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NATIONAL WATER RESEARCH INSTITUTE

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX

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MANAGEMENT PERSPECTIVE

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This report presents the results of a preliminary diffusion experiment undertaken in June/1997 as part of ongoing GWRP studies at Smithville, Ontario. Samples were obtained from 3 different geological zones during drilling in 1996. The primary purpose of the experiments was to provide information required to evaluate the effect of diffusional transport of specific chemical tracers. This data will provide information required to evaluate the effect of diffusional transport of solutes in the rock matrix underlying the Smithville area. This information will also aid in the interpretation of future field scale tracer experiments, as well as provide input parameters for use in numerical models of solute transport. The work is essential in developing techniques for effectively evaluating the radial diffusion experiments and improve on experimental techniques.

The results indicate that the radial diffusion method is well suited for the determination of the effective porosity of carbonate rock. However, the determination of the effective diffusion coefficients are subject to many interferences. The effective diffusion coefficients for some rocks may vary (in some cases, by an order of magnitude) depending on the tracer used. Considering that these differences can result in very significant differences in solute lost to the matrix in the field setting, this issue will be subject to continuing investigation.

This works supports EC priorities under COA Stream 1.6 (groundwater) and Stream 1.4 (contaminated sites). Additionally, it supports GWRP deliverables under Toxics Result #3.

Current Status:

The report is intended to be released as a NWRI contribution and will be incorporated into a journal manuscript later in the year after the completion of further experiments and interpretation.

Next Steps:

The results presented in the report are currently being used to plan another experimental session this fall. The results will be used to support future tracer experiments and predictive models at the Smithville site and will lead to a journal manuscript.

Executive Summary

Dolostone samples from various geological units which comprise the Lockport group formation at Smithville, Ontario were used to construct radial diffusion cells (Novakowski and van der Kamp, 1996; van der Kamp et al., 1996). Diffusion experiments were conducted by spiking the cell with tracer and monitoring the decrease in tracer concentration with time in the reservoir. Once equilibrium conditions were achieved (i.e. tracer concentration of the reservoir is equal to that of the rock), the experiment was reversed by removing the tracer remaining in the reservoir. This allows for reverse diffusion from the rock to the reservoir. The purpose of the experiment was to provide estimates of the effective porosity of the dolostone samples and the effective diffusion coefficients for specific chemical tracers. These data will provide information required to evaluate the effect of diffusional transport of solutes in the rock matrix underlying the Smithville area. This information will also aid in the interpretation of future field scale tracer experiments, as well as provide input parameters for use in numerical models of solute transport.

The results of the study indicate that the radial diffusion experiment is well suited for determination of the diffusional transport properties in the carbonate rock. Values of the effective porosity determined for the dolostone samples range from 1% to 18% which agrees favorably with other independent measurements of porosity. However, the determination of effective diffusion coefficients are subject to many interferences, thus the interpretation of the geometric factor (a parameter describing the geometry of the pore space) was found to be difficult. In addition, analytical errors, which may have resulted from the diffusion of sulfate or dissolution of sulfate bearing minerals into the reservoir, caused matrix interference during ion analyses. However, the results show that, should analytical measurements be improved, bromine is an effective tracer for the determination of both effective porosity and the geometric factor, as these were found to be similar in both the forward and reverse diffusion experiments. Lissamine was observed to behave in a non-conservative fashion during the forward diffusion experiments. However, Lissamine behavior during the reverse diffusion experiments showed little, if any, retardation. Therefore, use of Lissamine is warranted only when an additional tracer, such as bromine,

is used. This is supported by the results which show general agreement between the effective porosities determined from the reverse diffusion experiments for both tracers. It is important to note that the, geometric factors were found to be significantly different for each tracer, with Lissamine yielding values almost an order of magnitude greater than that for bromide. This finding is opposite to what would be predicted on the basis of the size of the tracer molecule (i.e. due to exclusion effects). Considering that differences in the estimate of effective diffusion coefficients by an order of magnitude can result in very significant differences in the estimate of solute lost to the matrix in the field setting, this issue will be subject to continuing investigation.

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Introduction

Dolostone samples from the geological units which comprise the Lockport group formation, were collected from drill core obtained from boreholes drilled in and around Smithville, Ontario. These samples were used in forward and reverse diffusion experiments. The experiments were conducted using radial diffusion cells (Novakowski and van der Kamp, 1996; van der Kamp et al., 1996). The purpose of the experiments was to estimate the effective porosity of the dolostone units and determine the effective diffusion coefficients for specific chemical tracers. From the estimates of the effective diffusion coefficient, a geometric factor, which represents the geometry of the pore structure, may be determined (Novakowski and van der Kamp, 1996). Measurements of the geometric factor allows for the estimation of effective diffusion coefficients for other solutes, such as the organic contaminants which are present in Smithville groundwater. This information is necessary for the accurate prediction of mass transfer from solutes located in fractures in the dolostone to the unfractured matrix. Small errors in the estimate of the effective diffusion coefficient can lead to significant errors in the estimates of mass transferred to the matrix. Thus, the results of the experiments are necessary for the correct interpretation of field tracer experiments which are used to directly measure the transfer process, and for use in numerical models which are used to simulate this transfer. Preliminary diffusion experiments were conducted on five samples in order to develop a sampling protocol and improve sampling techniques for future experimentation and to provide initial estimates of the aforementioned parameters.

Methods

Each of the samples used for this study was collected and preserved in the field at the time of drilling. The objective was to maintain sample saturation and prevent significant geochemical changes to the rock matrix porewater. In all cases, the samples were collected from the core tube immediately following the extraction of the tube from the drill rod and core barrel. The cores (4.5 cm in diameter) were collected in 10 - 30 cm

lengths and immediately placed in a 1L Nalgene jar containing groundwater. To inhibit bacterial growth, the host groundwater was treated with a 0.03 wt % solution of sodium azide. The containers were then placed in anaerobic gas packs and transferred to an anaerobic chamber, containing a mixture of NO_2 and CO_2 gases, to prevent any further contact with oxygen.

