

# MTBE, TBA, and TAME Attenuation in Diverse Hyporheic Zones

by James E. Landmeyer<sup>1</sup>, Paul M. Bradley<sup>2</sup>, Donald A. Trego<sup>3</sup>, Kevin G. Hale<sup>4</sup>, and Joseph E. Haas II<sup>4,5</sup>

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## Abstract

Groundwater contamination by fuel-related compounds such as the fuel oxygenates methyl *tert*-butyl ether (MTBE), *tert*-butyl alcohol (TBA), and *tert*-amyl methyl ether (TAME) presents a significant issue to managers and consumers of groundwater and surface water that receives groundwater discharge. Four sites were investigated on Long Island, New York, characterized by groundwater contaminated with gasoline and fuel oxygenates that ultimately discharge to fresh, brackish, or saline surface water. For each site, contaminated groundwater discharge zones were delineated using pore water geochemistry data from 15 feet (4.5 m) beneath the bottom of the surface water body in the hyporheic zone and seepage-meter tests were conducted to measure discharge rates. These data when combined indicate that MTBE, TBA, and TAME concentrations in groundwater discharge in a 5-foot (1.5-m) thick section of the hyporheic zone were attenuated between 34% and 95%, in contrast to immeasurable attenuation in the shallow aquifer during contaminant transport between 0.1 and 1.5 miles (0.1 to 2.4 km). The attenuation observed in the hyporheic zone occurred primarily by physical processes such as mixing of groundwater and surface water. Biodegradation also occurred as confirmed in laboratory microcosms by the mineralization of U-<sup>14</sup>C-MTBE and U-<sup>14</sup>C-TBA to <sup>14</sup>CO<sub>2</sub> and the novel biodegradation of U-<sup>14</sup>C-TAME to <sup>14</sup>CO<sub>2</sub> under oxic and anoxic conditions. The implication of fuel oxygenate attenuation observed in diverse hyporheic zones suggests an assessment of the hyporheic zone attenuation potential (HZAP) merits inclusion as part of site assessment strategies associated with monitored or engineered attenuation.

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## Introduction

The Clean Air Act Amendments of 1990 mandated the use of reformulated gasoline (RFG) and fuel oxygenates in areas of the United States that exceeded the air standards for carbon monoxide (Zogorski et al. 1997).

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<sup>1</sup>Corresponding author: U.S. Geological Survey, South Carolina Water Science Center, 720 Gracern Road, Suite 129, Columbia, SC 29210; (803) 750-6128; fax (803) 750-6181; jlandmey@usgs.gov

<sup>2</sup>U.S. Geological Survey, 720 Gracern Road, Suite 129, Columbia, SC 29210.

<sup>3</sup>Environmental Assessment & Remediations, 225 Atlantic Avenue, Patchogue, NY 11772.

<sup>4</sup>New York State Department of Environmental Conservation, Building 40, SUNY, Stony Brook, NY 11790.

<sup>5</sup>Currently at Environmental Protection Bureau, NY State Attorney General's Office, 120 Broadway, New York, NY 10271.

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The fuel oxygenates methyl *tert*-butyl ether (MTBE), *tert*-butyl alcohol (TBA), and *tert*-amyl methyl ether (TAME) were the most commonly used compounds added to gasoline. These compounds had been used previously in gasoline at low levels as octane enhancers after tetraethyl lead was removed from gasoline in the 1970s. Since then, MTBE has been added to gasoline, however, at greater volumes (up to 15%) than either TBA or TAME.

MTBE was thought to be recalcitrant in contaminated groundwater up until the 1990s. It is now recognized that MTBE undergoes oxidation by common heterotrophic microbes in the subsurface under oxic and anoxic conditions (Bradley et al. 2001a and references therein). TBA biodegradation also is significant under oxic conditions (Bradley et al. 1999). Little information exists, however, as to the biodegradation potential of TAME under either oxic or anoxic conditions.

The biodegradation of MTBE and TBA under oxic conditions in groundwater is controlled, in part, by dissolved oxygen (DO) levels. Significant fuel oxygenate

attenuation by biodegradation may occur at groundwater and surface water interfaces naturally characterized by sustainable levels of DO above 1 mg/L (Lendvay et al. 1998a; Norrström 1994). For example, up to 96% of MTBE in contaminated groundwater discharge was attenuated in the DO-rich hyporheic zone prior to discharge to a small stream in South Carolina (Landmeyer et al. 2001). This attenuation occurred in a vertical zone less than 5 feet (1.5 m) thick, in contrast to the lack of measurable attenuation along the more than 1000 foot (304 m) anoxic groundwater flowpath. Sediment cored from the oxic hyporheic zone and incubated in the laboratory under oxic conditions and fed uniformly (U) labeled U-<sup>14</sup>C-MTBE demonstrated rapid conversion to <sup>14</sup>CO<sub>2</sub> in 80 d with no conversion in sterile controls and no detection of intermediate compounds (Landmeyer et al. 2001). Streambed sediments collected from the hyporheic zone that degraded MTBE also mineralized TBA to carbon dioxide (Bradley et al. 1999). The effect of DO on TAME biodegradation in the hyporheic zone, however, has not been previously investigated.

The hyporheic zone is the highly variable zone beneath nearly all surface water bodies and lakes (Brunke and Gosner 1997; Sophocleous 2002; Biksey and Gross 2008), where surface water flows through parts of the bed and bank material and thus can interact with discharging groundwater (Winter et al. 1998; Cardenas 2008). Woessner (2000) states that from a physical and geochemical standpoint the hyporheic zone is that portion of saturated sediment where surface water and groundwater mix. The hyporheic zone also is a location of increased biological abundance and diversity because of (1) increased organic matter content and influx of DO primarily from surface water, (2) sharp chemical and redox gradients (Bencala 2000) that combine to act as a sink for many inorganic (Fuller and Harvey 2000; Moser et al. 2003; Gandy et al. 2007) and organic (Lendvay et al. 1998a, 1998b; Lendvay and Adrianes 1999; Smith and Lerner 2008) contaminants, and (3) mixing between surface water and groundwater (Winter et al. 1998; Baxter et al. 2003).

A review of the literature and results from Landmeyer et al. (2001) suggest the need to further evaluate the importance of natural attenuation processes such as advection, dispersion, and biodegradation relative to the rate of groundwater discharge at diverse hyporheic zones characterized by fuel oxygenate contamination. If the rate of all fuel oxygenate attenuation processes in the hyporheic zone is fast relative to groundwater discharge, the surface water quality may be protected. In contrast, if the rate of attenuation processes is slow relative to groundwater discharge then contaminants may discharge to surface water. Investigation of the relation between the natural attenuation of fuel oxygenates and groundwater discharge warrants documentation at diverse sites characterized by fresh water, brackish water, and saline water. Moreover, little information exists regarding the biodegradation of TAME under oxic and anoxic subsurface conditions or the fate of MTBE under saline pore water conditions.

