Fate of Methanol Spills into Rivers of Varying Geometry

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ABSTRACT: This paper describes the results of a study of potential environmental impacts of methanol releases into rivers. A number of hypothetical scenarios are defined, and dispersion of methanol in the selected rivers is investigated using a riverine dispersion-biodegradation model. The downstream variability of river flow and hydraulic geometry due to merging tributaries are included in the model. The model results are presented, and comparison is made with proposed allowable concentrations. An interesting finding is that the river variation has considerable effect on concentration distribution of methanol in the most critical scenario. A sensitivity analysis is made on the key modeling parameters such as the dispersion coefficient and the biodegradation rate. An analysis illustrating when water intake systems should potentially be shutdown in the event of a methanol release is also presented. In general, it is found the human health risks associated with the accidental release of methanol into riverine environments are low.

Keywords: methanol, dispersion model, impact assessment, regime equations, varying rivers.

INTRODUCTION

The possible widespread use of methanol as a fuel or a source of hydrogen for fuel-cell vehicles and stationary power applications has led to an interest in the potential water quality impacts of methanol releases into rivers. This paper presents the results of an analysis of the environmental impacts of accidental releases of methanol into rivers of different sizes. The assessment study consists of three components: selection of release scenarios, selection of concentrations of concern, and dispersion analysis. Methanol releases of different sizes into a number of hypothetical rivers comprise the release scenarios. The rivers are selected in such a way to be representative of a wide range of the natural rivers in terms of discharge. To define the hypothetical rivers, use is made of a large set of data on US rivers.

As the impact of a methanol release may extend to a point where both river cross-sectional area and discharge have increased considerably, variability of river geometry is taken into account in the dispersion analysis. An analytical variable-geometry dispersion model is used to predict methanol dispersion in the rivers.

In the following sections, the assessment study is described in detail.

SELECTION OF SCENARIOS

Selection of Rivers

Four hypothetical rivers of different sizes are selected for the assessment study. The selected rivers are “small”, “medium”, “large”, and “very large” with discharges of 10, 100, 1000, and 10,000 m^3/s, respectively. These discharges have been selected to cover the wide range of flows observed in natural rivers. The hydraulic geometry of each river is selected in such a way to represent the typical values for the corresponding river size category. To accomplish this, use is made of a large set of data available on US rivers (Keup, 1985). Based on a regression analysis of the data, the following hydraulic geometry relations, commonly referred to as regime equations, are obtained:

$$W = 8.088Q^{0.456}, \quad d = 0.245Q^{0.417}, \quad u = 0.505Q^{0.127} \tag{1}$$

which give the typical values of width w(m), depth d(m), and velocity u(m/s) of US rivers in terms of discharge Q(m^3/s). Using (1), the hydraulic geometry of the hypothetical rivers are summarized in table 1.

River	Discharge (m^3/s)	Width (m)	Depth (m)	Velocity (m/s)	L_0 (km)
Small	10	23.1	0.64	0.68	46
Medium	100	66.0	1.7	0.91	175
Large	1000	189	4.4	1.21	661
Very large	10,000	539	11.4	1.63	2494

Table 1. Hydraulic properties of the hypothetical rivers

River Geometry Variation

As a river flows downstream, tributaries add to the discharge and as a result, river width, depth, and velocity increase. These changes should be taken into account in modeling mixing of a solute in a natural river when the river properties change substantially before the solute disperses to below the concentration of concern. A preliminary analysis shows that the impact of a methanol release extends in some cases to a point where both river cross-sectional area and discharge have increased considerably. Accordingly, a variable-geometry dispersion model is used to obtain a more realistic prediction of methanol dispersion. The model is described below.

To quantify the variation of the hydraulic properties of the selected rivers, use is made again of the data available on US rivers (Keup, 1985). A regression analysis of the data indicates that the typical variation of river discharge with distance is given by

$$Q = 8.278 \times 10^{-8} \bar{x}^{1.732} \tag{2}$$

where $\bar{x}$ (m) denotes the distance from the river source. Combination of (1) and (2) yields the hydraulic properties of a river as functions of the distance x downstream of the spill location:

$$W = W_o (1 + x/L_o)^{0.79}, \quad d = d_o (1 + x/L_o)^{0.72}, \quad u = u_o (1 + x/L_o)^{0.22} \tag{3}$$

where the subscript $_o$ refers to the conditions at the release location as given by table 1, and L_o is the distance of the release location from the source of the river. This distance is computed from (2) and is listed in table 1 for each river.

