

# Hydrogen Release Compound **HRC**<sup>®</sup>

## Distribution of HRC in the Aquifer

### General Background

The placement of HRC deposition or injection points is a function of how HRC distributes in the aquifer. Molecular transport in a flow field is well defined in the engineering literature, and these Laws of Mass Transport are applied to the movement of substrate and/or contaminant molecules in an aquifer. Specifically, we would like to apply these laws to the movement of the substrate lactic acid and all its breakdown products, including hydrogen. The Laws of Mass Transport are a compellation and include Darcy's Law (which describes advective flow) and Fick's Law (which describes diffusion). The entire mass transport issue is conveniently presented in a single second order differential equation, generally called the Advection-Dispersion Equation, which ties all of the fundamental processes together, specifically advection, dispersion, diffusion, retardation and consumption.

Analytical solutions to the Advection-Dispersion Equation (Segol, 1994 – specifically Cleary-Ungs) were used early in the development of HRC to gain a basic theoretical understanding of its potential movement in an aquifer. For further details on the Advection-Dispersion Equation see a basic hydrogeology text such as Applied Hydrogeology by Fetter (1994). A more advanced discussion can be found in Contaminant Hydrogeology (1992), also by Fetter, or Ground Water Models (1990), a collective effort available from the National Research Council.

The use of models was part of a basic “sensitivity analysis” to gauge the relative importance of different parameters (advection, dispersion, diffusion, retardation and consumption) in the HRC distribution process. However, the need for this kind of analysis has now been superceded by actual laboratory and field data sets. As any one familiar with models realizes, the experimental data is worth more than the theoretical projections. While experimental data can be used to calibrate theoretical treatments and make them consistently more accurate, the cost and time that would be involved to gather the key variables at an actual site with enough accuracy is often prohibitive. Also, collecting the data with sufficient accuracy may be a difficult to impossible task.

Under these circumstances, what can we then do to understand the process?

First, as discussed, we have field evidence and this will be presented momentarily. Aside from that there is one theoretical excursion worthy of exploration and that concerns the effects of pure diffusion on the movement of HRC in the aquifer. This is an attractive avenue because it gives a concept of molecular movement independent of hydrogeological and biological conditions. It is a first approximation that grounds us in dealing with the more complex features of an advanced argument.

**Theoretical Considerations**

As discussed, diffusion is presented as a special case because it is fairly straightforward and manageable and gives an indication of the expected movement in an aquifer under ideal conditions. The important breakdown products of HRC (e.g., lactic acid, pyruvic acid and hydrogen) all extinct logarithmically in accordance with the equation for simple diffusion from a point source. This is the simplest case possible (point source in one dimension). It will be followed with experimentally derived values that will be applied to the more complex case of diffusion from a radial system (areal flux in one dimension). This is representative of a column of HRC dissolving in an enclosed tube perpendicular o to the length.

Returning to the simple case to illustrate a few fundamental concepts we have

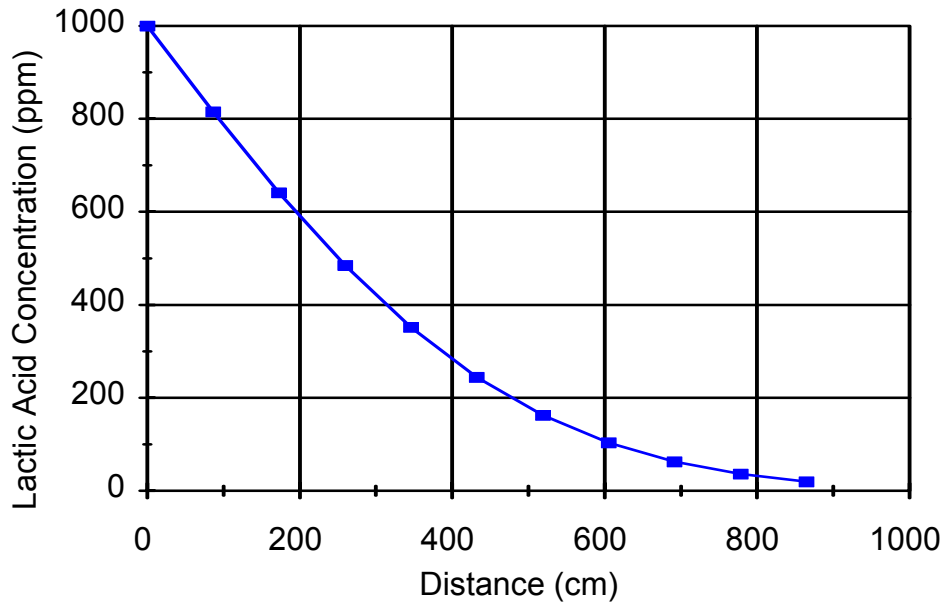
$$C(x,t) = C_0 [ \text{erf } c(x / 2*(D*t)^{0.5}) ]$$