The investigation reported here was designed to evaluate the natural attenuation of fuel oxygenates relative to groundwater discharge in diverse hyporheic zones.

## Background and Study Areas

This study was conducted between 2003 and 2005 on Long Island, New York (Figure 1), one of the most densely populated places in the United States; the 2000 census reported more than 2.8 million people in less than 1400 mi<sup>2</sup> (3628 km<sup>2</sup>). Residents on Long Island are dependent on groundwater as the sole source of drinking water. Also, New York along with California historically represented up to 40% of the U.S. consumption of MTBE (Zogorski et al. 1997).

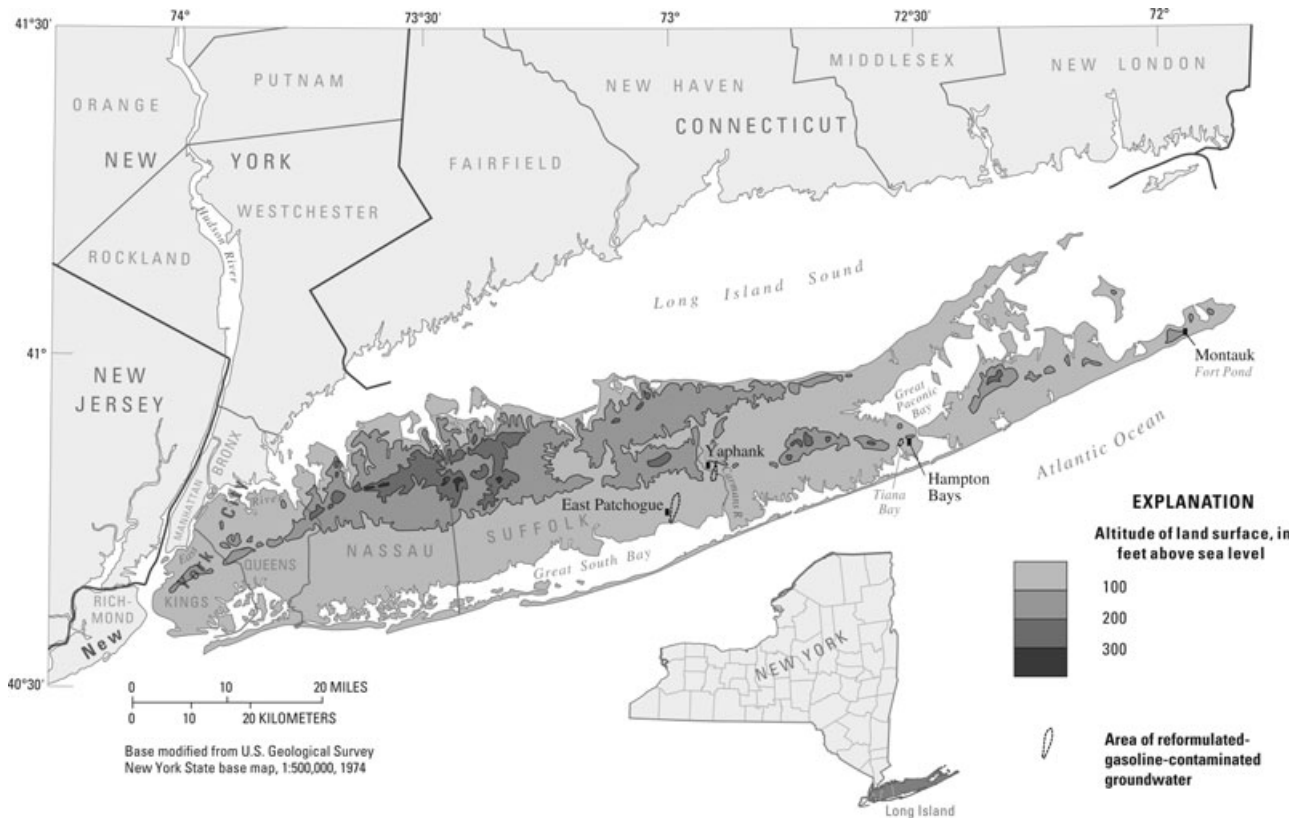
The geologic history of coastal New York produced aquifers characterized by fast groundwater flow rates, low sorption potentials (organic content less than 0.1%) (Prince 1986), and short residence times. Hydraulic conductivities of the shallow aquifer on Long Island range from 130 to 350 ft/d (39.6 to 107 m/d) (Prince 1986). Groundwater flow rates can be greater than 2 ft/d (3.6 m/d) and lead to lengthy plumes of dissolved contaminants. Because the base-flow index (BFI) for many streams on Long Island is near 0.90 (Pluhowski and Kantrowitz 1964; Wolock 2003; Simmons and Reynolds 2007), the water quality of streams is directly impacted by the quality of the groundwater discharge. The accidental release of contaminants to the water table, therefore, presents a challenge to managers of groundwater and surface water.

Four sites on Long Island characterized by leaking underground storage tanks (USTs) and dissolved phase plumes of MTBE, TBA, and TAME that have been transported downgradient to discharge into local surface water bodies were selected. The New York State Department of Environmental Conservation (NYSDEC) has established a discharge limit in surface water of 10 µg/L for MTBE and 50 µg/L for TBA and TAME based on best management practices and protection of ecological receptors. The four study sites included the following impacted surface water systems: the fresh water Carmans River near Yaphank, the fresh water Fort Pond near Montauk, the brackish water Tiana Bay near Hampton Bays, and the saline Great South Bay near East Patchogue (Figure 1). All sites were investigated using the same field and laboratory approaches. The Carmans River site will be discussed in detail but is representative of the work done at the other two sites. The Great South Bay site, however, provided only hyporheic zone sediment for the laboratory biodegradation study.

## Groundwater Discharge to Diverse Hyporheic Zones

### *Carmans River*

Carmans River is located on the eastern half of Long Island (Figure 1). It is a New York State statutorily designated and protected Scenic River and is used by catch-and-release trout fishermen. Flow in Carmans River is somewhat regulated by an upgradient lake but it is mostly



**Figure 1. Locations and approximate boundary of reformulated gasoline-contaminated groundwater that discharges to Carmans River (near Yaphank), Fort Pond (near Montauk), Tiana Bay (near Hampton Bays), and Great South Bay (near East Patchogue), Long Island, New York.**

controlled by groundwater discharge and rainfall (Schubert et al. 2006). Fuel-oxygenated gasoline-contaminated groundwater from a leaking UST discharges to the river. The boundary of the MTBE plume defined by concentrations greater than 5 µg/L is about 5400 feet (1645 m) long and narrow due to a lack of lateral dispersion. MTBE and TAME concentrations greater than 22 and 10 mg/L, respectively, have been detected in monitoring wells located within 300 feet (91.4 m) of the river, and bed-sediment pore water in the hyporheic zone and surface water also contained MTBE, TBA, and TAME at the milligrams per liter level (Environmental Assessment & Remediations [EAR] 2003, consulting report prepared for the NYSDEC).

