WSRC-RP-93-1545

Analysis of Volatile Organic Compounds (VOCs) in A/M Area Crouch Branch (Cretaceous) Aquifer Characterization Samples: 1993 (U)

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Westinghouse Savannah River Company
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Prepared for the U. S. Department of Energy under Contract No. DE-AC09-89SR18035

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Summary

Bulk samples (3 to 5 cm^3) were collected during the A/M Area Crouch Branch (Cretaceous) Aquifer Characterization (Phase I) Program. The samples were analyzed for chlorinated VOCs by the Savannah River Technology Center (SRTC) and MicroSeeps Ltd. All samples were sealed in the field immediately upon retrieval of the core and subsampling. A total of 113 samples locations were selected for analysis. The Environmental Sciences Section (ESS) of SRTC analyzed all locations in duplicate (226 samples). MicroSeeps Ltd was selected as the quality assurance (QA) check laboratory. MicroSeeps Ltd analyzed 40 locations with 4 duplicates (44 samples). The samples were collected from seven boreholes in A/M Area in the interval from 200 feet deep to the total depth of the boring (360 feet deep nominal); samples were collected every 10 feet within this interval. The sampling zone corresponds approximately to the Crouch Branch Aquifer in A/M Area. The overall A/M Area Crouch Branch Aquifer characterization objectives, a brief description of A/M Area geology and hydrology, and the sample locations, field notes, driller lithologic logs, and required procedural documentation are presented in WSRC (1993).

The primary analytes were trichloroethylene (TCE) and tetrachloroethylene (PCE). The sample data are summarized in Tables 1 and 2. All of the VOC concentrations were relatively low (less than approximately 0.1 ug/g) in this study. Approximately 70% of the samples were below detection (<0.001 ug/g) for both compounds. The maximum TCE concentration was 0.094 ug/g and the maximum PCE concentration was 0.030 ug/g. No detectable solvents were measured in MBCSB-1, MBCSB-6, and MBCSB-7. TCE was detected in each sample collected from MBCSB-3. Note that this boring is located near monitoring well cluster MSB-47, a location previously identified as a principal entry point of VOCs into the groundwater system. The TCE values in MBCSB-3 ranged from 0.003 ug/g to 0.051 ug/g. No PCE was detected in this boring. The rest of the borings (MBCSB-2, MBCSB-4, and MBCSB-5) showed a similar distribution of detected VOCs. These cores showed detectable VOCs near 220 feet deep and in the lower portion of the boring (e.g., 320 to 360 feet deep). Based on examination of the field geologic descriptions, these depths represent water bearing zones between or just above fine grained sediments (aquitards). The expected range of water concentrations associated with each depth discrete sample analyzed during the study is tabulated based on previus comparisons in A/M Area. These findings and additional observations are discussed below.

The quality assurance checks of the data suggest that the results are of high quality. There was a high degree of concordance between the intralaboratory duplicate samples. Additionally, the sample locations analyzed by both SRTC and MicroSeeps Ltd using different analytical methods yielded similar concentrations. SRTC analyzed the samples using a static headspace method developed to support SRS groundwater VOC remediation activities and documented in the EPA report on innovative VOC analysis methods (Looney et al., 1993). MicroSeeps Ltd utilized the

new (currently draft) EPA Method 5035 based on purge and trap of the suspended sediment sample using a special vial and laboratory apparatus (EPA, draft). The comparison data suggest that the heating of the sample vials in the SRTC sample set slightly improved the consistency and recovery of VOCs from the samples. Heating of the vials to encourage recovery of the VOCs into the purge gas is currently being examined by MicroSeeps to improve the performance of the new EPA method.

Methods

Depth Discrete bulk sediment samples were collected for chlorinated VOC analysis from the A/M Area Crouch Branch (Cretaceous) Aquifer Characterization. Samples were collected at ten foot intervals between 200 feet deep and the total depth of the boring (360 feet deep nominal) using a 94mm double tube wireline core. The cores were extruded into polyvinyl chloride troughs for immediate VOC sampling, followed by measuring, lithologic description, and archiving (WSRC, 1993). The driller and geological oversight informed the sampler of the drilling progress so that each target core could be sampled promptly. Bentonite based drilling fluids were utilized during the mud rotary drilling. Following extrusion of the samplers collected 3 to 5 cm^3 of the saturated bulk sediment using a 12 mm diameter sample tube (modified plastic syringe). As discussed below, all samples were sealed in the field immediately upon retrieval of the core and subsampling. The sampling syringes were decontaminated between samples by brushing and rinsing with isopropanol followed by deionized water.