Where C is the final concentration at distance x in cm. C<sub>0</sub> is the initial concentration, erf c is the complementary error function, D is the diffusion coefficient in cm<sup>2</sup>/sec and t is time in seconds.

A case is presented below for diffusion from a point source and is graphically represented in Figure 1. The initial concentration of lactic acid is fixed at 1,000 ppm, which is a conservative concentration for the zone of solubilized material at the interface of the HRC solids and the aquifer. In the example below, it is very important to also realize that this result is expressed in a “conservative background” with no biological or chemical consumption and no aquifer matrix tortuosity. Actual migration patterns will invariably be less than these theoretical maxima.

**Table 1. Lactic Acid Diffusion from a Point Source**

		<u>Concentration</u>	<u>Distance</u>	<u>Distance</u>
		<u>ppm</u>	<u>rad. in cm</u>	<u>rad. in ft</u>
		1000	0	0
		816	87	3
Temperature in °C	= 25	642	173	6
Time in Hours	= 8729 (1 Yr)	485	260	9
Maximum Distance in cm	= 865	352	346	11
Initial Lactic Acid Concentration	= 1,000	245	433	14
		163	519	17
		103	606	20
		63	692	23
		36	779	26
		20	865	28



**Figure 1. Diffusion of Lactic Acid from a Point Source over 1 Year.**

Results show that to achieve a lactic acid concentration of 20 ppm, provisionally enough to treat about 1 ppm of chlorinated hydrocarbon, sources can be as far apart as 56 feet as two 28 foot radii converge between application points. Again, this is in a non-consumptive environment with no path length tortuosity and in a one dimensional diffusion situation. As we will see the more exact result, which is connected to an actual experimental measurement of the diffusion coefficient and involves tortuosity and consumption, values are presented that are about 40 percent of those presented in the above analysis.

The point of this simple exercise is to emphasize that “diffusion matters”. Essentially, because the driving force is substantial at 1,000 ppm (versus, say, oxygen at 25 ppm), we can document a fairly vigorous movement of lactic acid and its breakdown products. Diffusion is actually a major driving force in low to moderate flow environments (noting that 0.1 ft/day = 36.5 ft/yr). It is also a valuable force in actually achieving contact between contaminant and substrate, because diffusion is an excellent way to distribute materials in the sub-surface relative to the injection of liquids – an activity that creates preferential flow paths and mixing problems.

### **Laboratory Results**

The next level to examine is laboratory performance. In this instance we performed an ASV test. For further details about the ASV macrocosm test please refer to TB 2.4.3; an illustration of this experimental system is provided in Figure 2.



**Figure 2. Aquifer Simulation Vessel (ASV)**

The purpose of this ASV study was to accomplish two goals. The first was to determine if the viscosity of the HRC affects the longevity of the product. A high viscosity “implant quality” GPL (approximately 200,000 cP) and the injectable HRC (20,000 cP) were compared. The second goal was to determine the diffusion rate for the two different materials in different compositions of soil. Details on the product viscosity issues and the longevity results are provided in TB 2.8.1.

In establishing the test, a soil sample with an active population of TCE degraders is homogenized by manual stirring and the soil is packed into a series of 6.0-foot long tubes with an internal diameter of 5.75 in. The tube therefore has a volume of 2,025 in<sup>3</sup>, and approximately 30% of that volume is pore space. A solution of 25 ppm of TCE was passed through the ASVs to make the concentration of TCE constant throughout. The pumps, which normally are used in the ASV for continuous flow experiments, were turned off and 15 g of HRC was loaded into the front end of each of tube. The ASVs were analyzed monthly until a reasonable diffusion rate was determined, and the experiment was continued to gather HRC longevity data.

Four ASV tubes were set up. Two were packed with 10% loam and 90% clay with 25 ppm of TCE. One of the ASVs was injected with HRC (20,000 cP) and the other with high viscosity GPL (200,000 cP). The other two ASVs were packed with 10% loam and 90% sand with 25 ppm of TCE and each received one of the two different viscosity materials. The flow of TCE solution was stopped once the HRC was injected and the movement of HRC and its by-products was left to diffusion.

