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SUBJECT: TRACKING ID 202841: REVIEW OF COMPARISON OF METHYL BROMIDE GAS CONCENTRATIONS IN THE TARP SOIL INTER-SPACE: DEEP BROADCAST TARPED VS. SHALLOW BROADCAST TARPED FUMIGATION (GILLIS AND SMITH 2003)

Summary

This study replicated within a single field the deep-tarped and shallow-tarped applications. The registrant requested that the emission ratio for deep-tarped be the same as for shallow-tarped. At this time, deep-tarped has a higher ratio because no sufficient studies for deep-tarped were submitted. The reviewed study supports the request to make the shallow- and deep-tarped emission factors the same.

Phase 1 Review

The text indicates that the samples were stored in an ice chest container at 'ambient conditions to minimize temperature fluctuations until analysis' (page 8).

QA/QC. Appendix 8 contains the calibration curve for the GC. The data were provided in Appendix 8. A regression in Excel gave the indicated equation with a slope of 0.202 and intercept of 265. The intercept was not significantly different from zero (p>.05). The multiplicative constant which I obtained (0.202) was different from that shown in Appendix 8 (0.2378). I tried forcing the regression

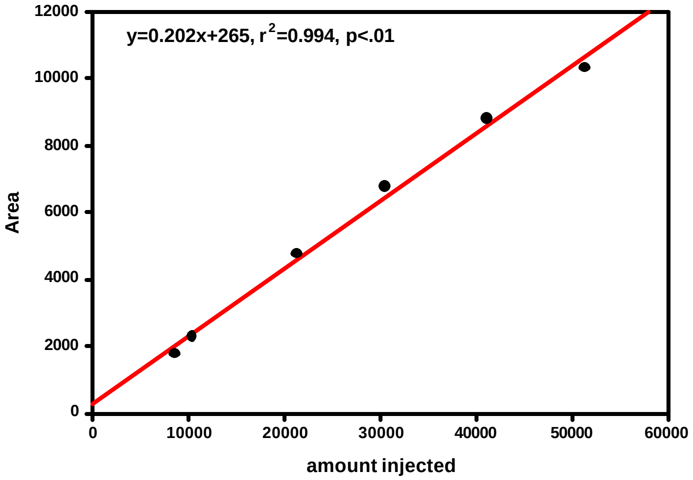

Figure 1. Attempt to replicate calibration calculations in Appendix 8.

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through the origin, but this only increased the slope slightly to 0.210. I do not understand where the 0.2378 constant comes from.

Table 1 presents the QA/QC results for interval 1. These data can be found in Table 4 shown on Appendix 5 (page 43). The time-dependant recovery equations derived from an analysis of these data were used to correct the measured concentrations. For this reason, it is important to understand these calculations.

Table 1. Excerpt from Table 4 in Appendix 5 of Gillis and Smith (2003)

	Time of Collection	Time of Analysis	Std. Concentration (ppmv)	Elapsed Time (HH:MM)	Elapsed Time (Decimal Hours)	Peak Area	Back Calculated Conc (ppmv)
1	7:15	12:15	30500	5:00	5.00	6370	28710
2	7:15	12:19	30500	5:04	5.07	6297	28381
3	7:15	12:21	30500	5:06	5.10	6222	28040
4	8:30	16:31	30500	8:01	8.02	6070	27349
5	8:30	16:33	30500	8:03	8.05	6395	28823
6	8:30	16:35	30500	8:05	8.08	6182	27860
7	12:24	12:24	30500	0:00	0.00	6575	29639
8	11:07	11:07	30500	0:00	0.00	6748	31136
9	11:10	11:10	30500	0:00	0.00	6782	31362
10	11:15	11:15	30500	0:00	0.00	6763	31318
11	15:55	15:55	30500	0:00	0.00	6438	29021
12	16:38	16:38	30500	0:00	0.00	6540	29482
13	17:18	17:18	30500	0:00	0.00	6426	28964

The first column is an artificial number to facilitate discussing the data. These samples were all taken from two standard cylinders of methyl bromide, which according to the text in Appendix 8 were "... tested extensively against other standards and against each other to validate their concentration before certifying for use in this test." Samples 1-6 were taken from cylinder SC31, while the remainder were from cylinder SC14. The peak area measurements presumably result from instrument variability and amount of time the sample was stored before being analyzed. The column title of the last column ("Back Calculated Conc.") is suggestive that a regression was used with the x axis being concentration (ppmv) and the y axis being peak area. After finding this regression, the equation was solved for x and used to calculate concentration based on peak area.

I utilized samples 1-6 (greater than zero time) and regressed the peak area on the back calculated concentration. The purpose in this analysis was to try to understand how the concentration estimates were derived. This regression gave an r2 of 0.99999, strongly suggesting that this was the equation used to convert peak into concentration. The equation was

$$P = 0.220574C + 37.16102 \tag{1}$$

where P is peak area and C is concentration (ppmv). Solving for C gives

$$C = \frac{P - 37.16102}{0.220574} \tag{2}$$

When I used equation (2) to calculate the concentrations, and compared them to the concentrations reported in Table 4 of Gillis and Smith (2003), I found good agreement except for three concentrations. These concentrations are bolded in Table 2. The samples 7-13 are used as basis for presenting other statistical results, which would change depending on which estimate for samples 8-10 were used. Why are the bolded estimates different?

Table 2. Comparison of concentrations based on peak area using equation 1.2 and as reported in Table 4 of Gillis and Smith (2003).

	Peak Area	Calculated Using Eq 1.2 (ppmv)	Table 4 (ppmv)
1	6370	28711	28710
2	6297	28380	28381
3	6222	28040	28040
4	6070	27351	27349
5	6395	28824	28823
6	6182	27858	27860
7	6575	29640	29639
8	6748	**30424**	**31136**
9	6782	**30579**	**31362**
10	6763	**30492**	**31318**
11	6438	29019	29021
12	6540	29481	29482
13	6426	28965	28964

I used the same procedure on Interval 2 data. In this case, there were 11 samples. The first 6 had non-zero storage times and were used for regression. The equation was very similar to equation (1) above.

$$P = 0.220487C + 39.44731 \qquad (3)$$

with an r2 of 0.99999. These two equations are probably the same, but differ only due to minor numerical differences in representation of the numbers. That is, the numbers reported in the spreadsheet have more digits than are shown in the table. When I type these numbers in and perform analysis on them, there will be minor differences due to my not having the full decimal representation available to me. The numbers I type in are essentially truncated compared to those which were used in the original calculations as found in Gillis and Smith (2003). Consequently, it is reasonable to see these minor differences between regression results.

Table 3. Comparison of concentrations for interval 2 based on peak area using C=(P-39.44731)/0.220487 in comparison to concentrations reported in Gillis and Smith (2003, Table 4). Bolded values differ.

	Estimated eq. 1.3	Table 4
5798	26117	26117
6224	28050	28048
6118	27569	27568
6093	27455	27457
6097	27474	27475
5897	26566	26566
6540	29483	29482
6426	28966	28964
6318	28476	28475
6431	28988	28990
6598	**29746**	**30477**

Table 3 presents the comparison for interval 2, analogous to Table 2 for interval 1. One sample differs from the estimate using equation (3). Given the four decimal place agreement between the reported and estimated concentrations in the other ten samples, why does the equation estimate for the last sample differ from that reported? This difference, as in the case of interval 1, appears to be too large to be the result of minor numerical issues.

Associated with each interval is an equation used to correct the recovery. The basis for the recovery correction is that concentrations in the sample tubes decline over time. No explanation is offered for this decline, but the data itself establishes that such a decline occurs. Figure 2 shows data from the first two intervals. All samples in this study were injected with the same standard. Samples were stored for various periods before analysis. Regressions for both intervals of peak area versus time were significant ($p<.05$). Table 4 in Gillis and Smith (2003) presents the regression results.

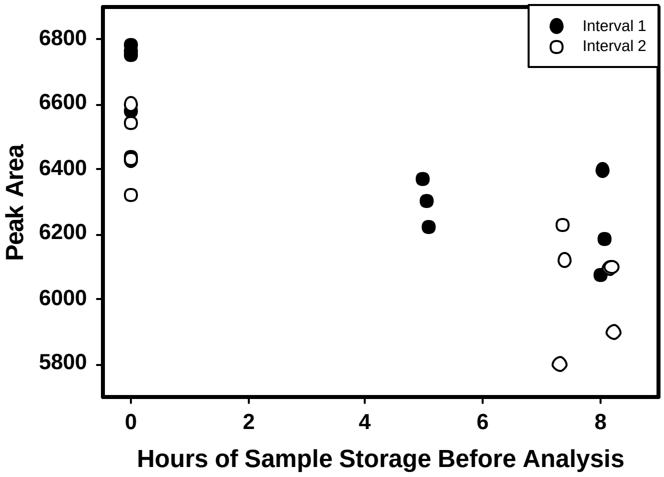


Figure 2. Concentration decline in stored samples as a function of storage time.

I was able to duplicate their regression results, but a caution is necessary. The regressions presented in Table 4 in Gillis and Smith (2003) utilize the raw time values, which are shown formatted as hh:mm in a column labeled “Elapsed Time from Collection to Analysis (ETA)”. In Table 1 above, this same column is labeled “Elapsed Time (HH:MM)”. In Table 1 above, the adjacent column is labeled “Elapsed Time (Decimal Hours)”. The Excel internal representation of time utilizes what it calls a ‘serial number’. This number represents one day as 1.0 and thus, one hour as $1/24=0.0417$. The regression equations shown in Table 4 of Gillis and Smith (2003) utilize the serial number representation. When I convert this representation into decimal hours, the multiplicative coefficient changes by a factor of 24. This conversion utilizes several Excel functions as follows:

```
=VALUE(LEFTB(TEXT(C16,"hh mm"),2))+VALUE(RIGHTB(TEXT(C16,"hh mm"),2))/60
```

The cell, C16, contains a serial number for a number of hours, represented, for example, as 8:01. The TEXT function converts the value into a text string with formatting as indicated. The LEFTB (RIGHTB) functions take the leftmost (rightmost) two characters and the VALUE function convert the characters into a number. The second part of the expression is in minutes, and so is divided by 60 to give a fraction of an hour, added to the hour.

Table 4 compares three regressions. The only difference, except for the minor effects of rounding and truncation, is in the slope. The slope using serial time is 24x the slope using decimal hours. This difference, as explained above, is due to the way Excel represents time.

I spot checked a few recovery adjustments and they seemed okay.

The 18-inch soil temperature measurements appear to be anomalous at about 5-6 a.m. on 8/7/03 and 8/8/03.

Table 4. Comparison of regression analyses of interval 1 data

		My Calculations	
	Reported in Gillis and Smith (2003)	Using 'serial' time	Using decimal hours
Slope	-1239.5	-1240.57	-51.69
Standard Error of Slope	272.103	272.451	11.352
Intercept	6603.03	6603.1	6603.1
Standard Error of Intercept	51.8304	51.8398	51.8398
r-squared	0.65353	0.65336	0.65336
Standard Error	140.025	140.043	140.043
F	20.7489	20.7331	20.7331
df	11	11	11
ss reg	406822	406616	406616
ss resid	215676	215732	215732

It is not clear if the reported concentrations are adjusted for temperature. The temperature under the tarps, based on Graph 8 (Gillis, page 72) ranged from 60-155F, or 16-68C, or 289-341K, which corresponds to a concentration difference of 68 percent from the middle temperature.

The statistical analyses presented in Section 7 consist of one way ANOVAs within each of the two areas (4401 and 4402) of the large field utilized for the study. An ANOVA is conducted for each ‘interval’ within each of the two areas (4401, 4402). There were twelve measurements taken from each sampling station over time. The sampling times were numbered 1 through 12 and each time was an interval. The applications and samples were started at approximately the same time, but there are some differences in timing after the application when the actual samples were drawn. The experimental unit in these analyses is the individual sample from each plot. Within each of the two sub-areas, there were six plots, consisting of three deep and three shallow treatments, which were randomly assigned in pairs within each sub-area. Within each plot, there were four sampling locations where below-tarp methyl bromide concentrations were sampled. The ANOVAs in Section 7 utilize these individual, within-plot samples as experimental units.

Pseudoreplication is an issue in these circumstances. It is clear that the use of the sub-plot samples for the ANOVAs is pseudoreplication because the four sub-plot samples do not represent replicates of the treatment. The mean of those four values represents one replicate of the treatment. Therefore, the ANOVA table would feature two treatments, and three replicates within each treatment for a total of six degrees of freedom relevant to testing the treatments.

For each area (4401 or 4402)

Treatment	1
Reps	5
Within reps	17
Total	23

The analysis reported in Gillis (2003) utilizes the following scheme:

Between groups	1
Within Groups	22
Total	23

The latter scheme mixes the within-plot variation and the between-plot variation and is not correct. The experimental unit in this study is the treated plot and in the entire field, there were six plots with shallow injection and 6 plots with deep injection.