The samples collected for this study were analyzed using two different methods to assist in assuring the quality of the data. All samples were analyzed by SRTC using a static headspace method. This method, originally developed to support VOC remediation technology demonstrations in A/M Area (Looney, 1993). A portion of the samples (approximately 20%) were analyzed by MicroSeeps Ltd as a quality check using the new EPA Method 5035 (EPA, draft). Each of these methods is summarized below. A full description of the SRTC method is provided in Appendix C and a copy of the draft EPA Method 5035 is provided in Appendix D.

Headspace Method (SRTC Analysis)

The depth discrete bulk sediment sample was extruded into a 22.5 mL borosilicate vial. Using a pipet, 5 mL of deionized water was added as a suspending solution and the vial was sealed by crimping an aluminum cap around a teflon lined butyl rubber septum. The sample was labeled and placed in a chilled ice chest for later analysis. Prior to field sampling, we determined the average weight of a sealed headspace vial containing 5 mL of suspending solution. Upon receipt of the sample vials from the field, the capped vials containing sediment samples were weighed. The amount of sediment in each vial was determined by subtracting the average weight from the sample weight. Each vial was then analyzed using a Hewlett Packard (HP) 5890 gas chromatograph (GC) equipped with an electron capture detector, a HP 19395 headspace sampler, and a 60m widebore capillary column coated with a nonpolar silicone phase. The flow and temperature conditions recommended by the manufacturers were used. The instrument was

calibrated using vials containing water of known concentrations. The conditions in the vials (headspace volume, suspension volume, etc.) were standardized to maintain the proportionality between the sediment concentration and the headspace concentration. For example, the heated (70 degrees Celsius) bath in the headspace bath maximizes the transfer of VOC into the headspace for analysis.

Standards were run corresponding to each of the seven cores collected in this study. All of the standards data, the equation for the relevant portion of the standard curve, and graphs of the data for TCE and PCE are provided in Appendix D. The concentration in each sample was estimated using the response factor from the appropriate portion of the calibration curve. All values are reported in units of micrograms of VOC per gram of bulk sediment (ug/g). The method is described further in Looney et al. (1993) -- Appendix C.

Modified Purge and Trap Analysis (MicroSeeps Ltd Analysis)

MicroSeeps Ltd recently implemented the new EPA Method 5035 (draft) in their laboratory and is providing this service to SRS under task order agreement. Samples were collected as described above and placed in specially designed vials. The vials allow sealing in the field and estimation of sample weight in the same fashion as the headspace method. The special sample container provides access from both ends and is designed to be mounted into a recently developed purge and trap GC interface (DynaSoils). At the present time, the capability to reproducibly heat the vials prior to analysis is not implemented in the method. The samples were analyzed using a HP GC equipped with both electron capture and flame ionization detectors. The concentration in each sample was determined using the response factor from the appropriate portion of the calibration curve. All values were originally reported in units of nanograms of VOC per gram of bulk sediment (ng/g). The summary table (Table 1) presents all data in units of ug/g for consistency. The method is described further in EPA (draft) -- Appendix D.

Results

The data for each sample location (core-depth) are summarized in Tables 1 and 2 for both laboratories. The full SRTC Dataset showing all duplicate results and supporting raw data are provided in Appendix A. The full MicroSeeps dataset is provided in Appendix B.

The primary analytes were trichloroethylene (TCE) and tetrachloroethylene (PCE). MicroSeeps Ltd analyzed for the following additional VOCs -- vinyl chloride, methylene chloride, trans 1,2 dichloroethylene, chloroform, 1,1,1 trichloroethane, and carbon tetrachloride. The detection limits for both laboratories are listed in Table 2. Those compounds marked with an asterisk were not detected in the samples analyzed.