The distance L_o can be also interpreted as a length-scale for variation of the hydraulic geometry of a river. Considering the selected releases typically impact a length of O(100 km), geometric variation is seen to be significant only in the small and medium river cases and almost insignificant in the large and very large river cases. On the other hand, in the small and medium rivers the cross-sectional mixing becomes complete within a short distance from the spill location. This suggests that the effects of river geometry variation on methanol dispersion can be satisfactorily modeled through a one-dimensional model.

From (3), the equation for river cross-sectional area is:

$$A = A_o(1 + x/L_o)^{1.51} \tag{4}$$

Longitudinal dispersion coefficient is an important parameter in mixing analysis. Based on data on USA rivers (Rutherford, 1994) this coefficient is estimated as

$$K = 1.8uW \tag{5}$$

From (3) dispersion coefficient is found to vary downstream as $K_0\left(1 + x / L_o\right)^{1.01}$.

Selection of Release Sizes

One of the key assumptions in this study is to determine appropriate release sizes. Anticipating the widespread use of methanol as a fuel for fuel cell vehicles, we choose gasoline as the surrogate. A statistical analysis of the gasoline releases to water as reported by the National Response Center (NRC), which is likely the most comprehensive spill database available, is presented in table 2.

Year	**Number of Spills**	**Total Spill Volume (gallons)**	**Average Spill Size (gallons)**	**Median Spill Size (gallons)**	**Maximum Spill Size (gallons)**	**Minimum Spill Size (gallons)**
1999	252	150,848	599	5	105,000	0.01
1998	253	60,794	240	5	8,300	0.03
1997	250	47,688	191	5	8,000	0.01
1996	341	343,143	1,006	6	315,000	0.01
1995	291	319,420	1,098	6	210,000	0.01
1994	251	44,968	179	7	10,000	0.03
1993	212	82,758	390	10	25,000	0.09
1992	250	43,540	174	6	8,950	0.10
1991	114	111,696	980	20	42,000	0.10
1990	285	149,935	526	10	40,000	0.02
Average	**250**	**135,479**	**538**	**8**	**77,225**	**0.04**

Table 2. Gasoline releases to water as reported by the NRC for years 1990–1999. Source: NRC Database

Over the ten-year period of 1990-1999, there appear to be on average 250 releases of gasoline to water. The average release size is 538 gallons and the median spill size is 8 gallons. Note that the median release size reveals that half of the releases to water are 8 gallons or less. The average maximum release and the average total volume of gasoline released to water over this period was ~77,000 gallons and ~135,500 gallons, respectively.

Through further analysis of the releases we are able to develop a distribution profile of release sizes. This is accomplished by assuming that releases occurred in one of the ranges: 0 to 10 gallons, 10 to 100 gallons, 100 to 500 gallons, 500 to 1,000 gallons, 1,000 to 10,000 gallons and greater than 10,000 gallons. The data from the NRC database is analyzed, and the results are summarized in table 3.

Size (gallons)	1999	1998	1997	1996	1995	1994	1993	1992	1991	1990
0 – 10	155	135	147	179	153	129	92	130	45	118
10 – 100	62	85	75	123	102	92	85	94	36	110
100 – 500	20	18	16	27	17	19	25	14	18	34
500 – 1000	6	2	2	5	3	4	0	5	0	2
1000 – 10000	8	13	10	6	13	6	7	7	14	17
>10,000	1	0	0	1	3	0	2	0	1	4
Total	252	253	250	341	291	251	212	250	114	285

Table 3. Distribution of gasoline release sizes to water as reported by the NRC for years 1990–1999. Source: NRC Database.

From this analysis we see that most spills occur in the 0 to 10-gallon range which coincides with the median spill size of 8 gallons. In addition, by performing a return period analysis on the data presented in table 3 we can anticipate that a single 10,000-gallon release occurs once per year. This analysis is illustrated below in figure 1.