Four samples were collected from 3 different geological units of the Lockport formation (Table 1): one from the Vinemount - Unit 1 (cell 9), two from the Goat Island (cells: 1 and C), and two from the Gasport member (cells:10 and D). A fifth sample was obtained from the Amherstburg formation, which was collected from core obtained at the Bruce Power Nuclear Plant near Kincardine, Ontario.

To construct radial diffusion cells, a 1.25 cm diameter reservoir was drilled through the center of the core samples, parallel to the core axis (Figure 1). The drilling was conducted using a diamond coring bit and water was circulated to keep the core saturated. Each end of the sample was lapped to 90° and then the entire sample was encapsulated using a Teflon sleeve and two stainless steel end caps. One of the end caps contained a sampling port through which samples were extracted from the reservoir. The Teflon coating was heat sealed to minimize leaking or evaporation of the liquid phase. The dimensions of each cell and a brief description are presented in table 1.

Table 1: Description of the diffusion cells

Sample	length (cm)	reservoir volume (mL)	Description
cell 1	8.8	11.5	brown/grey, fine grained dolostone, small vugs (1 - 2 cm diameter), discontinuous, black bituminus layer (~1 mm thick).
cell 9	11.48	14.7	brown/grey, fine grained, massive dolostone, contains some gypsum (1%).
cell 10	6.85	8.8	light grey, medium grained dolostone, highly fossilized, contains some gypsum nodules.
cell D	8.81	11.9	light grey, medium grained, dolostone, fossilized, large amounts of gypsum infilling features (~40 %).
cell OH3a	6.48	9.0	light brown, fine grained, limestone with mm scale bedding features.

To initiate the forward diffusion experiments, tracer was introduced into the center of the reservoir and agitated to achieve a complete mix. The subsequent decrease in tracer concentration in the reservoir was monitored by periodic sampling. It was assumed that free water diffusion resulted in uniform concentrations in the reservoir. For comparative purposes, a control cell was constructed using a stainless steel core.

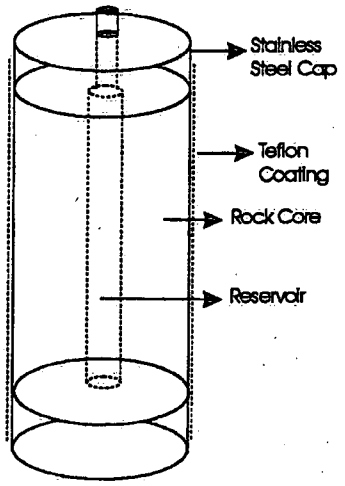

Figure 1: Schematic of the radial diffusion cell

The initial tracer concentrations were 50 mg/L solution of bromine (Br^-) in de-ionized water, in the form of potassium bromide (KBr), and a 500 µg/L solution of Lissamine FF (a conservative organic dye) in deionized water. Only tracers considered to be conservative were chosen so as to eliminate other potential sources of mass loss, such as decay and adsorption. Previous experiments (Shackelford et al., 1989) have shown that Br^- will behave conservatively in most soils and rocks. Although some organic dyes are known to interact with geological materials (Smart and Laidlaw, 1977), Lissamine was observed to behave conservatively in field scale tracer experiments conducted in rock similar to that used for the present experiments (Novakowski and Lapcevic, 1994).

Following the initiation of the experiment, the reservoir was periodically measured for tracer concentration. A 30 to 40 day period was required for the experiments to reach equilibrium (concentration within the reservoir is equal to the concentration in the rock). For each Br^- sample obtained, exactly 0.15 mL was abstracted from the reservoir and

replaced with deionized water. Lissamine analyses is non-destructive and sample volumes abstracted were immediately returned to the reservoir following analyses. Lissamine was analyzed using a Turner fluorometer, and concentrations of Br^- were determined using a Waters WISP 712 ion chromatograph.

Once the forward diffusion experiments were completed, reverse diffusion experiments were conducted using the same cells. These experiments were accomplished by replacing the reservoir fluid with deionized water and then monitoring the Lissamine and Br^- as they diffused back into the reservoir in a fashion following that of the forward diffusion experiments. The experiments were conducted to determine if the process of reverse diffusion is the same as that of diffusion from the reservoir into the matrix. In addition, in order to further asses the conservative nature of the tracers, the diffusion of Cl^- from the rock matrix into the reservoir was also monitored.

The weight of the cells was monitored over the entire experimental period. On basis of these measurements, the seals of the cells were adjusted to reduce or eliminate evaporative water loss. Cells 1, D and OH3a showed a maximum water loss in the forward diffusion experiments of 1.69 mL, 1.07 mL and 1.75 mL respectively, whereas a minimum water loss of 0.38 mL and 0.53 mL was observed in cells 9 and 10. Water loss during the reverse diffusion experiments was much less with the maximum water loss being 0.8 mL in cell 1.

Gravimetric porosity (total porosity) measurements of the rock cores were conducted on all cells after the diffusion experiments were completed. Inorganic chemical analyses of the porewater of each diffusion cell was determined at the National Laboratory for Environmental Testing, Burlington, Ontario.

To display the results of the diffusion experiments, the concentrations of each tracer were plotted relative to the initial concentrations (C_o) against time. The relative tracer concentrations were modeled using RADIF2 (Novakowski and van der Kamp, 1996) to obtain estimates of the effective diffusion coefficient and effective porosity. RADIF2 is a diffusion model that accounts for radial diffusion, mass balance in the reservoir, linear adsorption, decay and periodic volume extraction of reservoir samples.

