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A MODEL FOR THE DISPERSION OF CHEMICALS IN WATERWAYS

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ABSTRACT

This study is focused on the wide variety of chemical spills in waterways and shipped in bulk world-wide, raising concerns regarding the ecological and human health risks. In this research, a model is developed to predict the location of the spill at any point on a waterway and also to disperse the chemical in a safe place, beyond which water can be used without any harm. This paper discusses, axial dispersion model, which can be applied to waterways to quantify the distribution of chemicals spilt. The credibility of the model is to predict the concentration profile from the released area to any given distance.

Key words: Dispersion number; waterways; concentration profile

INTRODUCTION

With the increased use of the Nation's waterways for the transportation of materials, there is an increase in the probability of spills. Once such a spill has occurred, there is an immediate need to predict the concentration profile of the chemical as the spill travels in order to assess the impact to both; humans and the environment. Many untreated effluents containing toxic chemicals have been released in lakes, reservoirs, streams, rivers, estuaries and the sea. The characteristics of chemicals released to waterways have not been studied in detail. Very limited field study is carried out. In one such analysis, Neely et al.[1] applied the residence time distribution (RTD) models for water soluble chemical spills. Extension of such a study is necessary to quantify the extent of damage that can happen due to the presence of chemicals in waterways.

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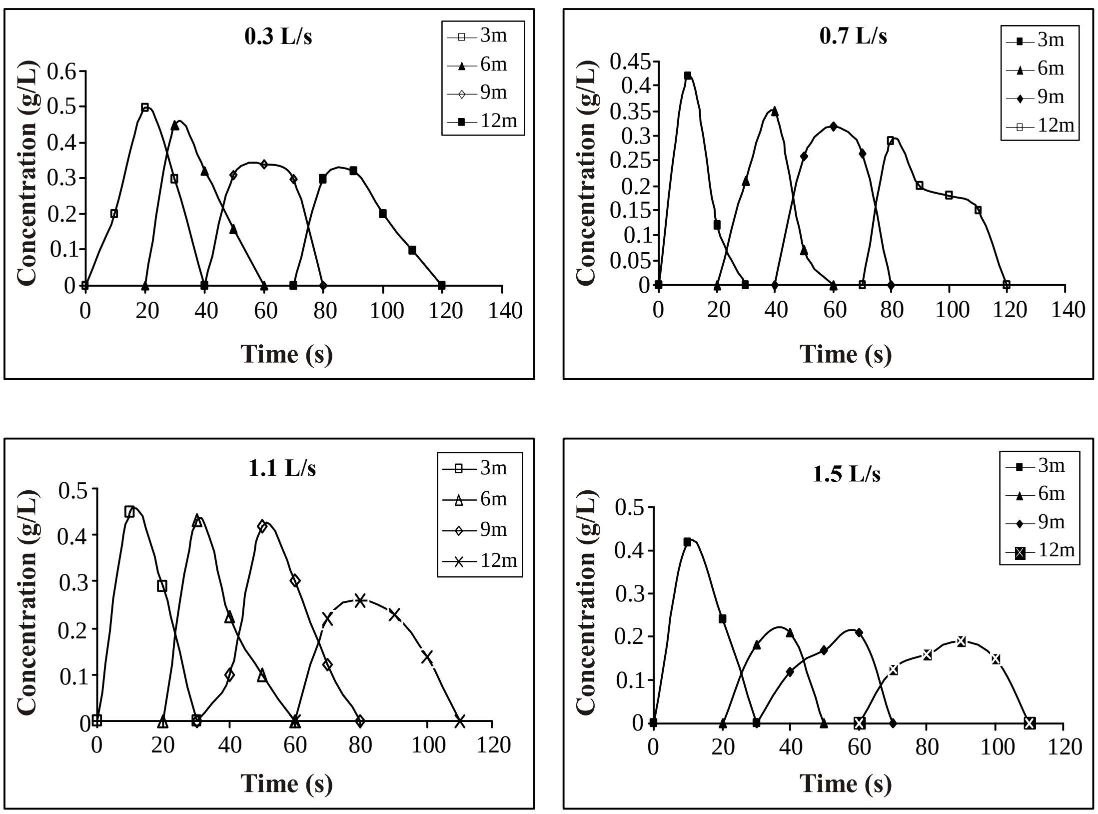
EXPERIMENTAL

Materials and methods

Studies are made on the dispersion of chemicals in water ways. The dispersion of the chemicals potassium permanganate, potassium dichromate and copper sulfate are considered for the experiments, which are widely used in dye, leather and glass industries, respectively. A site is selected, where there is provision for a stream of water to flow in a channel. The size of the channel considered for this study is of width 0.45 m, length 30 m and depth 0.23 m. A known amount of the chemical was dissolved in 5 litres of water and poured in the channel. Samples are taken at 3 m, 6 m, 9 m, and 12 m distances for every 10 seconds. The concentrations of the chemical in the samples are estimated using spectrophotometer. Experiments are done for the flow rates 0.3 L/s, 0.7 L/s, 1.1 L/s, 1.5 L/s and 1.8 L/s. The obtained concentration for the dispersed chemicals at 3 m intervals of the channel is plotted against time, and for one of the system $CuSO_4$ is given in the Fig. 1.