The sample data are summarized in Tables 1 and 2. All of the VOC concentrations were relatively low (less than approximately 0.1 ug/g) in this study. Approximately 70% of the samples were below detection (<0.001 ug/g) for both primary compounds. The maximum TCE

concentration was 0.094 ug/g and the maximum PCE concentration was 0.030 ug/g. No detectable solvents were measured in MBCSB-1, MBCSB-6, and MBCSB-7. TCE was detected in each sample collected from MBCSB-3. Note that this boring is located near monitoring well cluster MSB-47, a location previously identified as a principal entry point of VOCs into the groundwater system. The TCE values in MBCSB-3 ranged from 0.003 ug/g to 0.051 ug/g. No PCE was detected in this boring. The rest of the borings (MBCSB-2, MBCSB-4, and MBCSB-5) showed a similar distribution of detected VOCs. These cores showed detectable VOCs near 220 feet deep and in the lower portion of the boring (e.g., 320 to 360 feet deep). Based on examination of the field geologic descriptions, these depths represent water bearing zones between or just above fine grained sediments (aquitards). The concentrations in cores MBCSB-2, MBCSB-4, and MBCSB-5 ranged from <0.001 ug/g to 0.094 ug/g. Previous studies in A/M Area at SRS indicated that the depth discrete bulk sediment concentrations are related to the groundwater concentrations at the sample depth (Eddy et al., 1991). Typically, the groundwater concentration (in ug/L) is 2000 to 4000 times the bulk sediment concentration (in ug/g). Using these factors, the approximate range of expected groundwater concentration at each depth is calculated in Table 3.

The various quality assurance checks of the data suggest that the results are of high quality. There was a high degree of concordance between the intralaboratory duplicate samples. To assess the concordance of the duplicates, we calculated the normalized spread of each pair (S) in percent where:

$$S = 100 \times [(\text{maximum value} - \text{average value}) / (\text{average value})]$$
$$= 100 \times [(\text{average value} - \text{minimum value}) / (\text{average value})]$$

Figure 1 shows the percent spread as a function of average concentration for all 113 samples analyzed by SRTC. The average spread was 13.5% for TCE and 8% for PCE. The typical minimum and maximum values were typically within the average S% of the mean values.

The sample locations analyzed by both SRTC and MicroSeeps Ltd using different analytical methods yielded similar concentrations. The range of values for the interlaboratory comparison data sets were:

SRTC:	MicroSeeps Ltd
TCE: <0.001 to 0.094 ug/g	TCE: <0.001 to 0.078 ug/g
PCE: <0.001 to 0.030 ug/g	PCE: <0.001 to 0.015 ug/g

Figure 2 is a graph of the results from the two laboratories. There was an exact concordance between the laboratories in identifying the highest VOC concentrations and a good concordance in identifying samples below detection. SRTC analyzed the samples using a static headspace method developed to support SRS groundwater VOC remediation activities and documented in the EPA report on innovative VOC analysis methods (Looney, 1993). MicroSeeps Ltd utilized the new (currently draft) EPA Method 5035 based on purge and trap of the suspended sediment

sample using a special vial and laboratory apparatus (EPA, draft). The comparison data suggest that the heating of the sample vials in the SRTC sample set slightly improved the consistency and recovery of VOCs from the samples. Note for example the slightly lower PCE values in the MicroSeeps Ltd data. Also, the samples with the largest discrepancy, MBCSB-4 near 240 feet deep were clayey in nature. Both of these observations are consistent with the expected behavior of the methods based on the impact of heating. Heating of the vials to encourage recovery of the VOCs into the purge gas is currently being examined by MicroSeeps to improve the performance of the new EPA method.

Six of the samples analyzed by MicroSeeps Ltd contained traces (0.001 to 0.004 ug/g) of chloroform. This has been observed in past drilling studies at SRS in which depth discrete VOC samples were collected. Two causes have been identified for this observation. First, several natural organics coelute with chloroform increasing the likelihood of a false positive (note that the field notes indicate an trace OVA reading associated with this core suggesting the possibility of the presence of natural organic compounds). Second, chloroform is an indication (tracer) of minor infiltration of drilling fluids. The potable water used to mix the drilling mud, typical of most drinking water supplies, is treated using standard chlorination methods that result in generation of low concentrations of trihalomethanes (e.g., chloroform) during treatment. Two of the MicroSeeps Ltd analyses from MBCSB-1 (310' and 350') contain trace levels of TCE, PCE, and 1,1,1trichloroethane. The system blank for this core contains these same constituents in the same ratio. Thus, these two sample analyses should be viewed as suspect and are likely the result of a trace sample blank contamination associated with the initiation of the new EPA Method 5035. The MicroSeeps Ltd samples appear to be of extremely high quality, and the new method appears promising and viable for sample analysis of SRS sediments.

