from evapotranspiration data. Stand evapotranspiration was calculated using meteorological data from the California Irrigation Management Information System (CIMIS) applied in the Standardized Reference Evapotranspiration Equation.

KEY WORDS: phytovolatilization, stand evapotranspiration, methyl *tert*-butyl ether (MTBE), *tert*-butyl alcohol (TBA), phytoattenuation

INTRODUCTION

Phytovolatilization consists of one or more phytoattenuation processes that dilute a chemical from a plant's vascular system. Methyl *tert*-butyl ether (MTBE) has been shown to readily volatilize from foliage and through stem and root diffusion (Davis *et al.*, 2001; Hong *et al.*, 2001; Ma *et al.*, 2004; Rubin and Ramaswami, 2001; Zhang, Davis, and Erickson, 1998, 2001). Other MTBE studies including plant metabolism (Trapp, Yu, and Mosbaek, 2003; Newman *et al.*, 1999), rhizodegradation (Ramaswami, Rubin, and Bonola, 2003; Zhang, Davis, and Erickson, 2000) and phytoextraction (Hu, Davis, and Erickson, 1998; Ma *et al.*, 2004) have been conducted. These studies show little accumulation and

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Table 1 Physio-chemical properties of selected gasoline VOCs

	Vapor pressure (kPa)	Henry's Constant (Pa m ³ mol ⁻¹)	Solubility (mg L ⁻¹)	Water Diffusivity (cm ² s ⁻¹ 10 ⁻⁶)	Log K _{OW}	Log K _{OC}
MTBE	33.5	60	51,260	8.2	1.20	1.11
TBA	5.6	1	Miscible	8.7	0.37	1.57
Benzene	12.7	557	1780	10.9	2.13	1.92
Toluene	3.8	673	520	9.3	2.69	1.89
Ethylbenzene	1.3	854	152	9.0	3.15	2.41
Xylene-(m)	1.1	700	160	7.8	3.18	2.34

Octanol-water partition coefficient (K_{ow}) is a measure of chemical lipophilicity.

Organic-carbon partition coefficient (K_{oc})

All values reported at 20–25 C.

phytodegradation due to MTBE's low lipophilicity (Table 1) and general recalcitrance toward immediate degradation. In general, a contaminant's physical properties dictate which phyto-removal processes will dominate a plant system (Burken and Schnoor, 1999; Ma and Burken, 2002).

MTBE is capable of degrading in groundwater, both aerobically and anaerobically (Davis and Erickson, 2004). However, unlike other gasoline constituents, MTBE is very water-soluble and poorly adsorbed to soils, allowing it to migrate faster and farther in groundwater. TBA is a less widely used gasoline additive, but can also be introduced into gasoline as an impurity in commercial-grade MTBE (Deeb, Scow, and Alvarez-Cohen, 2000). *Tert*-butyl alcohol (TBA) is the main metabolite or breakdown product of MTBE.

Site Description

The project site is an operating self-serve gasoline fueling facility located near the White Slough in the city of Vallejo, California (Figure 1). This site is bounded by Austin Creek to the east and a main thoroughfare to the west. The climate in the area is characterized as coastal-mixed-fog with rainfall occurring predominantly in the winter months. Annual precipitation averages 47.2 cm yr⁻¹ (18.6 in) with 75% of the rainfall occurring in the winter. Five mature landscaped conifers, identified as T1 through T5, span a distance of about 15 m (50 ft) and border three 37,854 L (10,000 gal) underground storage tanks (USTs). The trees are approximately 3–6 m (10–20 ft) from the USTs and were 10–13 m (33–43 ft) tall with basal diameters ranging from 0.43 to 0.52 m (1.4 to 1.7 ft). A pavement area and structures around the trees create a significant amount of sensible heat in the nonwinter seasons, causing an oasis effect (Figure 2).

The root zone and area immediately northeast of the trees consist of artificial fill composed of silt, sand, and gravelly material to a depth of up to 2 m (7 ft) below the ground surface (bgs). Clayey sediments extending to a depth of at least 6 m (20 ft) underlie the remainder of the site. Groundwater flow is to the northeast toward Austin Creek, at elevations ranging from about 1.2 m (4 ft) to -0.9 m (-3 ft) mean sea level. The natural gradient southwest of the stand was reported to be approximately 0.05 m/m (SOMA, 2003). Groundwater at the site is impacted primarily with high concentrations