Results and Discussion

Visual comparison of the curves produced by forward diffusion, indicates that Lissamine, compared to Br^-, interacted significantly with the rock material (see Experimental Data, Appendix A). Lissamine retardation is most pronounced in cells 1 and 9 as illustrated by the lower final concentration of Lissamine relative to Br^-. Results from cell 10 showed evidence of only slight retardation. To illustrate this, the model simulations were conducted using a retardation factor of one. Resulting values of the effective porosity are significantly greater than the total porosity and are indicative of retardation. Model simulated results show effective porosities for the cells were as high as 49% which is equivalent to a Lissamine retardation of 4 (Table 2). Thus, Lissamine is observed not to behave conservatively in cells 1, 9 and 10 for the case of forward diffusion from the reservoir to the matrix. Lissamine retardation was less pronounced in cell D (see Experimental Data, Appendix A). Assuming a retardation of one, the effective porosity calculated for cell D, using the model RADIF2 and Lissamine reservoir concentrations, is 4%, which is only slightly larger than the effective porosity of 2.5% determined using Br^- concentrations (Table 2, Figure 2).

Table 2: Total and model-predicted porosity of the rock cores

Cell	Total Porosity (gravimetric) (%)	Forward Diffusion Lissamine (%)	Forward Diffusion Bromine (%)	Reverse Diffusion Lissamine (%)	Reverse Diffusion Bromine (%)	Lissamine Retardation (forward)*	Lissamine Retardation (reverse)*
1	8.2	49	11	9	11	3.8	1.0
9	10.2	47	8	9	10	4.1	1.0
10	15.7	22	11	15.4	17.9	1.8	1.0
D	7.5	4	2.5	1.2	4.6	1.2	1.0
OH 3a	20.0	11	12	-	-	1.0	-

* Where estimated effective porosity using Br^- concentrations are greater than those using Lissamine, retardation for Lissamine is considered equal to 1.0

Explanations for the retardation of Lissamine are not straight forward. For example, Smart and Laidlaw (1977) suggest that many dyes degrade as a result of photochemical decay with time. However, during the experiment, the reservoir is kept dark. In addition, previous studies show that photochemical decay of Lissamine does not occur within the time frame used in these experiments (Bickerton, *personal communication*, NWRI, 1997). The water quality used in the experiments may also influence Lissamine fluorescence. Smart and Laidlaw (1977) have determined that variations in pH values between 4 and 10 result in no significant changes in the fluorescence of Lissamine. However, the authors suggest that decay may occur in other organic dyes having long periods of contact (over 300 hours) with saline water (0.01 - 1.0 Molar concentration of NaCl).

The chemistry of the groundwater used in the diffusion cells gives an indication of the water quality before the introduction of the tracer solution (Table 3). The inorganic geochemical nature of all groundwaters are similar. Thus, it is unlikely that porewater salinity is the cause of the observed mass loss in Lissamine since Lissamine retardation is observed in some cells and not others.

Table 3: Porewater chemistry in diffusion cells

	Cell 1	Cell 9	Cell 10	Cell D	OH3a
Ca (mg/L)	301	292	287	521	68.5
Mg (mg/L)	96.1	108	108	222	39.5
Na (mg/L)	43.9	159	157	168	121
K (mg/L)	4.0	5.9	5.5	6.5	2.3
Cl (mg/L)	37.6	145	145	140	114
SO_4 (mg/L)	832	1100	1160	2360	242

Lissamine loss may also depend on the surface area of the porous media. Smart and Laidlaw (1977) provide evidence that Lissamine will weakly sorb to organic materials. The sorption mechanism was assumed to be related to the natural organic content of the porous media. After detailed investigations of organic content, it is now determined that the organic fraction of the majority of the rock matrix is negligible with some localized bands of material having higher organic content (stylolites). This was confirmed by conducting batch experiments using the compound trichloroethelyene (TCE), which has a

higher affinity for sorption on native organic material. No reactions were observed with samples having an absence of stylolitic material. Although some of the samples (cell 1) used in the present experiment have stylolitic banding, the volume of material cannot account for the magnitudes of retardation observed in the forward diffusion experiments.

In cell OH3a, both Lissamine and Br^- tracers were observed to behave as near-ideal tracers. Bromine, an ion smaller in size than the compound Lissamine, tends to diffuse at a more rapid rate into the porous media (see Experimental Data, Appendix A). Effective porosities for cell OH3a determined using RADIF2 are 11% and 12% for Lissamine and Br^- concentrations respectively (Table 2). However, it is important to note, that the diffusion experiment using cell OH3a was conducted under conditions slightly different than the others. The cell had been constructed one year prior to the others and initial concentration of Br^- tracer in the cell was 1000 ppm. Samples collected were then diluted one hundred fold in order to facilitate analyses with the ion chromatograph. Lissamine in this diffusion cell was not retarded, suggesting that this rock matrix has little tendency to sorb Lissamine.

Effective porosities predicted from both Lissamine and Br^- tracers in the reverse diffusion experiments are comparable (Table 2, Figures 3 and 4). This suggests that in the reverse diffusion experiments, Lissamine behaves conservatively. Thus, if sorption occurs, much of the Lissamine sorbed is irreversible. In general, sorption of organic dyes onto sediment surfaces has been suggested to be mainly irreversible (Smart and Laidlaw, 1977).

The effective porosities predicted using Br^-, in the forward radial diffusion and the reverse radial diffusion, compare favorably, with the exception of cell 10 (Table 2). The effective porosity predicted using Lissamine and Br^- tracers in the reverse radial diffusion cell experiments, with the exception of cell D, are also comparable (Table 2). The three independent measurements suggest that the radial diffusion experiments reasonably predict the effective porosity of the rock matrices.

Effective porosities determined by modeling the Br^- tracer for the forward and reverse radial diffusion experiments and by modeling Lissamine for the reverse diffusion experiments are similar to those determined using gravimetric techniques (Table 2). In most cases, it is anticipated that the effective porosity will be slightly less that total porosity, since the diffusive flux of tracer mass is unable to enter dead end or inaccessible

pores. For cells 9, D and OH3a, model simulated porosity is less than that of total porosity (Table 2).

