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CALCULATED VOLATILIZATION RATES OF FUEL OXYGENATE COMPOUNDS AND OTHER GASOLINE-RELATED COMPOUNDS FROM RIVERS AND STREAMS

James F. Pankow[a], Ronald E. Rathbun[b], and John S. Zogorski[c]

[a]Department of Environmental Science and Engineering
Oregon Graduate Institute
P.O. Box 91000
Portland, OR 97291-1000

[b]U.S. Geological Survey
Box 25046, M.S. 408
Denver, CO 80225

[c]U.S. Geological Survey
1608 Mt. View Rd.
Rapid City, SD 57702

ABSTRACT

Large amounts of the "fuel-oxygenate" compound methyl-*tert*-butyl ether (MTBE) are currently being used in gasoline to reduce carbon monoxide and ozone in urban air and to boost fuel octane. Because MTBE can be transported to surface waters in various ways, established theory was used to calculate half-lives for MTBE volatilizing from flowing surface waters. Similar calculations were made for benzene as a representative of the "BTEX" group of compounds (benzene, toluene, ethyl benzene, and the xylenes), and for *tert*-butyl alcohol (TBA). The calculations were made as a function of the mean flow velocity *u* (m/day), the mean flow depth *h* (m), the ambient temperature, and the wind speed. In deep, slow-moving flows, MTBE volatilizes at rates which are similar to those for the BTEX compounds. In shallow, fast-moving flows, MTBE volatilizes more slowly than benzene, though in such flows both MTBE and benzene volatilize quickly enough that these differences may often not have much practical significance. TBA was found to be essentially nonvolatile from water.

INTRODUCTION

When oxygen-containing compounds such as methyl-*tert*-butyl ether (MTBE), *tert*-butyl alcohol (TBA), and ethanol are added to gasoline, these and other "fuel oxygenates" (Table 1) reduce the levels of carbon monoxide and ozone in urban air, as required for some U.S. metropolitan areas by the Clean Air Act Amendments of 1990. The reduction of carbon monoxide is a result of the more complete combustion that is possible when oxygen is incorporated in the fuel. The reduction in ozone is a result of the fact that fuel oxygenates are octane boosters. Thus, the amounts of benzene and other aromatic octane-boosting (but ozone-forming) compounds in gasoline can be reduced.

Because high usage of fuel oxygenate compounds has occurred in the U.S. only fairly recently, many aspects of their environmental behavior, *e.g.*, their rates of volatilization from surface waters, are yet to be discussed in the literature. It is recognized that the oxygen in fuel oxygenate compounds makes each of them considerably more water soluble than the "BTEX" group (benzene, toluene, ethyl benzene, and the xylenes) which has been of conventional concern when gasoline is spilled into surface waters. Thus, the fuel oxygenate compounds exhibit lower Henry's Gas Law constants as compared to the BTEX group.

Inputs of fuel oxygenates to surface waters occur when: 1) gasoline is spilled into surface waters; 2) contaminated groundwater (or surface runoff) enters surface waters; and 3) precipitation falls through and equilibrates with contaminated urban air (Squillace *et al.*, 1996). The relatively low biodegradabilities of the alkyl ether fuel oxygenate compounds (OSTP, 1996) make it quite possible that compounds such as MTBE will reach surface waters following a release of gasoline to the subsurface. In contrast, BTEX compounds released to the subsurface can be degraded relatively quickly. In California, Rice *et al.* (1995) have concluded based on studies at over 1100 sites that *"benzene plume lengths [at the 10 ppb contour] rarely extend beyond 250 ft"*.

The manner in which the BTEX group and other familiar organic compounds volatilize from flowing surface waters has been clearly discussed in the literature (Rathbun, 1990; Schwarzenbach *et al.*, 1993). This is not the case for the fuel oxygenate compounds. Indeed, consider the following statement:

> *"Despite its relatively high solubility, MTBE is expected to partition largely to air. The Henry's law constant of 4.5×10^{-4} atm-m^3/mol indicates that any MTBE in surface water will have a half-life of about 9 hours before volatilizing."* (EPA, 1986).

Although quoted frequently in recent years, the above statement is misleading. First, it makes no distinction between surface waters which are flowing (*e.g.*, rivers and streams), and surface waters which are largely quiescent (*e.g.*, lakes, reservoirs, and ponds). Second, because volatilization rates are very dependent on the depth and velocity of any flow, the half-life for MTBE or any other fuel oxygenate compound will <u>never</u> be a single value: depending on the circumstances, it can be very much larger than 9 hours, or very much smaller.

This paper will use established theory to calculate half-lives for MTBE and TBA volatilizing from flowing surface waters, and will compare them with the half-lives for benzene as a representative of the BTEX group. The parameters of interest in the comparisons will be the mean flow velocity u (m/day), the mean flow depth h (m), the temperature, and the wind speed.

THEORY

The air/water partitioning of a given compound is parameterized by its temperature-dependent Henry's Gas Law constant H (atm/(mol/m^3)). When H is divided by the product of the gas constant R (= 8.2×10^{-5} m^3-atm/mol-K) and the ambient temperature T (K), the result is the "dimensionless" Henry's Gas Law constant which gives the air/water concentration ratio c_a/c_w at equilibrium:

$$\frac{H}{RT} = \frac{c_a\ (\text{mols/m}^3)}{c_w\ (\text{mols/m}^3)} \qquad (1)$$

From Table 2, at 25 °C, H/RT for the BTEX compounds ranges from 0.2 to 0.3; for the alkyl ether fuel oxygenates the range is 0.03 to 0.13; for TBA, it is only 0.000503 (the volatility of TBA from water is very low).