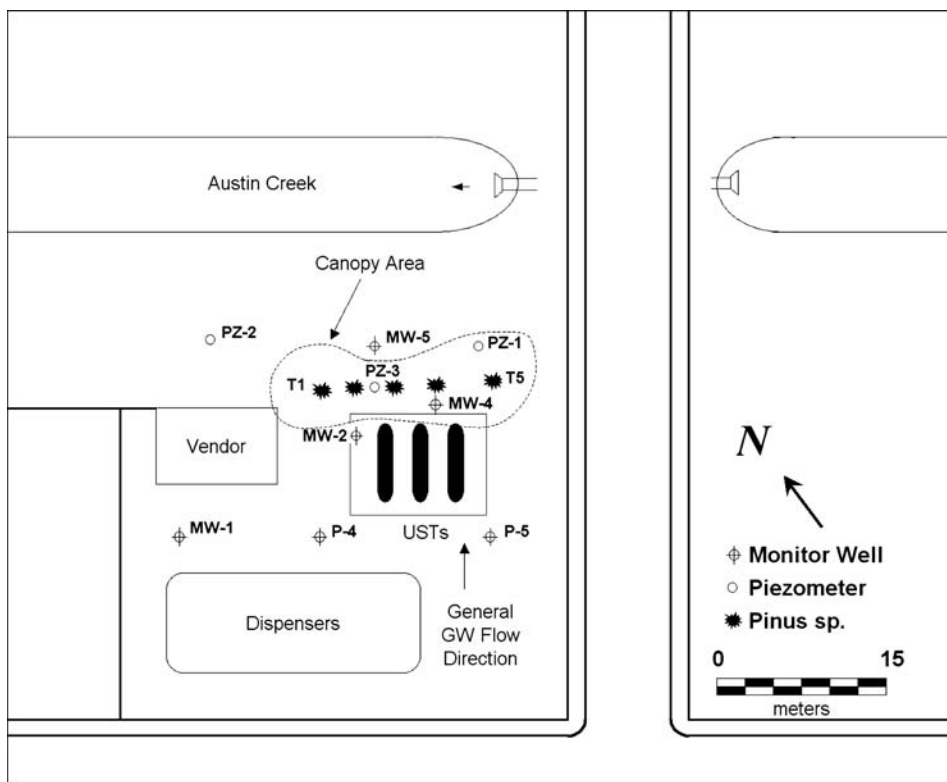


Figure 1 Site schematic.

of MTBE and TBA (Table 2) and low concentrations of other gasoline constituents (data not shown). At the site, high concentrations of dissolved phase oxygenates were contained to an unusually small area between the three USTs and the stand due to hydraulic control.

Table 2 Groundwater concentrations upgradient of the stand ($\mu\text{g/L } 10^5$)

	MW-2		MW-4	
	MTBE	TBA	MTBE	TBA
Mar. 1999	2.30 ± 0.050	0.25 ± 0.005	1.40 ± 0.050	0.27 ± 0.005
June 1999	1.70 ± 0.050	NA	1.10 ± 0.050	NA
Oct. 1999	2.40 ± 0.050	0.53 ± 0.005	0.65 ± 0.005	0.20 ± 0.005
Dec. 1999	1.40 ± 0.050	0.28 ± 0.005	0.88 ± 0.005	0.26 ± 0.005
Mar. 2000	0.74 ± 0.005	NA	1.60 ± 0.050	NA
May 2000	1.10 ± 0.050	0.32 ± 0.005	1.50 ± 0.050	0.50 ± 0.005
Sept. 2000	1.20 ± 0.050	0.51 ± 0.005	1.40 ± 0.050	0.51 ± 0.005
Nov. 2000	2.00 ± 0.050	0.29 ± 0.005	1.70 ± 0.050	0.71 ± 0.005

Mean MTBE, $1.4 \pm 0.27 \mu\text{g/L}$ ($n = 16$); mean TBA, $0.39 \pm 0.10 \mu\text{g/L}$ ($n = 12$). The \pm represents 95% confidence interval. Average MTBE in PZ-3 was $1.7 \pm 0.071 \mu\text{g/L}$ ($n = 2$); average TBA was $0.54 \pm 0.0071 \mu\text{g/L}$ ($n = 2$) in May/ Sept. 2000. NA—not analyzed.



Figure 2 A stand of pine trees is adjacent to underground storage tanks (foreground). The view is toward the northeast.

METHODS

Condensate Sampling and Analysis

Condensed vapor was captured in 125-L (0.85-mil) airtight plastic chambers sealed around distal branches. Condensate was collected from 19 branches at heights ranging from 2 to 5 m (7 to 16 ft) above ground from all five trees during the months of May and June, when light intensity is at its annual maximum. Accumulation occurred for 3–5 h under direct sunlight during the hours of 1000–1800. Six samples were collected in 1999 and 13 samples in 2000. Multiple samples from each tree were taken at different radial locations, to represent the transpiration stream concentration. Between 20 to 40 ml of aqueous solution was funneled into 20-ml glass vials and transported with trip blanks under chilled conditions to Kiff Analytical Laboratory in Davis, California, for analysis *via* EPA Method 8260. Samples were prepared with EPA Method 5030 (purge-and-trap) and were preheated to 70 °C for 3 min prior to purging. Method 8260 is a GC-MS method that yields excellent results for oxygenate quantification over a wide range of background total petroleum hydrocarbon (TPH) concentrations (Halden, Happel, and Schoen, 2001). Five of the 19 samples were also analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX). In addition to onsite samples, condensate from two offsite trees (one evergreen and one deciduous) was collected as upgradient and cross-gradient controls.

The mass accumulation for a chemical within the control volume, defined by the inside chamber walls and the foliar and woody biomass surfaces within the sealed chamber,

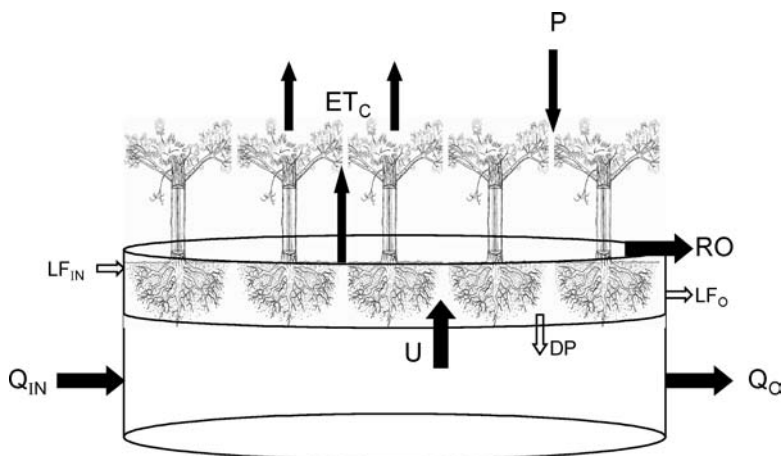


Figure 3 The canopy zone water mass balance.

is the sum of the mass inputs and internal sources, subtracted by the sum of the mass outputs and internal sinks (Schwarzenbach, Gschwend, and Imboden, 1993). Mass inputs consist of transpired, desorbed, or diffused oxygenates from plant tissues. The internal mass source is ambient oxygenate captured upon sealing the chamber. Possible mass outputs include adsorption to the chamber and adsorption and diffusion into plant tissues during chamber collection. Internal mass sinks include MTBE consumption and TBA generation due to chemical reactions.