Gravimetrically determined porosity for these rocks may slightly overestimate actual total porosity. Many of these geological units contain 3 to 7 % gypsum (Bickerton, 1997) which upon heating will loose most of the hydrating water bound loosely to the mineral. For example, theoretical calculations using the chemical structure of the mineral and the amount of gypsum in the matrix, shows that the de-hydration of gypsum would lead to an overestimate of total porosity by as much as 1.5%.

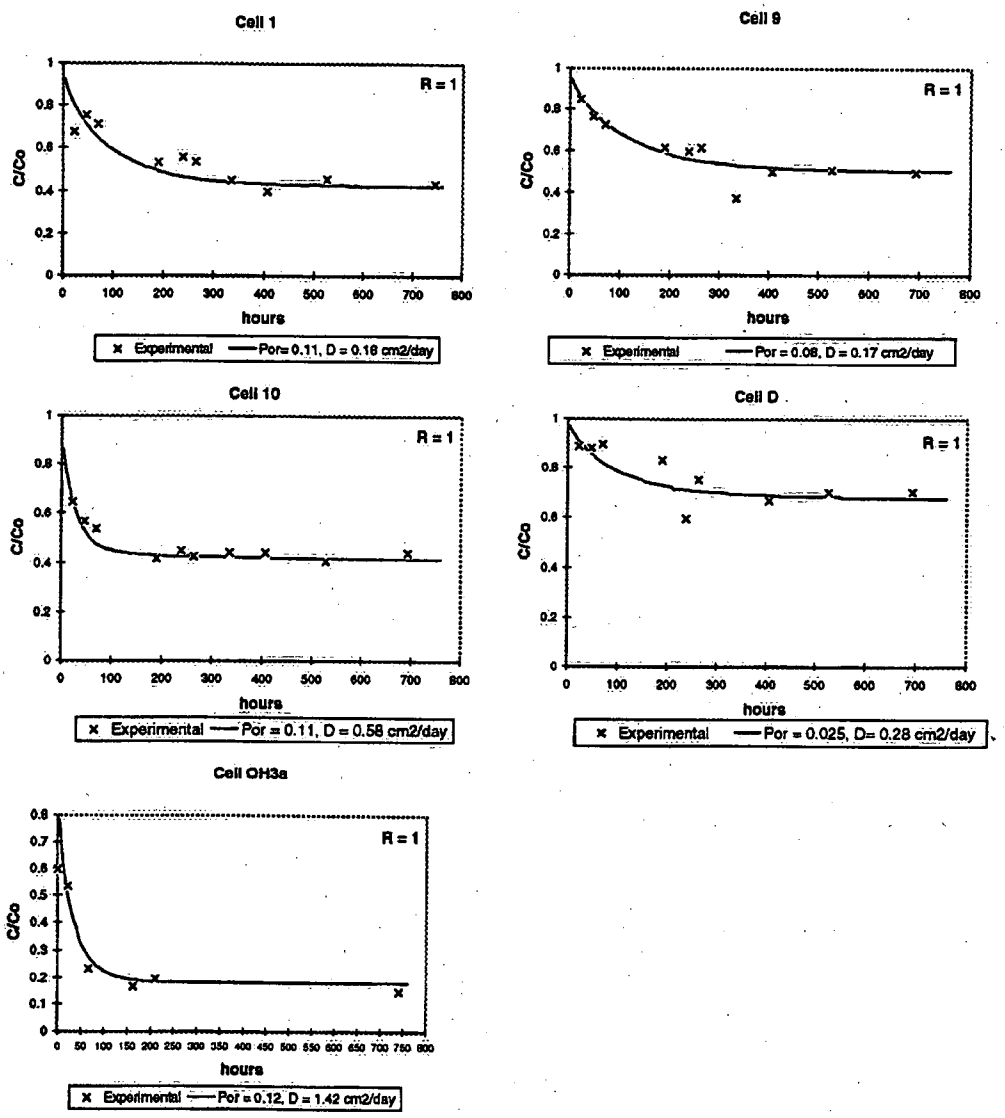

Figure 2: Bromine reservoir concentration with time in the forward radial diffusion experiments and modeled results

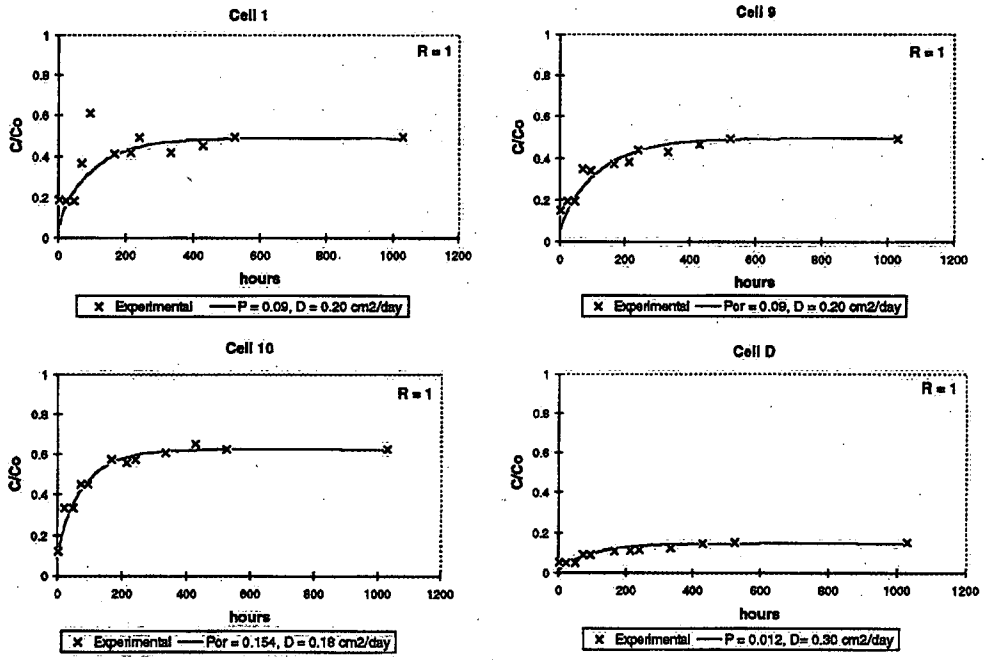

Figure 3: Lissamine reservoir concentration in reverse radial diffusion cell experiments with modeled results

