

SUBJECT: Plastic Pipe for Domestic Water Supply
: Implications of Pipe Use Simulation for Long-term Exposure.
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The Plastic Pipe Leaching Study conducted by SEHRL with Acurex laboratory showed persistent, high levels of solvents in the CPVC pipe systems. The results were the first available to show the likely rate of leaching over a moderate-term usage scenario. While it turns out that there was still significant leaching when the study was terminated (THF and MEK levels above 100 ppb) the longterm leaching can be reasonably inferred from the data.

Implications of Pipe Use Simulation for Long-term Exposure.

Four major solvents were found at high levels: tetrahydrofuran (THF), methylethylketone (MEK), cyclohexanone, and acetone. Initial levels of thousands of ppb declined during the preoccupancy phase. Going into the occupancy phase, THF and MEK were typically above 1000 ppb and declined slowly, falling a to a tenth of the initial value over the 60 day occupancy phase.

While the initial high levels are not unexpected, given the sheer quantity of solvent cement used to join the pipes, the persistence of the solvents was greater than suggested by previous shorter-term studies. Indeed, one of the motivations for the test protocol was to remedy the obvious deficiency of data on long-term leaching.

The four pipe cells behaved in a similar fashion, even though the pipe joint compound was different. All cells followed the same sharp initial decline during pre-occupancy (days 1 to 14) and the gradual decline during occupancy (days 16 to 75). A typical example is offered by Pipe Unit C, where MEK levels followed the curve shown in Figure 1.

Since the logical source of the solvent is the mass of cement in the joint, a simple leaching model would have solvent leaching undergo an exponential decay with the rate of leaching proportional to the amount of solvent still remaining in the joint. Such exponential decay, or first order kinetics, has the general form:

$$A_t = A_0 e^{-kt}$$

where A_t is the concentration of substance at time t ,
 A_0 is the initial concentration at time zero, start of leaching,
 e is the base of the natural logarithms
 $-k$ is the rate constant for decay, reflecting the diffusion rate

Logarithms of concentrations following first order kinetics will follow a straight line plot -- or may be graphed as a straight line on semi-log paper, as in Figure 2. Even on semi-log paper, there is an obvious curve to the plot, and this curve is exhibited for all solvents by all test units. When the sample data are fit to a line (see Figure 3), the curve is apparent, although the line is a good fit for the full 23 data points ($r = -0.9579$).

The shape of the curve is better illustrated when the semi-log plot is fit at three different periods: day 1 to 14 (5 samples), day 16 to 36 (9 samples), and day 39 to 75 (9 samples). Figure 4 shows the effect of estimating leaching behavior over the three separate periods. While the graph in Figure 4 shows only MEK from Unit C, all test data show the same phenomena. Table 1 lists the exponential curve fit for all compounds:

$\ln A_0$ is the natural log of the initial, day zero concentration,
 k is the exponential decay constant,
 r is the correlation coefficient (-1.00 is perfect fit)
 $\ln A_0 / -k$ is the time in days for the concentration to fall to 1 ppb.

In all cases, the value for k is less in the last study period than in the first study period -- often the k value is one quarter or one third, meaning that the leaching rate constant has declined abruptly. With a lower leaching rate constant, the solvent levels persist for a longer period of time. Thus the initial leaching rate of Unit C, MEK is -0.1225 which would have brought the leachate level to 1 ppb in 70 days, whereas between days 39 and 75 the leaching rate constant for the same cell fell to -0.0346 (28% of the earlier value) which projects levels above 1 ppb for 207 days.

The curve suggests deviation from pure first order leaching. The better description may be a higher order model, where the rate of leaching is proportional to the concentration of substance remaining raised to a power. There may be a plausible basis for such a phenomenon, such as the presence of the solvent altering the mechanical properties of the joint so that the diffusion rate through the joint is higher with higher solvent concentrations -- as the solvent dries up, the joint hardens and the remaining solvent is leached out more slowly.