#### *Fort Pond*

Fort Pond is located on the far eastern half of Long Island near the Village of Montauk (Figure 1). The south shore of this 5-acre (20,230-m<sup>2</sup>) pond is less than 500 feet (152 m) from the Atlantic Ocean, but the surface water level in the pond is not influenced by tides. Fort Pond is a kettle lake that receives water only from ground water discharge and precipitation and at rates sufficient to maintain lake levels even during droughts. Groundwater that contains MTBE, TBA, and TAME from a gasoline station located on the southern bank discharges to the pond. The length of the plume to the pond is less than 100 feet (30.4 m), but it extends about 500 feet (152 m)

beneath the pond under a clay layer until discharge. Previous remedial investigations indicated MTBE, TBA, and TAME in bed-sediment pore water at milligrams per liter concentrations (EAR 2003).

#### *Tiana Bay*

Tiana Bay is located on the eastern half of Long Island (Figure 1). It is an estuary that receives water from Tiana Creek and is isolated from the Atlantic Ocean by a barrier island. Groundwater that contains MTBE, TBA, and TAME from a gasoline station located about 4000 feet (1219 m) upgradient has reached Tiana Bay. Previous remedial work indicated MTBE concentrations greater than 250 mg/L in the brackish pore water of the bay sediments (EAR 2002, consulting report prepared for the NYSDEC).

## **Methods**

### **Hyporheic Zone Pore Water Sampling**

Pore water samples were collected during sampling events in 2003 to 2005 in the hyporheic zone at all sites. To collect the pore water samples, a 1-inch (2.5-cm) diameter rod was driven below the surface water and bed-sediment interface and advanced at 5 feet (1.5 m) intervals from surface to 15 feet (4.5 m) during sampling events in the summer of 2003, and advanced to

1 feet (0.3 m) and 5 feet (1.5 m) during sampling events in 2004 and 2005. The rod had a small screened drivepoint at the tip. The groundwater elevation was measured in the rod at each depth interval using an electric tape. Pore water was pumped from the drive point using a peristaltic pump and 1/4 inch (0.63 cm) tubing placed at the depth of the screened tip. Pore water samples taken for subsequent analysis of fuel oxygenates were collected using a low-flow rate and standard methods after stabilization of measured values of groundwater temperature, specific conductance, and pH. Pore water samples for MTBE, TBA, and TAME analysis were collected in 40-mL glass vials preserved with concentrated HCl to pH 2 and capped using Teflon®-lined septa. Concentrations of fuel oxygenates were quantified with purge-and-trap gas chromatography according to EPA method 8260B. Field parameters such as DO and chloride were measured during pore water collection using the CHEMets® colorimetric method (CHEMetrics Inc., Calverton, Virginia), and Hach® field kits (Hach, Loveland, Colorado), respectively. The 5-day biological oxygen demand (BOD5) of pore water samples was determined using standard methods. (Trade names are used for identification purposes only and do not constitute an endorsement by the U.S. government).

#### Hyporheic Zone Sediment Sampling

Samples of the hyporheic zone sediment at each site were collected during the sampling event in 2004 to provide material that contained microorganisms acclimated to the presence of MTBE, TBA, and TAME. At each location, sediments were collected with a hand auger to no deeper than 5 feet (1.5 m) beneath the streambed, lake bed, or beach face during pore water collection activities and placed in glass canning jars, sealed with canning caps with no headspace, and stored on ice in a cooler.

#### Laboratory Biodegradation Experiments

The sediments collected from the hyporheic zone were prepared as described previously (Bradley et al. 2002). In brief, 10-mL serum vials were amended with 5 to 6 g of saturated sediment sealed with Teflon-lined butyl rubber stoppers and flushed with 1000 mL of zero air (oxic treatments) or ultra high purity helium (anoxic treatments). Triplicate experimental vials were prepared for all treatments and the vials were stored in the dark. Duplicate sterile controls and a single sediment-free, container controls were prepared as described and then autoclaved twice for 1 h at 15 psi and 121°C. Each microcosm was amended with 0.11 µCi of uniformly radiolabeled (U) U-<sup>14</sup>C-MTBE (10.1 mCi/mmol; Perkin Elmer Life and Analytical Sciences, Boston, Massachusetts), 0.07 µCi of U-<sup>14</sup>C-TBA (5.0 mCi/mmol; Moravek Biochemicals, Brea, California), and 0.09 µCi of U-<sup>14</sup>C-TAME (9.6 mCi/mmol; Perkin Elmer Life and Analytical Sciences); this yielded 150 µg/L MTBE and TAME and 400 µg/L for TBA. All <sup>14</sup>C-substrates had radiochemical purities of 97% or greater. Headspace concentrations of labeled and unlabeled fuel oxygenates, CO<sub>2</sub>, and CH<sub>4</sub>

were quantified using gas chromatography radiometric detection as described in Bradley et al. (2001b).

#### Estimation of Groundwater Discharge to Surface Water

The occurrence and magnitude of groundwater discharge to surface water were quantified using two types of seepage meters at the sites. The first type of seepage meter was based on an ultrasound device (Chadwick et al. 1999, 2002; Paulsen et al. 2001). The device was placed inside a funnel of cross-sectional area of 0.209 m<sup>2</sup> and inserted into the surface water bed sediment. A datalogger was attached to the funnel via a flow tube of 1.3-inch (3.3-cm) ID (internal diameter) tygon tubing; the large diameter tubing was used to decrease resistance to flow. This seepage meter was used at the Tiana Bay site where previously conducted temperature and conductivity profiling in the bed sediment had delineated the location of contaminated groundwater discharge (Smith and Paulsen 2004). To summarize that work, a probe with temperature and conductivity meters was pushed about 6 inch (15 cm) into the bed sediment in transects in the suspected groundwater discharge area. This method was useful at this site because groundwater is characterized by a lower temperature and conductivity than surface water in Tiana Bay (Smith and Paulsen 2004). An area of lower temperature and conductivity was identified about 400 feet offshore where the local confining unit was absent (Smith and Paulsen 2004). Two seepage tests were done at this location; for test 1 three seepage meters were installed in July 2003 at the study location and for test 2 six seepage meters were deployed. Seepage was measured at each location for a minimum of 24 h and across multiple tidal cycles.