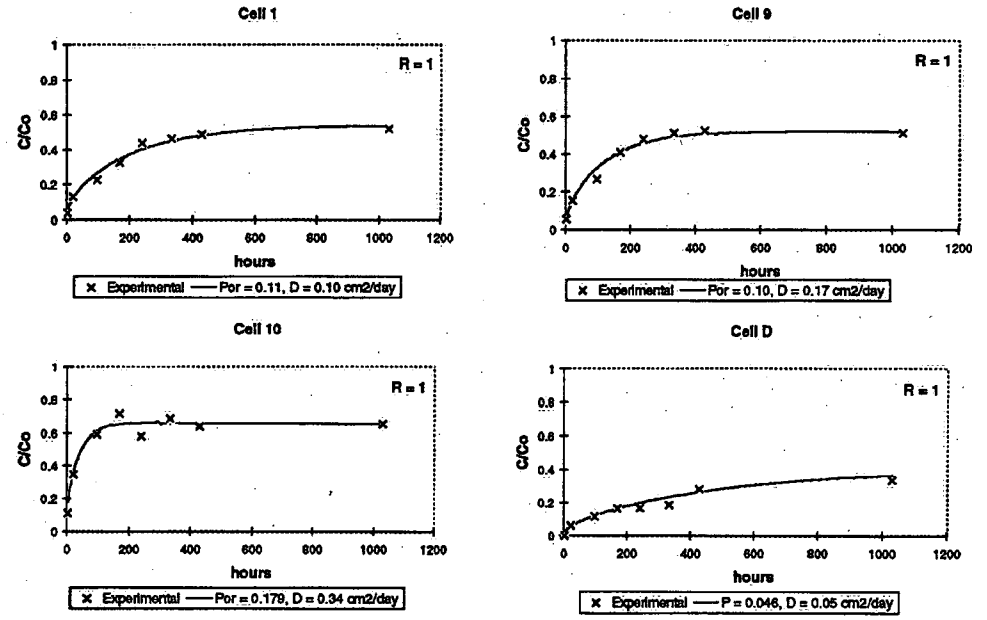

Figure 4: Bromine reservoir concentration in reverse radial diffusion experiments and modeled results

A comparison of effective porosity determined by model simulation, with that calculated using steady-state tracer concentrations, was also conducted. The effective porosity may be calculated using steady-state tracer concentrations values and the following equation (Novakowski and van der Kamp, 1996):

$$\beta_1 = V_r/R\theta_e\gamma_r r_r$$

where, β_1 is the dimensionless mixing coefficient, V_r is the reservoir volume, R is the dimensionless retardation factor (1.0 for a conservative tracer), θ_e is the effective porosity, γ_r is the cross-sectional area through which diffusion occurs, and r_r is the radius of the reservoir.

Table 4 shows the comparison between the modeled and steady-state estimates. This interpretation is highly dependent on the last few points in the relative concentration curves (Figures 3 and 4). If there is error in the sample analysis for these points, then this propagates the error through to the steady-state calculation. The estimates obtained from the forward diffusion experiments conducted using Lissamine were discarded because of the uncertainty regarding retardation. The calculated effective porosity, from the reverse radial diffusion experiments for cell 10, deviates considerably from that predicted by the model, for both Lissamine and Br^- tracers in the reverse radial diffusion experiments. This is likely due to significant amounts of tracer mass loss during the abstraction of samples for Br^- analyses. In cell D, the reservoir was depleted by 14% of its original volume compared to only 8 to 10% in all other cells. In all other cases, the calculated effective-porosity from steady-state concentrations are similar to that predicted by the model (Table 4).

Table 4: Calculated effective porosity using steady-state tracer concentrations and RADIF2

	Forward Diffusion Bromine		Reverse Diffusion Lissamine		Reverse Diffusion Bromine		
Cell	Steady State θe	Modeled θe	Steady State θe	Modeled θe	Steady State θe	Modeled θe	Total Porosity
1	9.4	11	10.4	9.0	10.9	11	8.2
9	7.5	8	10.0	9.0	11.1	10.0	10.2
10	9.4	11	23.3	15.4	28.7	17.9	15.7
D	1.7	2.5	1.4	1.2	3.5	4.6	17.5
OH3a	10.3	12	-	-	-	-	20.0

The effective diffusion coefficient is estimated for the diffusion process by the amount of curvature in the concentration versus time curves shown in Figures 2, 3 and 4 (Novakowski and van der Kamp, 1996). Accurate values of the effective-diffusion coefficients are necessary for the determination of a geometric factor using the equation:

$$D^* = \tau D_o$$

where D^* is the effective diffusion coefficient, τ is the geometric factor ($0<\tau<1$), and D_o is the free-water diffusion coefficient for the individual ion. D_o for Lissamine is estimated to be 4.5×10^{-9} m^2/s (Novakowski and van der Kamp, 1996) by comparison to a similar compound, Uranine (Skagius and Neretnieks, 1986) and for Br^- is 2.08×10^{-9} m^2/s (Lide, 1992). Geometric factors determined from Br^- concentrations, for both forward and reverse diffusion, are similar for cells 1 and 9 (Table 5). Significant differences in the geometric factor are observed in cells 10 and D. Similar deviations in the geometric factor determined from experiments in clay soils were observed by Shackelford et al. (1989, Table 6) using Br^- and Cl^- as tracers. Barone (1995) conducted several diffusion experiments using a Cl^- tracer on samples from the Eramosa unit in the same geological formation and found the geometric factor to range from 0.047 to 0.080 (Table 6).