Air-liquid partitioning in empty chambers was characterized onsite by dosing chambers with different aqueous concentrations of MTBE and analyzing the solution contents after approximately 3 h. Seven chambers were sealed with 40-ml stock solutions of different MTBE concentrations ranging from 5 to 200000 $\mu\text{g/L}$, in June 2000. One of the controls was dosed with TBA at a concentration of 3000 $\mu\text{g/L}$. Air for the chambers was captured at grade, onsite near the UST pad, where the highest concentrations of ambient VOCs would be expected (Figure 5). Periodic agitation facilitated partitioning between the liquid and vapor phases. After about 3 h, approximately 26 to 28 ml from each chamber was titrated into glass vials and transported under chilled conditions to Kiff Analytical Laboratory in Davis, California, for analyses *via* EPA Method 8260.

Ambient Air Sampling and Analysis

Ambient oxygenates and BTEX were investigated by collecting and analyzing ambient air samples. Ambient concentrations were assessed by two methods. First, gas samples were collected on multisorbent Carbotrap 300 tubes for 1–2 h intervals using a portable air sampling pump (Gilian, Inc.). The traps consist of hydrophobic sorbent packed in 6.35-mm (0.25-in) O.D., 20-cm (8-in) long stainless steel tubes. Three adsorbents were packed in the following order and amounts: 13-mm (0.51-in) Carboxipack C, 25-mm (0.98-in) Carboxipack B, and 13-mm (0.51-in) Carboxisieve S-III. The pumps were calibrated at the beginning of each sampling day and air was collected at a rate of 200 ml/min. Second, open chamber controls containing 0.5 L (0.1 gal) of water were subjected to ambient gas partitioning at the base of T3 (Figure 1). On each of three sampling days, 40 ml from each

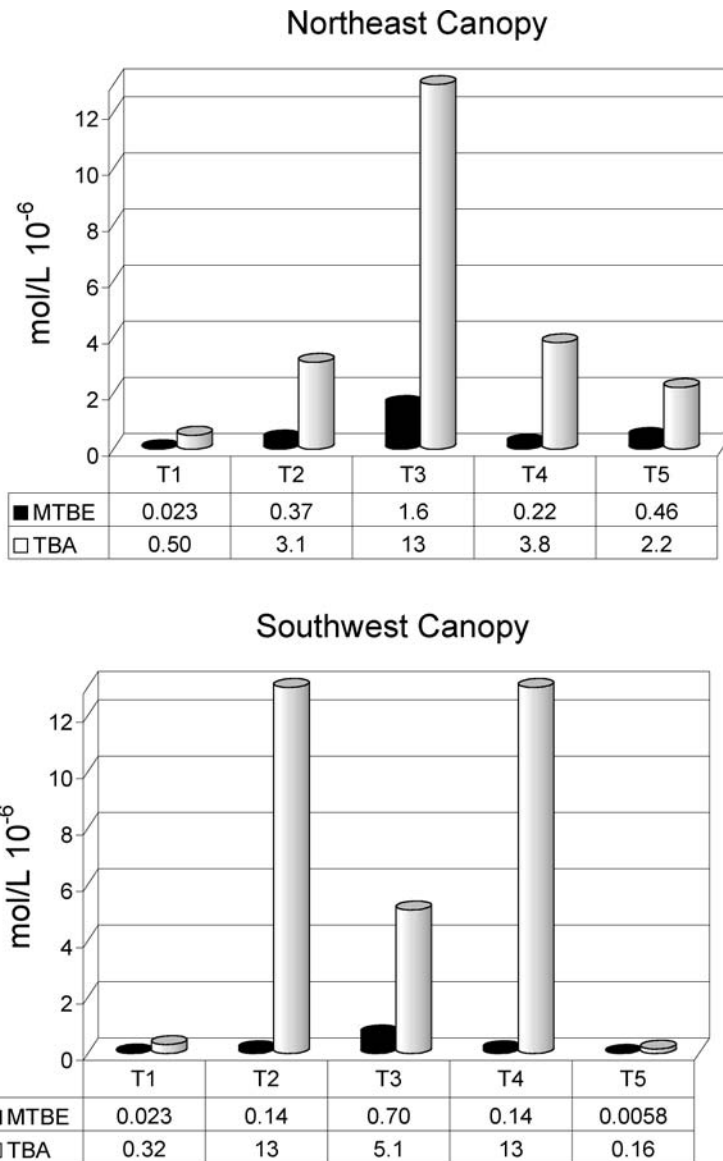


Figure 4 Condensed vapor concentrations are reported in closed chamber samples. Lower concentrations at the ends of the stand may reflect greater volumetric water usage due to competition from adjacent trees. Samples were collected June 2000.

open control solution was collected and analyzed for MTBE and TBA *via* EPA Method 8260 by Kiff Analytical Laboratory.