An alternative model is to consider the solvent as leaching from multiple sources, each with a separate solvent content and with different intrinsic diffusion rates. The result would be two or more exponential leaching sources which would sum to show higher order leaching phenomena. Figure 5 illustrates the simple case of two sources for the MEK, Unit C example. In Figure 5, two separate sources are plotted: MEK-f for the "fast" leaching source, and MEK-s for the "slow leaching source. It is obvious that the fast source contributes most to the total MEK level during the first 10 days, whereas the slow source continues to put MEK into the water long after the fast source is essentially depleted.

The total MEK value is a curve, labeled SUM, which fits the data well: the values for the fast and slow source leaching were derived by difference from the exponential curve fit for the period 1 and period 3 data. With a lower effective leaching rate constant, the slow source projects levels of MEK above 10 ppb at day 120 and above 1 ppb for nearly a year. A more complex

model, particularly one based on leaching studies longer than 75 days, would show a more pronounced decline in leaching rate and significantly more persistent levels of solvent.

The present Pipe Leaching Study data do not support such extrapolation, but in the absence of a longer series test, it must be assumed that solvent levels above 1 ppb for MEK and THF would be found for at least a year after the pipe was installed.

The persistent solvent levels will contribute a fairly reactive source of organic material for formation of chlorinated organic compounds by reaction with chlorine residual in the water supply. When the several solvents are considered as total volatile organic, the prospect for significant exposure is clear.

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Figure 1. LINEAR PLOT OF MEK CONCENTRATION (UNIT C)