Table 5: Effective diffusion coefficients and geometric factors for the diffusion cells and reverse diffusion cells

Cell	D^* (Br^-) Forward Diffusion (m^2/s)	τ	D^* (Lissamine) Reverse Diffusion (m^2/s)	τ	D^* (Br^-) Reverse Diffusion (m^2/s)	τ
1	2.08×10^{-10}	0.10	2.31×10^{-10}	0.51	1.16×10^{-10}	0.06
9	1.97×10^{-10}	0.09	2.31×10^{-10}	0.51	1.97×10^{-10}	0.09
10	6.71×10^{-10}	0.32	2.08×10^{-10}	0.46	3.94×10^{-10}	0.19
D	3.24×10^{-10}	0.16	3.47×10^{-10}	0.77	5.79×10^{-11}	0.03
OH3a	1.64×10^{-10}	0.79	-	-	-	-

In all cases, the geometric factors determined from Lissamine concentrations are very high and do not agree with those values determined using Br^-. Note that the differences observed in the geometric factors in cell D are likely due to low original

concentrations of tracer in the reverse diffusion experiments which have resulted in error in analytical measurements.

Table 6: Comparison of differing geometric factors determined in diffusion experiments of various porous media by other researchers

τ This Study Dolostone samples		τ Barone, 1995 Dolostone samples	τ Shackleford et al. (1986) Clay samples	
Br^-(forward)	**Br^- (reverse)**	**Cl^-**	**Br^-**	**Cl^-**
0.10	0.10	0.043	0.009	0.163
0.09	0.09	0.047	0.266	0.211
0.19	0.32	0.080	0.034	0.07
0.03	0.16	0.060	0.031	0.067
		0.063		
		0.073		

In three of four reverse diffusion experiments, the effective diffusion coefficient is observed to be smaller for Br^- than for Lissamine (Table 5). This is contrary to what would be expected based on the size of the tracer compound. Since Br^- has a smaller molecular weight and size, the rate at which diffusion will occur into the rock matrix with a porosity dominated by micro-cracks, should be greater than that for Lissamine. As this is not the case, there is uncertainty with respect to the meaning of the estimate for the geometric factor. It was observed, during analytical analyses for Br^-, that sulphate ion concentrations (and therefore salinity) were increasing steadily within the reservoir. This is most likely a result of the dissolution of gypsum bearing minerals. The change in water chemistry resulted in less accurate analytical measurements using ion chromatography. The increase in reservoir salinity over a long period of time may also affect Lissamine fluorescence (Smart and Laidlaw, 1977). This inaccuracy will greatly hinder accurate estimates in the effective diffusion coefficient. Since a precise estimate of this parameter is necessary for the interpretation of field tracer experiments and for the use in predictive numerical models, further investigation of this issue will be conducted.

Conclusions and Recommendations

The results of the study indicate that the radial diffusion method is suitable for determination of the diffusional transport properties in carbonate rock. The effective porosities determined for the dolostone samples range from 1% to 18% which agrees favorably with the gravimetric porosity measurements. In 3 of 5 forward radial diffusion experiments, the compound Lissamine was observed to behave non-conservatively. Yet, in the reverse diffusion experiments, Lissamine displays little, if any, retardation. Thus use of Lissamine as a conservative tracer is warranted only when an additional tracer, such as Br^-, is used.

The determination of the effective diffusion coefficients are imprecise and subject to many interferences. The effective diffusion coefficients for the same rock matrix can vary (in some cases, by almost an order of magnitude) depending on the tracer (Lissamine or Br^-) used. It was also observed that the effective diffusion coefficient for Lissamine was greater than that of Br^-, contrary to expectations based on the molecular mass of the two tracers. This results in inaccuracies in the determination of the geometric factor. An accurate estimate of this parameter is necessary for the interpretation of field tracer experiments and predictive models. However, the preliminary results show that, should analytical measurements be improved, Br^- is a satisfactory tracer for determination of both effective porosity and the geometric factor, as these were found to be similar in both the forward and reverse radial diffusion experiments.

To reduce analytical error, future experiments will be conducted with a solvent that is in close equilibrium with the porous media. This will help prevent possible dissolution of mineral phases. Also, tracer concentrations will be established at an initially high concentration and then diluted during sampling as a means to reduce analytical interference effects from high total dissolved ion (esp. sulphate) concentrations.

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Appendix A
Experimental Data