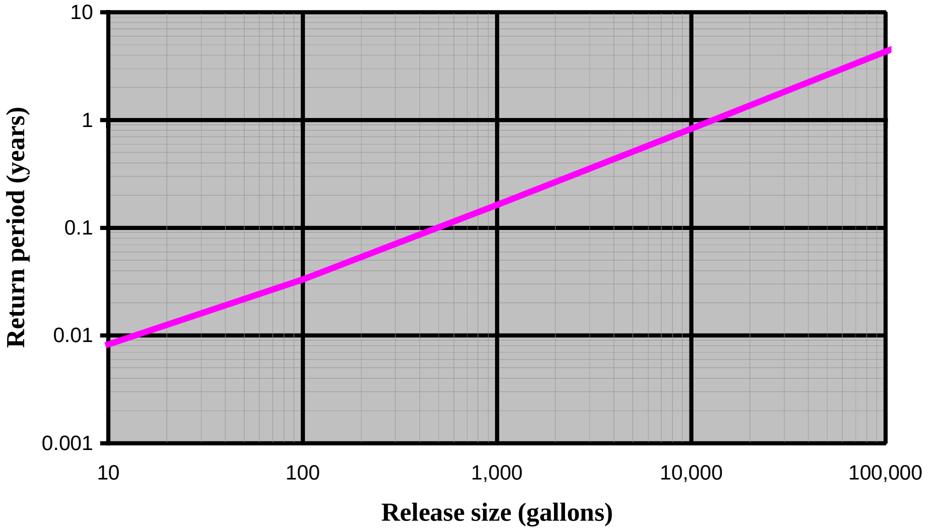

Figure 1. Return period (years) versus release size (gallons).

Based on the data presented above, the spill scenarios are selected to illustrate what the impacts of the potential worst spills could be on specific river environments. For the small, medium, and large rivers, the following spill scenarios are chosen:

1) 1,000 US gallons, which is close to the average spill size of gasoline into water based on data from National Response Center,
2) 10,000 US gallons, corresponding to the approximate size of a tanker truck and also corresponding to the once per year release, based upon the statistical analysis presented in figure 1, and
3) 30,000 US gallons, corresponding to the approximate size of a rail car and a two-year return period.

For the very large river, which corresponds to a navigable river like Mississippi, the methanol spill is assumed to be due to puncture of a barge releasing 300,000 gallons of methanol into the river. All the above releases are assumed to take place at riverbank on the water surface.

DEGRADATION MECHANISMS

There exists very little data on the rate of methanol biodegradation in surface water that would apply to the release scenarios selected for this assessment. In order to estimate the methanol biodegradation rate, a conservative assumption is made and the biodegradation rate is approximated assuming that the rate-limiting factor would be the rate of re-aeration of oxygen from the atmosphere to the surface water. By applying this assumption to the appropriate Monod kinetic equations, the methanol biodegradation rate is represented by a zero-order decay rate of 10 mg/l/day (Viessman and Hammer, 1993). This biodegradation rate is adopted for all the scenarios; however, this result is subject to considerable uncertainty, and a sensitivity analysis is performed below to examine the effects of other rates of decay on methanol dispersion. Volatilization effects are neglected.

CONCENTRATIONS OF CONCERN

Methanol, like other fuels, is a toxic substance and since methanol is completely miscible with water, it is necessary to examine the potential concentrations of concern of methanol/water mixture pertinent to human health. Marcus (1993) has proposed one-day and ten-day Drinking Water Health Advisory Limits (DWHAL's) for methanol of 200 and 100 mg/l for children, and 700 and 350 mg/l for adults. He proposed the concentration 3.5 mg/l as the lifetime DWHAL. These values are adopted here to be the appropriate concentrations of concern for the assessment study.

VARIABLE COEFFICIENT DISPERSION MODEL

River variation needs only to be considered in conjunction with a one-dimensional dispersion model. In its most general form the one-dimensional (longitudinal) advective-diffusion equation (conservation of solute mass) can be written as:

$$\frac{\partial C}{\partial t}+\frac{1}{A}\frac{\partial}{\partial x}(uAC)=\frac{1}{A}\frac{\partial}{\partial x}\left[KA\frac{\partial C}{\partial x}\right] \qquad (6)$$

where C is the concentration, t is time, and x is the downstream distance. In general, u, K, and A are functions of x as discussed above. Due to mathematical complexities, it is beyond the scope of the present study to allow more than one of these parameters to vary. The exponents of the downstream variations of A, K and u were found to be 1.51, 1.01 and 0.22, respectively. Little will be sacrificed if u is assumed constant. Also, an assumption of a constant K can be justified by noting that in analysis of one-dimensional dispersion in a uniform river, downstream concentrations are inversely proportional to the square root of K. On the other hand, intuitively it seems likely that downstream concentrations will be inversely proportional to A. Therefore, variation of K has much less impact on solute concentration than that of river cross-section and hence is assumed constant. However, the average value of *K* over the reach of concern will be used to take into account the effects of variation of *K*.