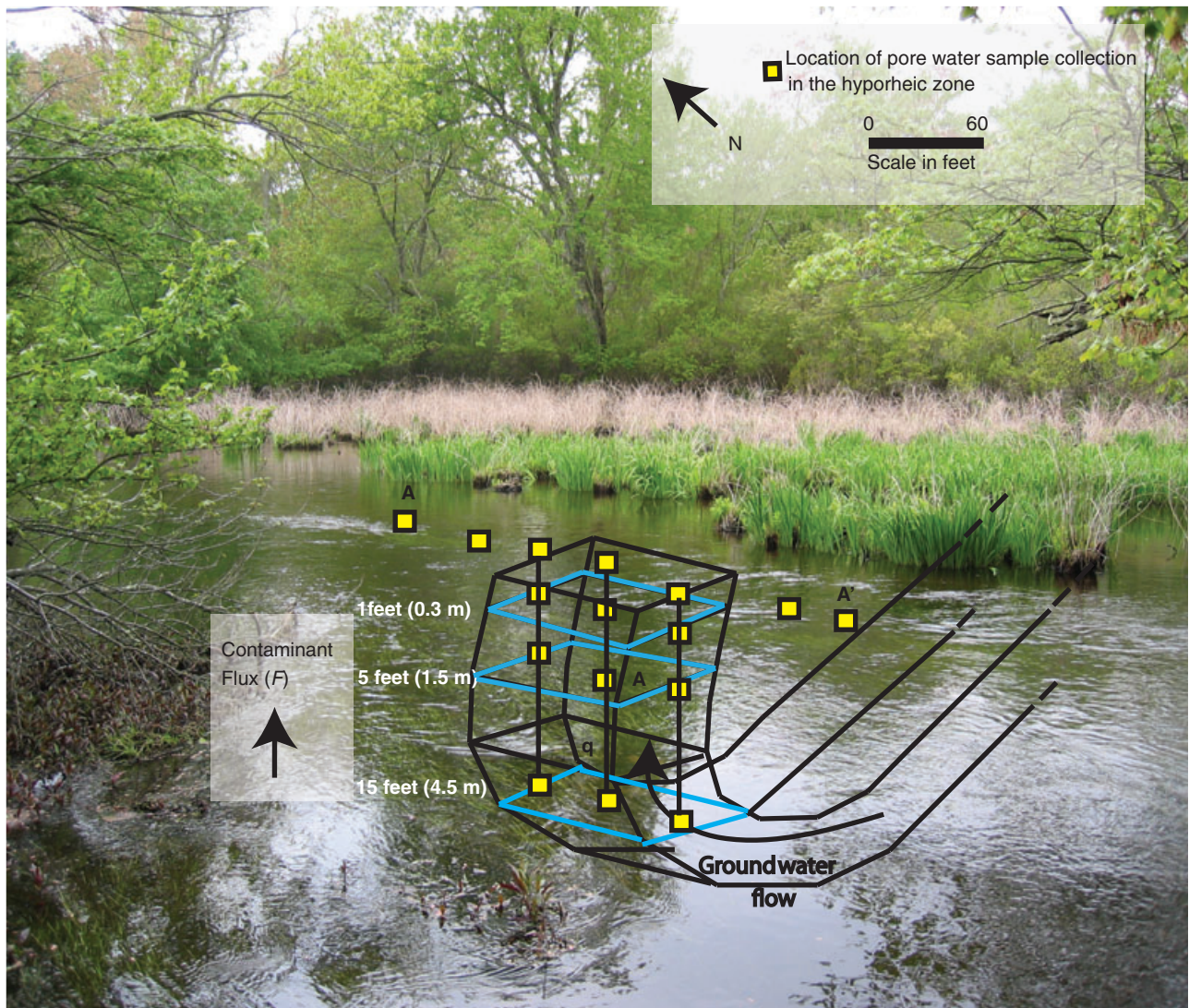
The second type of seepage meter used is similar to that described in Lee (1977); refer to Rosenberry and Menheer (2006) for a history of this meter. Basically, three quarters of a section of a 55-gallon drum was inserted into the bed sediment. A valve on a plastic bag was attached to the upturned highest end of the 55-gallon drum. Sample collection lasted no more than 24 h. The time that elapsed to collect a volume of water was used to determine the rate of groundwater seepage. This method was used at Carmans River, Fort Pond, and Great South Bay. At Carmans River two seepage meters tests were conducted. Test 1 commenced when three seepage meters were installed in July 2003 in a footprint area of 2.70 ft<sup>2</sup> (0.25 m<sup>2</sup>) of the stream bottom. A known volume of water was added to plastic bags attached to the valve on each of the three meters. Test 2 commenced when nine additional meters were installed in August 2003 and allowed to purge of trapped air and water. Late that same day, empty plastic bags were attached to each valve and after 24 h the volume of water measured. At Fort Pond the same strategy was used and three seepage meters were installed during two tests in August 2005. As noted in Rosenberry and Menheer (2006), measurements of seepage using most devices will tend to underrepresent groundwater discharge due to the resistance to flow created by the meter itself. Moreover,

the relatively small area of seepage measurement also will tend to limit the usefulness of seepage meter results (Rosenberry 2005) to considerably larger areas. Moreover, application of seepage meter test results in combination with pore water geochemical data collected on different dates is warranted given the groundwater plumes at the sites are under steady-state conditions and BFI exceeds 0.90 (Pluhowski and Kantrowitz 1964; Wolock 2003; Simmons and Reynolds 2007).

### Assessment of MTBE, TBA, and TAME Flux in the Hyporheic Zone

To couple measured groundwater discharge rates and pore water contaminant concentrations to understand contaminant attenuation in the hyporheic zone, the Theis polygon method (Bedient and Huber 1988) was used. This approach proved useful in investigating the fate of MTBE

in groundwater discharge to surface water (Landmeyer et al. 2001) and the remediation of MTBE plumes at various UST sites (Newell et al. 2003). The mass flux of a dissolved substance in groundwater discharge through the hyporheic zone can be quantified by dividing the hyporheic zone into a series of polygons of known area located at depth intervals that correlate to pore water sample collection and at a right angle to groundwater flow (Figure 2, blue polygons). Each polygon at each sample depth is centered on the pore water sampling point and the edges of the polygon delineated by contaminant detection in hyporheic zone pore water samples (Figure 2). This approach is useful because it is based on changes in total groundwater contaminant *fluxes* across a series of finite areas rather than based on changes in groundwater contaminant *concentrations* at single points (wells) along a groundwater flowline of constant direction; the latter