In addition, there is another level of pseudoreplication. From a regulatory standpoint, the ideal experimental unit is a single application to a field because DPR regulates at that level. Therefore, we are interested in treatment effects that persist over different fields at different times. In this sense, whenever DPR receives a single field study with replicates constructed within the field, it represents pseudoreplication with respect to DPR's domain of regulation. However, it is necessary to recognize that time and resources are not always sufficient to support multi-field studies. Moreover, in the special case of methyl bromide, many field studies located at different times and different locations *have already been conducted*.

Based on the phase 1 review, I submitted several questions to Matt Gillis of Tri-Cal. He responded to my questions. The questions and responses are listed in Appendix 1.

Phase 2 Review

In this study, the narrow question is whether the 24-hour emission factor assigned to the deep-tarped should be the same as emission factor assigned to the shallow-tarped application. Currently, the deep-tarped application receives a higher factor, an assignment based on lack of studies for the deep-tarped application. Thus the most relevant information would be the flux over the first 24 hours since the emission factor is based on such.

In order to examine this question and more properly utilize the information in the report, I created a FORTRAN program which estimated concentration at each time at each plot, utilized the temperature data from the deep-tarp, 4401 area (Graph 7), to adjust the tarp permeability, and together with the concentration data estimated a flux. The equation relating these various factors is

$$Flux = P * \Delta C \tag{4}$$

where flux is units of mass per area per time, P is permeability in units of length per time and Δ C is the difference in concentration (units of mass per volume) from beneath the tarp to above the tarp. Typically, the above tarp concentration is assumed to be zero since it is small in relation to the below-tarp concentration.

Tarp permeability was studied by Kolbezen and Abu-El Haj (1977) in a laboratory study on small tarp samples. One set of data generated by Kolbezen and Abu-El Haj (1977) was utilized to estimate permeability as a function of temperature (Table 5).

Table 5. Data from Kolbezena and Abu-E-Haj (1977) for high density polyethylene tarp, 1 mil. MBF units are ml gaseous methyl bromide per hour per meter squared per 1000ppm. There were two HDPE tarps tested. The data for tarp #1 were used in this report to estimate permeability as a function of temperature. The factor 2.8E-07 converts MBF to m/s.

Temperature (C)	Temperature (K)	Perm #1 (MBF)1	Perm #2 (MBF)2	Perm #1 (m/s)	Perm #2 m/s	Factor #1	Factor #2	ln(Factor#1)	ln(Factor #2)	1/T
23	296	2.70	1.40	7.56E-07	3.92E-07	1.000	1.000	0.000	0.000	0.00338
30	303	3.50	1.70	9.80E-07	4.76E-07	1.296	1.214	0.260	0.194	0.00330
40	313	5.00	2.90	1.40E-06	8.12E-07	1.852	2.071	0.616	0.728	0.00319
50	323	6.80	3.90	1.90E-06	1.09E-06	2.519	2.786	0.924	1.025	0.00310
60	333	8.80	5.20	2.46E-06	1.46E-06	3.259	3.714	1.181	1.312	0.00300

The natural logarithm of the permeability factor (normalized to 1 at 23C) was regressed on the reciprocal temperature (temperature in Kelvins). The resulting equation was ln(Factor)=10.7-3169*(1/T), (n=5, p<.01, $r^2=0.99$). Transformation to an estimator for factor gives

$$factor = e^{10.7}\left(e^{\left\{\frac{-3169}{T}\right\}}\right) \tag{5}$$

The conversion from MBF to m/s is accomplished as follows:

$$\frac{\frac{mlMB}{hr-m^2}}{1000\,ppmMB} = \frac{\frac{mlMB}{hr-m^2}}{1000\,ppmMB\left[\frac{\frac{(1E-3)LMB}{1m^3}}{ppmMB}\right]} = \frac{\frac{(3.88E-3)g}{hr(3600\frac{s}{hr})-m^2}}{1000\frac{(1E-3)LMB}{1m^3}} = \frac{\frac{(3.88E-3)g}{hr(3600\frac{s}{hr})-m^2}}{1000\frac{(1E-3)LMB\left[\frac{(3.88gMB}{LMB}\right]}{1m^3}} \tag{6}$$

$$= \frac{\frac{(3.88E-3)g}{hr(3600\frac{s}{hr})-m^2}}{1000\frac{\left[3.88E-3gMB\right]}{1m^3}} = \frac{\frac{(3.88E-3)g}{3600s-m^2}}{\frac{\left[3.88gMB\right]}{1m^3}} = \frac{(3.88E-3)g(1m^3)}{(3600s-m^2)\left[3.88gMB\right]} = 2.78E-7\frac{m}{s}$$

where 1 Liter of methyl bromide is estimated at 95g/24.5L=3.88g/L at approximately room temperature. The rate of escape of methyl bromide at 23C reported by KAH was 2.7MBF, which converts to 7.5E-7m/s.

When 7.57E-7m/s transfer factor is multiplied by a concentration differential, the result is a flux at 23C through the film. Another required conversion is from ppm to g/m^3. This conversion is embedded in the conversion above, as 3.88E-3g/m^3 per ppm, at approximately room temperature.

In order to perform the integrations, it is necessary to establish continuous functions which describe the measured concentration and temperature data. For the concentration data, Gillis and Smith (2003) use cubic spline functions to connect the data points. These functions begin with the first measured value. The interpolations look reasonable. However, I added a zero concentration point in order to represent the concentration the moment before application started and close off the left end of the curve. I utilized a cubic spline function from Press et al. (1996). The spline function worked well for 9 of the 12 data sets. However, for the shallow treatments in 4401, adding the zero point caused the spline curve to dip below zero (i.e., negative concentrations). In order to provide a realistic interpolation, for these three replications, a linear fit between zero time and the first measured value was used, with cubic spline thereafter. This modification yielded reasonable functions which followed the measured data.

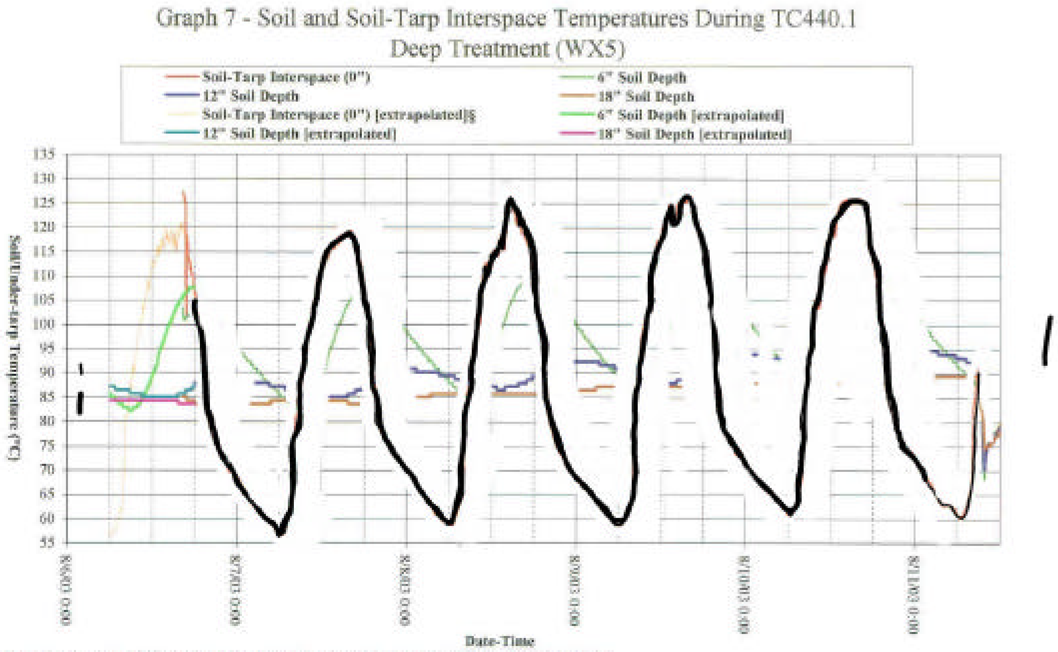
The temperature and concentration data had to be put onto a common time base. The time base chosen was days since 00:00 8/6/03. This was the midnight that preceded the applications, which were begun on the morning of 8/6/03. The concentration measurements include the time since application. The time since application was added to the time of application and normalized so that zero time was 00:00 8/6/03. The temperature measurements were already in these units. Table 6 details the calculations to put time units for the concentrations measurements onto a common footing.

Table 6. Table showing calculations to put concentration measurements on common time base using 00:00 8/6/03 as the start time.

Concentration Data Set	Start time in file (hours after application)	Estimated zero time for application, hours, minutes	Converted to string (in order to convert to decimal)	Estimated zero time for application, hours, fractional hours	Decimal hours past 00:00 when measurements taken	Decimal hours past 00:00 8/6/03 as fraction of days
4401D1.CSV	0.50	6:58	6:58	6.97	7.47	0.31
4401D2.CSV	0.50	7:08	7:08	7.13	7.63	0.32
4401D3.CSV	0.50	7:17	7:17	7.28	7.78	0.32
4401S1.CSV	0.53	7:29	7:29	7.48	8.01	0.33
4401S2.CSV	0.53	7:41	7:41	7.68	8.21	0.34
4401S3.CSV	0.53	7:47	7:47	7.78	8.31	0.35
4402D1.CSV	2.00	8:49	8:49	8.82	10.82	0.45
4402D2.CSV	2.00	8:58	8:58	8.97	10.97	0.46
4402D3.CSV	2.00	9:05	9:05	9.08	11.08	0.46
4402S1.CSV	1.80	8:19	8:19	8.32	10.12	0.42
4402S2.CSV	1.80	8:32	8:32	8.53	10.33	0.43
4402S3.CSV	1.80	8:37	8:37	8.62	10.42	0.43

To acquire the temperature data, I utilized Graph 7 (Gillis and Smith 2003 page 71), which consisted of the temperatures from TC440.1, deep treatment (Figure 3). While temperature graphs were also provided for TC440.1 shallow and TC440.2 deep (though not TC440.2 shallow), I only utilized this one set of temperatures for all calculations.

Figure 3. Graph prepared for digitization. Temperature line for interspace isolated and thickened



§ Data prior to ~5pm, 8/6/03 is extrapolated from the same time period on 8/7/03. Temperatures on 8/6/03 were slightly cooler with a subsequent warming trend over the course of the study.

Preparation of the graph for digitization was time-consuming. The soil-tarp interspace temperature was digitized by using Un-Scanit (Silk Scientific Corporation). The figure was prepared by erasing all lines near the line of interest, and widening and darkening the line of interest. After the points were digitized, I compared the original to a graph based on plotting the digitized points and they matched.

With the temperature and concentration functions, together with the permeability function, the elements necessary to calculate a flux were present. The four functions, concentration, temperature, permeability, and flux are presented in Figures 4-15 for the twelve plots. Throughout these figures, the temperature and permeability charts are the same since I utilized the same set of temperature data. To perform the function calculations and corresponding integrations, I wrote a FORTRAN program, FLUEXEST3.FOR (Appendix 2), which used Romberg integration scheme (Press et al. 1996).

The most relevant analysis is an integration over the first 24 hours of each flux curve. This period primarily corresponds to the greatest flux and to the most relevant period for assigning an emission ratio. The interest within the context of this study is the relative 24-hour flux between the shallow- and deep-tarped applications methods. The integrated flux functions for the first 24 hours are shown below in Table 7.

The third column in Table 7 corresponds to the area under the curve starting at the application time to 24 hours plus the application time. The fourth column is labeled ‘theoretical’ for reasons which will be described below. This column is obtained by multiplying the third column by 24x3600=86400, the number of seconds in 24 hours. For purposes of relative analysis, it is equivalent to analyze either the third or fourth columns with a one way ANOVA, using deep and shallow as treatments.

Table 7. Integration of flux function over 24 hours from application start time.