The volatilization half-life $t_{1/2}$ (days) is the *time* required to reduce the concentration of a compound by ½. In a flowing river, stream, or channel, the volatilization half-life distance $d_{1/2}$ is a measure of how far the water must travel for the concentration to drop by a factor of ½:

$$d_{1/2}\ (\text{km}) = \frac{u\, t_{1/2}}{1000} \qquad (2)$$

Movement of a chemical across an air/water interface is commonly modeled by assuming that the flux F (mols/m^2-day) is proportional to the difference between the bulk water concentration c_w (mols/m^3), and c_e (mols/m^3) which is the water concentration for equilibrium with the bulk air concentration (Rathbun, 1990):

$$F\ \ (\text{mols/m}^2\text{-d}) = -K_{OL}(c_w - c_e) \qquad (3)$$

K_{OL} is an overall mass transfer velocity for movement across the interface. When $c_w > c_e$, the flux of the compound is from the water to the air, and F is negative. When $c_w < c_e$, the flux of the compound is from the air to the water, and F is positive. K_{OL} is determined by a "two-film" transport process involving resistances in both the water and air phases (Lewis and Whitman, 1924) so that

$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{1}{k_G\ H/RT} \qquad (4)$$

where k_L (m/day) and k_G (m/day) are the liquid-side and gas-side mass transfer velocities, respectively.

For k_L, under conditions of isotropic turbulence, O'Connor and Dobbins (1958) have obtained for oxygen at 20 °C that

$$k_{L,20}^{O_2} = \left(\frac{D_{20}^{O_2}\, u}{h}\right)^{0.5} \qquad (5)$$

where $D_{20}^{O_2}$ (m^2/day) is the diffusion coefficient for dissolved oxygen in water at 20 °C (= 1.8×10^{-4} m^2/day).

Correction of $k_{L,20}^{O_2}$ to temperatures t_C (°C) other than 20 °C is usually carried out using (Elmore and West, 1961)

$$k_{L,t_c}^{O_2} = k_{L,20}^{O_2} \, 1.0241^{(t_c - 20)} \quad (6)$$

For compounds other than oxygen, k_L at t_C can be obtained by multiplying $k_{L,t_c}^{O_2}$ by a compound specific correction factor ϕ (Rathbun, 1990)

$$k_L = \phi \, k_{L,t_c}^{O_2} \quad (7)$$

For k_G, values for water vapor can be predicted as a function of wind speed (see Schwarzenbach *et al.*, 1993, for a review). For a compound other than water vapor, k_G can be obtained by multiplying $k_G^{H_2O}$ by a compound-specific correction factor φ (Rathbun, 1990)

$$k_G = \varphi \, k_G^{H_2O} \quad (8)$$

For a given stretch dx of river or stream of width w, the time rate of change of c_w will be given by

$$dc_w/dt = w\,dx\,F/(w\,dx\,h) = -K_{OL}(c_w - c_e)/h \quad (9)$$

When considering the volatilization of organic contaminants from water, it is frequently assumed that $c_e = 0$, *i.e.*, that the air is essentially free of the contaminant of interest. In this case,

$$dc_w/dt = -K_{OL}\, c_w / h \quad (10)$$

Integration of Equation 10 yields

$$c_w / c_w^{o} = \exp[-K_{OL}\, t / h] \quad (11)$$

where c_w^{o} is the concentration in the river or stream at time $t = 0$. In this simple first-order decay relation, the half-life $t_{1/2}$ is computed as usual as

$$t_{1/2} = 0.69/(K_{OL}/h) \quad (12)$$

and $d_{1/2}$ values are calculated using Equation 2.

RESULTS

General. Once the compound, temperature, and $k_G^{H_2O}$ value of interest are specified, the above equations can be used to calculate $t_{1/2}$ and $d_{1/2}$ values as functions of u and h. We considered two temperatures (winter, 5 °C; and summer, 25 °C), and $k_G^{H_2O}$ values for two different wind speeds. The $k_G^{H_2O}$ values are 300 m/d for a relatively low wind speed of about 0.25 m/s, and 1200 m/day for a relatively high wind speed of 5.5 m/s. (See Schwarzenbach *et al.* (1993) for a discussion of the dependence of $k_G^{H_2O}$ on wind speed.) The result was consideration of four cases for each of three compounds examined.

MTBE. Based on usage, MTBE is currently the most important alkyl ether oxygenate. Taking ϕ = 0.586 and φ = 0.558 (as based on Rathbun, 1990), the $t_{1/2}$ and $d_{1/2}$ values for the four temperature/wind combinations are given in Tables 3 and 4 under Cases 1-4. The results for calm conditions at 5 °C are illustrated in Figures 1a-1d. Increasing h for any specified u increases both $t_{1/2}$ and $d_{1/2}$. In contrast, increasing u for any specified h decreases $t_{1/2}$ but increases $d_{1/2}$.