References

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Table 1. Summary of A/M Area Crouch Branch (Cretaceous) Aquifer Characterization VOC Data

		SRTC DATA		MicroSeeps Data			
Core	Depth feet	TCE avg. conc. ug/g	PCE avg. conc. ug/g	TCE ug/g	PCE ug/g	chloroform ug/g	1,1,1 trichloroethane ug/g
MBCSB-1	200'	<0.001	<0.001				
MBCSB-1	210'	<0.001	<0.001				
MBCSB-1	220'	<0.001	<0.001				
MBCSB-1	230'	<0.001	<0.001				
MBCSB-1	240'	<0.001	<0.001				
MBCSB-1	250'	<0.001	<0.001				
MBCSB-1	260'	<0.001	<0.001				
MBCSB-1	270'	<0.001	<0.001				
MBCSB-1	280'	<0.001	<0.001				
MBCSB-1	290'	<0.001	<0.001				
MBCSB-1	300'	<0.001	<0.001				
MBCSB-1	310'	<0.001	<0.001	**0.008**	**0.002**	<0.001	**0.025**
MBCSB-1	320'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-1	330'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-1	340'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-1	350'	<0.001	<0.001	**0.005**	**0.001**	<0.001	**0.014**
MBCSB-1	360'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
replicate	360'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	200'	**0.001**	<0.001	<0.001	<0.001	<0.001	<0.001
replicate	200'	**0.001**	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	210'	**0.003**	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	220'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	230'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	240'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	250'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	260'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	270'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	280'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	290'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	300'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
replicate	300'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	310'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	320'	**0.002**	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	330'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	340'	**0.002**	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	350'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-2	360'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Table 1. Summary of A/M Area Crouch Branch (Cretaceous) Aquifer Characterization VOC Data (continued)

		SRTC DATA		MicroSeeps Data			
Core	Depth feet	TCE avg. conc. ug/g	PCE avg. conc. ug/g	TCE ug/g	PCE ug/g	chloroform ug/g	1,1,1 trichloroethane ug/g
MBCSB-3	200'	**0.015**	<0.001				
MBCSB-3	210'	**0.007**	<0.001				
MBCSB-3	220'	**0.006**	<0.001				
MBCSB-3	230'	**0.003**	<0.001				
MBCSB-3	240'	**0.003**	<0.001				
MBCSB-3	250'	**0.051**	<0.001				
MBCSB-3	260'	**0.011**	<0.001				
MBCSB-3	270'	**0.009**	<0.001				
MBCSB-4	200'	<0.001	<0.001	<0.001	<0.001	**0.004**	<0.001
replicate	200'	<0.001	<0.001	<0.001	<0.001	**0.003**	<0.001
MBCSB-4	210'	<0.001	<0.001	<0.001	<0.001	**0.002**	<0.001
MBCSB-4	220'	**0.001**	<0.001	<0.001	<0.001	**0.002**	<0.001
MBCSB-4	230'	**0.024**	<0.001	<0.001	<0.001	**0.002**	<0.001
MBCSB-4	240'	**0.026**	**0.003**	<0.001	<0.001	<0.001	<0.001
MBCSB-4	250'	**0.001**	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-4	260'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-4	270'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-4	280'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-4	290'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-4	300'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
replicate	300'	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
MBCSB-4	310'	**0.002**	<0.001	**0.001**	<0.001	<0.001	**0.001**
MBCSB-4	320'	**0.003**	**0.013**	**0.001**	**0.006**	<0.001	**0.001**
MBCSB-4	330'	**0.003**	**0.016**				
MBCSB-4	340'	**0.040**	**0.030**	**0.042**	**0.015**	**0.001**	<0.001
MBCSB-4	350'	**0.054**	**0.030**				
MBCSB-4	360'	**0.094**	**0.011**	**0.078**	**0.004**	<0.001	<0.001

Table 1. Summary of A/M Area Crouch Branch (Cretaceous) Aquifer Characterization VOC Data (continued)