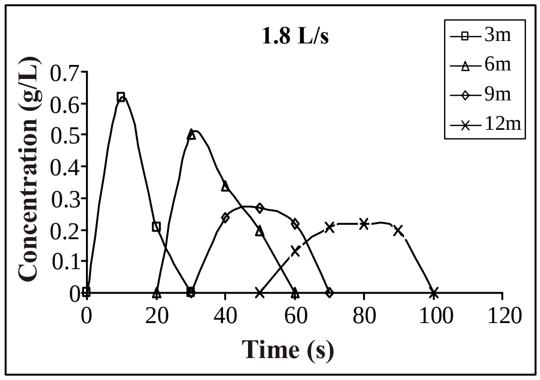


Fig. 1: Concentration vs time for $CuSO_4$ at different flow rates

Modeling

Dispersion model

The dispersion of chemicals can be characterised using axial dispersion model. Any distribution curve is fairly represented by the moments of the curve. The first moment, represented by the mean residence time ($\bar{t}$), and the second moment represented by the variance σ^2, are the two important values that charaterise the distribution curve. These are given by -

$$\bar{t} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \quad ...(1)$$

and

$$\sigma^2 = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}^2 \quad ...(2)$$

In the dimensionless form, $\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2}$ ...(3)

If axial dispersion model is assumed to truly represent the flow system, the concentration versus time relationship is given by

$$C_\theta = \frac{1}{2\sqrt{\pi(D/uL)}} exp^{\left[\frac{-(1-\theta)^2}{4(D/uL)}\right]} \quad ...(4)$$

If (D/uL) is known, dimensionless concentration C_θ can be estimated as a function of time (θ).

The results obtained from the various experimental studies are used to estimate the *D/uL*. The calculations are presented in the Table 1.

D/uL is estimated using the following relation,

(i) For closed vessels (C.V.)

$$\sigma_\theta{}^2 = 2\frac{D}{uL} - 2\left(\frac{D}{uL}\right)^2\left(1 - e^{-uL/D}\right) \qquad \text{...(5)}$$

(ii) For open vessels (D.V.)

$$\sigma_\theta{}^2 = 2\frac{D}{uL} + 8\left(\frac{D}{uL}\right)^2 \qquad \text{...(6)}$$

The Newton-Raphson technique is used to determine *D/uL* for the closed vessels and equation for the open vessel is quadrant in nature and from the roots of the equation *D/uL* is determined.

Table 1: Dispersion number – $CuSO_4$

$CuSO_4$ – Flow rate = 0.3 L/s											
Time (s)	**Conc. (g/L)**	**Δ t (s)**	**c Δt**	**Tc Δt**	$\bar{t}$	**t^2 c Δt**	$\bar{t}^2$	**σ^2**	**$\Delta\sigma\theta^2$**	**D/uL (O.V.)**	**D/uL (C.V.)**
Distance = 3 m											
0	0	10	0	0		0					
10	0.2	10	2	20		200					
20	0.5	10	5	100		2000					
30	0.3	10	3	90		2700					
40	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			10	**210**	**21**	**4900**	**441**	**49**	**0.111111**	**0.0468**	**0.059**
Distance = 6 m											
20	0	10	0	0		0					

Cont…

Time (s)	Conc. (g/L)	Δ t (s)	c Δt	Tc Δt	$\bar{t}$	t^2 c Δt	$\bar{t}^2$	σ^2	$\Delta\sigma\theta^2$	D/uL (O.V.)	D/uL (C.V.)
$CuSO_4$ – Flow rate = 0.3 L/s											
20	0	10	0	0		0					
30	0.45	10	4.5	135		4050					
40	0.32	10	3.2	128		5120					
50	0.16	10	1.6	80		4000					
60	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			9.3	**343**	**36.88172**	**13170**	**1360.261**	**55.86773**	**0.041071**	**0.0191**	**0.021**
Distance = 9 m											
40	0	10	0	0		0					
50	0.31	10	3.1	155		7750					
60	0.34	10	3.4	204		12240					
70	0.3	10	3	210		14700					
80	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			9.5	**569**	**59.89474**	**34690**	**3587.38**	**64.19945**	**0.017896**	**0.0086**	**0.009**
Distance = 12 m											
70	0	10	0	0		0					
80	0.3	10	3	240		19200					
90	0.32	10	3.2	288		25920					
100	0.2	10	2	200		20000					
110	0.1	10	1	110		12100					
120	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			9.2	**838**	**91.08696**	**77220**	**8296.834**	**96.64461**	**0.011648**	**0.0057**	**0.0059**