In general, when *A* varies as $A_0(1+x/L_0)^b$, and *K* and *u* are constant, a solution to (6) with the initial condition of release of a point mass M at $(x,t)=(0,0)$ is given by (Jamali, Lawrence, and Maloney, 2002)

$$C(x,t)=\frac{C_u(x,t)}{\sqrt{\left(A(x)/A_o\right)^{(1+ut/x)}}} \tag{7}$$

where

$$C_u(x,t)=\frac{M}{\sqrt{4\pi Kt}}\exp\left(\frac{-x^2}{4Kt}\right) \tag{8}$$

is the solution when the river is assumed to be uniform (Fischer et al., 1979).

Although the above solution was obtained for 1D dispersion, it can be approximately used for the 3D cases, e.g., the large and very large river cases, with C_u then being the corresponding 3D uniform-river solution.

RESULTS

The variation of the peak concentration with downstream distance is presented in figure 2 for the selected scenarios. It is seen that the 30,000-gallon release into the small river constitutes the most critical scenario. The impacted length of the river is approximately 180 km in this case. Given that for the small river L_o is 46 km, the variation of river hydraulic geometry is important in this case as anticipated above. This is also illustrated in figure 3, where the peak

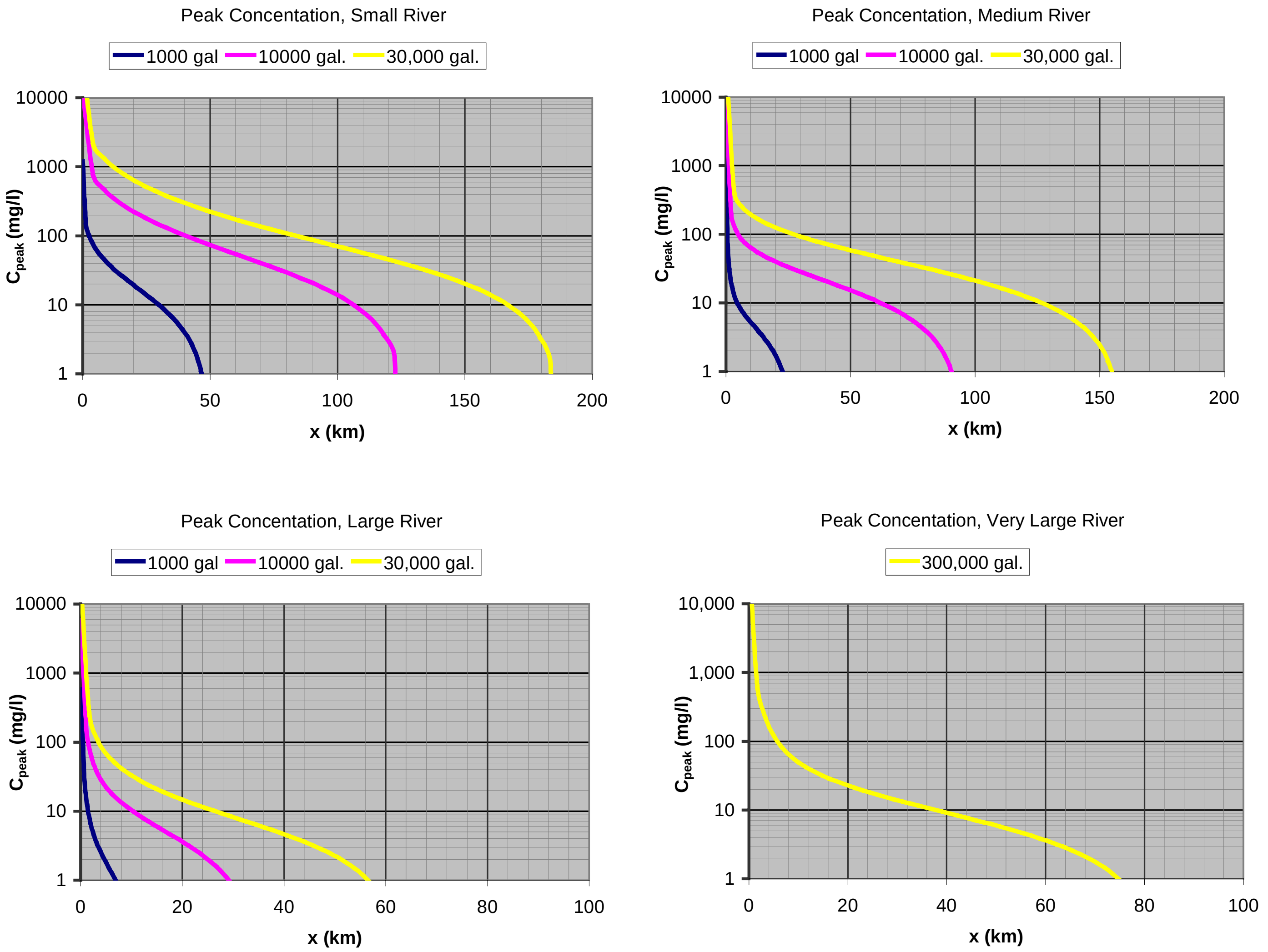

Figure 2. Variations of peak concentration with distance in the small, medium, large, and very large rivers.

concentration curves for the two cases of a uniform and a non-uniform small river are compared. It is seen that the uniform-river model overestimates the downstream concentrations, so the inclusion of river variation into the dispersion analysis proves to be important.

It is illustrative to estimate the required shutdown duration of a downstream drinking-water intake located at distance x from the release location when the concentration level in the river is above the one-day DWHAL for children of 200 mg/l. The shutdown start and end times are plotted in figure 4 for the case of 30,000-gallon methanol release into the small river. It is seen that the required shutdown duration is less a few hours at most.

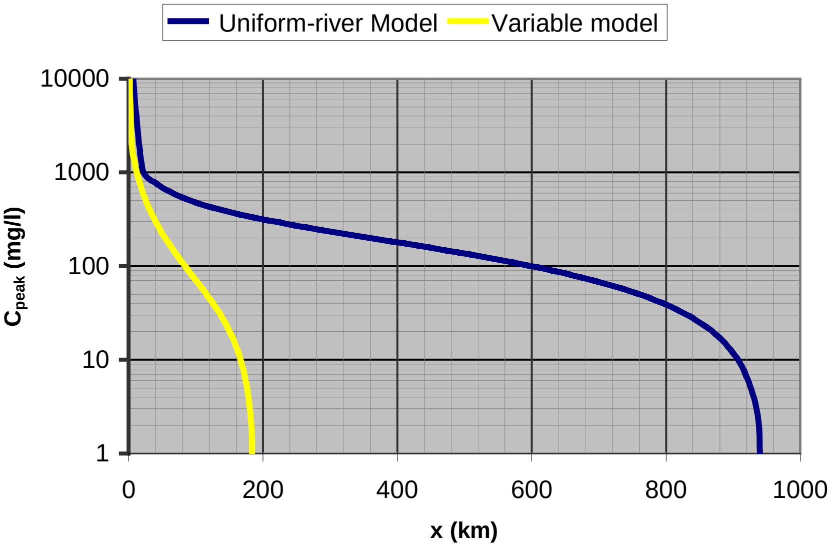

Figure 3. Comparison of variations of the peak concentration from the variable-river and the uniform-river solutions for the release scenario of 30,000 gallons into the small river (Q=10 m^3/s).