		SRTC DATA		MicroSeeps Data			
Core	Depth feet	TCE avg. conc. ug/g	PCE avg. conc. ug/g	TCE ug/g	PCE ug/g	chloroform ug/g	1,1,1 trichloroethane ug/g
MBCSB-5	200'	**0.003**	<0.001				
MBCSB-5	210'	<0.001	<0.001				
MBCSB-5	220'	<0.001	<0.001				
MBCSB-5	230'	<0.001	<0.001				
MBCSB-5	240'	<0.001	<0.001				
MBCSB-5	250'	**0.013**	<0.001				
MBCSB-5	260'	**0.017**	<0.001				
MBCSB-5	270'	<0.001	<0.001				
MBCSB-5	280'	<0.001	<0.001				
MBCSB-5	290'	<0.001	<0.001				
MBCSB-5	300'	<0.001	<0.001				
MBCSB-5	310'	<0.001	<0.001				
MBCSB-5	320'	<0.001	<0.001				
MBCSB-5	330'	<0.001	<0.001				
MBCSB-5	340'	<0.001	<0.001				
MBCSB-5	350'	**0.020**	**0.004**				
MBCSB-5	360'	**0.046**	**0.013**				
MBCSB-5	365'	**0.015**	**0.007**				
MBCSB-6	200'	<0.001	<0.001				
MBCSB-6	210'	<0.001	<0.001				
MBCSB-6	220'	<0.001	<0.001				
MBCSB-6	230'	<0.001	<0.001				
MBCSB-6	240'	<0.001	<0.001				
MBCSB-6	250'	<0.001	<0.001				
MBCSB-6	260'	<0.001	<0.001				
MBCSB-6	270'	<0.001	<0.001				
MBCSB-6	280'	<0.001	<0.001				
MBCSB-6	290'	<0.001	<0.001				
MBCSB-6	300'	<0.001	<0.001				
MBCSB-6	310'	<0.001	<0.001				
MBCSB-6	320'	<0.001	<0.001				
MBCSB-6	330'	<0.001	<0.001				
MBCSB-6	340'	<0.001	<0.001				
MBCSB-6	350'	<0.001	<0.001				
MBCSB-6	360'	<0.001	<0.001				

Table 1. Summary of A/M Area Crouch Branch (Cretaceous) Aquifer Characterization VOC Data (continued)

		SRTC DATA		MicroSeeps Data			
Core	Depth feet	TCE avg. conc. ug/g	PCE avg. conc. ug/g	TCE ug/g	PCE ug/g	chloroform ug/g	1,1,1 trichloroethane ug/g
MBCSB-7	200'	<0.001	<0.001				
MBCSB-7	205'	<0.001	<0.001				
MBCSB-7	210'	<0.001	<0.001				
MBCSB-7	220'	<0.001	<0.001				
MBCSB-7	230'	<0.001	<0.001				
MBCSB-7	240'	<0.001	<0.001				
MBCSB-7	250'	<0.001	<0.001				
MBCSB-7	260'	<0.001	<0.001				
MBCSB-7	270'	<0.001	<0.001				
MBCSB-7	280'	<0.001	<0.001				
MBCSB-7	290'	<0.001	<0.001				
MBCSB-7	300'	<0.001	<0.001				
MBCSB-7	310'	<0.001	<0.001				
MBCSB-7	320'	<0.001	<0.001				
MBCSB-7	330'	<0.001	<0.001				
MBCSB-7	340'	<0.001	<0.001				
MBCSB-7	350'	<0.001	<0.001				
MBCSB-7	360'	<0.001	<0.001				
MBCSB-7	365'	<0.001	<0.001				
SRTC Blanks		<0.001	<0.001				
MicroSeeps Blanks							
MBCSB-1	SB1			**0.009**	**0.002**	<0.001	**0.026**
MBCSB-2	SB1			<0.001	<0.001	<0.001	<0.001
MBCSB-2	SB2			<0.001	<0.001	<0.001	<0.001
MBCSB-4	SB1			<0.001	<0.001	<0.001	<0.001
MBCSB-4	SB2			<0.001	<0.001	<0.001	<0.001

Table 1. Summary of A/M Area Crouch Branch (Cretaceous) Aquifer Characterization VOC Data (continued)