The four ASVs were analyzed on day 3 after injection to see if there was any lactic acid present at the six-inch port in order to determine diffusion rates. Lactic acid was present and thus the 12-inch port was analyzed and used to determine the diffusion rates. The results are presented in Table 2.

**Table 2. Diffusion in an ASV.**

ASV Composition	Rate	GPL-HRC Viscosity
90% Sand-10% Loam	3 in/day	196,000 Cp
90% Clay-10% Loam	4 in/day	196,500 Cp
90% Sand-10% Loam	4 in/day	21,500 Cp
90% Clay-10% Loam	4 in/day	21,500 Cp

The lower viscosity material releases lactic acid at higher rate than the higher viscosity material (Table 3). The major difference between the low viscosity and high viscosity is the amount of lactic acid that diffuses out to a given location with time. As discussed in TB 2.8.1, all other conditions being equal, product viscosity combined with the nature of microbial activity in the aquifer are the ultimate key determinants of product degradation rates. This is essentially a surface area argument. The thinner the material the more it will spread out and be exposed to general chemical and biological degradation. Consequently, the low viscosity material can generate larger concentrations at greater distances from the source, but it will be consumed more readily.

Pyruvic acid is a breakdown product for lactic acid, on the way to acetic acid; a mole of hydrogen is produced at each step. For further details see TB 1.1.3. In Tables 3 through 6, the low viscosity material is already starting to convert to acetic acid, while the higher viscosity product does not have any acetic acid present and is still releasing lactic acid.

The major difference between the low viscosity (20,000 cP) and high viscosity (200,000 cP) products is the amount that diffuses out to a given location with time. This is exactly what is expected. Because bacteria metabolize the low viscosity material more quickly, the concentrations seen at various distances are larger. Of course, the “source” concentration will be used up sooner so that the higher concentrations of lactic acid are offset by the time the lactic acid will be present.

In both cases substantial concentrations of lactic acid (10 – 90 ppm) are seen 1 ft from the source in three days. By day 6, significant concentrations of lactic acid (14-132 ppm) were seen at 2 ft from the source. The concentrations of the low viscosity material are much higher, as would be expected.

**Table 3. Organic Acid Data for ASV #1-90% Sand-10% Loam-High Viscosity**

Days	Lactic Acid Results (mg/L)				Pyruvic Acid Results (mg/L)				Acetic Acid Results (mg/L)			
	3	6	36	66	3	6	36	66	3	6	36	66
1.0 ft	10.6				0				0			
1.5 ft		2.12				0				0		
2.0 ft			2.74	1.68			0.13	0.07			0	0
2.5 ft												

**Table 4. Organic Acid Data for ASV #4-90% Clay-10% Loam-High Viscosity**

Days	Lactic Acid Results (mg/L)				Pyruvic Acid Results (mg/L)				Acetic Acid Results (mg/L)			
	3	6	36	66	3	6	36	66	3	6	36	66
1.0 ft	13.3				0				0			
1.5 ft												
2.0 ft		14.2	8.79	23.2		0	0.07	0		0	0	0
2.5 ft												

**Table 5. Organic Acid Data for ASV #2-90% Sand-10% Loam-Low Viscosity**

Days	Lactic Acid Results (mg/L)				Pyruvic Acid Results (mg/L)				Acetic Acid Results (mg/L)			
	3	6	36	66	3	6	36	66	3	6	36	66
1.0 ft	12.3				0				0			
1.5 ft												
2.0 ft		59.9	1.64	1.26		0	0.09	0.07		0	0	46.4
2.5 ft												

**Table 6. Organic Acid Data for ASV #3-90% Clay-10% Loam-Low Viscosity HRC**

Days	Lactic Acid Results (mg/L)				Pyruvic Acid Results (mg/L)				Acetic Acid Results (mg/L)			
	3	6	36	66	3	6	36	66	3	6	36	66
1.0 ft	93.1				0				0			
1.5 ft												
2.0 ft		132	138	445		0	0	0		0	27.2	1498
2.5 ft												

In contrast to the previous treatment of diffusion we have here an actual experimental result. Since the diffusion is for a cylinder of HRC rather than a point source we refer to a different equation (Segol, 1994). The basis is:

$$0.02 = \frac{Dt}{r^2} \quad [1]$$

Where D is the diffusion coefficient in cm<sup>2</sup>/sec, t is time in seconds and r is the radius of diffusion in cm.