Cont…

$CuSO_4$ – Flow rate = 0.3 L/s											
Time (s)	**Conc. (g/L)**	**Δ t (s)**	**c Δt**	**Tc Δt**	$\bar{t}$	**t^2 c Δt**	$\bar{t}^2$	**σ^2**	**$\Delta\sigma\theta^2$**	**D/uL (O.V.)**	**D/uL (C.V.)**
Distance = 3 m											
0	0	10	0	0		0					
10	0.42	10	4.2	42		420					
20	0.12	10	1.2	24		480					
30	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			5.4	**66**	**12.22222**	**900**	**149.3827**	**17.28395**	**0.11570 2479**	**0.0485**	**0.0617**
Distance = 6 m											
20	0	10	0	0		0					
30	0.21	10	2.1	63		1890					
40	0.35	10	3.5	140		5600					
50	0.07	10	0.7	35		1750					
60	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			6.3	**238**	**37.77778**	**9240**	**1427.16**	**39.50617**	**0.02768 1661**	**0.0131**	**0.014**
Distance = 9 m											
40	0	10	0	0		0					
50	0.26	10	2.6	130		6500					
60	0.32	10	3.2	192		11520					
70	0.265	10	2.65	185.5		12985					
80	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			8.45	**507.5**	**60.05917**	**31005**	**3607.104**	**62.12668**	**0.01722 3422**	**0.0083**	**0.0087**

Cont…

$CuSO_4$ – Flow rate = 0.3 L/s											
Time (s)	**Conc. (g/L)**	**Δ t (s)**	**c Δt**	**Tc Δt**	$\bar{t}$	**t^2 c Δt**	$\bar{t}^2$	**σ^2**	**$\Delta\sigma\theta^2$**	**D/uL (O.V.)**	**D/uL (C.V.)**
Distance = 12 m											
70	0	10	0	0		0					
80	0.29	10	2.9	232		18560					
90	0.2	10	2	180		16200					
100	0.18	10	1.8	180		18000					
110	0.15	10	1.5	165		18150					
120	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			8.2	**757**	**92.31707**	**70910**	**8522.442**	**125.119**	**0.014681118**	**0.0071**	**0.0074**
Distance = 3 m											
0	0	10	0	0		0					
10	0.45	10	4.5	45		450					
20	0.29	10	2.9	58		1160					
30	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			7.4	**103**	**13.91892**	**1610**	**193.7363**	**23.83126**	**0.123008766**	**0.0511**	**0.0658**
Distance = 6 m											
20	0	10	0	0		0					
30	0.43	10	4.3	129		3870					
40	0.225	10	2.25	90		3600					
50	0.1	10	1	50		2500					
60	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			7.55	**269**	**35.62914**	**9970**	**1269.436**	**51.09425**	**0.040249582**	**0.0187**	**0.0205**

Cont…

$CuSO_4$ – Flow rate = 0.3 L/s											
Time (s)	**Conc. (g/L)**	**Δ t (s)**	**c Δt**	**Tc Δt**	$\bar{t}$	**t^2 c Δt**	$\bar{t}^2$	**σ^2**	**$\Delta\sigma\theta^2$**	**D/uL (O.V.)**	**D/uL (C.V.)**
Distance = 9 m											
30	0	10	0	0		0					
40	0.1	10	1	40		1600					
50	0.42	10	4.2	210		10500					
60	0.3	10	3	180		10800					
70	0.12	10	1.2	84		5880					
80	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			9.4	**514**	**54.68085**	**28780**	**2989.995**	**71.70665**	**0.023982195**	**0.0115**	**0.0121**
Distance = 12 m											
60	0	10	0	0		0					
70	0.22	10	2.2	154		10780					
80	0.26	10	2.6	208		16640					
90	0.23	10	2.3	207		18630					
100	0.14	10	1.4	140		14000					
110	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			8.5	**709**	**83.41176**	**60050**	**6957.522**	**107.1834**	**0.015405396**	**0.0075**	**0.0078**
Distance = 3 m											
0	0	10	0	0		0					
10	0.42	10	4.2	42		420					
20	0.24	10	2.4	48		960					
30	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			6.6	**90**	**13.63636**	**1380**	**185.9504**	**23.1405**	**0.124444444**	**0.0516**	**0.0667**