At both 5 °C and 25 °C, for deep, slow-moving flows, there are only small differences in the $t_{1/2}$ values between the calm and windy conditions. For example, at 5 °C, for h = 10 m and u = 2,732 m/d (0.0316 m/s), then $t_{1/2}$ = 85 and 78 days for calm and windy conditions, respectively. This is due to the fact that MTBE is sufficiently volatile from water (*i.e.*, H/RT is large enough) that under these conditions, the overall mass transport process is limited largely by transport on the liquid side ($k_L << k_G(H/RT)$). While h and u affect $t_{1/2}$ (and $d_{1/2}$), increasing wind speed has relatively little effect. The same conclusions apply at 25 °C. For shallow, fast-moving flows, the situation is largely reversed ($k_L >> k_G(H/RT)$) so that changing from calm to windy conditions provides a significant acceleration in the volatilization rate. For example, for h = 0.1 m and u = 273,200 m/d (3.16 m/s), then $t_{1/2}$ = 0.10 and 0.03 days for Cases 1 and 2, respectively. Similar large differences are evident at 25 °C. As regards the effect of increasing the temperature from 5 to 25 °C, for deep, slow-moving flows, the acceleration in the volatilization rate is due largely to the temperature effect on k_L as embodied in Equation 6. For shallow, fast-moving flows, the acceleration in the volatilization rate due to increasing the temperature is caused by the temperature effect on H/RT. Overall, it is clear that $t_{1/2}$ values for MTBE are very dependent on h and u: quite large as well as very small $t_{1/2}$ values are possible.

Benzene. At a given temperature, all of the BTEX compounds exhibit similar H/RT values. Therefore, benzene has been selected as a representative of this group. Taking ϕ = 0.655 (experimentally determined by Rathbun and Tai, 1981) and φ = 0.590 (as based on Rathbun, 1990), the $t_{1/2}$ and $d_{1/2}$ values for the four temperature/wind combinations are given in Tables 3 and 4 under Cases 5-8.

At both 5 °C and 25 °C, there are only small differences in the $t_{1/2}$ values between the calm and windy conditions for the whole range of h and u values considered. This is because benzene is sufficiently volatile from water (*i.e.*, H/RT is large enough) that under all of these conditions, the overall mass transport process remains limited by transport on the liquid side ($k_L << k_G(H/RT)$). (The nature of the transport control under these conditions means that the effects of increasing the temperature from 5 to 25 °C are due largely to the effect of temperature on k_L as embodied in Equation 6.) For the deep, slow-moving flows, the $t_{1/2}$ values for benzene are similar to those for MTBE, which is also rate-limited in the liquid phase under these conditions. For the shallow, fast-moving flows, the $t_{1/2}$ values are smaller for benzene than for MTBE because gas-side resistance does not become important for benzene: it is too volatile from water for gas-side resistance to be important under the range of h and u considered here.

TBA. In addition to being a compound that can be used directly as a fuel oxygenate, TBA is an important degradation product of both MTBE and ETBE. Estimating that $\phi = 0.623$ and $\varphi = 0.606$ for TBA (as based on Rathbun and Tai, 1981), the $t_{1/2}$ and $d_{1/2}$ values for the four temperature/wind combinations are given in Tables 3 and 4 under Cases 9-12.

At both 5 °C and 25 °C, there are significant differences in the $t_{1/2}$ values between the calm and windy conditions for the whole range of h and u conditions considered here. This is because TBA exhibits very limited volatility from water (*i.e.*, H/RT is very small) so that except for the condition of very large h and low u, the overall mass transport process is essentially completely limited by transport on the gas side ($k_L >> k_G(H/RT)$). This means that the effects of increasing the temperature from 5 to 25 °C are due largely to the effects of temperature on H/RT for all h and u considered. This limitation by the gas-side transport can be observed in the near independence in the $t_{1/2}$ values as u increases at a given depth: the changes in k_L (see Equation 5) result in little change in $t_{1/2}$. Overall, the $t_{1/2}$ values for TBA are much larger than those for MTBE and benzene. Many of the $t_{1/2}$ values for TBA are quite large. When these $t_{1/2}$ values are multiplied by u to obtain the $d_{1/2}$ values, it becomes clear that TBA can be considered to be essentially nonvolatile in surface waters except when the flows are very shallow.

MTBE/Benzene Half-Life Ratios. Table 5 gives the calculated values of the ratio of the MTBE half-life ($t_{1/2,M}$) to the benzene half-life ($t_{1/2,b}$). Because of the nature of the definition of $d_{1/2}$, we note that $t_{1/2,M}/t_{1/2,b} = d_{1/2,M}/d_{1/2,b}$. Table 5 shows that for all h and u conditions, $t_{1/2,M}/t_{1/2,b} > 1.0$, reflecting the lower value of H/RT of MTBE relative to that of benzene. However, in most cases, this ratio is less than 2.0, except for shallow and fast-moving flows for which $t_{1/2,M}$ is in all cases quite short.

CONCLUSIONS

MTBE and the other alkyl ether oxygenates in flowing surface waters will volatilize at rates which depend on the depth and velocity of the flow. No single volatilization half-life will characterize the loss process. In deep and slow-moving flows, MTBE and the other alkyl ether fuel oxygenates will volatilize at rates which are similar to those for the BTEX compounds. In shallow and fast-moving flows, they will volatilize at rates which are significantly less than those for the BTEX compounds. The low volatility of TBA from water makes its loss from water much slower than that for both the alkyl ether oxygenates and the BTEX compounds.

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Table 1. Fuel oxygenate compounds.

Compound	Formula
alkyl ethers	
methyl-*tert*-butyl ether (MTBE)	CH_3-O-C$(CH_3)_3$
ethyl-*tert*-butyl ether (ETBE)	CH_3-CH_2-O-C$(CH_3)_3$
tert-amyl methyl ether (TAME)	CH_3-CH_2-C$(CH_3)_2$-O-CH_3
di-isopropyl ether (DIPE)	$(CH_3)_2$CH-O-CH$(CH_3)_2$
alcohols	
ethanol	CH_3-CH_2-OH
tert-butyl alcohol (TBA)	$(CH_3)_3$-C-OH

Table 2. Selected properties of compounds of interest.