Data Source	Treatment	Integration over first 24 hours starting from application time ((g/m2s)-day)	Theoretical Mass g/m2
4401D1.CSV	Deep	2.92E-05	2.5
4401D2.CSV	Deep	2.94E-05	2.5
4401D3.CSV	Deep	2.40E-05	2.1
4401S1.CSV	Shallow	5.03E-05	4.3
4401S2.CSV	Shallow	4.18E-05	3.6
4401S3.CSV	Shallow	4.86E-05	4.2
4402D1.CSV	Deep	2.21E-05	1.9
4402D2.CSV	Deep	2.48E-05	2.1
4402D3.CSV	Deep	4.00E-05	3.5
4402S1.CSV	Shallow	4.04E-05	3.5
4402S2.CSV	Shallow	5.83E-05	5.0
4402S3.CSV	Shallow	5.74E-05	5.0

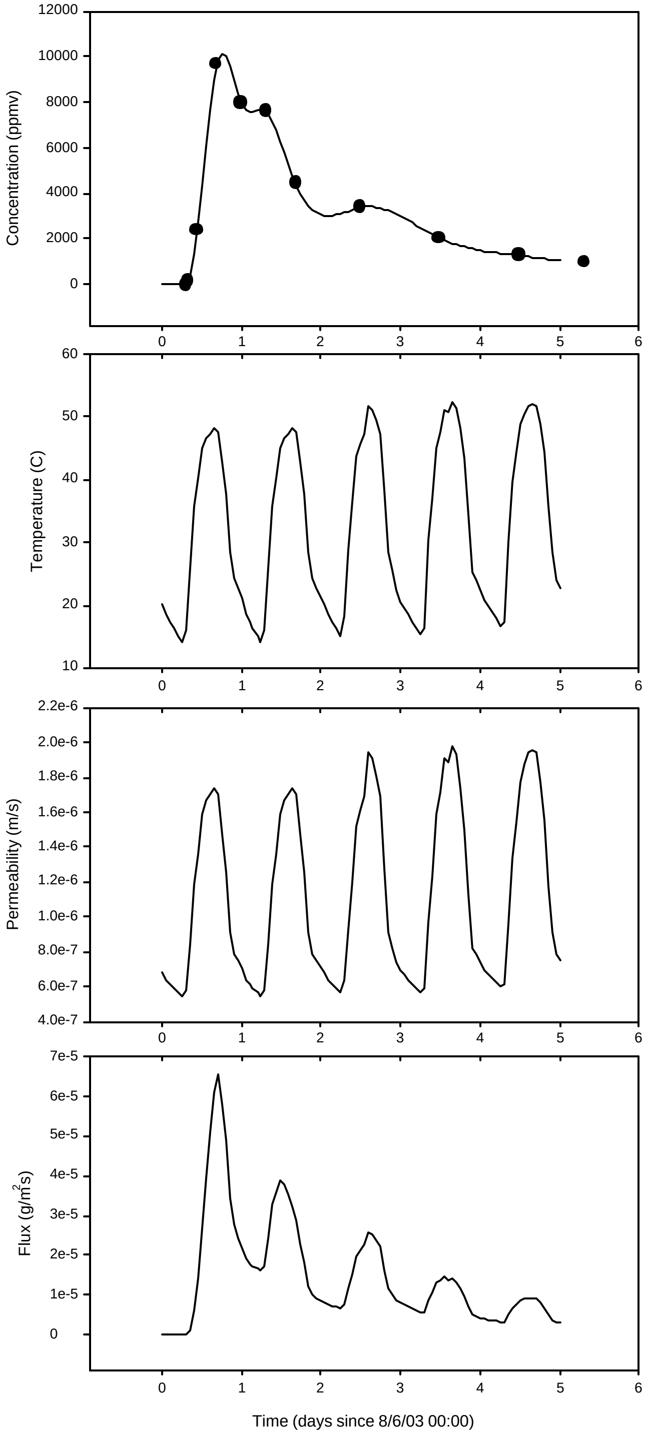


Figure 4.Components of estimating flux from FORTRAN program FLUXEST3.FOR. Temperature data from TC440.1, deep treatment. Concentration data from deep, plot 1 TC440.1 with concentrations adjusted to an application rate of 400 lbs/acre based on weighed cylindar masses. [In this case, reported concentrations were multiplied by 400/455.] Lines above based uniformly spaced, estimations of functions. Data points in concentration are measured values except 0 point, if present.

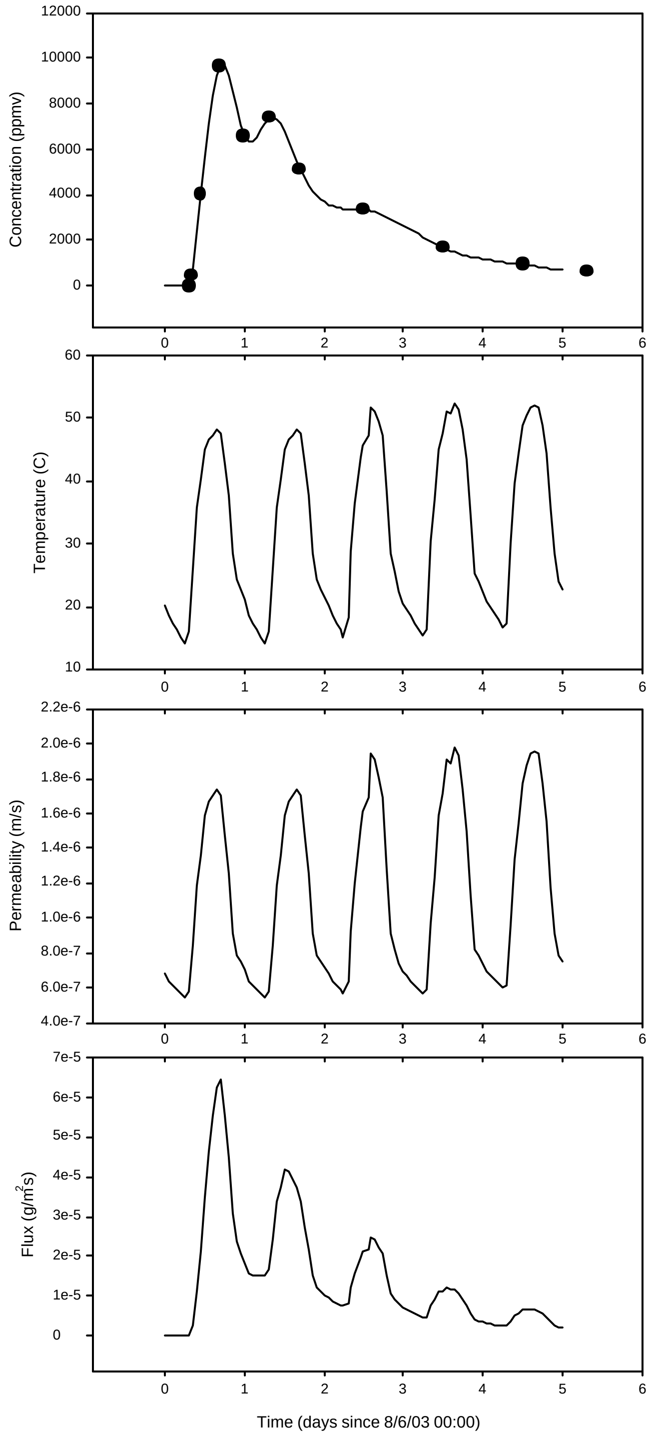


Figure 5. Deep tarped 440.1. Replicate #2. See Figure 4 caption.

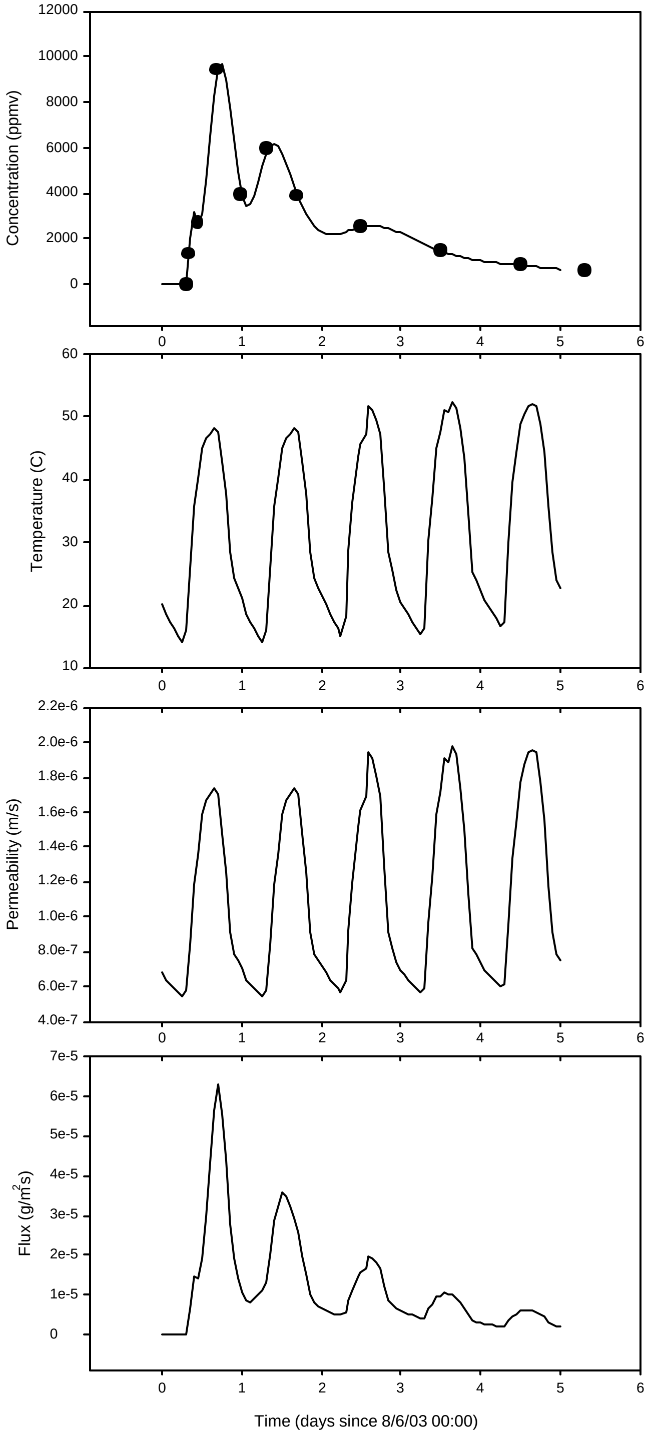


Figure 6. Deep tarped, replicate #3. See Figure 4 caption.

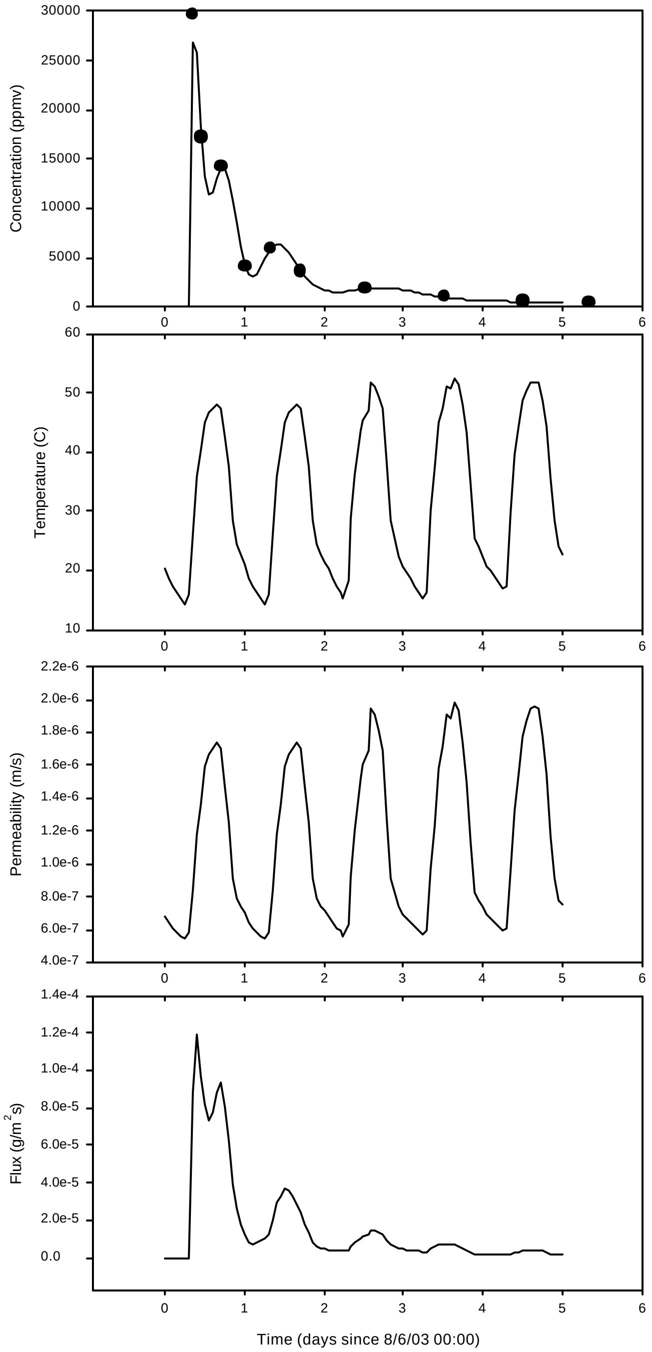


Figure 7. Shallow tarped, replicate #1, 4401. See Figure 4 caption.