Cont…

Time (s)	Conc. (g/L)	Δ t (s)	c Δt	Tc Δt	$\bar{t}$	t^2 c Δt	$\bar{t}^2$	σ^2	$\Delta\sigma\theta^2$	D/uL (O.V.)	D/uL (C.V.)
$CuSO_4$ – Flow rate = 0.3 L/s											
Distance = 6 m											
20	0	10	0	0		0					
30	0.18	10	1.8	54		1620					
40	0.21	10	2.1	84		3360					
50	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			3.9	**138**	**35.38462**	**4980**	**1252.071**	**24.85207**	**0.019848771**	**0.0096**	**0.01**
Distance = 9 m											
30	0	10	0	0		0					
40	0.12	10	1.2	48		1920					
50	0.17	10	1.7	85		4250					
60	0.21	10	2.1	126		7560					
70	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			5	**259**	**51.8**	**13730**	**2683.24**	**62.76**	**0.023389633**	**0.0112**	**0.0118**
Distance = 12 m											
60	0	10	0	0		0					
70	0.125	10	1.25	87.5		6125					
80	0.16	10	1.6	128		10240					
90	0.19	10	1.9	171		15390					
100	0.15	10	1.5	150		15000					
110	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			6.25	**536.5**	**85.84**	**46755**	**7368.506**	**112.2944**	**0.015239779**	**0.0074**	**0.0077**

Cont…

$CuSO_4$ – Flow rate = 0.3 L/s											
Time (s)	**Conc. (g/L)**	**Δ t (s)**	**c Δt**	**Tc Δt**	$\bar{t}$	**t^2 c Δt**	$\bar{t}^2$	**σ^2**	**$\Delta\sigma\theta^2$**	**D/uL (O.V.)**	**D/uL (C.V.)**
Distance = 3 m											
0	0	10	0	0		0					
10	0.62	10	6.2	62		620					
20	0.21	10	2.1	42		840					
30	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			8.3	**104**	**12.53012**	**1460**	**157.0039**	**18.8997**	**0.12037 7219**	**0.0501**	**0.0643**
Distance = 6 m											
20	0	10	0	0		0					
30	0.5	10	5	150		4500					
40	0.34	10	3.4	136		5440					
50	0.2	10	2	100		5000					
60	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			10.4	**386**	**37.11538**	**14940**	**1377.552**	**58.98669**	**0.04281 9941**	**0.0198**	**0.0219**
Distance = 9 m											
30	0	10	0	0		0					
40	0.24	10	2.4	96		3840					
50	0.27	10	2.7	135		6750					
60	0.22	10	2.2	132		7920					
70	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			7.3	**363**	**49.72603**	**18510**	**2472.678**	**62.93864**	**0.0254 53635**	**0.0121**	**0.0129**

Cont…

CuSO$_4$ – Flow rate = 0.3 L/s											
Time (s)	**Conc. (g/L)**	**Δ t (s)**	**c Δt**	**Tc Δt**	$\bar{t}$	**t^2 c Δt**	$\bar{t}^2$	**σ^2**	**$\Delta\sigma\theta^2$**	**D/uL (O.V.)**	**D/uL (C.V.)**
Distance = 12 m											
50	0	10	0	0		0					
60	0.13	10	1.3	78		4680					
70	0.21	10	2.1	147		10290					
80	0.22	10	2.2	176		14080					
90	0.2	10	2	180		16200					
100	0	0	0	0		0					
			Σ =	Σ =		Σ =					
			7.6	**581**	**76.44737**	**45250**	**5844.2**	**109.7472**	**0.01877 8828**	**0.0091**	**0.0095**

RESULTS AND DISCUSSION

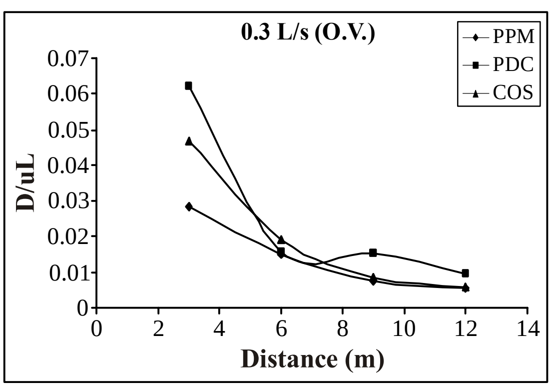
The dispersion number (*D/uL*) values for open vessel boundary conditions for the all the systems studied in the work are given in Table 2. Fig. 2 explains, how the dispersion number varies with respect to the distance from the place of the spill ? Table 3 and Fig. 3 represent the same for the closed vessel conditions.