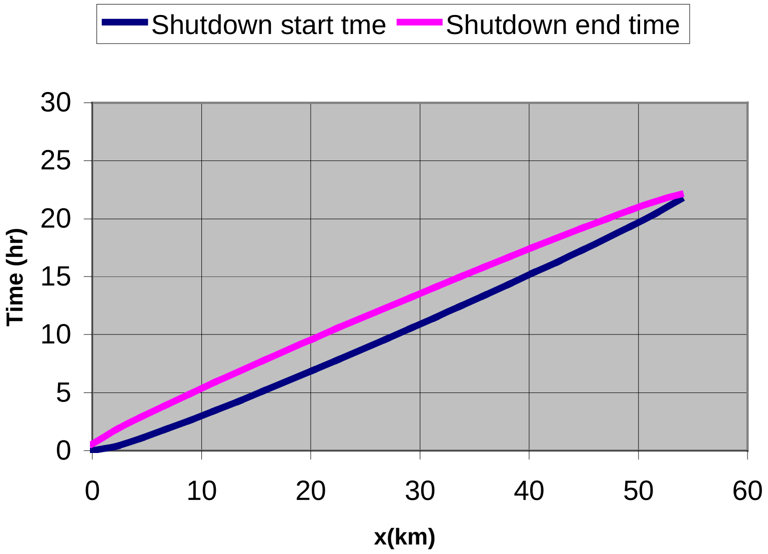

Figure 4. The start and end times for the shutdown of a water intake station located at distance x after a release of 30,000 gallons of methanol into the small river; C=200 mg/l.

It is interesting to look at the distance *x* and the time *t* at which the peak concentration drops below a certain level in the given scenarios. These values are summarized in table 4 for the life-time DWHAL of 3.5 mg/l. The required time for the peak concentration to fall below the life-time DWHAL ranges from less than a few hours to 3 days at worst. The corresponding values for the concentration level of 200 mg/l are given in table 5. As seen, in all cases the concentration falls below the one-day DWHAL for children in less than a day.

River/Release	**1,000-gal**		**10,000-gal**		**30,000-gal**		**300,000-gal**	
	x (km)	**t(hr)**	**x (km)**	**t(hr)**	**x (km)**	**t(hr)**	**x (km)**	**t(hr)**
Small	42	17	117	48	177	72		
Medium	14	4.3	81	25	146	45		
Large	3.2	0.8	20	4.6	44	10		
Very Large							60	10

Table 4. Distance (km) and time (hr) at which the concentration drops below 3.5 mg/l in each scenario.

River/Release	**1,000-gal**		**10,000-gal**		**30,000-gal**		**300,000-gal**	
	x (km)	**t(hr)**	**x (km)**	**t(hr)**	**x (km)**	**t(hr)**	**x (km)**	**t(hr)**
Small	1.0	0.4	22	9.0	54	22		
Medium	0.3	0.1	2.1	0.6	9.5	2.9		
Large	0.2	0.1	1.0	0.2	2.0	0.5		
Very Large							3.6	0.6

Table 5. Distance (km) and time (hr) at which the concentration drops below 200 mg/l in each scenario.

Finally, the dispersion analysis of a 8-gallon spill, which is the median release size according to NRC data, into the small river shows that methanol peak concentration drops below the children one-day DWHAL in less than a few meters from the spill location, and below 1 mg/l in about 1 km. Therefore, the potential impact of a median-size release is almost zero.

Sensitivity Analysis

Considering the uncertainties associated with the parameters used in this study, it is appropriate to conduct a sensitivity analysis on the parameters of concern. Here the results of the sensitivity analysis on longitudinal dispersion coefficient and biodegradation rate, which are the two most important parameters determining the persistence of methanol in the riverine environment, are presented.

Equation 5 gives the longitudinal dispersion coefficient in a river within a factor of four. The results of a sensitivity analysis on dispersion coefficient in the small river (K=82 m^2/s) are illustrated in figure 5 for the worst case of the 30,000-gallon release. The dispersion coefficients have been changed by factors of two and four. It is seen that when the dispersion