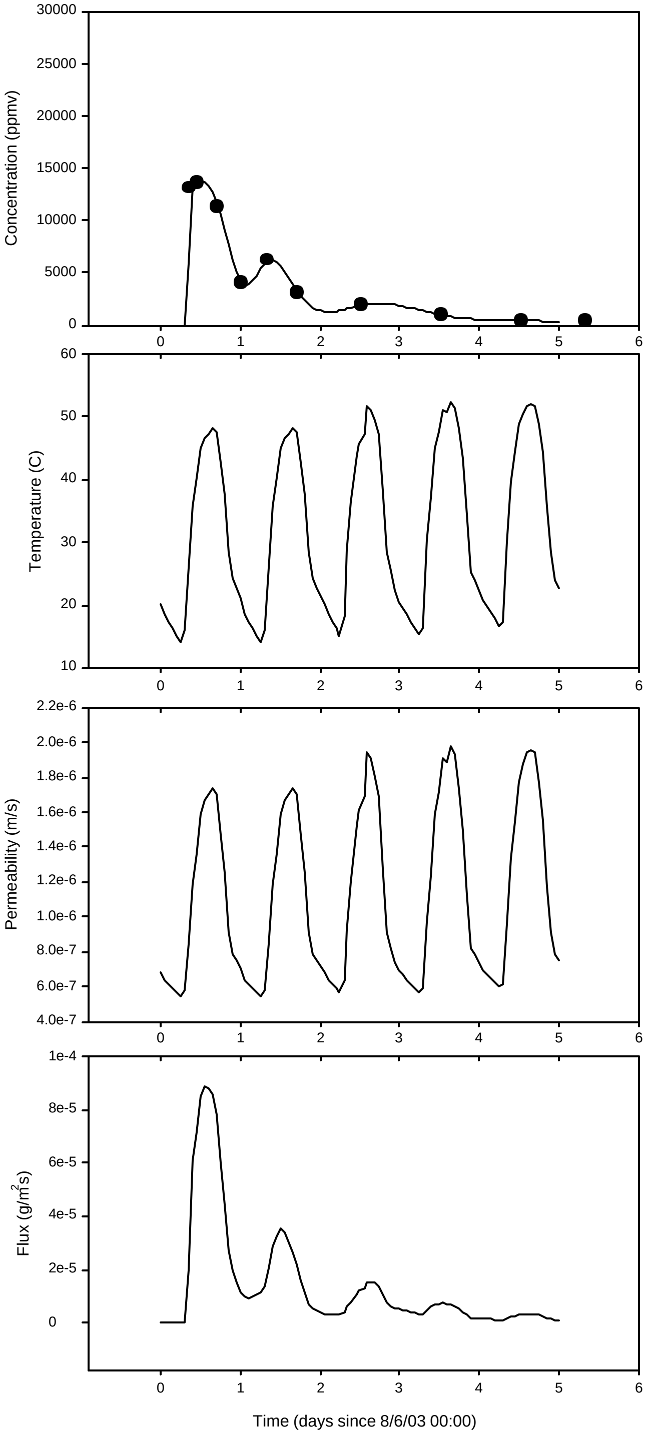


Figure 8. Shallow tarped, replicate #2, 4401. See Figure 4 caption.

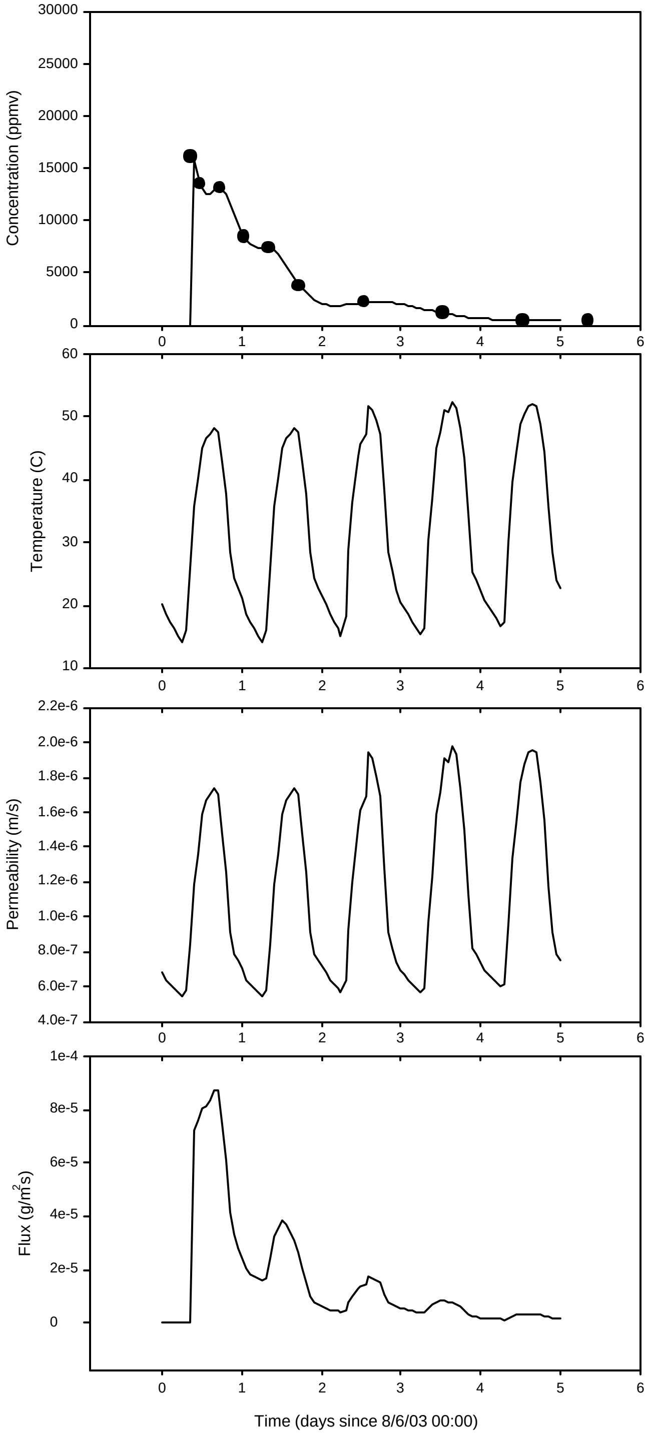


Figure 9. Shallow tarped, replicate #3. 4401. See Figure 4 caption.

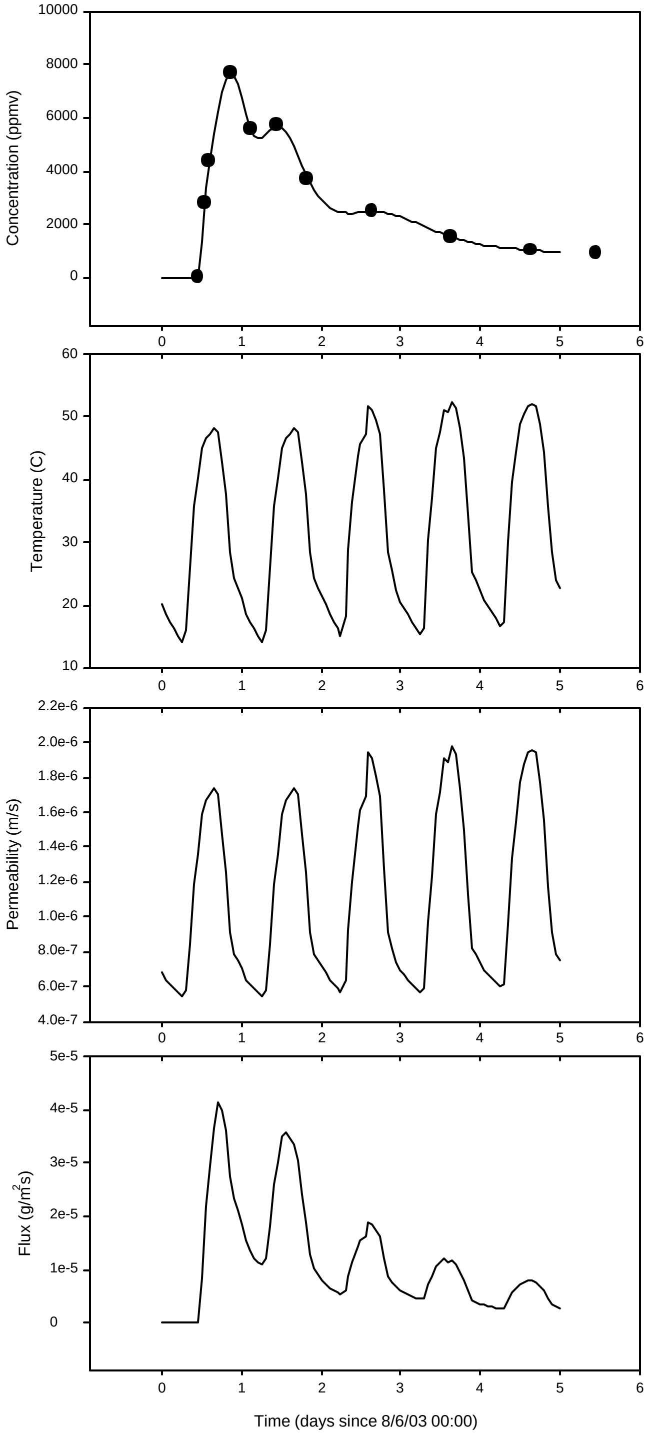


Figure 10. Deep tarped, replicate #1, 4402. See Figure 4 caption.

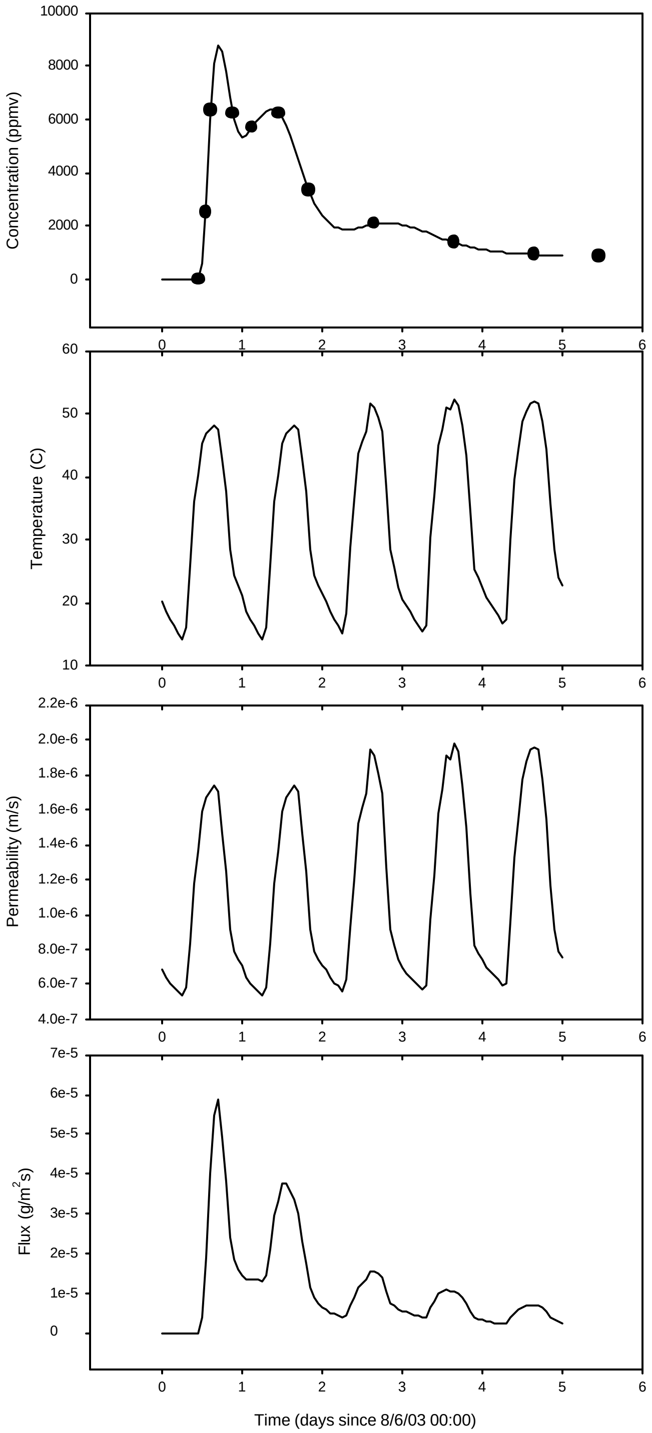


Figure 11. Deep tarped, replicate #2, 4402. See Figure 4 caption.