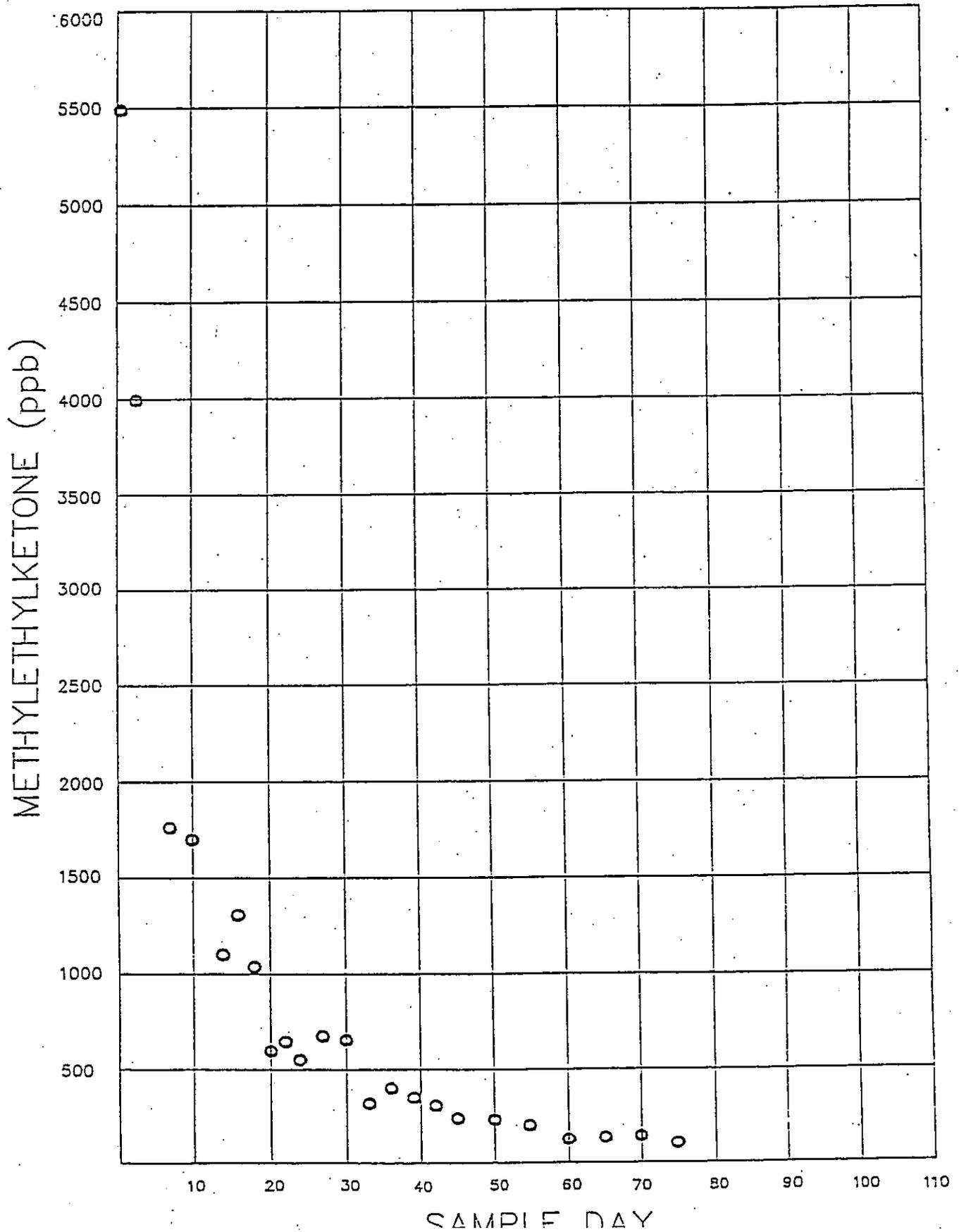


Figure 2. SEMILOG PLOT OF MEK CONCENTRATION (UNIT C)