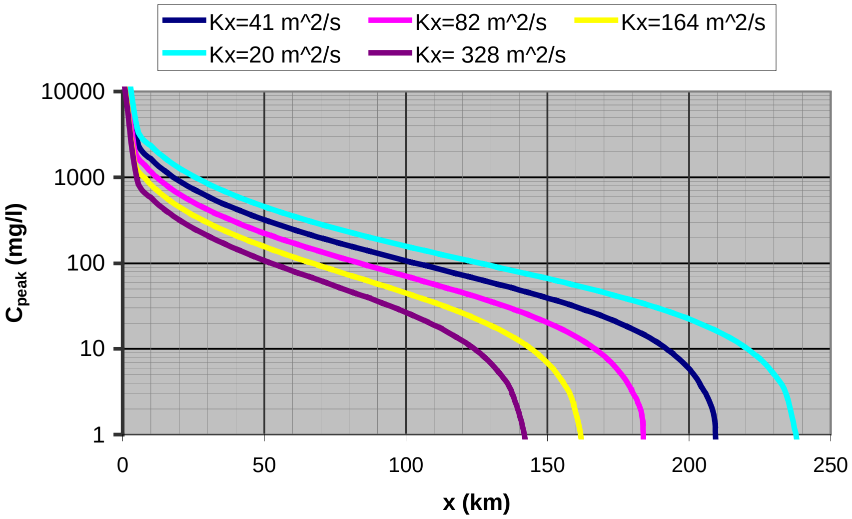

Figure 5. Sensitivity analysis on *K* for the case of the spill of 30,000 gallons into the small river.

coefficient is reduced by a factor of two, the required distance for the peak concentration to fall below the one-day children DWHAL increase by 30%. When the dispersion coefficient is reduced by a factor of four, the increase is 55%.

The effects of biodegradation rates of 0, 1, 10, and 100 mg/l/day are compared in figure 6. The curves start to drop rapidly from the zero biodegradation curve when the concentration becomes low enough to vanish in a few days through biodegradation. The plots suggest that biodegradation rate has a minor effect on the distance required for the concentration level to drop below the one-day children DWHAL. However, it affects considerably the required distance for the life-time DWHAL.

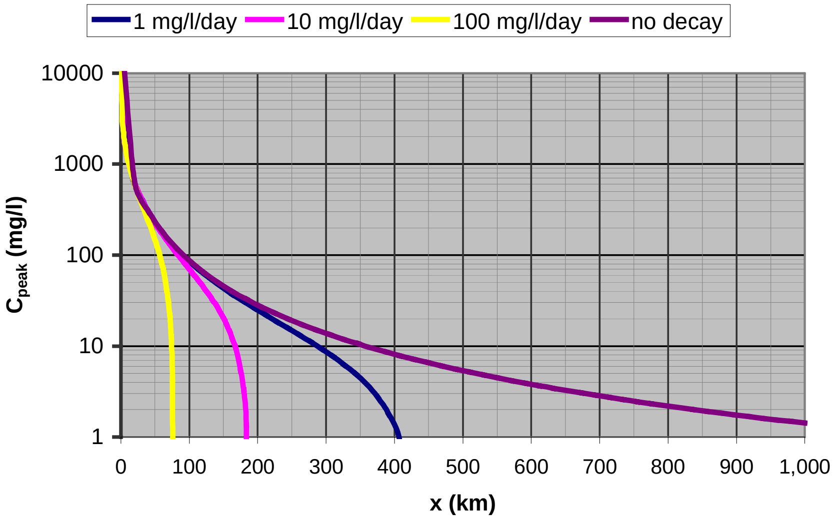

Figure 6. Downstream variations of the peak concentration for different biodegradation rates for the case of the spill of 30,000 gallons into the small river.

CONCLUSIONS

For this assessment study, appropriate release sizes were selected and evaluated for four hypothetical rivers to determine the potential impact a methanol release could have on human health. In general, it was found that the downstream variation of river cross-sectional area has a considerable effect on dispersion in a small river. River enlargement greatly reduces downstream concentrations of methanol.

From this analysis, the human health and environmental risks associated with an accidental release of methanol into a river appears to be low. For example, in the most critical scenario, a 30,000-gal release into a small (10 m^3/s) river, the peak methanol concentration falls below the estimated one-day drinking water health advisory limit for children (200 mg/l) in less than one day.

In addition, it was estimated that the entire 30,000-gal methanol release would be virtually eliminated from the small river (i.e., less than 1 mg/l) in approximately three days. The short-lived duration of the methanol release is not only due to the speed of dilution but also to the rapid rate of methanol biodegradation. Methanol biodegradation plays an important role in ensuring the complete elimination of methanol from the river environment.

Closer to the release location the potential exists for observers to experience higher concentrations of methanol. While we feel that the potential for this is low we acknowledge that peak concentrations above the 200 mg/l DWHAL could be experienced a few kilometers to approximately 50 km from the release location depending upon the release scenario. In all likelihood, potentially toxic concentrations of methanol will only be experienced by the aquatic species within the vicinity of the release zone.

Finally, no long-term toxic effects are expected from a methanol release in a river environment, as methanol will not persist in water due to the rapid rate of dilution and biodegradation.

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