**Figure 2.** Idealized representation of groundwater flow through the hyporheic zone to discharge to surface water (Carmans River as an example). Polygons of known area ( $A$ ) and at a right angle to groundwater flow and seepage ( $q$ ) were centered around vertically discretized pore water sample locations between 1 and 15 feet (0.3 and 4.5 m) in 2003 and 1 and 5 feet (0.3 and 1.5 m) in 2004 and used to calculate contaminant mass flux ( $F$ ) and attenuation between polygons. The yellow squares at the surface are locations where pore water samples were collected at depth but not shown.

being an assumption required by the dispersion model (Chapelle et al. 1996) and the conservative tracer model (Weidemeier et al. 1996). For example, if the concentration of a particular contaminant changes over time in a well, it is uncertain if the change is indicative of natural attenuation or simply an artifact of a deviation in the groundwater flow direction away from the well. With the flux approach, the presence of multiple wells placed in a cross section of the predicted changes in groundwater flow direction reduces the uncertainty surrounding contaminant concentration changes in a single well, because a decrease in contaminant concentration caused by changes in flow direction would permit the contaminant to be measured in adjacent wells.

At each study site, the contaminant mass flux,  $F$ , of MTBE, TBA, and TAME was related to the groundwater discharge by:

$$F = CAq \quad (1)$$

where

$F$  = total mass (M, or concentration) of MTBE, TBA, or TAME (M/T);

$C$  = MTBE, TBA, or TAME mass or concentration per polygon at each depth interval (M/L<sup>3</sup>);

$A$  = area of each polygon (L<sup>2</sup>), and;

$q$  = specific discharge of groundwater through each polygon ([L<sup>3</sup>/T]/L<sup>2</sup>)

The contaminant mass flux data were computed for each depth interval. The contaminant mass flux data were log transformed and plotted against the depth of each pore water sample to provide the total contaminant mass attenuation rate ( $K_{\text{atten}}$ ) in per day (d<sup>-1</sup>) from the slope ( $m = K/v$ ) of the line; this is the hyporheic zone attenuation potential (HZAP). This decrease in contaminant mass between increasingly shallower depth intervals also was used to estimate the percentage of total attenuation observed. Comparison of the loss of contaminant observed in the laboratory microcosm study converted to  $K_{\text{bio}}$  (d<sup>-1</sup>) with  $K_{\text{atten}}$  (d<sup>-1</sup>) was used to determine the percentage of total attenuation observed in the field due to apparent biodegradation.

## Results and Discussion

### Contaminated Groundwater Discharge to Diverse Hyporheic Zones

The occurrence of fuel-oxygenated contaminated groundwater discharge was examined at all sites between 2003 and 2005 except Great South Bay, which was characterized by surface water recharge to groundwater. Specific field results from Carmans River will be discussed here in detail.

The footprint of contaminated groundwater discharge beneath Carmans River was roughly 150 feet (45.7 m) by 23.5 feet (7.3 m) for a total area of 3525 ft<sup>2</sup> (327 m<sup>2</sup>), to a depth of 15 feet (4.5 m) as defined by the 2003 results of pore water analysis for fuel oxygenates such as MTBE,

TBA, and TAME (Figures 3a, 3b, and 3c, respectively) collected at the locations shown in Figure 2. Groundwater discharge in this area was confirmed by the two seepage meter tests. During test 1, two seepage meter bags gained between 133 and 480 mL of water suggesting active groundwater discharge between 0.69 and 2.51 gal/d/ft<sup>2</sup>; the third bag was located beyond the zone of contaminant discharge and was not used. The average groundwater discharge rate was 1.51 gal/d/ft<sup>2</sup>. For test 2, all bags (except one that had become dislodged from the valve) had gained between 140 and 2010 mL of water, indicating groundwater discharge between 0.11 and 1.66 gal/d/ft<sup>2</sup> for an average groundwater discharge rate of 0.93 gal/d/ft<sup>2</sup>; the nonweighted average from both seepage meter tests was 1.22 gal/d/ft<sup>2</sup> (Table 1). Results of the range of contaminant concentrations detected and the occurrence and magnitude of groundwater discharge for Carmans River, Fort Pond, and Tiana Bay are summarized in Table 1.

### Evidence for Biodegradation of Fuel Oxygenates in Hyporheic Zone Sediments under Oxidic and Anoxic Laboratory Conditions

Hyporheic zone sediment from all sites mineralized U-<sup>14</sup>C-MTBE, U-<sup>14</sup>C-TBA, and U-<sup>14</sup>C-TAME to <sup>14</sup>CO<sub>2</sub> under oxidic conditions (Table 2). Anoxic mineralization observed was lower for each compound at each site (Table 2). The percentage of added U-<sup>14</sup>C-MTBE converted to <sup>14</sup>CO<sub>2</sub> was highest (39% ± 26%) in the Great South Bay beach sediments, even though the pore water was saline and uncontaminated. The mineralization of TAME under oxidic and anoxic conditions (and at equal or greater percentage than MTBE) is believed by the authors to be the first report of this occurrence under natural conditions.

### MTBE, TBA, and TAME Hyporheic Zone Attenuation Potential (HZAP)

The measurements of groundwater discharge, pore water geochemistry, and laboratory biodegradation rates were used to assess the flux and attenuation of contaminants in the hyporheic zone at three of the four sites. The results of the investigation at Carmans River are described in detail; results for the other sites are listed in Table 3.

At Carmans River the concentration of MTBE decreased in the hyporheic zone sediments as groundwater flow approached surface water (Figure 3a), and this trend was observed during each sampling event between 2003 and 2005. In 2003, for example, the concentration of MTBE in groundwater sampled at 5 feet (1.5 m) beneath the streambed at Carmans River decreased from a high of 43,000 to 34,000 µg/L at the 1-foot (0.3-m) sampling location and then to 340 µg/L at the bottom of the streambed (Figure 3a). The calculated flux of MTBE through the 3525 ft<sup>2</sup> (327 m<sup>2</sup>) section of hyporheic zone at these depths decreased from 6.11 × 10<sup>8</sup> at 5 feet (1.5 m) to 5.01 × 10<sup>8</sup> at 1 foot (0.3 m) to 1.47 × 10<sup>7</sup> µg/d at the stream water column. The mass