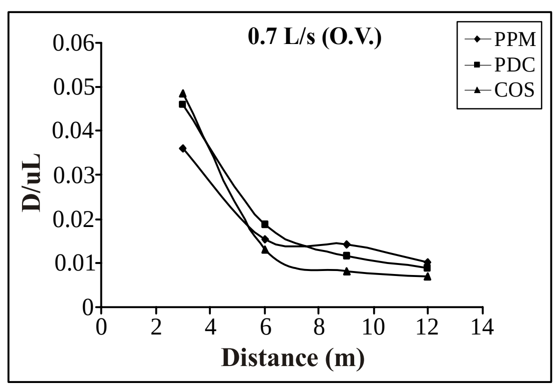
Table 2: D/uL for the systems at open vessel conditions

Flow rate (L/s)	Distance (m)	D/uL		
		KMnO$_4$	K$_2$Cr$_2$O$_7$	CuSO$_4$
0.3	3	0.0282	0.062	0.0468
	6	0.0151	0.0156	0.0191
	9	0.0076	0.0152	0.0086
	12	0.0055	0.0097	0.0057

Cont…

Flow rate (L/s)	Distance (m)	D/uL		
		$KMnO_4$	$K_2Cr_2O_7$	Cu SO_4
0.7	3	0.0361	0.046	0.0485
	6	0.0155	0.0188	0.0131
	9	0.0143	0.0118	0.0083
	12	0.0103	0.009	0.0071
1.1	3	0.072	0.0414	0.0511
	6	0.0417	0.0171	0.0187
	9	0.019	0.0133	0.0115
	12	0.012	0.0069	0.0075
1.5	3	0.0416	0.05114	0.0516
	6	0.0192	0.01	0.0096
	9	0.0219	0.0034	0.0112
	12	0.0115	0.0027	0.0074
1.8	3	0.0651	0.0291	0.0501
	6	0.0301	0.019	0.0198
	9	0.0312	0.0235	0.0121
	12	0.0135	0.0125	0.0091





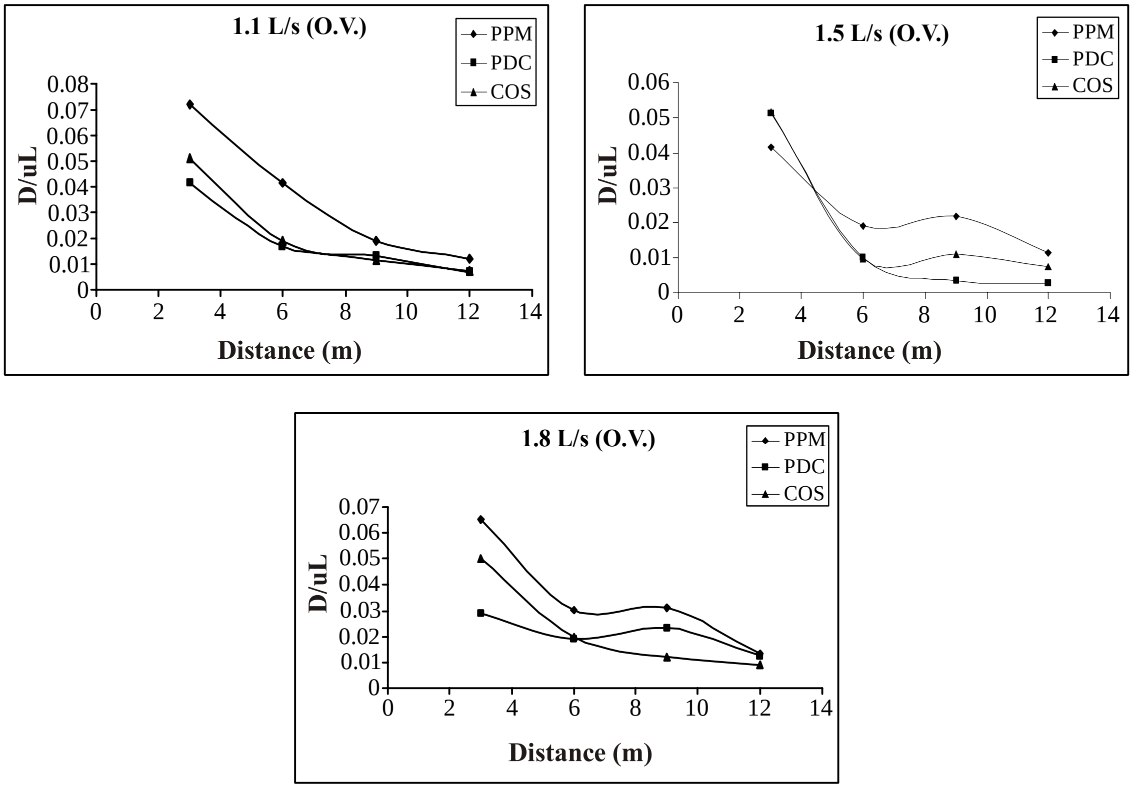


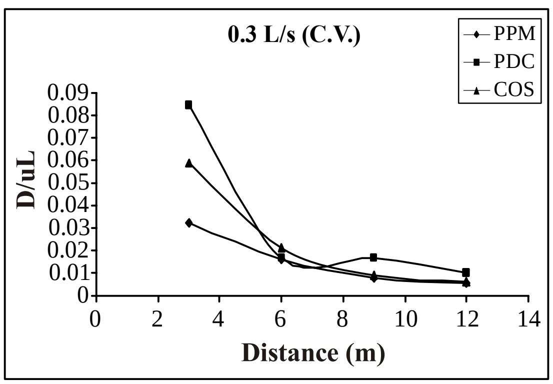
Fig. 2: Variation of dispersion number at open vessel (O.V.) conditions (PPM- $KMnO_4$; PDC- $K_2Cr_2O_7$; COS- $CuSO_4$)