Compound	*H/RT* at 5 °C	*H/RT* at 25 °C	ϕ (see Eq. 7)	φ (see Eq. 8)
alkyl ethers				
MTBE	0.0044[a]	0.026[a]	0.586	0.558
ETBE	0.019	0.11	0.557	0.521
TAME	0.014	0.081	0.556	0.521
DIPE	0.030[b]	0.13[b]	0.556	0.521
alcohols				
ethanol	-	0.000257[c]	0.738	0.753
TBA	0.000113[d]	0.000503[d]	0.623	0.605
BTEX compounds				
benzene	0.114[e]	0.230[e]	0.655	0.590
toluene	0.140[e]	0.273[e]	0.655	0.547
ethyl benzene	0.105[e]	0.325[e]	0.569	0.512
o-xylene	0.157[e]	0.301[e]	0.569	0.512
m-xylene	0.143[e]	0.312[e]	0.569	0.512
p-xylene	0.105[e]	0.213[e]	0.569	0.512

[a]Robbins *et al.* (1993); [b]Stull (1947) and Stephenson (1992); [c]Nirmalakhandan and Speece (1988); [d]Rathbun and Tai (1988); [e]Ashworth *et al.* (1988).

Table 3. **Half-life ($t_{1/2}$, days) values for MTBE, benzene, and TBA as a function of flow velocity u (m/d), flow depth h (m), temperature, and wind conditions.**

Velocity u (m/d)	→ 2732	8640	27300	86400	273200
Velocity (ft/s)	→ 0.104	0.328	1.037	3.281	10.375
Velocity (m/s)	→ 0.032	0.100	0.316	1.000	3.162

$t_{1/2}$ (days)

Depth (ft)	Depth h (m)					
Case 1. MTBE, 5 °C, calm				MTBE		
32.8	10.0	85.3	52.0	33.4	22.9	17.0
10.4	3.2	16.5	10.6	7.23	5.36	4.31
3.3	1.0	3.34	2.29	1.70	1.36	1.18
1.0	0.3	0.723	0.536	0.431	0.372	0.339
0.3	0.1	0.170	0.136	0.118	0.107	0.101
Case 2. MTBE, 5 °C, windy						
32.8	10.0	78.2	45.0	26.3	15.8	9.93
10.4	3.2	14.2	8.32	5.01	3.14	2.09
3.3	1.0	2.63	1.58	0.993	0.661	0.474
1.0	0.3	0.501	0.314	0.209	0.150	0.117
0.3	0.1	0.0993	0.0661	0.0474	0.0369	0.0310
Case 3. MTBE, 25 °C, calm						
32.8	10.0	48.7	28.1	16.5	9.97	6.30
10.4	3.2	8.88	5.21	3.15	1.99	1.34
3.3	1.0	1.65	0.997	0.630	0.424	0.308
1.0	0.3	0.315	0.199	0.134	0.0973	0.0766
0.3	0.1	0.0630	0.0424	0.0308	0.0242	0.0206
Case 4. MTBE, 25 °C, windy						
32.8	10.0	47.5	26.9	15.3	8.78	5.11
10.4	3.2	8.51	4.84	2.78	1.62	0.964
3.3	1.0	1.53	0.878	0.511	0.305	0.189
1.0	0.3	0.278	0.162	0.0964	0.0597	0.0390
0.3	0.1	0.0511	0.0305	0.0189	0.0123	0.00868
Case 5. benzene, 5 °C, calm				benzene		
32.8	10.0	68.2	38.5	21.8	12.4	7.13
10.4	3.2	12.2	6.90	3.93	2.26	1.32
3.3	1.0	2.18	1.24	0.713	0.416	0.249
1.0	0.3	0.393	0.226	0.132	0.0787	0.0490
0.3	0.1	0.0713	0.0416	0.0249	0.0155	0.0102
Case 6. benzene, 5 °C, windy						
32.8	10.0	68.0	38.3	21.6	12.2	6.88
10.4	3.2	12.1	6.82	3.85	2.17	1.23
3.3	1.0	2.16	1.22	0.688	0.390	0.223
1.0	0.3	0.385	0.217	0.123	0.0706	0.0409
0.3	0.1	0.0688	0.0390	0.0223	0.0129	0.00764
Case 7. benzene, 25 °C, calm						
32.8	10.0	42.3	23.9	13.5	7.67	4.39
10.4	3.2	7.55	4.27	2.42	1.39	0.803
3.3	1.0	1.35	0.767	0.439	0.254	0.150
1.0	0.3	0.242	0.139	0.0803	0.0475	0.0291
0.3	0.1	0.0439	0.0254	0.0150	0.00919	0.00591
Case 8. benzene, 25 °C, windy						
32.8	10.0	42.2	23.8	13.4	7.54	4.26
10.4	3.2	7.51	4.23	2.38	1.35	0.763
3.3	1.0	1.34	0.754	0.426	0.241	0.138
1.0	0.3	0.238	0.135	0.0763	0.0435	0.0251
0.3	0.1	0.0426	0.0241	0.0138	0.00792	0.00464

Table 3. Continued. Half-life ($t_{1/2}$, days) as a function of flow velocity u (m/d), flow depth h (m), temperature, and wind conditions.