Corehole Details (WSRC, 1993)

Core	SRS Northing feet	SRS Easting feet	Surface Elevation feet above MSL	Total Depth feet
MBCSB-1	108450	52780	372.0	365
MBCSB-2	107750	52975	380.2	365
MBCSB-3	107178	52035	367.2	270
MBCSB-4	105008	51445	381.2	365
MBCSB-5	103983	51641	370.5	365
MBCSB-6	104750	50600	na	365
MBCSB-7	100850	48750	328.6	365

na = not available

Table 2. Detection Limits and Identification of VOCs not Detected in Study

Headspace Method (SRTC Analysis)

trichloroethylene	<0.001 ug/g
tetrachloroethylene	<0.001 ug/g

Purge and Trap Method (MicroSeeps Ltd Analysis)

trichloroethylene	<0.001 ug/g
tetrachloroethylene	<0.001 ug/g
vinyl chloride	<0.001 ug/g
methylene chloride	<0.020 ug/g *
trans 1,2 dichloroethylene	<0.020 ug/g *
chloroform	<0.001 ug/g
1,1,1 trichloroethane	<0.001 ug/g **
carbon tetrachloride	<0.001 ug/g *

* = not detected in any sample
** = detected in only 2 samples and the associated system blank

Table 3. Water Concentrations Estimated from Depth Discrete Bulk Sediment Results

		SEDIMENT CONCENTRATION		ESTIMATED WATER CONCENTRATIONS					
Well ID	Depth feet	TCE avg. conc. ug/g	PCE avg. conc. ug/g	TCE estimated conc. range (ug/L)			PCE estimated conc. range (ug/L)		
MBCSB-1	200'-360'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-2	200'	0.001	<0.001	2	to	6	< 2	to	< 5
MBCSB-2	210'	0.003	<0.001	5	to	13	< 2	to	< 5
MBCSB-2	220'-310'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-2	320'	0.002	<0.001	3	to	8	< 2	to	< 5
MBCSB-2	330'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-2	340'	0.002	<0.001	4	to	10	< 2	to	< 5
MBCSB-2	350'-360'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-3	200'	0.015	<0.001	30	to	75	< 2	to	< 5
MBCSB-3	210'	0.007	<0.001	14	to	34	< 2	to	< 5
MBCSB-3	220'	0.006	<0.001	12	to	31	< 2	to	< 5
MBCSB-3	230'	0.003	<0.001	5	to	13	< 2	to	< 5
MBCSB-3	240'	0.003	<0.001	7	to	17	< 2	to	< 5
MBCSB-3	250'	0.051	<0.001	101	to	253	< 2	to	< 5
MBCSB-3	260'	0.011	<0.001	22	to	54	< 2	to	< 5
MBCSB-3	270'	0.009	<0.001	18	to	45	< 2	to	< 5
MBCSB-4	200'-210'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-4	220'	0.001	<0.001	2	to	6	< 2	to	< 5
MBCSB-4	230'	0.024	<0.001	49	to	122	< 2	to	< 5
MBCSB-4	240'	0.026	0.003	53	to	132	6	to	14
MBCSB-4	250'	0.001	<0.001	2	to	5	< 2	to	< 5
MBCSB-4	260'-300'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-4	310'	0.002	<0.001	4	to	10	< 2	to	< 5
MBCSB-4	320'	0.003	0.013	6	to	14	26	to	64
MBCSB-4	330'	0.003	0.016	5	to	13	31	to	79
MBCSB-4	340'	0.040	0.030	80	to	199	61	to	152
MBCSB-4	350'	0.054	0.030	109	to	272	60	to	151
MBCSB-4	360'	0.094	0.011	188	to	470	21	to	53
MBCSB-5	200'	0.003	<0.001	6	to	15	< 2	to	< 5
MBCSB-5	210'-240'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-5	250'	0.013	<0.001	25	to	63	< 2	to	< 5
MBCSB-5	260'	0.017	<0.001	33	to	83	< 2	to	< 5
MBCSB-5	270'-340'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-5	350'	0.020	0.004	41	to	102	8	to	19
MBCSB-5	360'	0.046	0.013	92	to	230	26	to	65
MBCSB-5	365'	0.015	0.007	29	to	73	14	to	35
MBCSB-6	200'-360'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-7	200'-360'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5
MBCSB-7	365'	<0.001	<0.001	< 2	to	< 5	< 2	to	< 5

Where a depth range is indicated, discrete samples were collected every 10 feet.