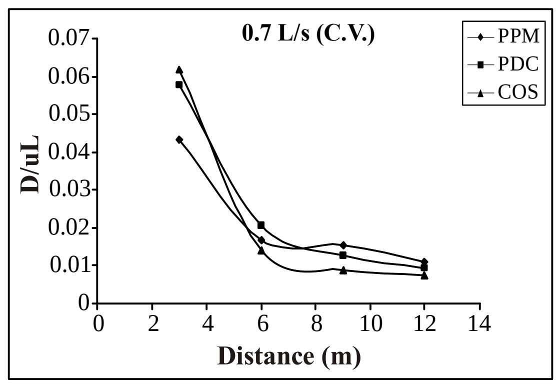
Table 3: D/uL for the systems at closed vessel conditions

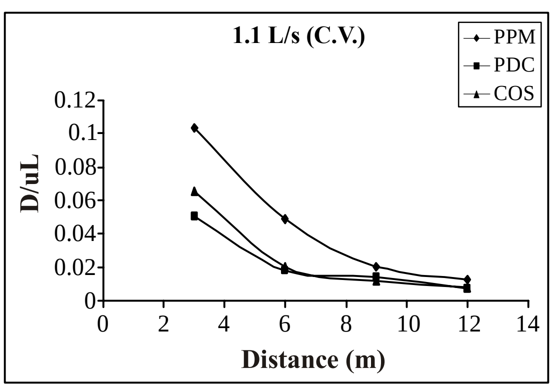
Distance (m)	Distance (m)	D/uL		
		$KMnO_4$	$K_2Cr_2O_7$	$CuSO_4$
0.3	3	0.0324	0.0845	0.059
	6	0.0163	0.0168	0.021
	9	0.0079	0.0164	0.009
	12	0.0057	0.0102	0.0059
0.7	3	0.0431	0.0577	0.0617
	6	0.0168	0.0206	0.014
	9	0.0153	0.0125	0.0087
	12	0.0109	0.0094	0.0074

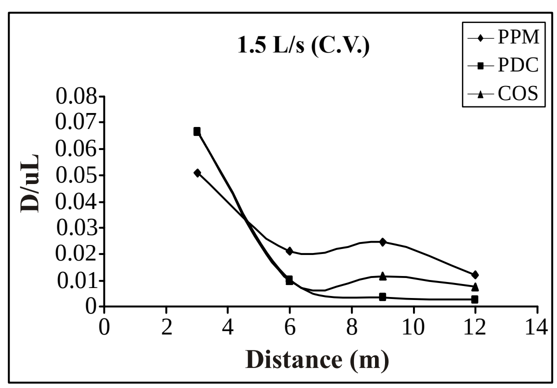
Cont…

Distance (m)	Distance (m)	D/uL		
		$KMnO_4$	$K_2Cr_2O_7$	$CuSO_4$
1.1	3	0.1035	0.0508	0.0658
	6	0.0487	0.0185	0.0205
	9	0.0209	0.0142	0.0121
	12	0.0127	0.0071	0.0078
1.5	3	0.0511	0.0664	0.0667
	6	0.0212	0.0105	0.01
	9	0.0244	0.0035	0.0118
	12	0.0122	0.0028	0.0077
1.8	3	0.0901	0.0337	0.0643
	6	0.0349	0.0208	0.0219
	9	0.0365	0.0264	0.0129
	12	0.0145	0.0133	0.0095









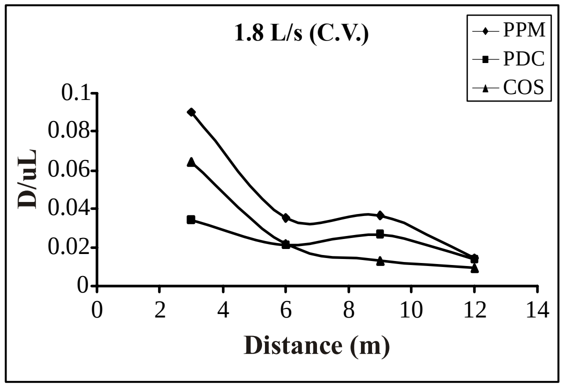


Fig. 3: Variation of dispersion number at closed vessel (C.V.) conditions (PPM- $KMnO_4$; PDC- $K_2Cr_2O_7$; COS- $CuSO_4$)