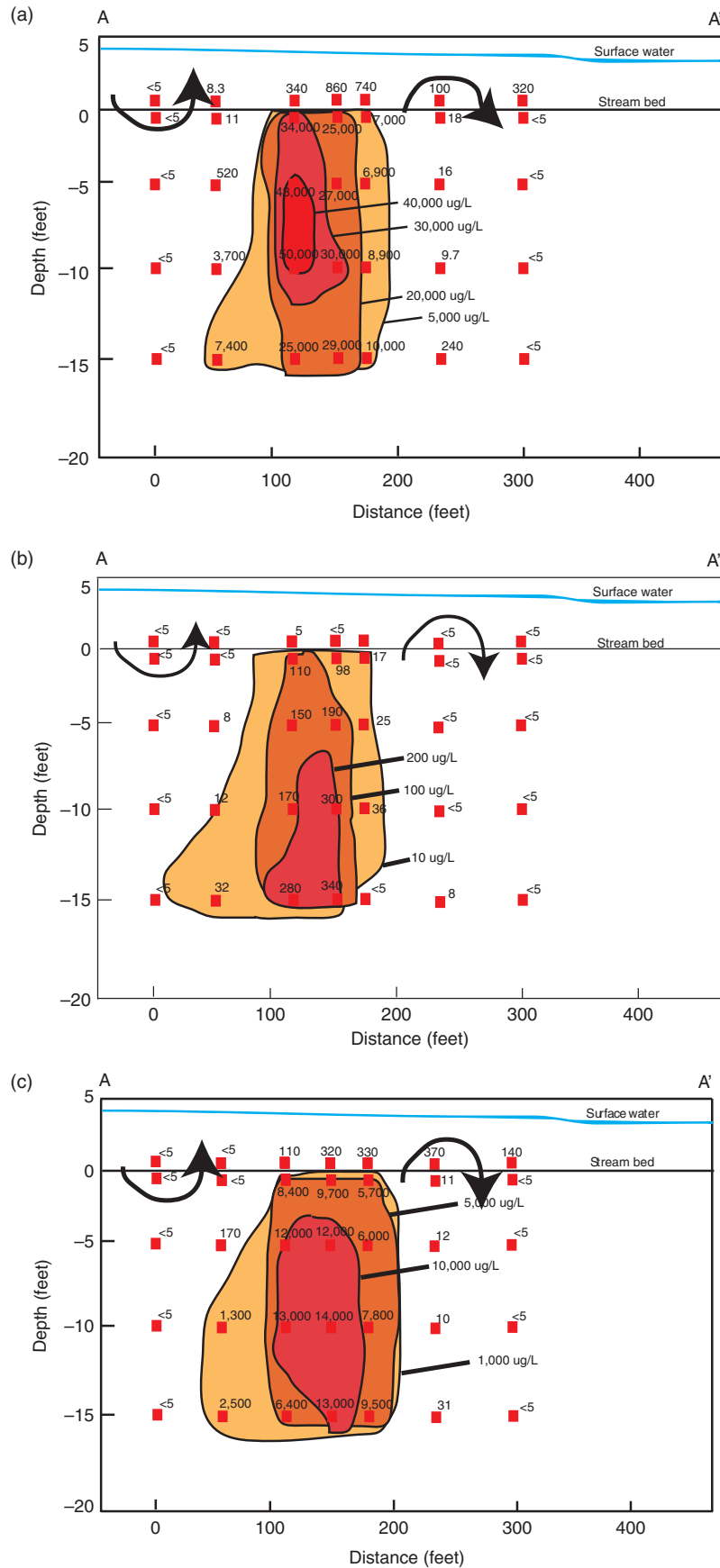


Figure 3. Pore water concentrations in micrograms per liter of (a) MTBE, (b) TBA, and (c) TAME in the hyporheic zone as measured in pore water samples located parallel to the bank (A to A' in Figure 2), Carmans River, New York, 2003. The arrows represent the potential mixing of surface water and groundwater.

**Table 1**  
**Groundwater Discharge and Fuel Oxygenate Contamination Range in the Hyporheic Zone**

Site	Fuel Oxygenate Concentration Range (µg/L)		Discharge Area (ft <sup>2</sup> )	Discharge (gal/d/ft <sup>2</sup> )
Fort Pond	MTBE	ND–81,000	12,600 (1170 m <sup>2</sup> )	0.47
	TBA	ND–21,000		
	TAME	ND–8700		
Carmans River	MTBE	Figure 3	3525 ft <sup>2</sup> (327 m <sup>2</sup> )	1.22
	TBA			
	TAME			
Tiana Bay	MTBE	ND–11,000	1500 ft <sup>2</sup> (140 m <sup>2</sup> )	10.20
	TBA	ND–190		
	TAME	ND–33		

Notes: Groundwater did not discharge to surface water at Great South Bay.  
Fuel oxygenate concentration data are from 2003 sampling events.  
ND is nondetection.

**Table 2**  
**Fuel Oxygenate Mineralization after 83 Days**

Site	Surface Water Quality	MTBE <sup>1</sup>		TBA <sup>2</sup>		TAME <sup>3</sup>	
		(Percent ± standard deviation)					
		Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic
Fort Pond	Fresh	27 ± 9	15 ± 1	8 ± 2	4 ± 1	89 ± 20	4 ± 0
Carmans River	Fresh	36 ± 5	12 ± 2	100 ± 0	2 ± 2	88 ± 17	2 ± 1
Tiana Bay	Brackish	24 ± 6	20 ± 1	14 ± 14	3 ± 4	25 ± 17	5 ± 1
Great South Bay (Tidal Creek)	Brackish	31 ± 4	14 ± 1	11 ± 2	2 ± 0	59 ± 16	3 ± 1
Great South Bay (Beach)	Saline	39 ± 26	2 ± 3	87 ± 6	0 ± 0	26 ± 17	0 ± 0

<sup>1</sup>% <sup>14</sup>C-MTBE converted to <sup>14</sup>CO<sub>2</sub> under oxic conditions or <sup>14</sup>CO<sub>2</sub> and <sup>14</sup>CH<sub>4</sub> under anoxic conditions.  
<sup>2</sup>% <sup>14</sup>C-TBA converted to <sup>14</sup>CO<sub>2</sub> under oxic conditions or <sup>14</sup>CO<sub>2</sub> and <sup>14</sup>CH<sub>4</sub> under anoxic conditions.  
<sup>3</sup>% <sup>14</sup>C-TAME converted to <sup>14</sup>CO<sub>2</sub> under oxic conditions or <sup>14</sup>CO<sub>2</sub> and <sup>14</sup>CH<sub>4</sub> under anoxic conditions.  
Note: No <sup>14</sup>CO<sub>2</sub> was detected in sterile or sediment-free control microcosms.