	Velocity u (m/d) →	2732	8640	27300	86400	273200
	Velocity (ft/s) →	0.104	0.328	1.037	3.281	10.375
	Velocity (m/s) →	0.032	0.100	0.316	1.000	3.162
				$t_{1/2}$ (days)		
Case 9.	TBA, 5 °C, calm			TBA		
Depth (ft)	Depth h (m)					
32.8	10.0	408	377	359	349	344
10.4	3.2	119	114	110	109	108
3.3	1.0	35.9	34.9	34.4	34.0	33.9
1.0	0.3	11.0	10.9	10.8	10.7	10.7
0.3	0.1	3.44	3.40	3.39	3.38	3.37
Case 10.	TBA, 5 °C, windy					
Depth (ft)	Depth h (m)					
32.8	10.0	155	124	107	96.8	91.2
10.4	3.2	39.3	33.7	30.6	28.9	27.9
3.3	1.0	10.7	9.68	9.12	8.81	8.64
1.0	0.3	3.06	2.88	2.79	2.73	2.70
0.3	0.1	0.912	0.881	0.864	0.854	0.848
Case 11.	TBA, 25 °C, calm					
Depth (ft)	Depth h (m)					
32.8	10.0	120	101	89.6	83.5	80.0
10.4	3.2	31.8	28.3	26.4	25.3	24.7
3.3	1.0	8.96	8.35	8.00	7.81	7.70
1.0	0.3	2.64	2.53	2.47	2.43	2.41
0.3	0.1	0.800	0.781	0.770	0.764	0.760
Case 12.	TBA, 25 °C, windy					
Depth (ft)	Depth h (m)					
32.8	10.0	63.2	43.8	32.9	26.8	23.3
10.4	3.2	13.9	10.4	8.47	7.38	6.76
3.3	1.0	3.29	2.68	2.33	2.14	2.03
1.0	0.3	0.847	0.738	0.676	0.642	0.620
0.3	0.1	0.233	0.214	0.203	0.197	0.193

Table 4. Half-life Distance ($d_{1/2}$, km) values for MTBE, benzene, and TBA as a function of flow velocity u (m/d), flow depth h (m), temperature, and wind conditions.

	Velocity u (m/d) →	2732	8640	27300	86400	273200
	Velocity (ft/s) →	0.104	0.328	1.037	3.281	10.375
	Velocity (m/s) →	0.032	0.100	0.316	1.000	3.162
				$d_{1/2}$ (km)		
Case 1.	MTBE, 5 °C, calm			MTBE		
Depth (ft)	Depth h (m)					
32.8	10.0	233	450	912	1980	4630
10.4	3.2	45.0	91.2	198	463	1180
3.3	1.0	9.10	19.8	46.3	118	322
1.0	0.3	1.98	4.63	11.8	32.2	92.6
0.3	0.1	0.463	1.18	3.22	9.26	27.7
Case 2.	MTBE, 5 °C, windy					
Depth (ft)	Depth h (m)					
32.8	10.0	214	389	720	1370	2710
10.4	3.2	38.9	72.0	137	271	571
3.3	1.0	7.20	13.7	27.1	57.1	130
1.0	0.3	1.37	2.71	5.71	13.0	31.9
0.3	0.1	0.271	0.571	1.30	3.19	8.47
Case 3.	MTBE, 25 °C, calm					
Depth (ft)	Depth h (m)					
32.8	10.0	133	243	451	861	1721
10.4	3.2	24.3	45.1	86.1	172	366
3.3	1.0	4.51	8.61	17.2	36.6	84.0
1.0	0.3	0.861	1.72	3.66	8.40	20.9
0.3	0.1	0.172	0.366	0.840	2.09	5.62
Case 4.	MTBE, 25 °C, windy					
Depth (ft)	Depth h (m)					
32.8	10.0	130	232	418	758	1400
10.4	3.2	23.2	41.8	75.8	140	263
3.3	1.0	4.18	7.58	14.0	26.3	51.6
1.0	0.3	0.758	1.40	2.63	5.16	10.7
0.3	0.1	0.140	0.263	0.516	1.07	2.37
Case 5.	benzene, 5 °C, calm			benzene		
Depth (ft)	Depth h (m)					
32.8	10.0	186	333	596	1070	1950
10.4	3.2	33.3	59.6	107	195	359
3.3	1.0	5.96	10.7	19.5	35.9	68.0
1.0	0.3	1.07	1.95	3.59	6.80	13.4
0.3	0.1	0.195	0.359	0.680	1.34	2.79
Case 6.	benzene, 5 °C, windy					
Depth (ft)	Depth h (m)					
32.8	10.0	186	331	589	1050	1880
10.4	3.2	33.1	58.9	105	188	337
3.3	1.0	5.89	10.5	18.8	33.7	61.0
1.0	0.3	1.05	1.88	3.37	6.10	11.2
0.3	0.1	0.188	0.337	0.610	1.12	2.09
Case 7.	benzene, 25 °C, calm					
Depth (ft)	Depth h (m)					
32.8	10.0	116	206	369	663	1200
10.4	3.2	20.6	36.9	66.3	120	220
3.3	1.0	3.69	6.63	12.0	22.0	41.1
1.0	0.3	0.663	1.20	2.20	4.11	7.94
0.3	0.1	0.120	0.220	0.411	0.794	1.62
Case 8.	benzene, 25 °C, windy					
Depth (ft)	Depth h (m)					
32.8	10.0	115	205	366	652	1160
10.4	3.2	20.5	36.6	65.2	116	209
3.3	1.0	3.66	6.52	11.6	20.9	37.6
1.0	0.3	0.652	1.16	2.09	3.76	6.85
0.3	0.1	0.116	0.209	0.376	0.685	1.27

Table 4. Continued. Half-life distance ($d_{1/2}$, km) values as a function of flow velocity u (m/d), flow depth h (m), temperature, and wind conditions.