D/uL is a very strong function of the distance during the initial stage. However, at

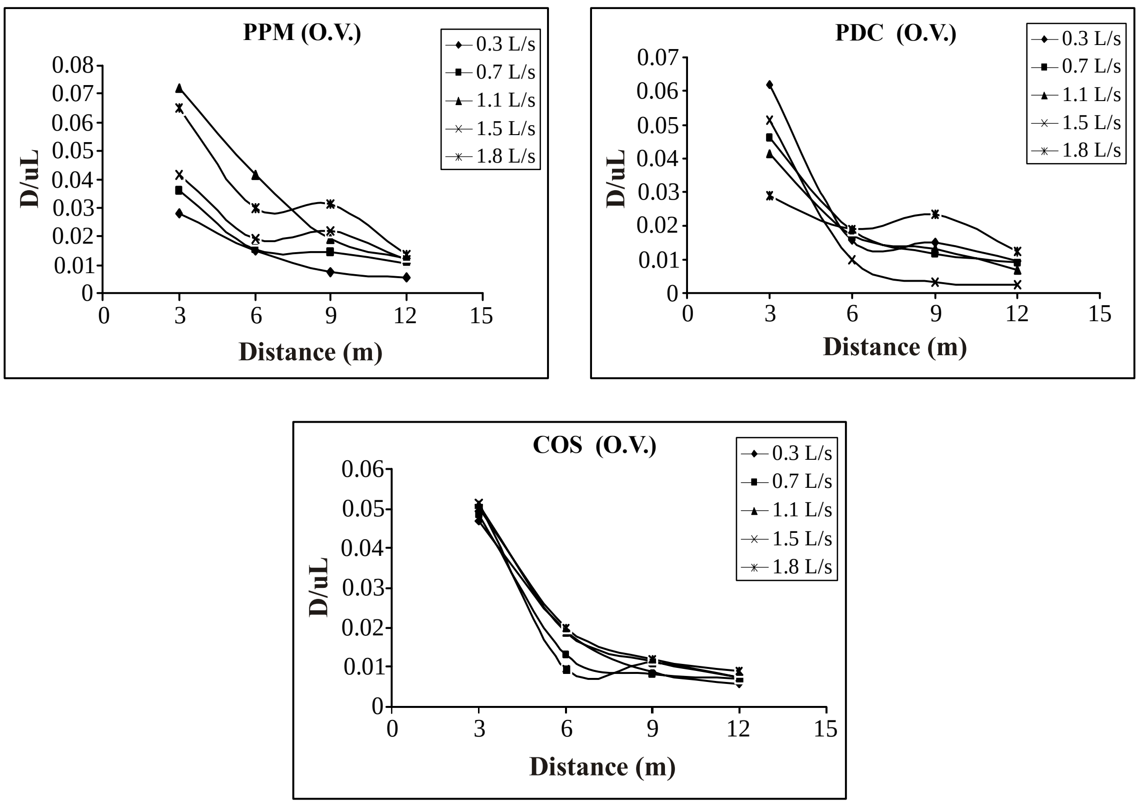


Fig. 4: D/uL vs distance at various distances for the chemicals at open vessel (O.V.) conditions (PPM- $KMnO_4$; PDC- $K_2Cr_2O_7$; COS-$CuSO_4$)

the distances far away from the place of spill, flow rate has very less influence on the dispersion number. Moreover, all the chemicals that spill have same dispersion number. Fig. 4 and 5 represent the dispersion number versus distance for chemicals spilled at different flow rates of the stream under open and closed vessel conditions, respectively.