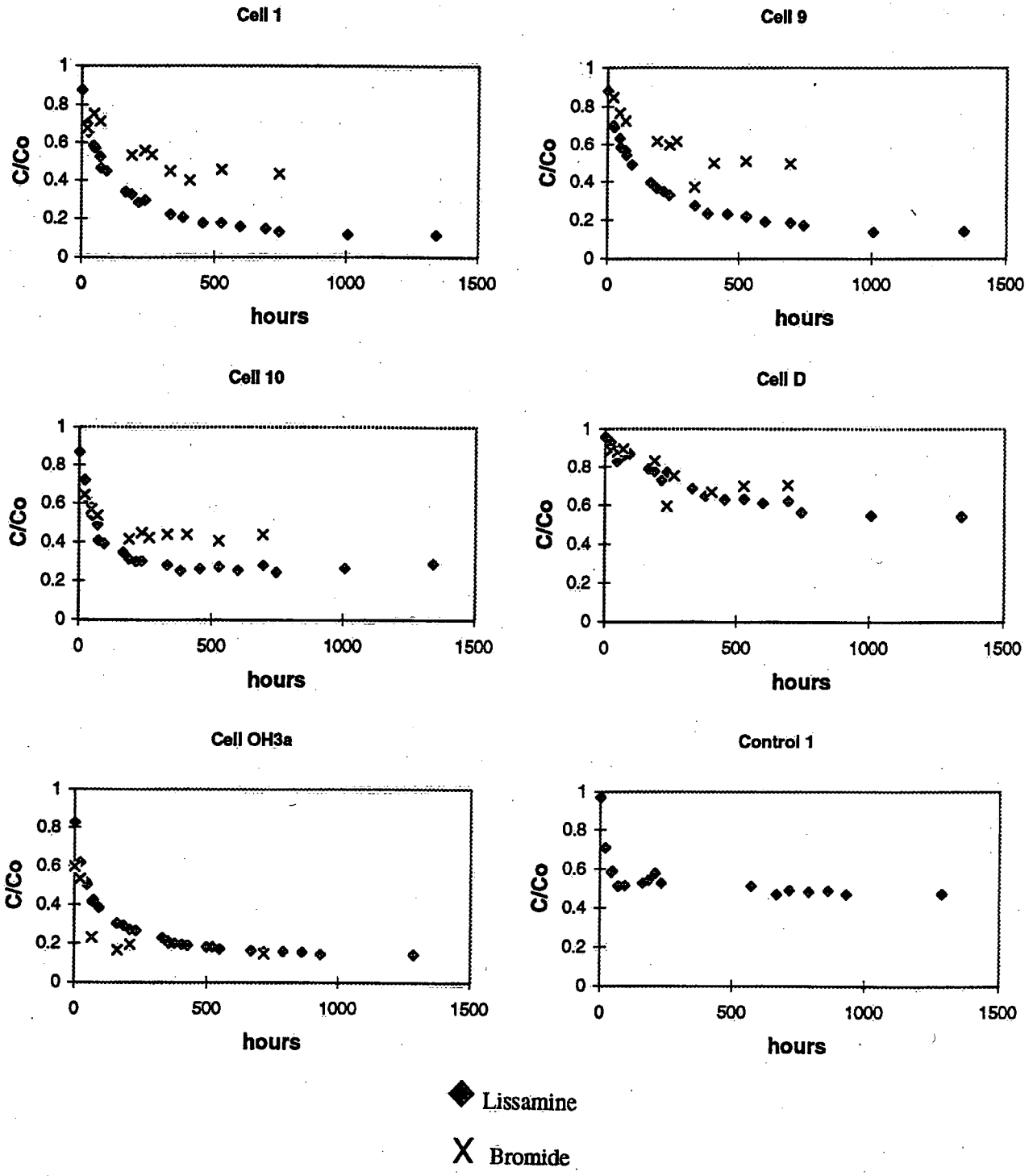

Figure A-1. Experimental data for forward radial diffusion cells

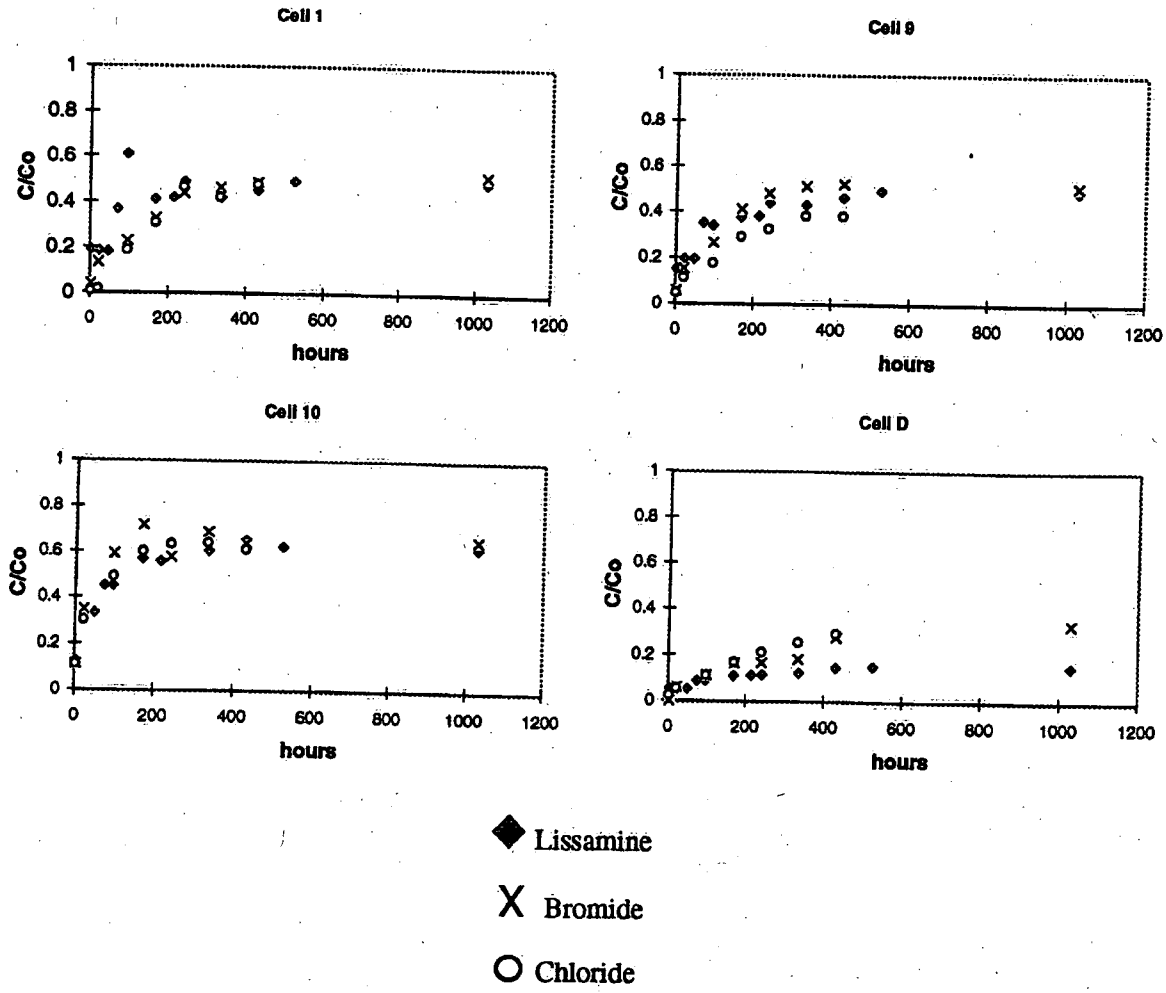

Figure A-2: Experimental data for reverse radial diffusion cells

Table A-1: Experimental data for forward radial diffusion experiments–lissamine

Cell 1		cell 9		cell 10		cell D		OH3a		Control	
Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co
1.50	0.88	1.50	0.88	1.50	0.87	1.50	0.96	1.47	0.83	2.13	0.97
22.67	0.70	22.72	0.70	22.62	0.72	22.70	0.93	22.60	0.62	21.05	0.71
26.93	0.66	27.00	0.69	26.92	0.63	27.00	0.88	44.45	0.52	44.58	0.58
46.75	0.58	46.85	0.63	46.85	0.58	46.92	0.83	47.25	0.51	47.47	0.59
50.88	0.57	50.97	0.58	50.88	0.54	50.93	0.88	69.08	0.42	69.20	0.51
70.70	0.52	70.77	0.57	70.68	0.49	70.67	0.88	72.63	0.42	72.72	0.51
73.92	0.46	74.00	0.54	73.88	0.41	73.78	0.86	94.50	0.38	95.23	0.52
95.03	0.45	94.95	0.49	94.83	0.39	94.75	0.87	163.00	0.30	163.80	0.53
167.58	0.34	167.50	0.39	167.33	0.35	167.27	0.79	187.63	0.29	187.73	0.54
190.88	0.33	190.83	0.37	190.72	0.31	190.65	0.78	211.50	0.27	211.63	0.58
217.67	0.29	217.57	0.35	217.37	0.30	217.38	0.73	235.55	0.26	235.67	0.53
239.83	0.29	239.75	0.33	239.55	0.30	239.53	0.77	333.76	0.23	572.97	0.51
335.53	0.22	335.42	0.27	335.30	0.28	335.20	0.69	355.65	0.21	668.68	0.47
382.58	0.21	384.50	0.23	384.38	0.25	384.28	0.65	359.01	0.20	715.80	0.49
455.82	0.18	457.68	0.23	457.57	0.26	457.50	0.63	379.90	0.20	788.97	0.49
527.75	0.18	529.63	0.22	529.50	0.27	529.45	0.63	406.97	0.19	860.97	0.49
598.30	0.16	600.23	0.19	600.08	0.26	600.03	0.61	427.70	0.19	931.48	0.47
694.00	0.15	695.92	0.18	695.78	0.28	695.70	0.62	500.38	0.18	1287.24	0.47
746.02	0.13	745.92	0.17	745.78	0.25	745.87	0.56	523.80	0.18		
1006.62	0.12	1006.52	0.14	1006.38	0.27	1006.32	0.55	550.58	0.17		
1343.35	0.11	1343.38	0.14	1343.41	0.29	1343.43	0.54	669.30	0.16		
								716.41	0.16		
								789.60	0.16		
								861.65	0.16		
								932.10	0.14		
								1287.20	0.14		

Table A-2: Experimental data for forward radial diffusion experiments–Bromide