		Velocity u (m/d) →	2732	8640	27300	86400	273200
		Velocity (ft/s) →	0.104	0.328	1.037	3.281	10.375
		Velocity (m/s) →	0.032	0.100	0.316	1.000	3.162
					$d_{1/2}$ (km)		
Case 9. TBA, 5 °C, calm					TBA		
Depth (ft)	Depth h (m)						
32.8	10.0		1100	3250	9800	30200	94000
10.4	3.2		325	981	3020	9390	29000
3.3	1.0		98.1	302	939	2940	9250
1.0	0.3		30.2	93.9	294	925	2920
0.3	0.1		9.40	29.4	92.5	292	921
Case 10. TBA, 5 °C, windy							
Depth (ft)	Depth h (m)						
32.8	10.0		425	1070	2920	8360	25000
10.4	3.2		107	292	836	2490	7610
3.3	1.0		29.1	83.6	249	761	2360
1.0	0.3		8.36	24.9	76.1	236	738
0.3	0.1		2.49	7.61	23.6	73.8	232
Case 11. TBA, 25 °C, calm							
Depth (ft)	Depth h (m)						
32.8	10.0		328	868	2450	7210	21900
10.4	3.2		86.8	245	721	2190	6750
3.3	1.0		24.5	72.1	219	675	2100
1.0	0.3		7.21	21.9	67.5	210	660
0.3	0.1		2.19	6.75	21.0	66.0	210
Case 12. TBA, 25 °C, windy							
Depth (ft)	Depth h (m)						
32.8	10.0		173	379	899	2310	6370
10.4	3.2		37.9	89.9	231	637	1850
3.3	1.0		8.99	23.1	63.7	185	555
1.0	0.3		2.31	6.37	18.5	55.5	170
0.3	0.1		0.637	1.85	5.55	17.0	52.8

Table 5. MTBE/benzene half-life ratios as a function of flow velocity *u* (m/d) and flow depth *d* (m) for four temperature and wind combinations.

	Velocity *u* (m/d) →	2732	8640	27300	86400	273200
	Velocity (ft/s) →	0.104	0.328	1.037	3.281	10.375
	Velocity (m/s) →	0.032	0.100	0.316	1.000	3.162
		$t_{1/2,M}/t_{1/2,b} = d_{1/2,M}/d_{1/2,b}$				
5 °C, calm						
Depth (ft)	Depth *h* (m)					
32.8	10.0	1.2	1.4	1.5	1.8	2.4
10.4	3.2	1.4	1.5	1.8	2.4	3.3
3.3	1.0	1.5	1.8	2.4	3.3	4.7
1.0	0.3	1.8	2.4	3.3	4.7	6.9
0.3	0.1	2.4	3.3	4.7	6.9	9.9
5 °C, windy						
Depth (ft)	Depth *h* (m)					
32.8	10.0	1.2	1.2	1.2	1.3	1.4
10.4	3.2	1.2	1.2	1.3	1.4	1.7
3.3	1.0	1.2	1.3	1.4	1.7	2.1
1.0	0.3	1.3	1.4	1.7	2.1	2.9
0.3	0.1	1.4	1.7	2.1	2.9	4.1
25 °C, calm						
Depth (ft)	Depth *h* (m)					
32.8	10.0	1.2	1.2	1.2	1.3	1.4
10.4	3.2	1.2	1.2	1.3	1.4	1.7
3.3	1.0	1.2	1.3	1.4	1.7	2.0
1.0	0.3	1.3	1.4	1.7	2.0	2.6
0.3	0.1	1.4	1.7	2.0	2.6	3.5
25 °C, windy						
Depth (ft)	Depth *h* (m)					
32.8	10.0	1.1	1.1	1.1	1.2	1.2
10.4	3.2	1.1	1.1	1.2	1.2	1.3
3.3	1.0	1.1	1.2	1.2	1.3	1.4
1.0	0.3	1.2	1.2	1.3	1.4	1.6
0.3	0.1	1.2	1.3	1.4	1.6	1.9