Air samples were collected on four Carbotrap tubes under near-halcyon conditions in October and November 1999, when the average wind velocity was near its annual minimum. Two ambient samples were collected below the stand at ground level and two were collected at the base of the canopy, 1.5–1.8 m (5–6 ft) above ground. Each sample tube was individually recapped and sealed in a clean, airtight container and chilled during

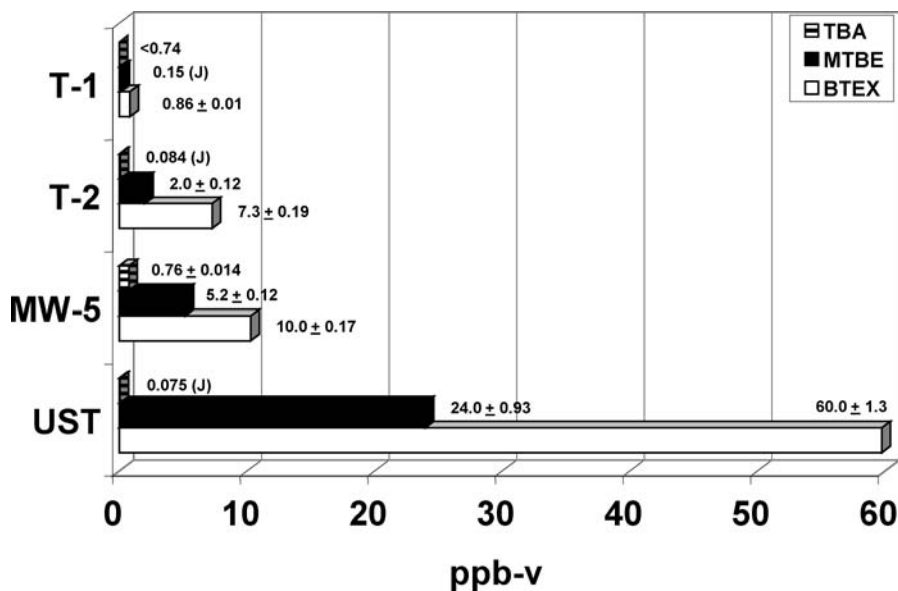


Figure 5 Time-weighted average ambient VOC concentrations. UST and MW-5 samples were collected at ground level. T1 and T2 were collected at the base of the canopy from 5–6 ft (1.5–1.8 m) above ground. The \pm represents absolute uncertainty. The “J” flag indicates that the results are below the laboratory reporting limit.

transport to the lab. Tubes were thermo-desorbed into 1-L tedlar bags and analyzed *via* EPA Method TO-14 (GC/MS) for MTBE, TBA, and BTEX by Air Toxics Laboratory in Folsom, California. Time-weighted average ambient concentrations over the monitoring period were calculated by dividing the total mass of analyte (nanograms) retained on the carbon by the specific air volume sampled.

Groundwater Data Collection

Groundwater concentrations and elevations were assessed using monitor wells and piezometers. Monitor wells were installed prior to the study period and are constructed of 5-cm (2-in) Sch 40 poly-vinyl chloride (PVC) pipe screened from 1.5 to 4.6 m (5 to 15 ft) bgs, with the exception of well MW-5, which is screened from 1.5 to 3.1 m (10 to 15 ft) bgs. Piezometers PZ-1 and PZ-2 were installed in 1999 and PZ-3 was installed in 2000. Piezometers are constructed of 2.5-cm (1-in) Sch 40 PVC screened from 2.4 to 3.1 m (8 to 10 ft) bgs. Groundwater samples were collected and analyzed numerous times during the study period for MTBE, TBA, BTEX, and TPH in the gasoline (C_2 to C_{12}) range *via* EPA Method 8260 (Tables 2 and 3). Environmental consultants (SOMA, 2003; TRC, 2001) were responsible for collecting and analyzing groundwater samples on behalf of the site owner and under the direction of the Solano County Department of Resource Management (the local regulatory agency).

Transpiration Estimates

The energy balance method (*i.e.*, Penman–Monteith) was used to estimate stand evapotranspiration. Since the Penman–Monteith equation does not separate water losses

Table 3 Groundwater analytical results downgradient of the stand ($\mu\text{g/L}$)

	MW-5		PZ-1		PZ-2	
	MTBE	TBA	MTBE	TBA	MTBE	TBA
Mar. 1999	33.0 \pm 0.50	19.0 \pm 0.50	NA	NA	NA	NA
June 1999	40.0 \pm 0.50	NA	NA	NA	NA	NA
Oct. 1999	26.0 \pm 0.50	21.0 \pm 0.50	19.00 \pm 0.50	28.0 \pm 0.50	8.00 \pm 0.50	<5.0
Dec. 1999	20.0 \pm 0.50	20.0 \pm 0.50	NA	NA	NA	NA
Mar. 2000	9.10 \pm 0.05	NA	NA	NA	NA	NA
May 2000	12.0 \pm 0.50	20.0 \pm 0.50	1200 \pm 50.0	450 \pm 5.0	130 \pm 5.0	22.0 \pm 0.50
Sept. 2000	12.0 \pm 0.50	21.0 \pm 0.50	950.0 \pm 5.00	400 \pm 5.0	90 \pm 0.5	18.0 \pm 0.50
Nov. 2000	NA	NA	NA	NA	NA	NA

Mean MTBE, 200 \pm 240/ $\mu\text{g/L}$ ($n = 13$); mean TBA, 93 \pm 110/ $\mu\text{g/L}$ ($n = 11$). The \pm represents the 95% confidence interval. NA—not analyzed.

from the vadose vs. non-vadose zone, a water balance was performed to differentiate between soil and groundwater root uptake. Figure 3 illustrates the general site conceptual model for the mass balance. A general water balance around a control volume extending from the soil surface to the depth of the first water bearing zone or aquifer, over some defined surface area, gives the net groundwater flux ($Q_I - Q_O$) through the control volume