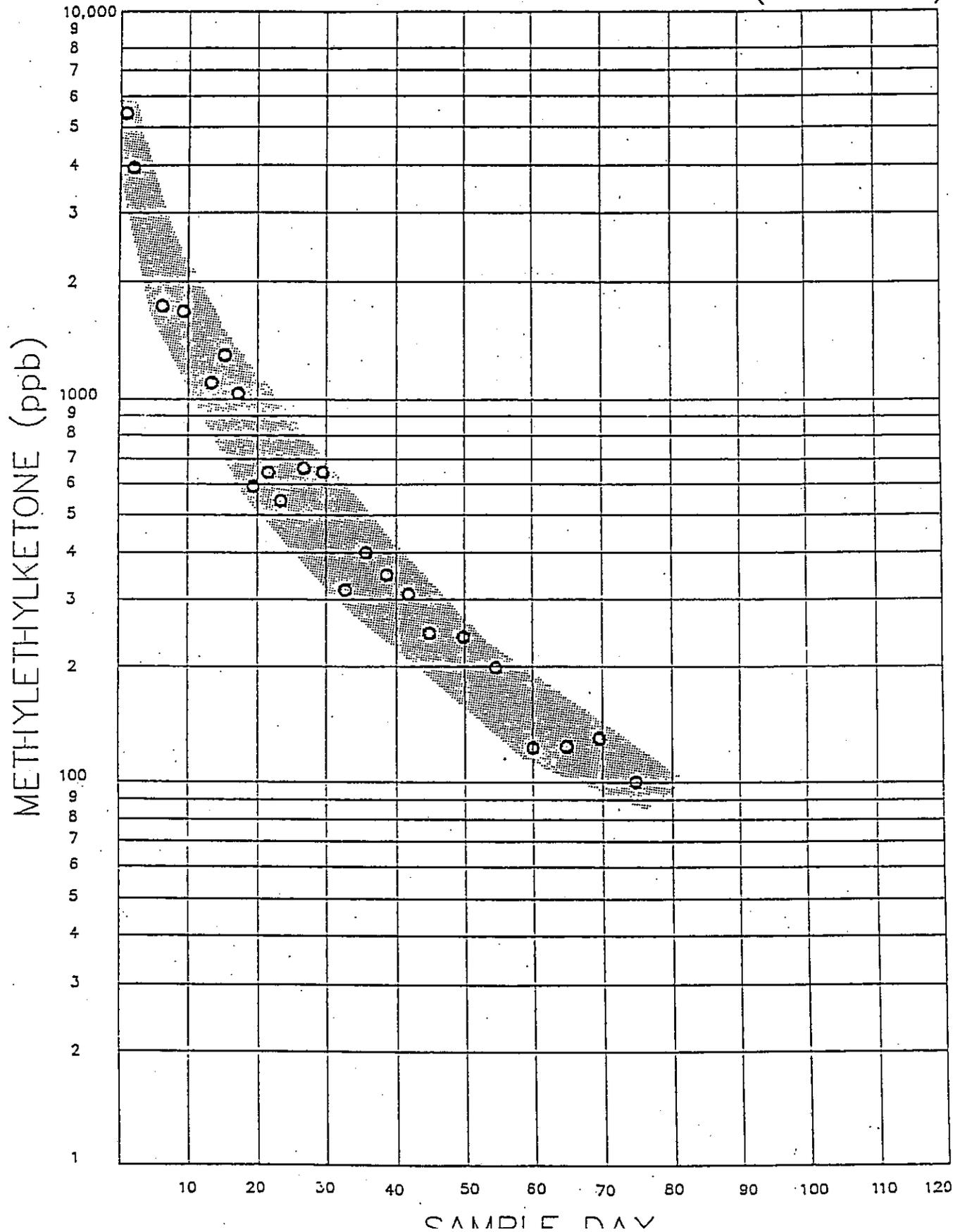


Figure 3. EXPONENTIAL CURVE FIT OF ALL SAMPLES

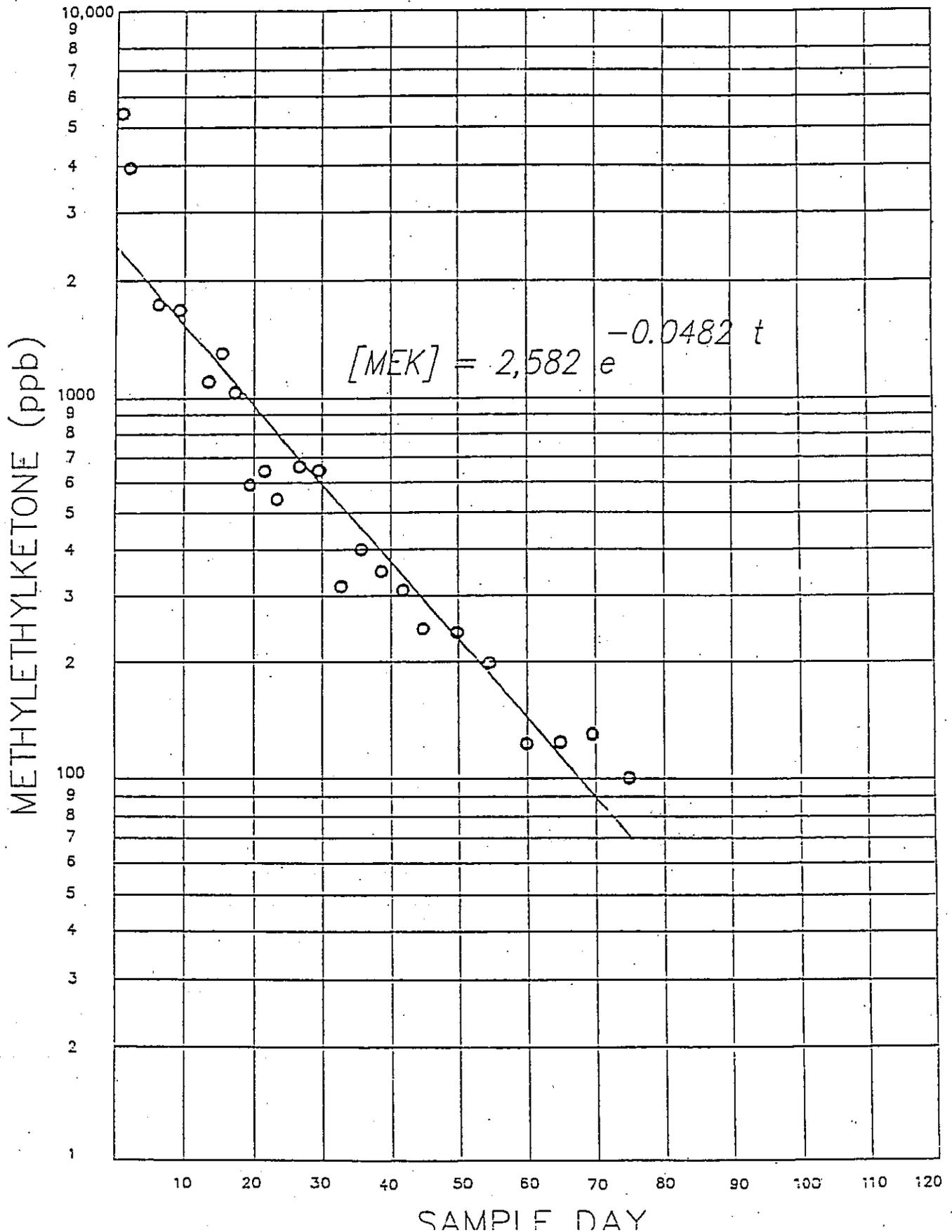


Figure 4. EXPONENTIAL CURVE FIT OF THREE SAMPLE GROUPS

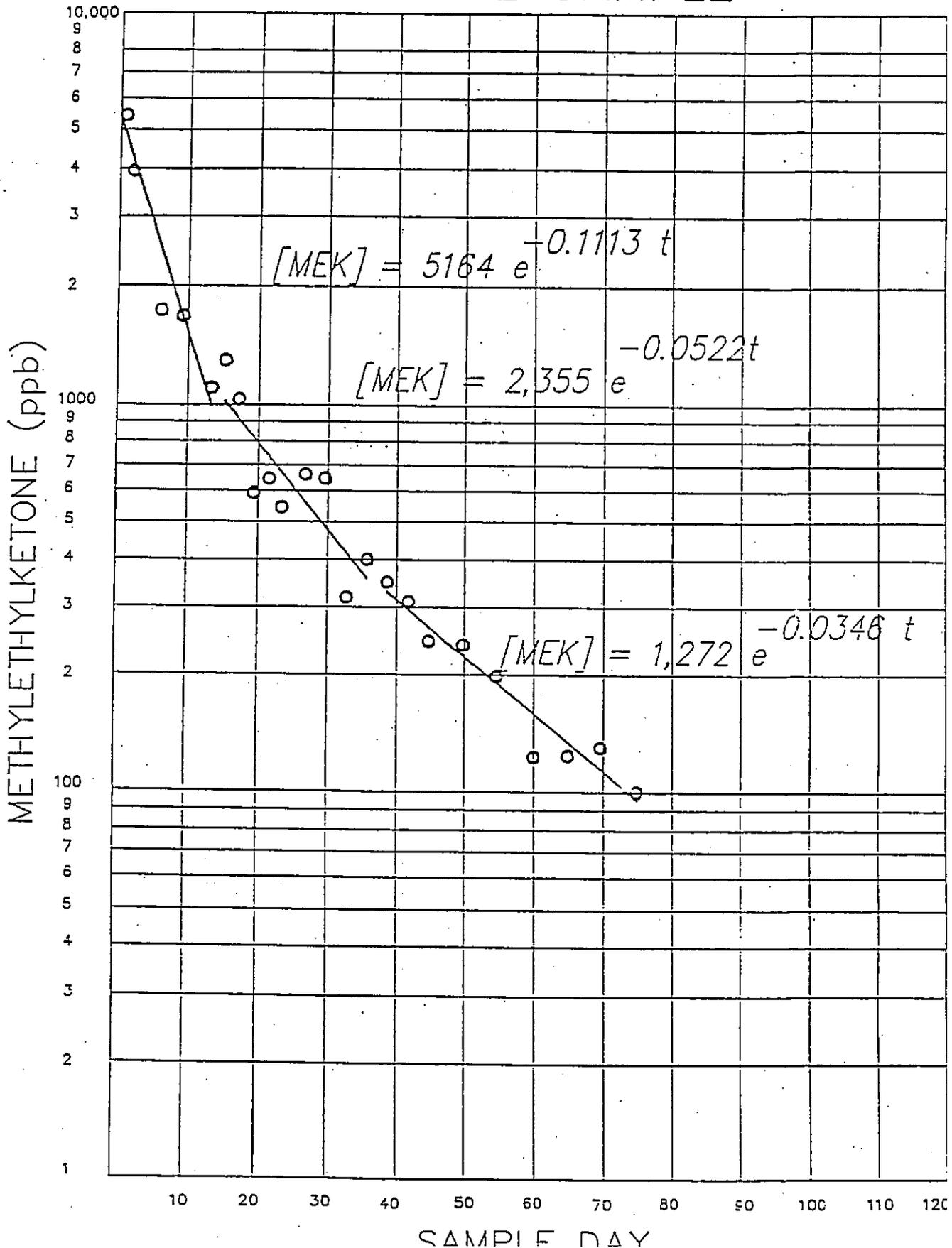


Figure 5. TWO SOURCE MODEL

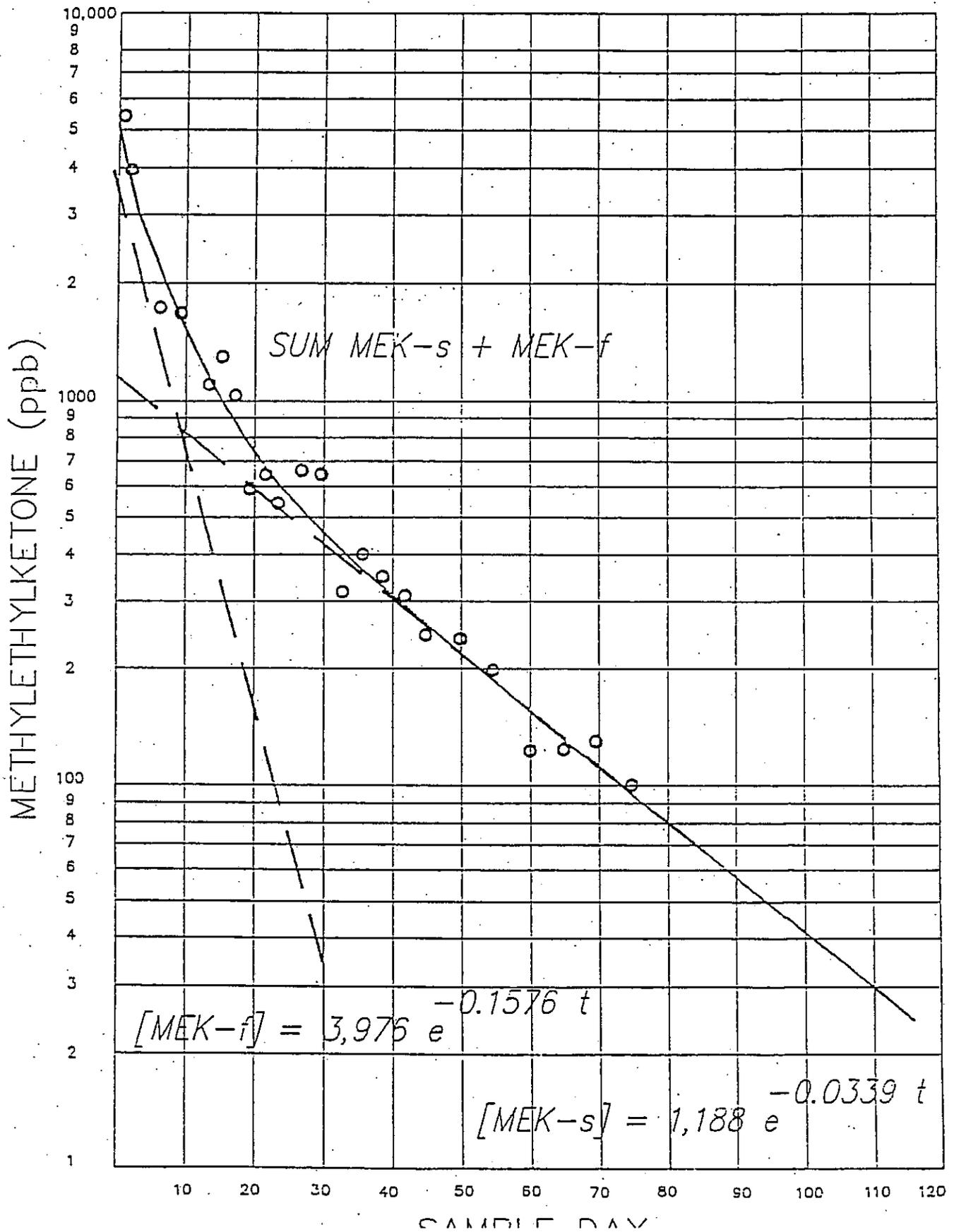


Table 1: Solvent Leaching Rates

TETRAHYDROFURAN

SAMPLING PERIOD	k	$\ln A_0$	r	$\ln A_0 / -k$
UNIT A				
Period 1	-0.1762	8.5165	-0.8741	48.3343
Period 2	-0.0662	7.5931	-0.7306	114.6994
Period 3	-0.0320	6.7894	-0.8490	212.1688
UNIT B				
Period 1	-0.1348	8.7767	-0.9152	65.1091
Period 2	-0.0673	7.8943	-0.8011	117.3001