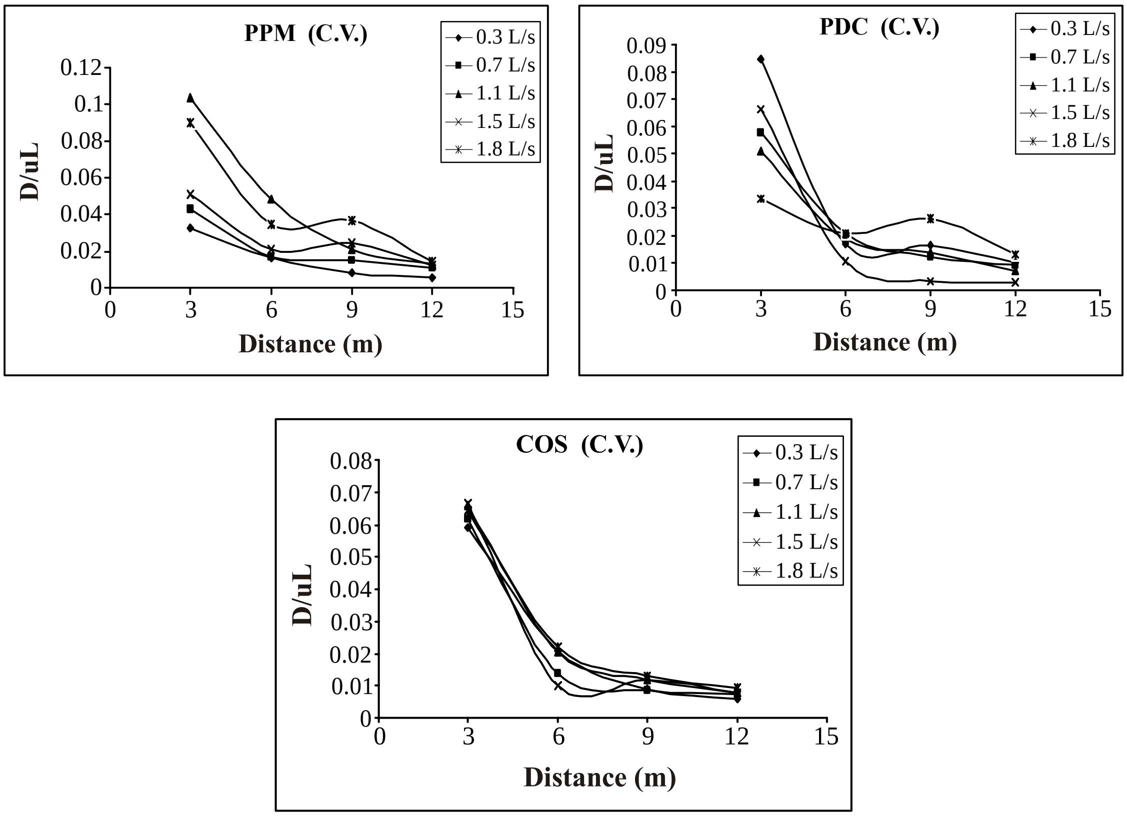


Fig. 5: D/uL vs distance at various distances for the chemicals at closed vessel (C.V.) conditions (PPM- $KMnO_4$; PDC- $K_2Cr_2O_7$; COS- $CuSO_4$)

There are atleast two ways, by which dispersion model can be effectively used -

(i) By taking samples at different locations in a waterway, which will be helpful to determine the location, where the chemical is dumped into the waterways, and

(ii) If the spill occurs at a known location, it is possible to determine the concentration of the toxic chemical along the waterway and hence, to identify the safe distance at which the water in the river can be used.

If the chemical does not vaporize, the dispersion model can be directly employed. Otherwise, the rate of vapourization can be superimposed over dispersion and the resulting equation can be used.

CONCLUSIONS

Quantitative measures to describe the spread of the spills are scarce in literature. The characteristics of chemicals released into water ways have not been studied in detail. Very limited field study has been carried out.

The dispersion of chemicals can be characterised using axial dispersion model. It is assumed that normal distribution curve truly represents the dispersion. The first moment, represented by the mean residence time ($\bar{t}$), and the second moment represented by the variance σ^2, are the two important values that charaterise the distribution curve. They are given by -

$$\bar{t} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \quad \ldots(7)$$

and $$\sigma^2 = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}^2 \quad \ldots(8)$$

In the dimensionless form, $\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2}$

If axial dispersion model is assumed to represent truly the flow system, the concentration versus time relationship is given by -

$$C_\theta = \frac{1}{2\sqrt{\pi(D/uL)}} exp^{\left[\frac{-(1-\theta)^2}{4(D/uL)}\right]} \quad \ldots(9)$$

If D/uL is known, dimensionless concentration C_θ can be estimated as a function of time (θ).

D/uL is estimated using the following relation,

(i) For closed vessels

$$\sigma_\theta^{\,2} = 2\frac{D}{uL} - 2\left(\frac{D}{uL}\right)^2\left(1 - e^{-uL/D}\right) \qquad \ldots(10)$$

(ii) For open vessels

$$\sigma_\theta^{\,2} = 2\frac{D}{uL} + 8\left(\frac{D}{uL}\right)^2 \qquad \ldots(11)$$

The results obtained from the various experimental studies are used to estimate the *D/uL*. The results indicate that *D/uL* is a very strong function of the distance during the initial stage. However, at the distances far away from the place of spill, flow rate has very less influence on the dispersion number. Moreover, all the chemicals that spill have same dispersion number.

Experiments similar to the ones discussed here can be carried out for different groups of chemicals, in different sizes of waterways at different flow conditions and the results; thus obtained can be used to correlate the dispersion number in terms of Reynolds number. Such correlation can be used to determine the concentration of the chemicals dispersed in waterways. The dispersion model can be used to determine the location of the spill if the distribution of the chemical at any point on location and the flow condition of the waterway are known. It can also be used to determine the concentration of the dispersed chemical along the waterway. This will help in the design of *in situ* treatment methods and locating safe distances along the river, beyond which water can be used without any harm.

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