$$Q_I - Q_O = \iint_A ET_c dA - (P - RO + \Delta SW) A. \quad (1)$$

The integrand represents the species evapotranspiration as a function of location within some defined area A (mm^2). Here, we define A as the canopy area projected onto the soil surface as observed from nadir (overhead). The control volume therefore takes the form of a cylindrical shape as define by the projected canopy area. Eq. 1 was applied during the period from April to November, herein referred to as the dry season. Precipitation (P) (mm) data was collected from a nearby weather station and runoff (RO) (mm) is defined as rainfall that breaks through the canopy and is shed by the pavement. The fraction of annual precipitation that is intercepted by the pavement area directly beneath the canopy is defined as α , so that the precipitation penetrating the control volume is $P(1 - \alpha)$. Over the dry season period, the average change in the soil water content in the vadose zone ΔSW (mm) is equivalent to the sum of the total available water in soil storage for root uptake; $(\theta_{FC} - \theta_{WP})(Z_R - Z_E)$ and the total evaporable water from the soil surface; $(\theta_{FC} - 0.5\theta_{WP})(Z_E)$ (Allen *et al.*, 1998). The corresponding volumetric quantity is obtained by multiplying by the surface area A . Here, soil water accumulation is defined as a negative quantity. We conservatively assumed that the soil water content began at field capacity θ_{FC} (mm^3/mm^3) and ended at the wilting point θ_{WP} (mm^3/mm^3). The soil depth subject to drying by evaporation is defined as Z_E (mm), with Z_R (mm) being the approximate rooting depth. Irrigation was not applied at the site and a 4-in concrete curb provided a barrier, separating the tank pit and stand from any potential surface water runoff. Deep percolation (DP) and lateral flux ($LF_I - LF_O$) did not occur during the dry season and, therefore, do not appear in Eq. 1. Therefore, the net groundwater flux is equivalent to the volumetric groundwater uptake U (mm^3). After substituting these variables into Eq. 1, the water balance becomes

$$U = \iint_A ET_c dA - (P(1 - \alpha) + \theta_{FC} Z_R + \theta_{WP}(0.5Z_E - Z_R))A. \quad (2)$$

Allen *et al.* (1998) noted that, for row crops, most of the water extracted by the roots is taken from beneath the plants' canopy. Assuming this is also true for landscaped conifers, the volume of water evapotranspired can be approximated by multiplying the stand evapotranspiration ($K_C ET_O$) by the canopy area A . This allows simplification of the integral in Eq. 2, obtaining a final expression for the mass balance where the groundwater transpiration U/A (mm) is equivalent to the stand evapotranspiration (ET_C) subtracted by the vadose zone evaporation

$$U/A = ET_C - P(1 - \alpha) - \theta_{FC} Z_R - \theta_{WP}(0.5Z_E - Z_R). \quad (3)$$

Stand evapotranspiration was calculated by multiplying the stand coefficient (K_C) by the reference evapotranspiration (ET_O) for a 0.12-m (0.4-ft) grass surface. Hourly ET_O was computed using ASCE's standardized reference evapotranspiration equation in a software application developed by Snyder and Eching (2004). The standardized equation is a derivative of the ASCE—Penman—Monteith equation. The required weather data includes hourly solar radiation, air temperature, wind speed, and dew point temperature. Meteorological data for ET_O calculations were downloaded from the California Irrigation Management Information System (CIMIS) reported by the California Department of Water Resources. The CIMIS Carneros weather station reports hourly weather data calculated from minute-by-minute weather measurements and is located 8.5 mil northeast of the project site.

Below the stand, dead vegetation, dry bare soil, and pavement generate large amounts of sensible heat, creating an oasis effect during the dry season. Small expanses of tall vegetation that are surrounded by shorter cover or dry land can have a K_C that exceeds the grass reference by 100% or more (Allen *et al.*, 1998). As long as the trees are not under water stress, K_C can increase to up to 2.5 under the oasis effect, resulting in unusually high transpiration rates. For a single row of tall trees serving as a windbreak, K_C can range from 1.2 to 2.5, as presented by Allen *et al.* (1998).

$$K_C = \min(1.2 + F_R h_C / W, 2.5) \quad (4)$$

where h_C is the mean vertical height of the canopy (m), W is the horizontal thickness of the canopy (m), and F_R is a resistance correction factor based on the FAO Penman—Monteith equation.

Since evergreen trees have low transpiration rates in the winter as a result of the shorter days, lower light levels, and colder temperatures (Doucette *et al.*, 2003), the majority of groundwater uptake was presumed during the nonwinter months. This is reasonable, since rain infiltration into soil becomes the major source of water for trees in the winter (Caldwell and Virginia, 1998) and forest stands composed of trees > 10 m (33 ft) tend to transpire only groundwater over the growing season (Dawson, 1996).

RESULTS

Root Uptake

Concentrations in upgradient monitor wells MW-2 and MW-4 (Table 2) were considered to be representative of concentrations in the immediate vicinity of the USTs due to higher oxygenate mobility in the pea gravel surrounding the USTs (Figure 1). The encompassing pea gravel zone constitutes a single-source distribution zone feeding the

center stand area. In wells MW-2 and MW-4, mean MTBE and TBA concentrations during the sampling period were $140,000 \pm 27,000 \mu\text{g/L}$ ($n = 16$); and $39,000 \pm 10,000 \mu\text{g/L}$ ($n = 12$). The \pm represents the 95% confidence interval. We applied t-distribution parameters $t_{0.05} = 2.131$ and 2.201 assuming a standard normal distribution. The mean MTBE and TBA concentrations downgradient of the stand were $200 \pm 240 \mu\text{g/L}$ ($n = 13$) and $93 \pm 110 \mu\text{g/L}$ ($n = 11$) (Table 3). The reduction in oxygenate concentrations indicate that root uptake is capturing a significant quantity of contaminated groundwater. On average, the concentration decline exhibited in groundwater concentrations across the stand was 99% for both oxygenates. Although maximum total BTEX concentrations reported in wells MW-4 and PZ-3 were $510 \mu\text{g/L}$ and $420 \mu\text{g/L}$, none were detected downgradient of the stand above the $0.5 \mu\text{g/L}$ detection limit.