Period 3	-0.0334	7.2314	-0.9483	216.5090
UNIT C				
Period 1	-0.1612	8.4928	-0.9223	52.6849
Period 2	-0.0502	7.2958	-0.8432	145.3347
Period 3	-0.0218	6.4267	-0.8298	294.8028
UNIT D				
Period 1	-0.1471	8.4108	-0.8656	57.1774
Period 2	-0.0668	7.6977	-0.7274	115.2350
Period 3	-0.0264	6.5326	-0.8402	247.4470

METHYLETHYLKETONE

SAMPLING PERIOD	k	$\ln A_0$	r	$\ln A_0 / -k$
UNIT A				
Period 1	-0.1136	8.2337	-0.9646	72.4793
Period 2	-0.0565	7.4569	-0.8769	131.9805
Period 3	-0.0236	6.0303	-0.6933	255.5212
UNIT B				
Period 1	-0.1113	8.5495	-0.9483	76.8149
Period 2	-0.0603	7.9311	-0.8893	131.5274
Period 3	-0.0420	7.5616	-0.9709	180.0381
UNIT C				
Period 1	-0.1225	8.6235	-0.9625	70.3959
Period 2	-0.0522	7.7644	-0.8408	148.7433
Period 3	-0.0346	7.1483	-0.9637	206.5983
UNIT D				
Period 1	-0.0691	8.1132	-0.9450	117.4124
Period 2	-0.0502	7.6626	-0.8961	152.6414
Period 3	-0.0350	7.0410	-0.9344	201.1714

CYCLOHEXANONE

<u>SAMPLING PERIOD</u>	<u>k</u>	<u>lnA₀</u>	<u>r</u>	<u>lnA₀/-k</u>
UNIT A				
Period 1	-0.2033	7.6316	-0.8316	37.5386
Period 2	--	--	--	--
Period 3	--	--	--	--
UNIT B				
Period 1	-0.2051	8.4660	-0.9015	41.2774
Period 2	-0.0739	6.4382	-0.6239	87.1204
Period 3	--	--	--	--
UNIT C				
Period 1	-0.2656	8.8106	-0.9187	33.1724
Period 2	-0.0688	6.2116	-0.5190	90.2849
Period 3	--	--	--	--
UNIT D				
Period 1	-0.1985	7.7077	-0.7760	38.8297
Period 2	-0.1105	7.2707	-0.9749	65.7982
Period 3	--	--	--	--

ACETONE

<u>SAMPLING PERIOD</u>	<u>k</u>	<u>$\ln A_0$</u>	<u>r</u>	<u>$\ln A_0 / -k$</u>
UNIT A				
Period 1	-0.1751	6.1150	-0.7354	34.9229
Period 2	-0.0234	3.2478	-0.4851	138.7949
Period 3	--	--	--	--
UNIT B				
Period 1	-0.2787	6.6203	-0.9528	23.7542
Period 2	-0.0263	3.2567	-0.4597	123.8289
Period 3	--	--	--	--
UNIT C				
Period 1	-0.1799	3.5566	-0.9630	19.7699
Period 2	--	--	--	--
Period 3	--	--	--	--
UNIT D				
Period 1	--	--	--	--
Period 2	--	--	--	--
Period 3	--	--	--	--