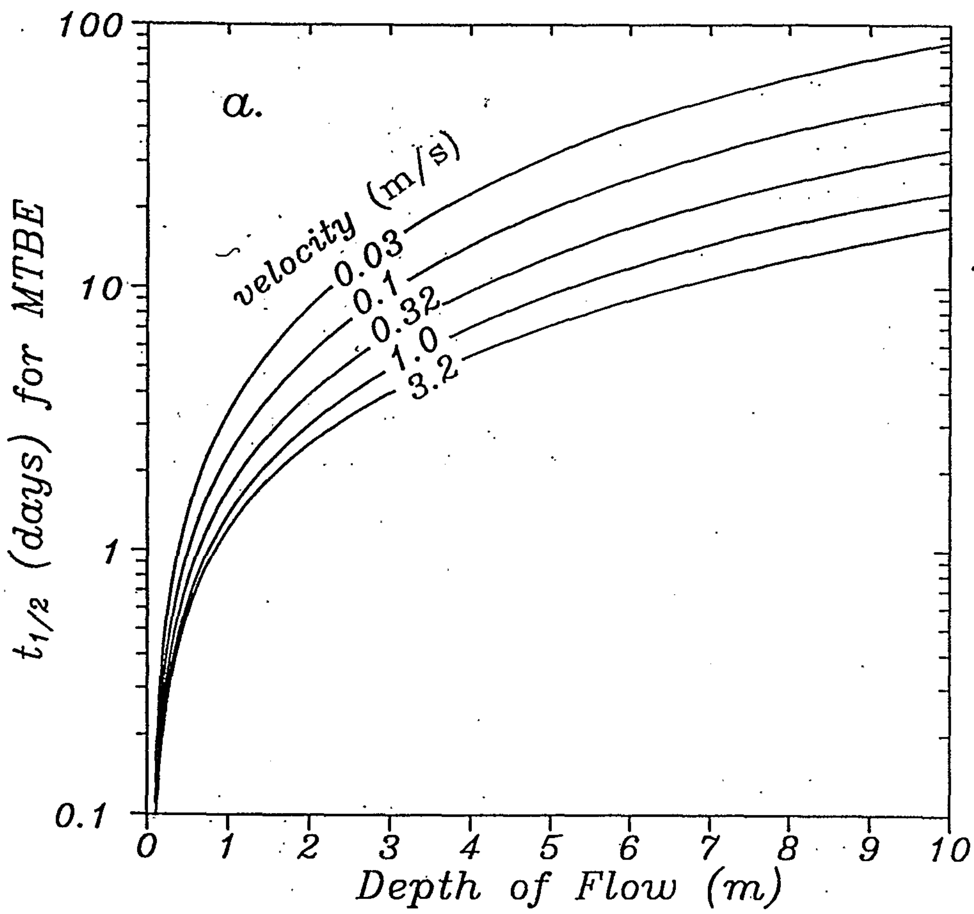

Figure 1.a. Case 1: MTBE, 5 °C, calm wind conditions. Half-life $t_{1/2}$ (days) *vs*. depth of flow *h* (m) for five different flow velocities.

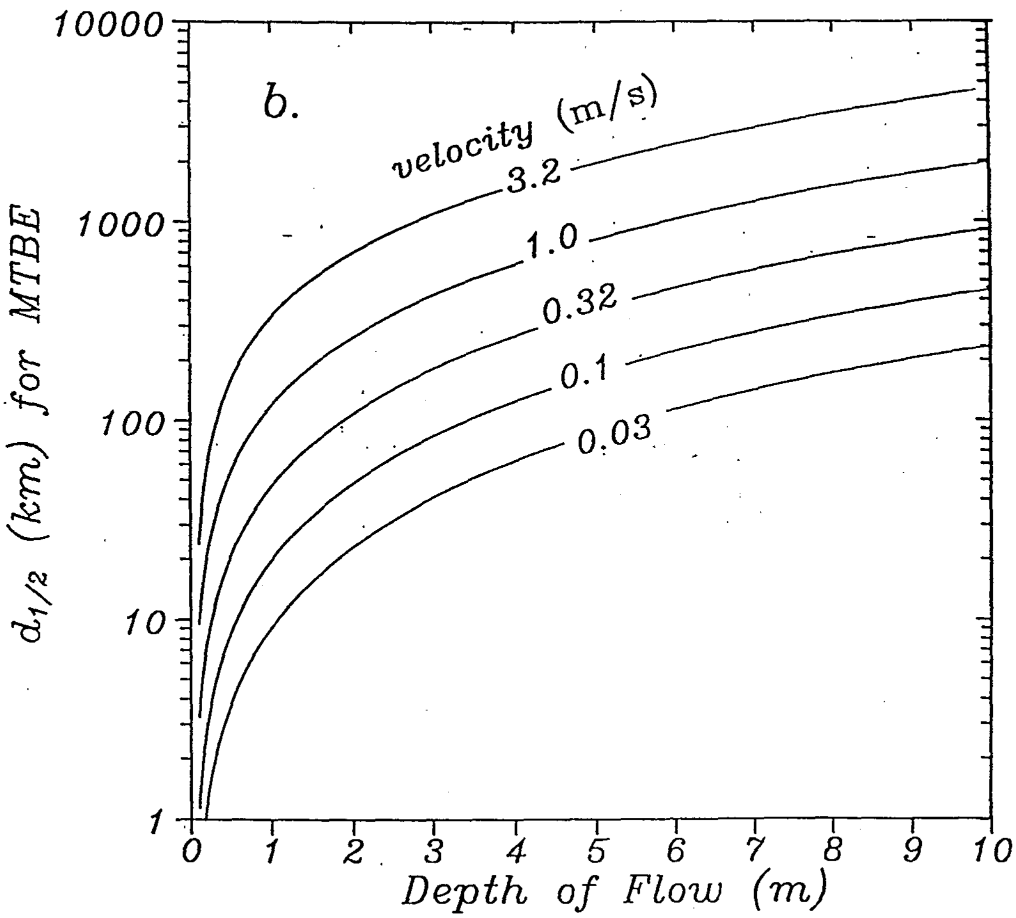

Figure 1.b. Case 1: MTBE, 5 °C, calm wind conditions. Half-life distance $d_{1/2}$ (km) *vs*. depth of flow *h* (m) for five different flow velocities.