flux attenuation from 1 feet (0.3 m) to the stream bottom was  $4.86 \times 10^8$  µg MTBE/d. Expressed as a first-order attenuation rate normalized to the groundwater seepage rate, the MTBE  $K_{\text{atten}}$  gives rise to the HZAPs listed in Table 3. Prior to the 2005 pore water sampling event, oxygen had been injected into monitoring wells along the eastern bank of Carmans River as part of a more aggressive remediation strategy. The concentration of MTBE in the pore water down to 15 feet (4.5 m) of the hyporheic zone decreased after oxygen injection to concentrations no greater than 1000 µg/L (EAR 2005, consulting report prepared for the NYSDEC). Perhaps because of the lowered MTBE concentrations, the MTBE mass attenuation rate decreased by a factor of 2 relative to the rate measured prior to oxygen injection (Table 3). The pore water concentration of TBA measured in 2003 decreased in the hyporheic zone as groundwater flow approached surface

water (Figure 3b) but increased during 2004. In 2003, for example, the concentration of TBA in groundwater sampled at 5 feet (1.5 m) beneath the streambed decreased from a high of 190.2 to 98 µg/L at the 1 foot (0.3 m) location and to <5 µg/L at the bottom of the streambed (Figure 3b). The attenuation of TBA at these depths was  $2.62 \times 10^6$  µg TBA/d, with a resultant HZAP similar to that of MTBE (Table 3). For the 2005 sampling event, the HZAP is positive because the TBA flux to the river increased by  $5.00 \times 10^4$  µg TBA/d, suggesting the possible conversion of MTBE to TBA under microanoxic conditions in the hyporheic zone. The pore water TAME concentration also decreased in the hyporheic zone as groundwater flow approached surface water (Figure 3c). The TAME attenuation was  $2.14 \times 10^8$  µg TAME/d and an HZAP similar to MTBE and TBA (Table 3). The data for the HZAP calculated at Fort Pond and Tiana Bay are

**Table 3**  
**Fuel Oxygenate Hyporheic Zone Attenuation Potential (HZAP) ( $K_{\text{atten}}$ ) ( $\text{d}^{-1}$ )**

Site	MTBE			TBA			TAME		
	2003	2004	2005	2003	2004	2005	2003	2004	2005
Fort Pond	<sup>1</sup>	-0.050	-0.160	<sup>1</sup>	-0.078	-0.165	<sup>1</sup>	-0.070	-0.071
Carmans River	-0.780	-0.702	-0.327 <sup>2</sup>	<sup>3</sup>	-0.760	+0.104	<sup>3</sup>	-0.769	-0.544
Tiana Bay	-4.88	<sup>4</sup>	<sup>4</sup>	-15.83	<sup>4</sup>	<sup>4</sup>	-11.13	<sup>4</sup>	<sup>4</sup>

<sup>1</sup>Indicates that pore water samples were not collected.  
<sup>2</sup>Data were collected but not representative of natural conditions due to oxygen injection. Negative sign of  $K_{\text{atten}}$  indicates loss.  
<sup>3</sup>Indicates that pore water samples were collected but not used as part of HZAP determination.  
<sup>4</sup>Indicates that fuel oxygenate concentrations were below detection.  
Notes: Pore water data were from 1 to 15 feet (0.3 to 4.5 m) in the hyporheic zone (2003).  
Pore water data were from 1 foot (0.3 m) in the hyporheic zone (2004, 2005).

**Table 4**  
**Fuel Oxygenate Hyporheic Zone Total Attenuation and Apparent Biodegradation**

Site (date)	Fuel Oxygenate	Total Attenuation Observed (%)	Apparent Biodegradation (%)	Groundwater Discharge ( $\text{gal/d/ft}^2$ )
Carmans River (2003–2004)	MTBE	85.4	0.56	1.22
	TBA	66.9	1.57	
	TAME	92.4	1.60	
Fort Pond (2003–2004)	MTBE	86.9	3.75	0.93
	TBA	94.2	1.31	
	TAME	34.0	15.9	
Tiana Bay (2003–2004)	MTBE	84.5	0.50	10.2
	TBA	48.7	1.31	
	TAME	49.5	0.50	

shown in Table 3. The HZAP was lower in the Fort Pond hyporheic zone but higher at Tiana Bay.

**Attenuation of MTBE, TBA, and TAME in the Hyporheic Zone and Influence of Groundwater Discharge Rate**

At all sites the total mass attenuation of fuel oxygenates in a 5-foot (1.5 m) thick part of the hyporheic zone ranged from 34% to 95% (Table 4). The total MTBE attenuation in the hyporheic zone of Fort Pond, Carmans River, and Tiana Bay was 86.9%, 85.4%, and 84.5%, respectively (Table 4). The fraction of this total MTBE attenuation due to apparent biodegradation was highest in Fort Pond at 3.75%, then Carmans River (0.56%), and Tiana Bay (0.50%) (Table 4). The total TBA attenuation in the hyporheic zone of Fort Pond, Carmans River, and Tiana Bay was 94.2%, 66.9%, and 48.7%, respectively (Table 4). The total TBA attenuation due to biodegradation was highest in Carmans River at 1.57%, then Fort Pond (1.31%), and then Tiana Bay (0.50%). The total TAME attenuation in the hyporheic zone of Fort Pond, Carmans River, and Tiana Bay was 34%, 92.4%, and 49.5%, respectively (Table 4). The total TAME attenuation due to biodegradation was highest in Fort Pond

at 15.9%, then Carmans River (1.6%), and then Tiana Bays (0.5%).

The percent total attenuation attributed to biodegradation was highest for MTBE and TAME when the groundwater discharge rate was the lowest (Table 4). This occurred at the Fort Pond site where groundwater discharge was 0.93 gal/d/ft<sup>2</sup>. The lower groundwater discharge rate may provide more residence time for biodegradation in the hyporheic zone to occur. The laboratory-based apparent biodegradation estimates are best taken as a lower bound for biological contribution to contaminant loss because the microcosms represent static conditions rather than the dynamic conditions found in the field. As such, laboratory biodegradation rates may be lower than field rates due to oxygen limitations typically encountered over time in microcosm studies. These estimates also should be considered to be a lower bound because not all potential biologically mediated processes were examined as part of this study. For example, under anoxic conditions MTBE can undergo abiotic reduction to TBA by molecular hydrogen (H<sub>2</sub>) produced by heterotrophic microbes during fermentative heterotrophy (Bradley et al. 2006) and at higher concentrations under methanogenic

conditions. These processes were not specifically examined as part of the experimental setup, although the anoxic treatments for MTBE were at ambient hydrogen concentrations.