cell 1		cell 9		cell 10		cell D		OH3a	
Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co
22.58	0.68	22.75	0.85	22.75	0.64	22.75	0.89	1.47	0.60
47.08	0.75	47.08	0.76	47.18	0.57	47.18	0.88	22.60	0.53
70.62	0.71	70.62	0.72	70.62	0.54	70.62	0.90	66.32	0.23
190.50	0.53	190.50	0.62	190.50	0.42	190.50	0.83	163.65	0.17
239.42	0.56	239.50	0.60	239.53	0.45	239.58	0.60	211.72	0.19
264.75	0.54	264.75	0.62	264.75	0.42	264.75	0.75	740.80	0.15
335.20	0.45	335.20	0.37	335.25	0.44	407.42	0.67		
407.15	0.40	407.33	0.50	407.42	0.44	527.50	0.70		
527.23	0.46	527.33	0.51	527.50	0.41	693.83	0.70		
693.57	0.44	693.67	0.50	693.83	0.44				

Table A-3: Experimental data for reverse radial diffusion experiments--lissamine

Cell 1		cell 9		cell 10		cell D	
Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co
3.27	0.19	3.30	0.15	3.38	0.12	3.43	0.05
23.68	0.18	23.68	0.20	23.65	0.33	23.70	0.05
47.52	0.18	47.52	0.20	50.35	0.33	50.38	0.05
71.25	0.37	71.25	0.35	73.38	0.45	74.42	0.09
95.93	0.61	96.02	0.34	96.07	0.45	96.13	0.09
168.18	0.41	168.23	0.37	168.28	0.57	168.33	0.11
215.62	0.42	215.67	0.38	215.72	0.56	215.77	0.11
242.57	0.49	242.62	0.44	242.67	0.57	242.72	0.11
336.10	0.42	336.15	0.43	336.20	0.61	336.25	0.12
430.45	0.45	430.50	0.46	430.57	0.65	430.62	0.15
526.15	0.49	526.20	0.49	526.25	0.62	526.30	0.15
1031.40	0.49	1031.45	0.49	1031.50	0.62	1031.55	0.15
1200.50	0.37	1200.55	0.40	1200.60	0.53	1200.65	0.18
1536.23	0.36	1536.28	0.33	1536.33	0.46	1536.38	0.17

Table A-4: Experimental data for reverse radial diffusion cells -- Bromide.

Cell 1		cell 9		cell 10		cell D	
Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co	Time (hr)	C/Co
3.17	0.04	3.17	0.06	3.17	0.11	3.17	0.00
22.67	0.13	22.67	0.15	22.67	0.35	22.67	0.06
98.22	0.23	98.22	0.26	98.22	0.59	98.22	0.11
169.72	0.33	169.72	0.41	169.72	0.72	169.72	0.16
241.55	0.44	241.55	0.48	241.55	0.58	241.55	0.17
335.13	0.46	335.13	0.51	335.13	0.69	335.13	0.18
430.38	0.49	430.38	0.52	430.38	0.64	430.38	0.28
1031.80	0.52	1031.80	0.51	1031.80	0.66	1031.80	0.34

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