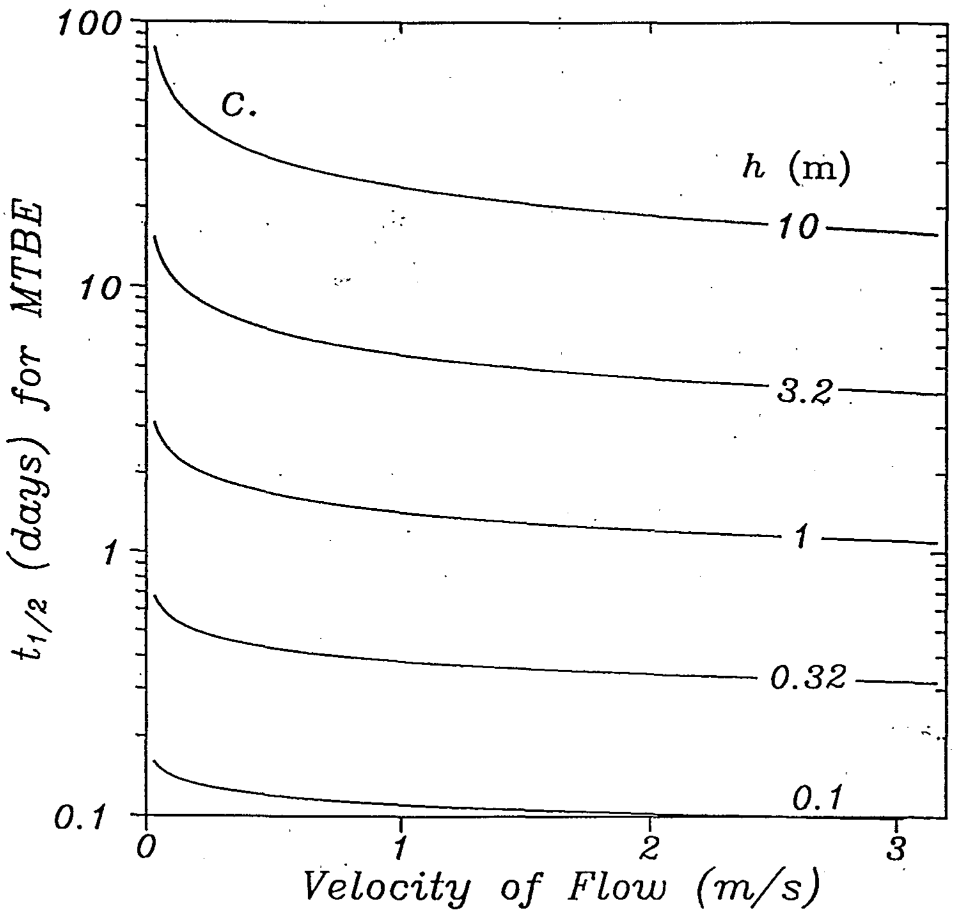

Figure 1.c. Case 1: MTBE, 5 °C, calm wind conditions. Half-life $t_{1/2}$ (days) *vs.* flow velocity for five different flow depths h (m).

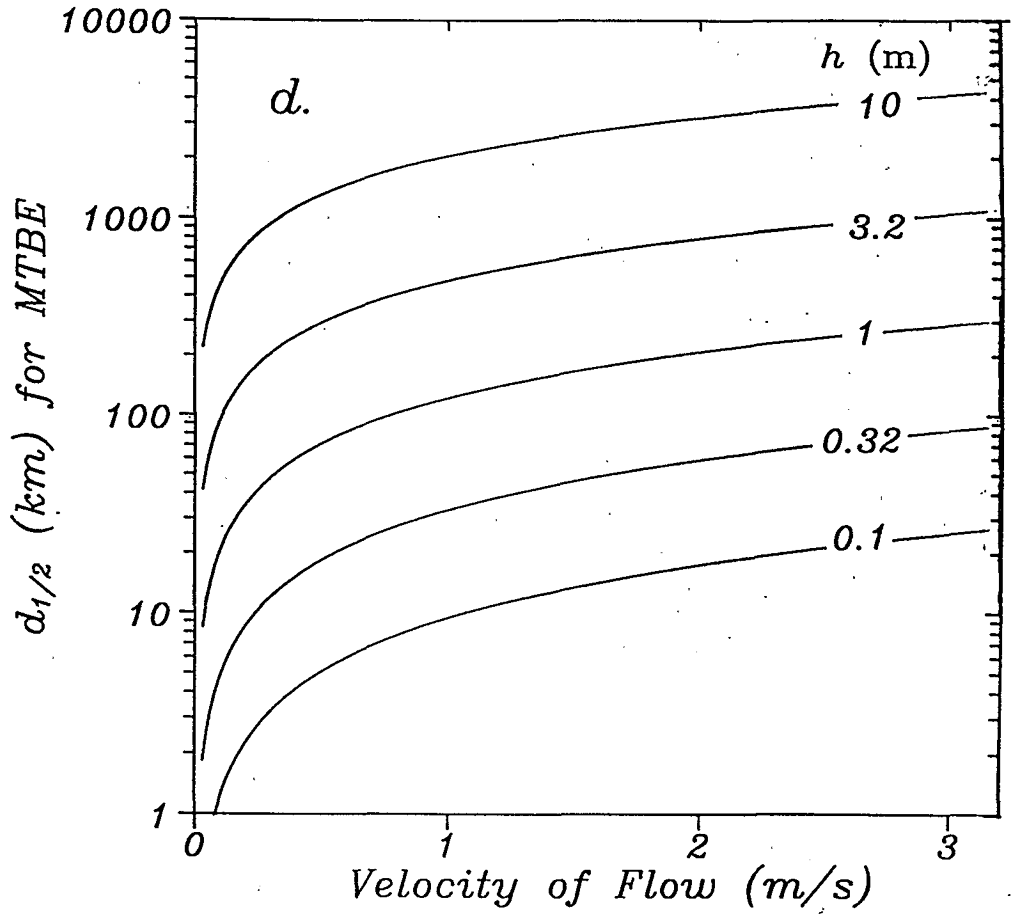

Figure 1.d. Case 1: MTBE, 5 °C, calm wind conditions. Half-life distance $d_{1/2}$ (km) *vs*. flow velocity for five different flow depths *h* (m).