The in situ redox status of the hyporheic zone presumably affected the biodegradation component of natural attenuation. The laboratory study indicated that fuel oxygenate degradation under oxic conditions was favored relative to anoxic conditions. The ambient, background redox status of the hyporheic zone at the Carmans River site in 2003, for example, had measurable concentrations of DO down to 15 feet (4.5 m) (Figure 4) but was DO depleted where the highest fuel oxygenate concentrations were detected (Figures 3 and 4). The lack of DO may explain the positive HZAP for Carmans River during 2005 (Table 3). These results indicate that the availability of oxygen in the hyporheic zone is a driver for the biological component of fuel oxygenate biodegradation. Because the decrease in contaminant level at the four sites caused by apparent biodegradation is generally less than 3% of the total attenuation, the prevailing processes for controlling the decrease in fuel oxygenate concentrations in the hyporheic zones of the sites studies are the physical processes of natural attenuation.

Even though the contribution of microbial processes to overall contaminant attenuation is small relative to the physical processes of natural attenuation at these sites, the activity of aerobic microorganisms in the hyporheic zone is evident by the levels of DO less than 1 mg/L in the presence of the contaminants (Figure 4) and as an increase in biological oxygen demand (as BOD<sub>5</sub>) from average ambient concentrations of 4.0 mg/L to a high of 34 mg/L at the 15-foot (4.5-m) sample depth in Carmans River where contaminant concentrations also were at milligrams per liter levels.

### Implication of the Hyporheic Zone Attenuation Potential for Remediation Strategies for MTBE-, TBA-, and TAME-Contaminated Groundwater Discharge

At contaminated sites characterized by rates of groundwater flow that are faster than rates of natural attenuation processes, the use of monitored natural attenuation (MNA) is not effective in limiting plume growth or mitigating pollution risks and is typically not selected. This is especially the case at sites where the plume can intersect or has intersected a downgradient surface water body. However, this study indicates that natural attenuation processes can be significant for groundwater contamination in the hyporheic zone prior to discharge to surface water. Currently, attempts to quantify such contaminant attenuation in the hyporheic zone as part of site assessments required by state environmental regulations are often limited or not performed at all.

At several of the sites studied as part of this investigation, groundwater flow and solute transport had occurred more than 1 mile (1.6 km) from the source areas with little contaminant attenuation. Conversely, attenuation in the relative thin hyporheic zone resulted in an average decrease in fuel oxygenate concentrations of 71% (Table 4). This attenuation occurred predominately by nonbiological processes such as mixing with uncontaminated surface water in the hyporheic zone. Although biological processes were occurring as demonstrated by the laboratory experiments, the apparent impact of such biodegradation was about 3% of the total mass attenuation observed in the field.

These results of significant attenuation of fuel oxygenates in the hyporheic zone suggest that site characterization activities where gasoline contains fuel oxygenates should include assessment of the HZAP if adjacent surface water sources are currently or are anticipated to be

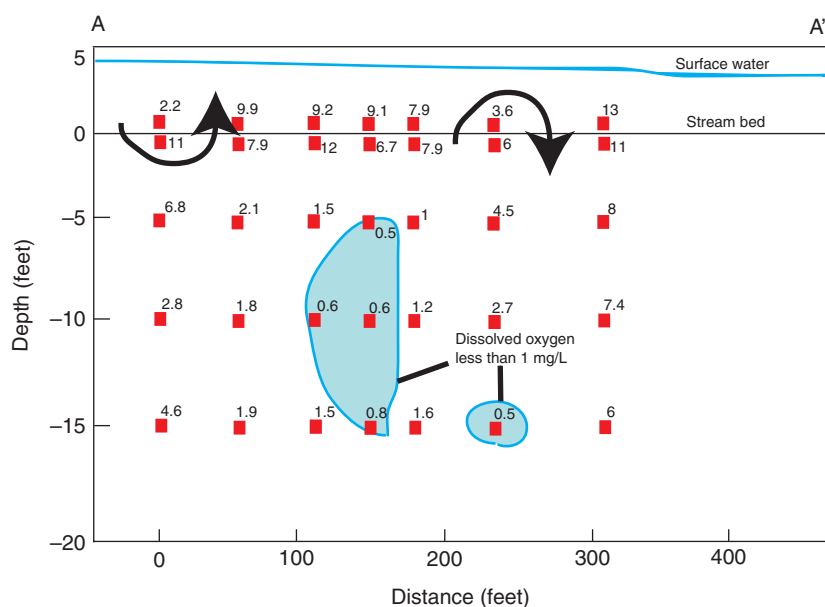


Figure 4. Pore water concentrations of dissolved oxygen in milligrams per liter in the hyporheic zone as measured in pore water samples located parallel to the bank, Carmans River (A to A' in Figure 2), New York, June 2003.

impacted. Focused efforts to characterize the hyporheic zone may require a shift in site characterization and plume monitoring strategies where typically much resource is devoted to the installation and monitoring of wells, both horizontally and vertically, to delineate and monitor the plume dimensions near the source area. The fact that even deep groundwater may ultimately discharge to surface water suggests that at least commensurate effort should be focused here because this is where the majority of the attenuation will likely occur. If assessment of the HZAP confirms these processes to be protective of the surface water quality, then MNA may be an appropriate remedial option. Conversely, conventional site assessment and characterization activities that do not include the hyporheic zone may lead to selection of unnecessarily costly and less sustainable remedial strategies.

## Conclusions

This study was designed to provide more information on how to investigate the biological and physical processes of natural attenuation that occur in the hyporheic zone using four sites where fuel-oxygenated contaminated groundwater discharged to diverse surface water bodies. At each site, plumes of fuel oxygenates have been determined to be between 0.1 (0.16 km) and 1.5 miles (2.4 km) long, because groundwater flow rates exceed 2 ft/d (0.6 m/d) and biodegradation rates within the contaminated aquifer were low. At the point of local groundwater discharge at each site ranging from fresh to saline surface water, attenuation of the fuel oxygenates was observed to occur over a short vertical distance relative to the distance of contaminant transport in groundwater. Some of this attenuation (3%) was direct loss by biodegradation of MTBE and TBA, even under saline conditions, and the novel biodegradation of TAME. However, the primary mechanisms of natural attenuation observed in the hyporheic zone were dilution and dispersion.

The implication of these findings of rapid attenuation in the hyporheic zone suggest that common site characterization strategies may benefit by including a focus on the hyporheic zone when concerns exist for surface water impacts arising from the discharge of contaminated groundwater. At sites where MNA is not considered appropriate because of perceived impacts to surface water, additional investigation to quantify the magnitude of natural attenuation in the hyporheic zone is potentially warranted. In such scenarios, it may be more efficient to focus investigations on locations of plume discharge to potential surface water receptors and to determine the rate of attenuation in these areas rather than to intensively delineate and monitor extensive plume in aquifers where little attenuation is likely occurring. Moreover, in areas characterized by fast groundwater flow rates and therefore shorter groundwater residence time, assessment of the hyporheic zone would permit the effectiveness of any source removal/remediation activities to be monitored over time, as the groundwater plume would become “purged” from the aquifer.

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