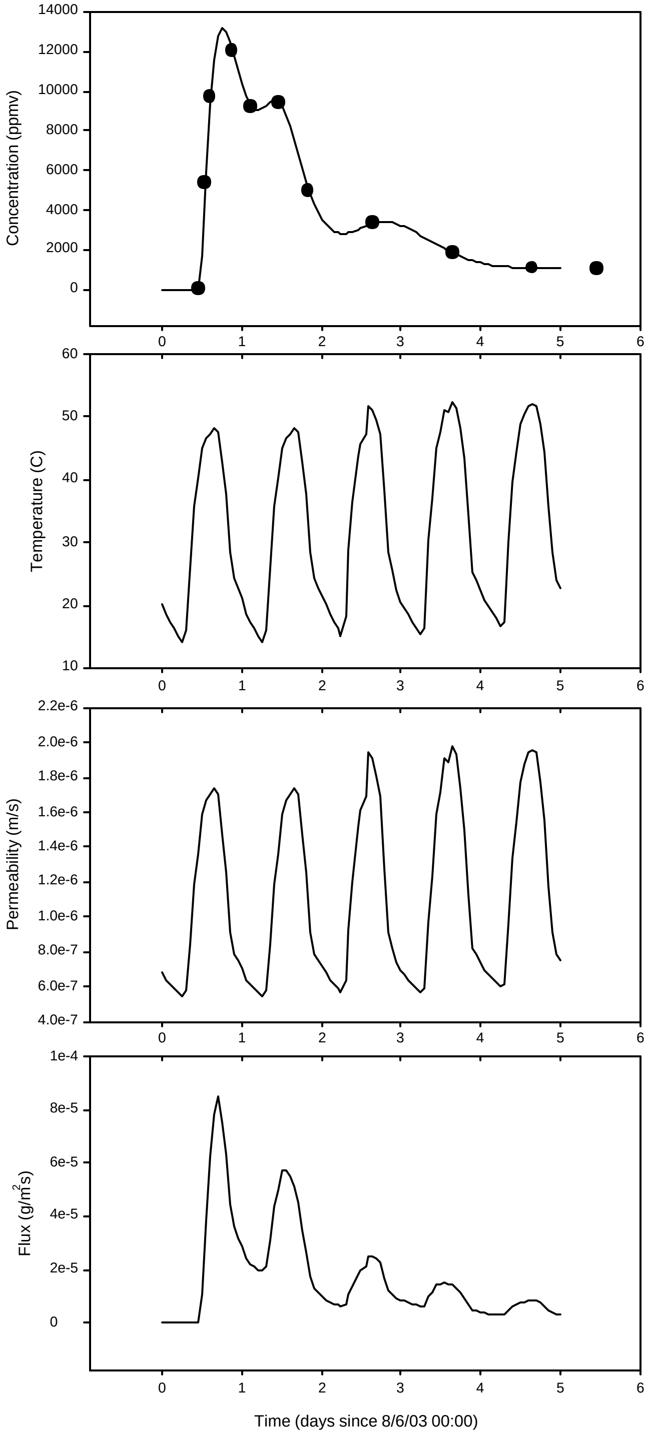


Figure 12. Deep tarped, replicate #3, 4402. See Figure 4 caption.

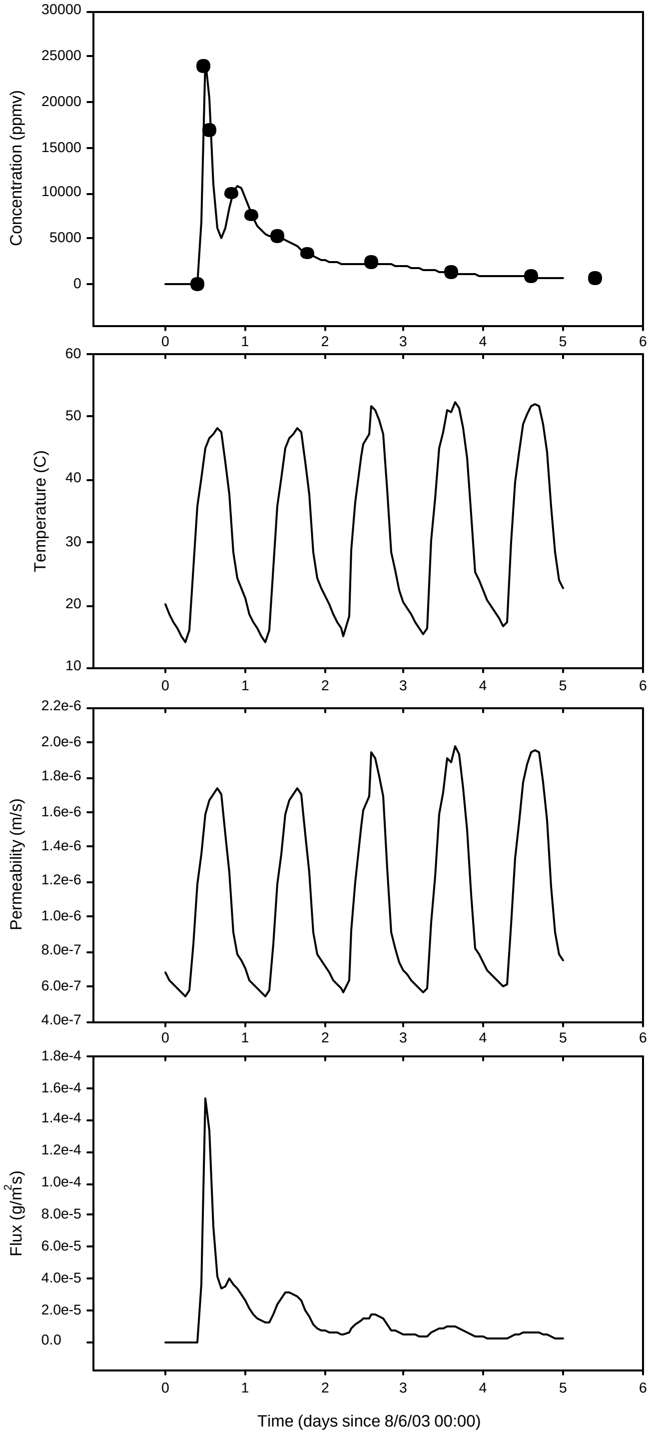


Figure 13. Shallow tarped, replicate #1, 4402. See Figure 4 caption.

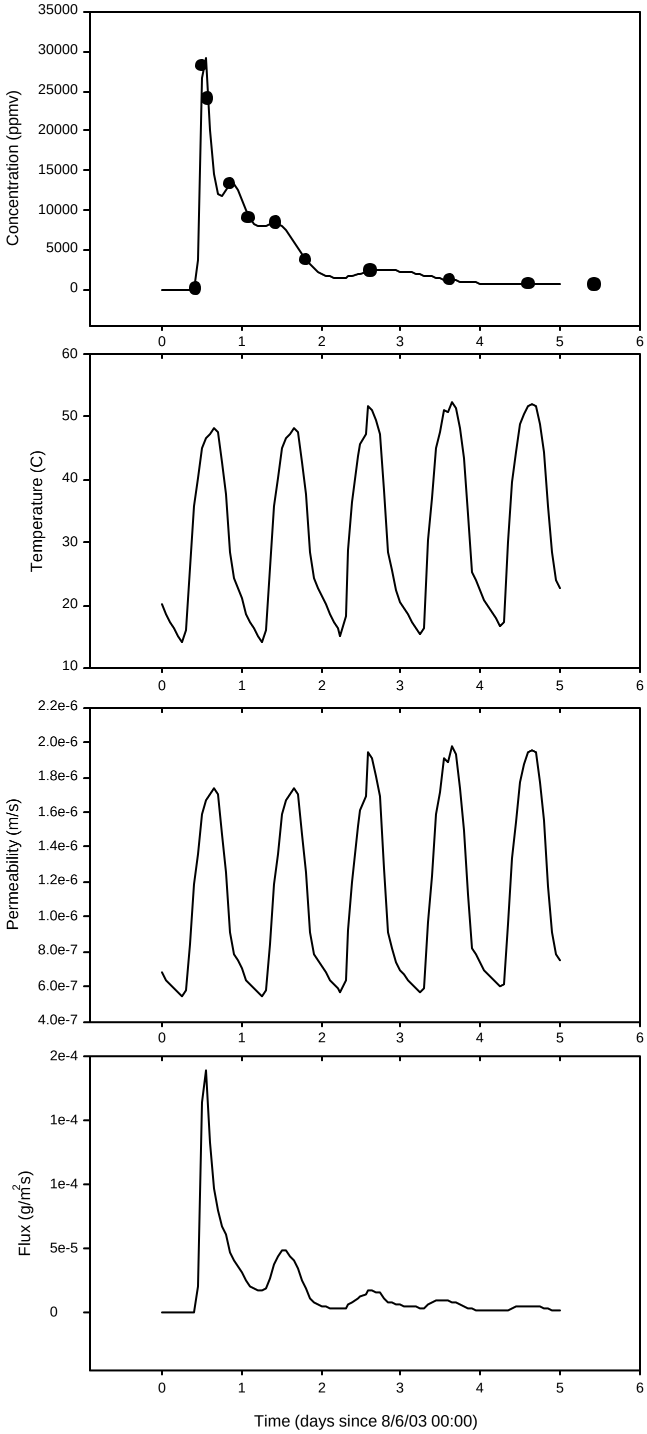


Figure 14. Shallow tarp, replicate #2, 4402. See Figure 4 caption.

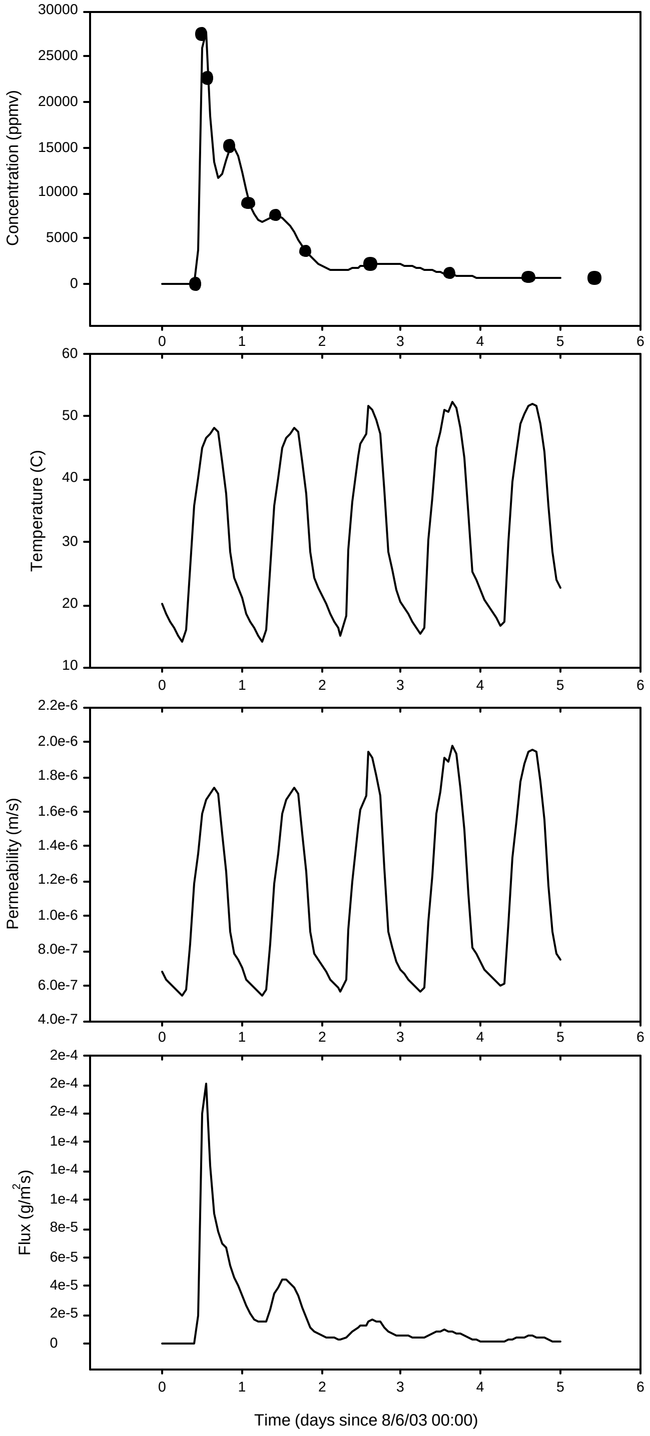


Figure 15. Shallow tarped, replicate #3, 4402. See Figure 4 caption.

Table 8 depicts the analysis of variance using the theoretical mass evolved from Table 7. The treatments were statistically different (p<.01) with the shallow treatment about 1.8x the deep treatment. Based solely on laboratory measured permeability relationships in combination with the concentration difference, these results support the case for reducing the deep-tarped emission ratio.

Table 8. Analysis of variance of integrated 24-hour theoretical flux for deep vs shallow treatments.

```
Analysis of Variance for C4
Source     DF        SS        MS        F        P
Treatment   1    10.083    10.083    26.77    0.000
Error      10     3.767     0.377
Total      11    13.850
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Treatment        Mean      StDev   -------+---------+---------+---------
Deep        6    2.4333    0.5750  (------*------)
Shallow     6    4.2667    0.6501                       (------*------)
                                   -------+---------+---------+---------
Pooled StDev =   0.6137                 2.40      3.20      4.00
```

While these calculated flux values are useful for comparing the two treatments in this particular study, they cannot be used for calculating off-site air concentrations and, hence, I have used the phrase ‘theoretical mass’ in Table 7. There are difficulties that occur in field situations, which are not present in the laboratory measurement of permeability. Protocols for the study of tarp permeability require careful scrutiny of tarping material in order to avoid testing samples which contain rips, tiny holes, folds, stretched areas or other anomalies. Rolling out the tarp during application probably creates microscopic holes, folds, or other features, which would increase tarp permeability. I have seen applications where noticeable tears were taped shut. Yagi et al. (1993) found with low density polyethylene tarp that over four flux-sampling locations the tarp thickness varied from 2.6 to 4.1 mil with consequent flux varying by a factor of 2.5 between the thinnest and thickest of the four locations. In addition to stretching, the presence of tiny holes could lead to large fluxes from small areas. Off-gassing is also likely from under the edge of the tarp, though tarp edges are typically buried beneath soil, which would slow down methyl bromide escape at the edge. Other circumstances may also arise such as animal activity on the tarp. I have observed tarp damage by crows. The manufacturing quality and additives can also affect tarp permeability. Gamliel et al. (1998) specifically cite ‘production quality’ (page 146) to be a major determinant of permeability. In addition, the presence of absence of various metal additives changed the permeability of high density polyethylene films by a factor of about ten (Gamliel et al, 1998 Table 3). While initial laboratory measurements indicated very low permeability for virtually impermeable film (VIF), a subsequent side-by-side field trial using off-site air concentration field measurements comparing high density polypropylene to VIF showed no differences (Segawa and Kim 1998). Possible reasons for the lack of difference included tarp quality. Besides factors which may increase tarp permeability, there can be wind-induced flapping of tarps, which may result in higher rates of flux. For these reasons, predicting off-site air concentrations based on laboratory measured permeability is not reliable. However, within the context of this field study, the relative flux between the two treatments does seem like a reasonable comparison because all other conditions were held constant.