Groundwater elevation data compiled from January 1999 through June 2003 were used to calculate average elevations upgradient and downgradient of the stand. The average groundwater elevation immediately upgradient of the trees in monitor well MW-4 was 0.96 m ($3.1 \text{ ft} \pm 0.35$) MSL ($n = 15$). The average elevation downgradient of the stand in MW-5 was -0.21 m ($-0.7 \text{ ft} \pm 0.68$) MSL ($n = 16$) (SOMA, 2002, 2003; TRC, 2001). The \pm represents the 95% confidence interval. The difference between average elevations directly across the stand over a distance of about 6 m (20 ft) is 1.2 m (3.9 ft). Due to the fine-grained nature of the soil material along with periods of high transpiration, the roots are able to depress the saturated zone.

When soils are stressed, water uptake by forest stands composed of trees $>10 \text{ m}$ (33 ft) can be enhanced by night-time root water transfer to the upper soil layers by a phenomena known as “hydraulic lift” (Dawson, 1996). Hydraulic lift may have significant implications for phytoremediation (Negri *et al.*, 2003) by supplementing water uptake by deep roots during the day.

Condensed Vapor Analysis

Closed chamber controls. Closed chamber controls (Table 5) indicate that most of the spiked MTBE analyte partitions into the vapor phase. The average MTBE concentration reduction among controls in Table 5 was $96 \pm 2.9\%$ ($n = 8$). The \pm represents the average deviation, which includes uncertainty introduced by an assumed 24-ppbv ambient MTBE ($\sim 1 \mu\text{g/L}$) contribution, as determined from ambient air samples (Figure 5). Under this assumption, any aqueous detection less than $1 \mu\text{g/L}$ (*e.g.*, C-1) would not represent an emitted quantity. Nevertheless, concentrations less than $1 \mu\text{g/L}$ were included in the averages, to be conservative. Estimated MTBE transpirate concentrations for each tree were calculated based on a 96% reduction in the chamber. TBA was spiked in one control and was not replicated experimentally. Therefore, the reduction exhibited in control C-6 (*i.e.*, 76%) was not used as a basis to determine TBA transpirate concentrations.

Six closed controls (C-1, 2, 3, 4, 5, and 8) spiked only with MTBE exhibited low concentration TBA (Table 5). Several explanations may account for this, including degradation to stoichiometric production of TBA (Steffan *et al.*, 1997) by acid hydrolysis or photolysis, or TBA may have also been introduced into the chamber through ambient air collected onsite near the tank pit.

A molar MTBE conversion of $0.13 \pm 0.03\%$ was calculated in control C-8, generating a final aqueous TBA concentration of $160 \mu\text{g/L}$, presumably through photolysis. Photolysis of MTBE can occur in the atmosphere if a hydroxide ion or other radicals are present. Assuming an average tropospheric hydroxide ion concentration of $10^6 \text{ radicals cm}^{-3}$, the

Table 4 Transpirate vapor condensed in sealed chambers ($\mu\text{g/L}$)

T1 ($n = 4$)		T2 ($n = 6$)		T3 ($n = 3$)		T4 ($n = 3$)		T5 ($n = 3$)	
MTBE	TEA	MTBE	TEA	MTBE	TEA	MTBE	TEA	MTBE	TEA
5.60 \pm 0.05	99 \pm 0.5	41 \pm 0.5	4000 \pm 50	460 \pm 5.0	2200 \pm 50	41 \pm 0.5	1200 \pm 50	6.50 \pm 0.05	280 \pm 5.0
1.9 \pm 0.05	42 \pm 0.5	30 \pm 0.5	4100 \pm 50	140 \pm 5.0	1000 \pm 50	19 \pm 0.5	280.0 \pm 5.0	41.0 \pm 0.50	160 \pm 5.0
2.0 \pm 0.05	37 \pm 0.5	46 \pm 0.5	2800 \pm 50	62.0 \pm 0.5	380.0 \pm 5.0	12 \pm 0.5	990.0 \pm 5.0	0.51 \pm 0.005	12 \pm 0.5
2.0 \pm 0.05	24 \pm 0.5	24 \pm 0.5	2100 \pm 50						
		33 \pm 0.5	230.0 \pm 5.0						
		12 \pm 0.5	1000 \pm 50						

MTBE concentrations shown may represent approximately 4% of the transpirate concentration based on data from controls in Table 5. BTEX was not detected ($< 5 \mu\text{g/L}$) in five condensate samples taken from T2, T3, and T5, although it was detected in groundwater at concentrations of up to 510 $\mu\text{g/L}$ within the canopy area. Analysis for total petroleum hydrocarbons (C_2 to C_{12}) from T3 showed a concentration of 570 $\mu\text{g/L}$ which may be a composition of gasoline constituents, plant lipids, and/or biogenic VOCs.

Table 5 MTBE Partitioning in empty chambers

	T (C)	Initial Aq. Phase ($\mu\text{g/L}$)		Final Aq. Phase ($\mu\text{g/L}$)		Conc. Reduction ^a (%)
		MTBE	TBA	MTBE	TBA	MTBE
C-1	33	5.0000 \pm 0.500	0	0.820 \pm 0.005	7.80 \pm 0.05	88 \pm 12
C-2	33	50.000 \pm 0.500	0	1.50 \pm 0.050	8.70 \pm 0.05	98 \pm 1.9
C-3	33	100.00 \pm 5.000	0	3.00 \pm 0.050	7.20 \pm 0.05	96 \pm 3.8
C-4	33	300.00 \pm 5.000	0	3.60 \pm 0.050	12.0 \pm 0.50	98 \pm 1.4
C-5	33	500.00 \pm 5.000	0	5.10 \pm 0.050	7.00 \pm 0.05	99 \pm 1.0
C-6	33	500.00 \pm 5.000	3000 \pm 50	9.50 \pm 0.050	730 \pm 5.00	99 \pm 1.1
C-7	24	10000 \pm 500.0	0	710 \pm 5.000	<10	93 \pm 4.7
C-8	24	200000 \pm 5000	0	12,000 \pm 500.0	160 \pm 5.00	94 \pm 2.4

^aThe \pm represents absolute uncertainty and includes uncertainty introduced by ambient background MTBE.

atmospheric half-lives of MTBE and TBA are approximately 4 and 11 d (Wallington *et al.*, 1988). MTBE also decomposes upon photoirradiation with UV light (Miyake and Shibamoto, 1999). Because the conversion rate is not large enough to produce TBA concentrations that are distinguishable from ambient contributions (*i.e.*, detectable) in controls C-1 through C-5, photolysis does not appear to be a significant factor at lower concentrations.