This is for a cylinder where we want the average concentration to be 2% of the source, e.g. 20 ppm if the source is 1,000 ppm. Fitting the data and converting to the English System, using an average value from the experiments of 1 foot in 3 days, gives an effective diffusion coefficient of 0.007 ft<sup>2</sup>/day or (7 x 10<sup>-5</sup> cm<sup>2</sup>/s) and thus a fairly straightforward and usable diffusion rule is derived:

$$t = 3 x^2 \quad [2]$$

Where t is the time in days it takes the front to move out a distance x in feet. Thus, it takes about 300 days to move 10 feet or about 11 feet per year. If a higher concentration is used at the source, the time will decrease. We cannot really project exact amounts at various distances from the data because it is difficult to gauge bacterial utilization rates and localized substrate concentrations. What we do get is a sense of diffusional movement as a function of time at a level quite adequate for project design purposes.

Other observations from the data are as follows. Recall that the soil was infused with a solution of 25 ppm of TCE. For the low viscosity HRC, for example, about 3 times more acetic acid than lactic appears at 2.0 ft on day 66 compared to a ratio of 1 acetic acid to 5 of lactic acid on day 36. There is very little acetic acid seen with the high viscosity material. This indicates a larger potential “waste” factor for very low viscosity materials, such that more hydrogen is produced per unit time than can be used for reductive dechlorination. This would lead to off-gassing of hydrogen and/or the production of excess methane with implications for using liquid substrates like lactic acid or molasses.

Ultimately the point of all this is to determine injection point spacing. A highly detailed answer depends on the bacterial activity and product viscosity, but nominally it appears that diffusion alone

will drive the lactic acid out several feet in two months. The data suggest that 10 ft points will work if coverage is desired in two to three months. The distance between 10 ft points where coverage occurs is where the two fronts meet at a 5 ft distance from both injection points. Placing 5 for x in equation [2] results in a time of 75 days. If injection wells were placed 20 feet apart they would meet at a distance of 10 feet from each point. This would occur in 300 days according to equation [2]. In a year the distance increases to 11 feet. Note that this assumes no advection whatsoever. The motive force is simply diffusion.

### **Field Results**

The data in Table 7 provide an excellent cross section of results across 10 sites. These are the same 10 sites referenced in the longevity Technical Bulletin (TB 2.8.1). The sites have a range of groundwater velocities from essentially static (Site 1) to moderate flow rates of about 128 ft/yr. (Site 5). All of these sites were treated with 20,000 cP HRC injections, noting that an “injection” is not a process that sends material as far from the injection point as might happen with thin liquids. Therefore, the movement as measured is due to the net mass transport forces of advection, dispersion, diffusion, retardation and consumption. Overall it seems that HRC applied to an aquifer can move quite readily.

**Table 7. Movement of Organic Acids in the Field.**

<b>ID</b>	<b>Distances and Days to Wells</b>	<b>GW Velocity (ft/yr)</b>	<b>Potential Yearly Movement (ft)</b>
Site 1	8' in 89 days (OW-201-S)	0.15	33
Site 2	20' in 32 days (MW-8, 23 and 27)	110	228
Site 3	16' in 35 days (MW-31)	110	167
Site 4	15' in 154 days (MW-3)	27.4	36
Site 5	32' in 31 days (IMP-6)	128	377
Site 6	NA*	14.6	NA
Site 7	5' in 33 days (TWM-B)	< 36.5	55
Site 8	20' in 30 days (MW-26)	102	243
Site 9	140' in 140 days (MW-9)	< 36.5	365
Site 10	25' in 120 days (RW-68)	73	76

\* NA (not applicable): acids data, which was supposed to be collected at 30 days was not collected until 77 days post-application. At this time acids were detected in monitoring wells, but they were all within a few feet from the HRC grid area. There were no monitoring points downgradient from the grid that were useful in this analysis.

One of the most interesting observations from this data set is the fact that Site 1 is essentially driven by diffusion and is also affected by retardation and, more importantly, consumption. Therefore, we note that there is at least 33 ft of movement per year under these conditions. Recognize that the thesis throughout the entire presentation is the justification for placing 20,000 cP material at 10 ft centers and 200,000 cP material at 20 ft centers.

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