Two further questions arise from this study: Are off-site air concentrations likely to be a problem after tarp-cutting and how does the deep-tarp application affect worker exposure at tarp-cutting.

The deep application delayed and reduced the peak concentrations underneath the tarp. The general concentration function over time of deep versus shallow treatment showed a sudden, high peak for the shallow applications, followed by a relatively rapid tail-off. The deep treatments showed concentration peaks which were lower and delayed (skewed to right) compared to the shallow. However, the tail-off was not as abrupt, and from about day 3-5 the concentrations beneath the tarp in the deep treatments were higher than for shallow treatments.

In this study, off-site air concentrations were not made. It is not possible to directly estimate air concentrations. The off-site air concentrations would consist of a transient spike associated with tarp cutting and a longer tail-off due to continued release of methyl bromide from the soil. There is indirect evidence that methyl bromide soil storage levels at tarp cutting would be approximately similar between the two treatments. An analysis of variance of the cumulative flux over the five days of the study showed that there was no statistical difference between the deep- and shallow-tarped treatments (p>0.1). This is weak evidence that off-site air concentrations will not be problematical from the deep-tarped application since shallow-tarped application do not pose such a problem and the lack of significant different between the cumulative fluxes hints that the soil storage of methyl bromide is also approximately the same.

With regard to immediate air concentrations of methyl bromide associated with tarp cutting, I have analyzed the concentrations under the tarp during the final interval. Table 9 shows this analysis. The concentrations below the tarp are statistically significantly different (p<.01) with

```
Table 9. Analysis of Variance for Deep vs Shallow, Concentration (ppmv)
during final interval
Source     DF        SS        MS        F        P
Treatment   1    665052    665052    21.46    0.001
Error      10    309879     30988
Total      11    974931
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ----------+---------+---------+------
Deep        6     902.8     230.9                     (-----*------)
Shallow     6     432.0      93.1   (-----*------)
                                   ----------+---------+---------+------
Pooled StDev =    176.0                    500       750      1000
```

the concentrations for the deep-tarped application approximately twice magnitude of the shallow-tarped application.. This indicates that the immediate, and transient release of gas from tarp cutting would lead to concentrations approximately twice as large as air concentrations from the shallow-tarped application.

cc: Kean S. Goh, Ph.D., Agriculture Program Supervisor IV
Sally Powell, Senior Environmental Research Scientist

bcc: Johnson Surname File

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Appendix 1. Questions posed to Matt Gillis of Tri-Cal based on Phase 1 review. Responses from Matt Gillis indented below question.

Questions on study: Comparison of methyl bromide gas concentrations in the tarp soil inter-space: Deep broadcast tarped vs shallow broadcast tarped fumigation.

1. Appendix 8, pg 70 shows a sample (?) calibration file. When I regress the first column (Lvl.Area/ht.) on the second column (Amount), I get Y=0.202X+265. The analysis printed below the graph shows Y=0.0000Xy+0.2378X. Why are these equations different?

   The selected calibration method was non-linear, "Quadratic through the origin ($Ax^2 + Bx$)". In printing out the curve, the print font was different than the screen font, the Ax2 was printed as "AXy", with "A" being 0.0000 and "x^{2}" as Xy. The software we use to interface with the GC allows for several regression types for calibration. The regression type used was selected because it provided the best r². Linear regression may provide good r², however, it does not necessarily follow real world instrument response over a wide range of concentrations. GC with FID often has a slight convex slope over a wide range of concentrations; i.e., it is not truly linear. We typically choose the regression type that gives the best r², since we have that option.

2. Table 4 (Appendix 5, pg 43) lists QC data. The samples with sort codes 5,6,7 appear to come from a different calibration equation than the other 10 samples for interval 1. How does this occur?

   These values were used because they were from the same standard matrix and also the analysis of the standard injections fell within the range or bracketed the sample analysis period, so all of those samples were utilized. In this table, the value of interest is the peak area, which does not depend upon a calibration equation, and as such allows these samples to be used without biasing the results.

3. Table 4 (pg43), the coefficient of variations are based on the peak. Since different calibration equations are used on different samples, shouldn't the coefficient of variation be based on the estimated concentration, instead of on peak area?

   The coefficients of variation in Table 4 are based upon the data used in the recovery calculations in preceding columns as an estimate of the variation in those means. See answer to 4 below

4. Table 4 (pg43), the recovery calculations are based on peak area. Since different calibration equations are used on different samples, shouldn't the recovery calculations be based on concentration instead of peak area?

   No, because the concentration is a constant since we are evaluating the same apple not comparing different apples. The same gas standard matrix from the same source cylinder is used for the field recovery samples as for “time 0” samples run during the analysis for each interval. The purpose of using peak area is that it is independent of calibration and takes into account variations in instrument response, as well, which accounts for that source of variability. The primary variable is the average magnitude of instrument response to the sample matrix. Using concentrations would factor out short term variation due to instrument response because determination of concentration is secondary to the GC response to the same matrix.

5. Are the concentrations shown in Table 3 adjusted to a standard set of conditions? That is, the temperatures at which the samples were collected varied as much as 90F (Graph 9, pg73 from 65 to 155F). Are the calculated concentrations normalized for temperature effects.

   As referenced in the protocol this study compares relative differences between treatments over time. Because samples for each interval were collected under the same conditions, normalizing the data would not change the relative differences between treatments. So, although overall normalization would provide some relevance on an academic level, it was unnecessary for the purpose of this study.

6. The 18 inch soil temperatures in Graph 8 (pg72) appear to take unexpected and potentially anomalous dips, for example, at 6AM 8/7/03 where the temperature drops from about 83 to 71F. Why is this?

   I don’t know. The 5 spikes that appear in the graphs do not appear with the other two data loggers data sets, so they were probably voltage spikes.

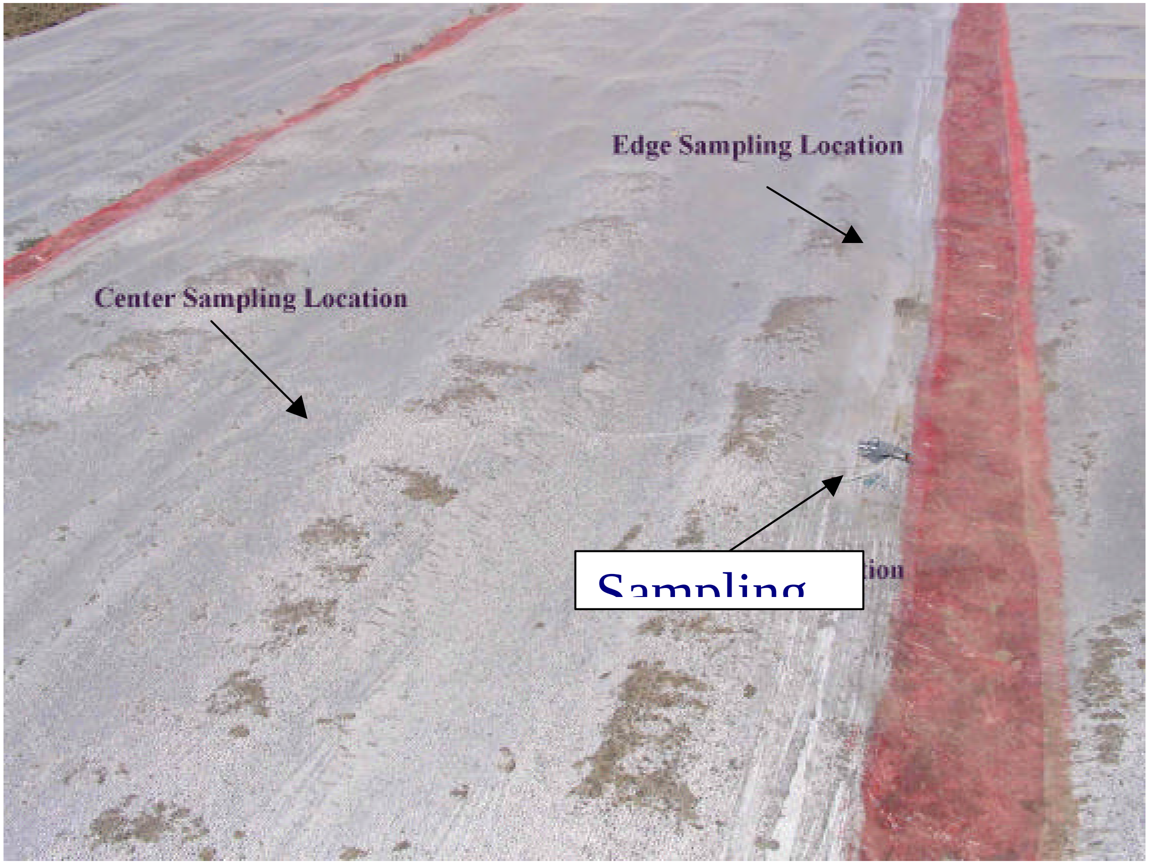
7. Pg 71, units of temperature shown as C, but are probably F.

   You are correct, it is °F. That graph did not get changed.

8. How often did you run a calibration curve?

   On the 1st day of analysis, 6 calibration curves were generated before the days’ analysis was complete. The validity of the final curve was verified daily and after every 10 samples by use of QC check standards.

9. Can you provide more exact map of where the samples were taken? Both field maps indicate that they were not drawn to scale and it's not clear to me where the samples were drawn.
   Yes, I can provide a more detailed map of the sampling locations, although the map is reasonably descriptive. The sampling locations were selected based upon sampling across the swath and away from the ends of the passes. The photo below that may help with the description.



10. The SOP #BR-FD-03, section 8.1 Syringe gas sample storage stability and recovery describes a recovery method which uses the estimated and standard gas concentrations instead of the peak areas. How does this recovery method based on estimated and known concentrations relate to the peak area method which was described in the study?
    The SOP says either concentration or response (peak area), *"The ratio of the SSFR to the gas standard concentration (**or response**) is the correction factor:"* See answer to #3 above.

11. The SOP #BR-AP-001 (pg3) states "Examine the sheet of film to be tested and select portions for sampling that are representative of undamaged film; i.e., free of holes, abrasions, creases, etc." and "Be careful not to stretch the film during the unrolling/sampling process." In conducting permeability studies, what percentage of the film is acceptable for testing?

    Usually most of the film is acceptable. Generally speaking, it is very seldom that film samples are rejected. These procedures were developed for personnel to select representative samples of film. Only a small area is tested in the apparatus, so it is important that it is not collected from damaged or unrepresentative portions, since this would disproportionately impact permeability measurements.

    Do you have studies indicating the effect of stretching on the permeability?

    No, we do not have studies indicating the effect of stretching on permeability. The reason this is stated in the SOP is that we consider it good procedure.

12. Did either shallow or deep application use closing shoes and/or compaction roller?

    No.