Rong and Kerfoot (2003) have noted that acidic conditions and high temperatures are necessary for significant hydrolysis to occur. The samples in this study were heated to high temperatures during laboratory analyses (at least 70 °C), but acid preservative was not introduced during sample preparation or analysis. Without the presence of acidic conditions, we conclude that aqueous TBA concentrations produced in the controls were not attributed to acid hydrolysis.

With respect to ambient background TBA, we noted an average concentration of $8.5 \pm 1.4 \mu\text{g/L}$ ($n = 5$) in controls C-1 through C-5, spiked only with pure MTBE. The \pm represents the average deviation. Comparable TBA concentrations were produced in these controls, independent of a wide range of spiked MTBE concentrations. Photolysis was ruled out based on the minimal conversion exhibited in control C-8 ($\sim 0.13\%$), which is too low to produce detectable concentrations in the other controls, on the basis that control C-1 produced more TBA than could theoretically be converted from the initial $5.0 \mu\text{g/L}$ MTBE spike. We conclude that the controls reflect ambient background TBA from a single ambient source (*i.e.*, near the UST pit).

Condensate samples. Oxygenate concentrations in condensate are reported in Table 4. Graphical analysis in Figure 4 show that concentrations decrease significantly at both ends of the stand. The higher concentrations exhibited in the stand interior may be a result of root competition from adjacent trees, facilitating a greater chemical uptake. The condensate concentrations under-represent transpirate concentrations, primarily due to the quantity of oxygenate distributed in the nonaqueous phase (*e.g.*, the vapor phase). Estimated transpirate concentrations were derived from condensate concentrations in Table 4, assuming that $96\% \pm 2.9\%$ of the transpired MTBE concentration was reduced by partitioning out of the free aqueous phase (Table 5) and then averaged for each tree.

Analysis for TPH_G was performed in only one sample, with a resultant concentration of $570 \mu\text{g/L}$ from T3, which may be a composition of gasoline-range constituents, plant lipids, and biogenic compounds. BTEX was not detected above laboratory detection limits ranging from 0.5 to $5 \mu\text{g/L}$ among the five condensate samples selected for analyses from

trees T2, T3, and T5. Neither oxygenates nor BTEX were detected in condensate collected from the offsite tree controls, with the exception of toluene detected at $1.1 \mu\text{g/L}$ in the upgradient control. Toluene is present in gasoline at a relatively high volume and is a common environmental contaminant.

Ambient Air Assessment

Tube samples collected at ground level were highest among all samples collected (Figure 5). The maximum MTBE concentration of 24 ± 0.93 parts per billion by volume (ppbv) at ground level at the UST pit could theoretically partition into the aqueous phase at concentrations ranging from 0.81 to $2.1 \mu\text{g/L}$ at the system temperatures (Robbins, Wang, and Stuart, 1993). MTBE was reported at 2.0 ± 0.12 ppbv and at 0.15 ppbv (J) at the base of canopies T1 and T2, at 1.5 – 1.8 m (5 – 6 ft) above ground. The highest calculated TBA concentration from the tube samples was 0.76 ± 0.014 ppbv, at MW-5 at ground level. This gas phase concentration could theoretically produce an aqueous phase concentration ranging from 1.5 to $3.2 \mu\text{g/L}$ at the system temperatures, according to Henry's constants reported by Rathbun and Tai (1988). In the open container controls, MTBE was detected in only one sample at a concentration of $1.2 \pm 0.05 \mu\text{g/L}$. Oxygenates were not detected in any other open control above $0.5 \pm 0.5 \mu\text{g/L}$ detection limits for MTBE and $5.0 \mu\text{g/L}$ detection limits for TBA.

Although the chamber-collection method is a relatively simple way to collect transpire, VOC emissions must be high enough in concentration to partition back into the aqueous phase. In this study, transpire concentrations were indeed high enough to produce concentrations in all but one condensate sample. Sample 3, T5 (Table 4) exhibited concentrations of $0.51 \pm 0.005 \mu\text{g/L}$ MTBE and $12 \pm 0.5 \mu\text{g/L}$ TBA, which is believed to be a manifestation of ambient oxygenates captured upon sealing the chamber. This conclusion is conservatively based upon oxygenate concentrations exhibited in the controls that closely resemble this sample. We selected the maximum ambient oxygenate concentrations exhibited among the controls, of 24 ppbv MTBE (*i.e.*, $1.0 \mu\text{g/L}$ aqueous at 39 C) and $12 \mu\text{g/L}$ TBA to represent the quantity of ambient oxygenates contributing to condensate samples, and incorporated these values into the uncertainty analyses.

Atmospheric deposition of MTBE is typical in urban air from vehicle emissions and from evaporative losses at service stations. A mean concentration of 4 ppbv was reported in Southern California urban air (Cal/EPA, 1997) among detection's ranging from 1 to 11 ppbv. Squillance *et al.* (1996) reported median concentrations of MTBE in the urban atmosphere that varied from less than 0.025 to 8.4 ppbv, in contrast to air at the perimeter of refueling stations that varied from 3 to 14 ppbv. It has been shown in the literature that atmospheric VOCs from phytoremedial applications lead to trivial concentrations in the atmosphere (EPA-RTDF, 2005; Davis and Erickson, 2004). Based on measured ambient MTBE concentrations in this study that are typical of urban air, we conclude that MTBE emitted from the stand had no significant impact to ambient air quality.