Appendix 2. FORTRAN source code listing for FLUXEST3.FOR.

```
C     Last change:  BJ   14 Jan 2004    9:41 am
        program fluxest3
cccccccccccccccccccccccccccccccc
c
c 1/13/04 there was a problem with fluxest2.  The cubic spline interpolator gave
c negative values for two of the shallow treatments in the group 4401.  This
c is a function of the cubic spline algorithm becuase i input thedata into table
c curve and asked for spline interpolation and the same thing happeneed.
c therefore, to fix this, i will use linear interpolator for region from
c start of app (conc=0) to first measured value, then cublic spline after
c that based on that set of points, because those seemed to interpolate pretty
c well, the cubic sline for 4402 shalow and for all of deep seemed ok
c
c i will use the fluxest2 algorithms for the 9 cases as before, and for the
c three cases where 4401 and shallow i will use the linear segment followed by
c the cublic spline based on those measured values
c the output files will be .OF3 (fluxest3) instead of OUT
C THE T,C ARRAYS FOR THE THREE SHALLOW ONES WILL BE SET UP TO ONLY REFLECT
C THE MEASUREMENTS USED IN THE SPLIN, I.E. THE FIRST 'MEASUREMENT' WHICH I AM
C ACTRUALLY ADDING IS THE 0 CONCENTRATION AT THE START OF THE APPLICATION TIME
C HOWEVER THE ESTIM FUNCTION WILL NOW NEED TO KNOW WHICH CASE IT IS WORKING
C ON, AND WILL NEED THE TIME THAT THE APPLICATION STARTED, SINCE THAT WILL NO
C LONGER BE IN T,C

cccccccccccccccccccccccccccccccccccc
c
c
c fluxest2, based on fluxest1, adds a loop to cycle through the 12 csv files
containing
c the concentration information, for each file, fluxest2 will create an output file
c using the first six characters of the input file name and containing a data table
with
c the time (days since 8/6/03 00:00) and concentration, temperature, permeability, and
c flux.  This file can be used for graphing.
c
c also a community output file will be created which gives the integral of the flux
c over each day of positive concentrations, the final integral may be for less than 24
hours
c together with the starting time value, and the integral over the entire period,
c along with the identifying characters of the data set
c i examineed th eoutput from fluxest2 by grahing and by handcalculting a selected set
of vlues
c the results seemed to be ok
C THE INPUT FILES ARE 4401D1.CSV, 4401D2.CSV ETC
C THE INDIVIDUALOUTPUT FILES FOR GRAPHING ARE 4401D1.OUT, 4401D2.OUT ETC
C THE COMMON OUPTUT FILE IS FLUXEST2.OUT
C
C
c
c a new function, flux, was created which is used to calculate the flux and is
c set up as an external function in order to be called by qromb, the
c integration routine
c
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
```

```
c combining conc24 (spline interpolated concentration) and permeab (time and
temperature
c during study and estimated permeability as a function of temperature)
c into a single program to estimate the flux
c
c the concentration, time function needs to have the x values converted to
c fractional days and to reset the starting point to 00;00 8/6/03 in order to
c match the temperature function
c
c  i introduced a linear interpolator to give me the temperature functions
c at points of my choosing
c
cfirst stab will be simply going at 100 intervals, estimating the relevant quantitites
c and priting out table so that i can graph and assess
c
cccccccccccccccccccccccccccccccccccccccccccccomments below for program predecessor
conc24
c program conc24 reads a file containing concentration
c measurements and hooks the measurements into a cubic
c spline interpolator to set up a function, which is then
c integrated over 24 hours since application to estimate
c something that is proportional to flux
c
cccccccccccccccccccccccccccccccc
        implicit none
        REAL t(100),c(100)  !time after app and concentration
        REAL Y2(100),YP1,YPN  !Y2 IS TABLE OF 2ND DERIVITIVES, YP1,YP2 FIRST
DERIVITIVE AT FIRST AND LAST POINTS
        CHARACTER*50 FIN,FOUT
        REAL DX ,DY,ESTIM,FLUXF
        INTEGER COUNT, I,J,K,L,M,IK
        COMMON /KEY/T,C,Y2,COUNT,TTHRES  !COMMON TO COMMUNICATE WITH FUNCTION
        COMMON /LINSHALL/SHAL4401  !PASSES INFO TO ESTIM NEEDED TO LINEARIZE FIRST
SEGMENT OF 4401 SHALLOW CASES
        LOGICAL SHAL4401  !TRUE IF WORKING ON IBIG=4,5, OR 6 (I.E. SHALLOW 4401)
        EXTERNAL ESTIM,FLUXF  !ESTIM FUNCTION ESTIMATES CONCENTRATION, FLUXF ESTIMATES
FLUX

        COMMON /FORFLUX/UNSCAN,IUNSCAN
        REAL SS24,SS120
        CHARACTER*10 TMPC
        CHARACTER*10 FINS(12)
        REAL ZERTIM(12)
        INTEGER IBIG
        DATA FINS/'4401D1.CSV','4401D2.CSV','4401D3.CSV','4401S1.CSV',
     1       '4401S2.CSV','4401S3.CSV','4402D1.CSV','4402D2.CSV',
     1       '4402D3.CSV','4402S1.CSV','4402S2.CSV','4402S3.CSV'/
        DATA ZERTIM/.31,.32,.32,.33,.34,.35,.45,.46,.46,.42,.43,.43/
        REAL unscan(2,2000) !arrayunscan will hold fahrenheit temperatures from unscan
it 1=time,2=temperature F
        INTEGER IUNSCAN
        REAL TM(501),CNC(501),TEMPX(501),PERMEA(501),FLUX(501)
        REAL TFACT
        REAL INTERP,ST,TTHRES
        REAL INTSTRT,INTEND,QRINT(5),LENINT(5),DAY5
```

```
        REAL tttx,ttty


C
C  CREATE COMMON OUTPUT FILE WHICH WILL HOLD THE INTEGRALS, START TIMES AND FILE NAME
        OPEN(UNIT=12,STATUS='UNKNOWN',FILE='FLUXEST3.OUT')  !COMMON OUTPUT FILE IS
UNIT 12
        WRITE(12,444)

444     FORMAT(1X,'FILENAME    INTDAY1       INTDAY2        INTDAY3',
     1  6x,
     1'INTDAY4      INTDAY5      LENDAY1      LENDAY2      LENDAY3    ',
     2' LENDAY4      LENDAY5      FULLQ       FULLLENDAY')

C
C GET TEMPERATURE DATA, SAME TEMPERATURE DATA USED FOR ALL DATA SETS
C NOW READ IN UNSCANIT INFO AND GET IT READY FOR USE

        OPEN(UNIT=1,STATUS='OLD',FILE='401D.CSV')  !THIS FILE CONTAINS TIME,TEMPRATURE
DATA FOR 4401 DEEP 5 DAYS
        IUNSCAN=0
1111   CONTINUE
         READ(1,*,END=115)UNSCAN(1,IUNSCAN+1),UNSCAN(2,IUNSCAN+1)
          IUNSCAN=IUNSCAN+1
          GOTO1111
115     CONTINUE
        WRITE(6,116)IUNSCAN
116     FORMAT(1X,'TEMPERATURE FILE READ IN WITH ',I6,' POINTS....')
        CLOSE(1)
        WRITE(6,119)
119     FORMAT(1X,'CONVERTING FAHRENHEIT VALUES TO CENTIGRADE.........')
        DO I=1,IUNSCAN
          UNSCAN(2,I)=(UNSCAN(2,I)-32)*(5./9.)  !CONVERT FROM FAHRENHEIT TO CENTIGRADE
        END DO
C
C NOW SET UP BIG LOOP TO RUN THROUGH 12 CONCENTRATION DATA FILES
        DO 9999 IBIG=1,12
         IF(IBIG.GE.4.AND.IBIG.LE.6)THEN
           SHAL4401=.TRUE.  !THIS IS ONE OF THE SHALLOW TTMNTS IN 4401
         ELSE
           SHAL4401=.FALSE.
         ENDIF
         TMPC=FINS(IBIG)
C        TMPC='4401D1.CSV'
         FIN(1:10)=TMPC(1:10)
         OPEN(UNIT=1,STATUS='OLD',FILE=TMPC)  !UNIT 1 IS INPUT FILE FOR CONCENTRATIONS
         FOUT(1:6)=FIN(1:6)
         FOUT(7:10)='.OF3'
         OPEN(UNIT=10,STATUS='unknown',FILE=fout(1:10))  !UNIT 10 IS OUTPUT FOR THIS
SPECIFIC DATA TABLE


C
C AND ZERO THE REMAINING VALUES
```

```
         DO L=1,100
          T(L)=0.
          C(L)=0.
         END DO
C
C READ IN REMAINING VALUES AND KEEP TRACK OF HOW MANY
         COUNT=1 !COUNT 1 FOR THE FIRST 0 WHICH THE PROGRAM FORCED
1        CONTINUE
          READ(1,*,END=50)T(COUNT+1),C(COUNT+1) !NOTE INDEX STARTS AT 2
          COUNT=COUNT+1
          GOTO1
50       CONTINUE
         CLOSE(1)
         WRITE(6,51)COUNT-1,COUNT,TMPC
51       FORMAT(1X,I4,' TIME/CONC VALUES READ IN, TOTAL OF ',I4,
     1   ' VALUES'/,
     1    'IN FILE ',A10)

C FOLLOWING CODE ADJUSTS THE T,C ARRAYS AND COUNT IF WORKING ON SHALLOW 4401 PLOTS
        IF(SHAL4401)THEN   !NEED TO GET RID OF 0 VALUE AND REDUCE COUNT BY 1
          DO IK=1,COUNT-1
           T(IK)=T(IK+1)
           C(IK)=C(IK+1)
          END DO
          T(IK+1)=0.  !THIS WONT GET USED NOW, ARRAY SIZE IS 1 LESS THAN
          C(IK+1)=0.
          COUNT=COUNT-1
        ENDIF
C
C NOW FIX UP TIME VALUES in the concentration measurement data sets
C convert from hours to days and reset starting point
C FIRST DETERMINE WHICH DATA FILE WE ARE WORKING ON AND USE THAT
C CORRESPONDING START TIME ADJUSTMENT FROM TABLE ABOVE

          ST=ZERTIM(IBIG)  !SET STARTING VALUE FOR THIS DATA SET AND THRESHOLD VALUE
FOR CUBIC SPLINE TO START INTERPOLATING
          TTHRES=ST

         DO I=1,COUNT
          T(I)=ST+T(I)/24.  !CONVERT "HOURS PAST APP" TO "DAYS PAST 00:00 8/6/03"
         END DO

C I WANT TO GET THE MEASURED VALUES PLOTTED OUT ON THE SAME GRAPHS AS THE
C ESTIMATED CONC/TEMP/PERM/FLUX GRAPHS
C SO I NEED TO PRINT OUT THE CONCENTRATION DATA AFTER IT'S BEEN CHANGED INTO THE
C COMMON TIME UNITS.  USE THE STRING FOUT, JUST CHANGE THE EXTENSION A BIT
        FOUT(8:10)='CTU' !CHANGED TIME UNIT
        OPEN(UNIT=15,STATUS='UNKNOWN',FILE=FOUT(1:10))
        DO I=1,COUNT
         WRITE(15,1015)T(I),C(I)
1015     FORMAT(1X,F10.3,',',F10.3)
        END DO
        CLOSE(15)
C
C AT THIS POINT, THE CONCENTRATION MEASUREMENTS HAVE THE CORRECT TIME UNITS
```

```
C AND CAN GO AHEAD AND MAKE CALLS TO CUBIC SPLINE ROUTINES TO GET THAT SET UP


C
C GET SET UP FOR CUBIC SPLINE
C MUST SPECIFY FIRST DERIVITIVES AT FIRST AND LAST POINTS
C WILL SET FIRST DERIVITIVE EQUAL TO ZERO, SINCE FUNCTION MUST COME
C REST AT 0 (IE F(0)=0)
C AND WILL SET LAST DERIVITIVE EQUAL TO ZERO, EVEN THOUGH IT PROBABLY IS A
C SMALL NEGATIVE VALUE (TAIL OF SKEWED FUNCTION LIKE LOGNORMAL)
C ALSO FOR FIRST 24 HOURS, LAST DERIVITIVE WONT GET USED, BUT MAY
C WISH TO INTEGRATE THE WHOLE THING JUST FOR KICKS LATER ON
C
         YP1=0
         YPN=0
         CALL SPLINE(T,C,COUNT,YP1,YPN,Y2)

C FUNCTION ESTIM IS NOW READY TO ESTIMATE THE CONCENTRATIONS



          DO I=0,100  !RUN THROUGH TIME, EVEN INTERVALS AND PRINT OUT GRAPHS
           TM(I+1)=5.*FLOAT(I)/100.  !THIS IS THE TIME TO USE FOR X
           CNC(I+1)=ESTIM(TM(I+1))   !THIS IS ESTIMATED CONCENTRATION IN PPMV
           TEMPX(I+1)=INTERP(TM(I+1),UNSCAN,IUNSCAN,K)  !interpolated temperature at