DISCUSSION

Water Use Estimates

Volumetric groundwater uptake was estimated using Eq. 3. A rooting depth of 1.5 m (5 ft) was applied to conifers in the total available water calculations as referenced by Allen *et al.* (1998). This rooting depth correlates well with the average depth of the capillary fringe ranging from 1.2 to 1.8 m (4 to 6 ft) bisecting MW-4 and MW-5. Therefore, it is

likely, and we presumed, that a portion of the root system penetrates the saturated zone such that the tree is not under water stress during high transpiration demand. Total available water was calculated based on the condition that soil moisture began at field capacity at the beginning of the dry season (36%) and was depleted to the wilting point at the end of the dry season (9%) for a silt loam soil classification. The soil depth for the total evaporable water calculation recommended by Allen *et al.* (1998) is 0.15 m (0.5 ft). The soil water depleted from the canopy area control volume under the aforementioned assumptions during the dry season was 412 mm (16.2 in).

We conservatively selected the maximum leaf resistance of 910 s m^{-1} from a group of nine pinus species (Körner, Scheel, and Bauer, 1979) for application in Eq. 4. Assuming that the affects of water stress were negligible, daily stand coefficients ranged from 1.7 to 2.2. Pavement interception was 21%, resulting in an average soil through-fall of 92 mm (3.6 in). The average annual dry season ET_O was calculated at 893 mm (35.2 in). The daily ET_C , summed over the dry season yielded a stand evapotranspiration of 1704 mm (67.8 in), which equates to an average volumetric water use of 638 L (168 gal) $\text{stand}^{-1} \text{ day}^{-1}$. The fraction of ET_C attributed to groundwater transpiration was calculated at 1200 mm (47 in).

Emission Rates

Dry season MTBE emission rates were estimated by multiplying the uptake volume for each tree by its average transpirate concentration, resulting in a range of emissions (Table 6). The annual dry season MTBE emitted from all trees ranged from 170 to 490 g. Here we differentiate between emission rate and phytovolatilization rate, since the latter may include diffusion through tissue walls or from the soil surface following upward transport into the vadose zone by root uptake, which were not measured. Concentrations have been shown to decrease exponentially with increasing height along plant stems by diffusion, as demonstrated in laboratory scale studies (Ma *et al.*, 2004; Zhang *et al.*, 2001). Zhang *et al.* (2001) developed a mathematical model that predicts MTBE diffusion rates as a function of stem height and water velocity. It has been presumed that VOCs are capable of escaping through tree bark, similar to the process of water vapor escaping through lenticels (Vroblesky, Nietch, and Morris, 1999). If this presumption is applicable to MTBE, a significantly higher quantity of MTBE could have been removed from groundwater than estimated by emissions in this study.

Transpirate emissions were not estimated for TBA based on data from the single control (C-6). Based strictly on average condensate concentrations for each tree, the

Table 6 Annual dry season needle emissions

U/A (mm)		A (m^2)	U (L)	Avg. MTBE Trans. Conc. ($\mu\text{g/L}$)	MTBE Emissions (g)
1200	T1	29	35,015	120 ± 92	4.2 ± 3.3
	T2	17	20,295	1300 ± 920	26 ± 19
	T3	20	23,752	9500 ± 6500	230 ± 160
	T4	33	39,698	1000 ± 720	40 ± 29
	T5	31	36,799	680 ± 470	25 ± 17
Totals		130	155,559		330 ± 160

U/A groundwater transpiration; A , projected canopy area; U , volumetric groundwater uptake.

The \pm represents absolute uncertainty.

minimum total dry season TBA produced from the stand is approximately 120 g. This value should not be relied upon as a measure upon which to base TBA emissions, since it assumes no reduction in aqueous concentration, when in fact an unknown but significant quantity resided in the chamber vapor space.

CONCLUSIONS

Phytovolatilization processes remove a substantial quantity of gasoline oxygenates from groundwater, partly due to the high transpiration demand relative to the natural groundwater flow rate. Transpiration is believed to be the primary removal process facilitated by possible diffusion to ambient air through tissues. Based on laboratory studies, very little MTBE is phytodegraded or accumulated.

Evaluating phytohydraulic control with trees requires an understanding of how the hydrogeologic flow system responds to groundwater uptake. Changes in light intensity and other environmental variables such as site-specific evapotranspiration requirements cause fluctuations in daily and seasonal transpiration and vary by tree species. For larger trees, species that perform hydraulic lift can significantly increase the uptake rate. Although the trees in this study were limited to a single row perpendicular to groundwater flow, migration of contaminants past the trees could theoretically be minimized by extending the length of the stand and staggering multiple rows of trees over a larger area, or by using species that demand greater rooting depths and higher transpiration rates.

Ambient MTBE concentrations at the site were not found to be elevated and were consistent with those typically reported in urban air. Emissions do not function as a point source, because the volatilization process distributes the contaminant over a large foliage area, where it is dispersed to trivial concentrations in the atmospheric. The atmospheric half-lives of MTBE and TBA are approximately 4 and 11 d, respectively.

Phytoremediation with trees is ideal at sites where exposure to human receptors is unlikely and there is sufficient time to implement a cleanup. For sites that pose acute risks for human and other ecological receptors, phytoremediation alone may not be the most feasible alternative. Under circumstances when contaminant mass must be reduced quickly, certain phytoremedial applications may take longer than traditional approaches to reach cleanup goals, but may still be considered in conjunction with traditional remedial techniques or natural attenuation processes.

ACKNOWLEDGMENTS

The authors wish to thank Klaus Scott (California Air Resources Board) for his assistance in this project.

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