tm(i)
           IF(K.NE.0)THEN  !check flag, and for now halt with error message
            WRITE(6,1221)TM(I+1),I
1221        FORMAT(1X,'AT TIME ',F6.2,' LINEAR INTERP BNDS EXC ',I4)
            STOP
           ENDIF
           PERMEA(I+1)=(7.56E-7)*TFACT(TEMPX(I+1))  !PERMEABILITY IN M/S
           FLUX(I+1)=PERMEA(I+1)*CNC(I+1)*(3.9E-3)  !PEREMABILITY TIMES CONCENTRTION
(CONVERTED TO G/M3)
          !FLUX ABOVE IN G/M2S, 3.9E-3 CONVERTS 1 ML/M3 TO 3.9E-3G/M3 AT BETWEEN 20-
25C
          END DO

C WRITE OUT CALCULATION RESULTS NOW IN FORM CONVENIENT TO POP INTO SIGMAPLOT
          DO I=1,101
           WRITE(10,423)TM(I),CNC(I),TEMPX(I),PERMEA(I),FLUX(I)
423        FORMAT(4(G12.4,','),G12.4)
          END DO

C testing section
C          tttx=1.
C          call testf(fluxf,tttx,ttty)
C
C NOW DO THE INTEGRATIONS THAT ARE NEEDED
          DO I=1,5
            WRITE(6,377)FINS(IBIG),I
377         FORMAT(1X,'STARTING INTEGRATION ON ',A10,' FOR DAY# ',I2)
            INTSTRT=FLOAT(I-1)+ST
            INTEND=MIN(FLOAT(I)+ST,5.)  !CAN ONLY INTEGRATE UP TO 5 DAYS, LAST DAY
WILL BE A BIT SHORT
```

```
            CALL QROMB(FLUXF,INTSTRT,INTEND,QRINT(I))
            LENINT(I)=INTEND-INTSTRT
          END DO
C
C DO AN INTEGRATION OVER THE WHOLE INTERVAL TO COMPARE WITH SUM OF INTGRATIONS
          CALL QROMB(FLUXF,ST,5.,DAY5)
          WRITE(12,589)FINS(IBIG),(QRINT(I),I=1,5),
     1                 (LENINT(I),I=1,5),DAY5,5.-ST
589       FORMAT(A10,1X,11(G12.3,','),G12.3)
C        CALL QROMB(ESTIM,0.,24.,SS24)
C        CALL QROMB(ESTIM,0.,120.,SS120)
C        WRITE(6,300)FOUT(1:6),SS24,SS120
C        WRITE(10,300)FOUT(1:6),SS24,SS120
C300     FORMAT(1X,A6,2X,F15.2,2X,F15.2)
C        DO I=1,COUNT
C         WRITE(6,301)T(I),C(I)
C301      FORMAT(1X,F15.2,F15.2)
C        END DO
         CLOSE(10)  !CLOSE THE SPECIAL OUTPUT FILE
9999    CONTINUE  !THIS IS END OF LOOP THAT CYCLES THROUGH THE 12 FILES
        STOP
        END PROGRAM
CCCCCCCCCCCCCCCSPECIALTEST SUBROUTINE TO DEBUG PROBLEM
        subroutine testf(func,x,y)
        REAL func
        EXTERNAL func
1        write(6,*)'enter x value time '
        read(5,*,end=1000)x
        y=func(x)
        write(6,100)x,y
100     format(2f10.4)
        goto1
1000    stop

        END SUBROUTINE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
        REAL FUNCTION FLUXF(X)
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C  THIS FUNCTION CALCULATES THE FLUX BASED ON TEMPERATURE, PERMEABILITY, CONCENTRATION
AND TIME
C 'X', WHICH IS IN UNITS OF DAYS SINCE 8/6/03 00:00.  THE CONCENTRATION DATA HAS BEEN
RESET
C SO THAT THE TIMES ARE CONSISTENT WITH THIS TIME DEFINITION, THE VARIABLE ST
C IS THE STARTING TIME IN TERMS OF THSI TIME DEFINITION
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
        IMPLICIT NONE
        REAL X   !TIME IN SPECIAL UNITS
        COMMON /FORFLUX/UNSCAN,IUNSCAN
        REAL UNSCAN(2,2000)
        REAL ESTIM
        REAL INTERP
        INTEGER KERR
        INTEGER IUNSCAN
        REAL TTX,TFACT,PERM,CNC
        CNC=ESTIM(X)
```

```
        TTX=INTERP(X,UNSCAN,IUNSCAN,KERR)
          IF(KERR.NE.0)THEN
            WRITE(6,100)X,TTX
100         FORMAT(1X,'ERROR FROM FLUXF: X OUT OF RANGE (X,TTX) ',2F7.3)
            STOP
          ENDIF
        PERM=(7.56E-7)*TFACT(TTX)
        FLUXF=PERM*CNC*(3.93E-3)
        RETURN
        END
CCCCCCCCCCCCCCCCCCCCCCCCCCCC
        REAL FUNCTION ESTIM(X)
        REAL T(100),C(100),Y2(100)
        INTEGER COUNT
        REAL X ,TTHRES
        COMMON /KEY/T,C,Y2,COUNT,TTHRES

        COMMON /LINSHALL/SHAL4401  !PASSES INFO TO ESTIM NEEDED TO LINEARIZE FIRST
SEGMENT OF 4401 SHALLOW CASES
        LOGICAL SHAL4401  !TRUE IF WORKING ON IBIG=4,5, OR 6 (I.E. SHALLOW 4401)

        REAL SLOPE,CONST

        IF (X.GT.TTHRES) THEN  !THIS IS STILL VALID EVEN FOR SHALL0W 4401
          IF(SHAL4401)THEN  !IN THIS CASE WE WANT LINEAR ESTIMATE BETWEEN TTHRES,0 AND
T(1),C(1)
            IF(X.LT.T(1))THEN  !IF HERE, THEN TTHRES.LE.X.LE.T(1)
              SLOPE=(C(1))/(T(1)-TTHRES)  !LINEARLY INTERPOLATE
              CONST=C(1)-T(1)*SLOPE
              ESTIM=SLOPE*X+CONST
            ELSE
             CALL SPLINT(T,C,Y2,COUNT,X,Y)  !OK, X > T(1), SO USE CUBLIC SPLINE
             ESTIM=Y
            ENDIF
          ELSE
           CALL SPLINT(T,C,Y2,COUNT,X,Y) !THIS IS NOT SHALL4401, SO PROCEED AS  BEFORE
           ESTIM=Y
          ENDIF
        ELSEIF (X.LT.TTHRES)THEN
          ESTIM=0  !IF BEFORE APPLICATION, THEN CONC DIFF IS ZERO
        ENDIF
        RETURN
        END
CCCCCCCCCCCCCCCCCCCCCCC
        SUBROUTINE SPLINE(X,Y,N,YP1,YPN,Y2)
      PARAMETER (NMAX=100)
      DIMENSION X(N),Y(N),Y2(N),U(NMAX)
      IF (YP1.GT..99E30) THEN
        Y2(1)=0.
        U(1)=0.
      ELSE
        Y2(1)=-0.5
        U(1)=(3./(X(2)-X(1)))*((Y(2)-Y(1))/(X(2)-X(1))-YP1)
      ENDIF
      DO 11 I=2,N-1
```

```
        SIG=(X(I)-X(I-1))/(X(I+1)-X(I-1))
        P=SIG*Y2(I-1)+2.
        Y2(I)=(SIG-1.)/P
        U(I)=(6.*((Y(I+1)-Y(I))/(X(I+1)-X(I))-(Y(I)-Y(I-1))
     *      /(X(I)-X(I-1)))/(X(I+1)-X(I-1))-SIG*U(I-1))/P
11    CONTINUE
      IF (YPN.GT..99E30) THEN
        QN=0.
        UN=0.
      ELSE
        QN=0.5
        UN=(3./(X(N)-X(N-1)))*(YPN-(Y(N)-Y(N-1))/(X(N)-X(N-1)))
      ENDIF
      Y2(N)=(UN-QN*U(N-1))/(QN*Y2(N-1)+1.)
      DO 12 K=N-1,1,-1
        Y2(K)=Y2(K)*Y2(K+1)+U(K)
12    CONTINUE
      RETURN
      END
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccccccccccc
      SUBROUTINE SPLINT(XA,YA,Y2A,N,X,Y)
      DIMENSION XA(N),YA(N),Y2A(N)
      KLO=1
      KHI=N
1     IF (KHI-KLO.GT.1) THEN
        K=(KHI+KLO)/2
        IF(XA(K).GT.X)THEN
          KHI=K
        ELSE
          KLO=K
        ENDIF
      GOTO 1
      ENDIF
      H=XA(KHI)-XA(KLO)
      IF (H.EQ.0.) PAUSE 'Bad XA input.'
      A=(XA(KHI)-X)/H
      B=(X-XA(KLO))/H
      Y=A*YA(KLO)+B*YA(KHI)+
     *      ((A**3-A)*Y2A(KLO)+(B**3-B)*Y2A(KHI))*(H**2)/6.
      RETURN
      END
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccccc
      REAL FUNCTION INTERP(X,A,N,I)
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
c linear interpolation of a table
C X IS PROVIDED, A(2,N) IS PROVIDED
C INTERP INTERPOLATES IN THE TABLE A(2,N)
C WHERE A(1,N) ARE THE X VALUES AND A(2,N) ARE
C THE Y VALUES, INTERP IS SET EQUAL TO THE
C INTERPOLATED TABULAR VALUE OVER X.
C THE TABLE A(2,N) IS ASSUMED TO HAVE THE
C A(1,N) VALUES ORDERED FROM LOWEST TO HIGHEST
```

```
C SO THAT A(1,1) IS MIN (A(1,I)) AND A(1,N) IS
C GREATEST.  I IS A FLAG SET EQUAL TO -1 IF
C X<A(1,1) OR +1 IF X>(A(1,N)) OR 0 OTHERWISE
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      IMPLICIT INTEGER(A-Z)
      REAL X,A(2,2000)  !CHANGED FROM A(2,N) brj JAN 05, 2004


C DETERMINE IF X OUTSIDE OF RANGE

      IF(X.LT.A(1,1))THEN
        I=-1
        INTERP=A(2,1)
        RETURN
      ELSEIF(X.GT.A(1,N))THEN
        I=1
        INTERP=A(2,N)
        RETURN
      ENDIF
      I=0

C USE BISECTION TO DETERMINE WHERE IN TABLE X IS

      KLO=1
      KHI=N
1     IF(KHI-KLO.GT.1)THEN
       K=(KHI+KLO)/2
       IF(A(1,K).GT.X)THEN
        KHI=K
       ELSE
        KLO=K
       ENDIF
      GOTO1
      ENDIF

C KHI,KLO NOW BRACKET INPUT VALUE OF X
C PERFORM LINEAR INTERPOLATION

      INTERP=A(2,KLO)+(X-A(1,KLO))*(A(2,KHI)-A(2,KLO))/(A(1,KHI)
     1        -A(1,KLO))
      RETURN
      END
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c
        REAL function tfact(temper)
cccccccccccccccccccccccccccccccccccccccccc
c
c provides factor to adjust permeability at 23 degrees to
c permeability at a different temperature
c temper is temperature in degrees centigrade
c the allowable range is 10-99, though the data for the equation
c came from 23 to 60C
c
ccccccccccccccccccccccccccccccccccccccccccc
```

```
        implicit none
        REAL temper, t
c do some checking
       if (temper.lt.10.or.temper.gt.99.) then
                WRITE(6,100)temper
100             FORMAT(1x,'tfact: temperature outside bounds ',f10.1)
                stop
        endif
        t=273+temper
        tfact=EXP(10.7)*EXP(-3168./t)
        return
        end
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccccccccccccccc
      SUBROUTINE POLINT(XA,YA,N,X,Y,DY)
      PARAMETER (NMAX=10)
      DIMENSION XA(N),YA(N),C(NMAX),D(NMAX)
      NS=1
      DIF=ABS(X-XA(1))
      DO 11 I=1,N
        DIFT=ABS(X-XA(I))
        IF (DIFT.LT.DIF) THEN
          NS=I
          DIF=DIFT
        ENDIF
        C(I)=YA(I)
        D(I)=YA(I)
11    CONTINUE
      Y=YA(NS)
      NS=NS-1
      DO 13 M=1,N-1
        DO 12 I=1,N-M
          HO=XA(I)-X
          HP=XA(I+M)-X
          W=C(I+1)-D(I)
          DEN=HO-HP
          IF(DEN.EQ.0.)PAUSE
          DEN=W/DEN
          D(I)=HP*DEN
          C(I)=HO*DEN
12      CONTINUE
        IF (2*NS.LT.N-M)THEN
          DY=C(NS+1)
        ELSE
          DY=D(NS)
          NS=NS-1
        ENDIF
        Y=Y+DY
13    CONTINUE
      RETURN
      END
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccccccccccccccccc
      SUBROUTINE QROMB(FUNC,A,B,SS)
      PARAMETER(EPS=1.E-6,JMAX=20,JMAXP=JMAX+1,K=5,KM=4)
```

```
      DIMENSION S(JMAXP),H(JMAXP)
      REAL FUNC  !BRJ ADDED 1/04
      EXTERNAL FUNC  !BRJ ADDED 1/04
      H(1)=1.
      DO 11 J=1,JMAX
        CALL TRAPZD(FUNC,A,B,S(J),J)
        IF (J.GE.K) THEN
          L=J-KM
          CALL POLINT(H(L),S(L),K,0.,SS,DSS)
          IF (ABS(DSS).LT.EPS*ABS(SS)) RETURN
        ENDIF
        S(J+1)=S(J)
        H(J+1)=0.25*H(J)
11    CONTINUE
      PAUSE 'Too many steps.'
      END
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccccccc
      SUBROUTINE TRAPZD(FUNC,A,B,S,N)
      IF (N.EQ.1) THEN
        S=0.5*(B-A)*(FUNC(A)+FUNC(B))
        IT=1
      ELSE
        TNM=IT
        DEL=(B-A)/TNM
        X=A+0.5*DEL
        SUM=0.
        DO 11 J=1,IT
          SUM=SUM+FUNC(X)
          X=X+DEL
11      CONTINUE
        S=0.5*(S+(B-A)*SUM/TNM)
        IT=2*IT
      ENDIF
      RETURN
      END
```