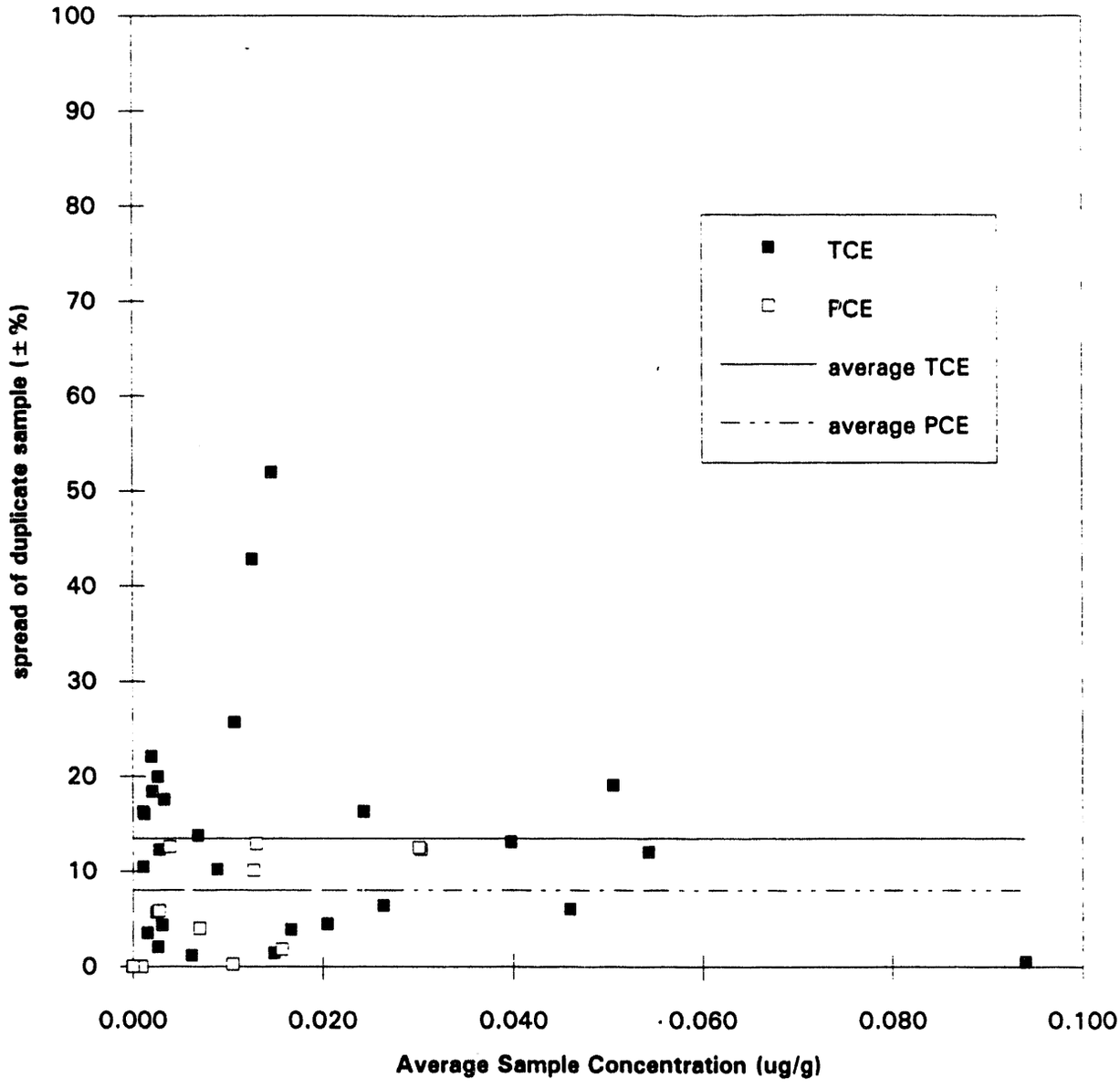

Figure 1. Evaluation of the concordance of the 113 duplicate samples analyzed by the headspace method (SRTC)

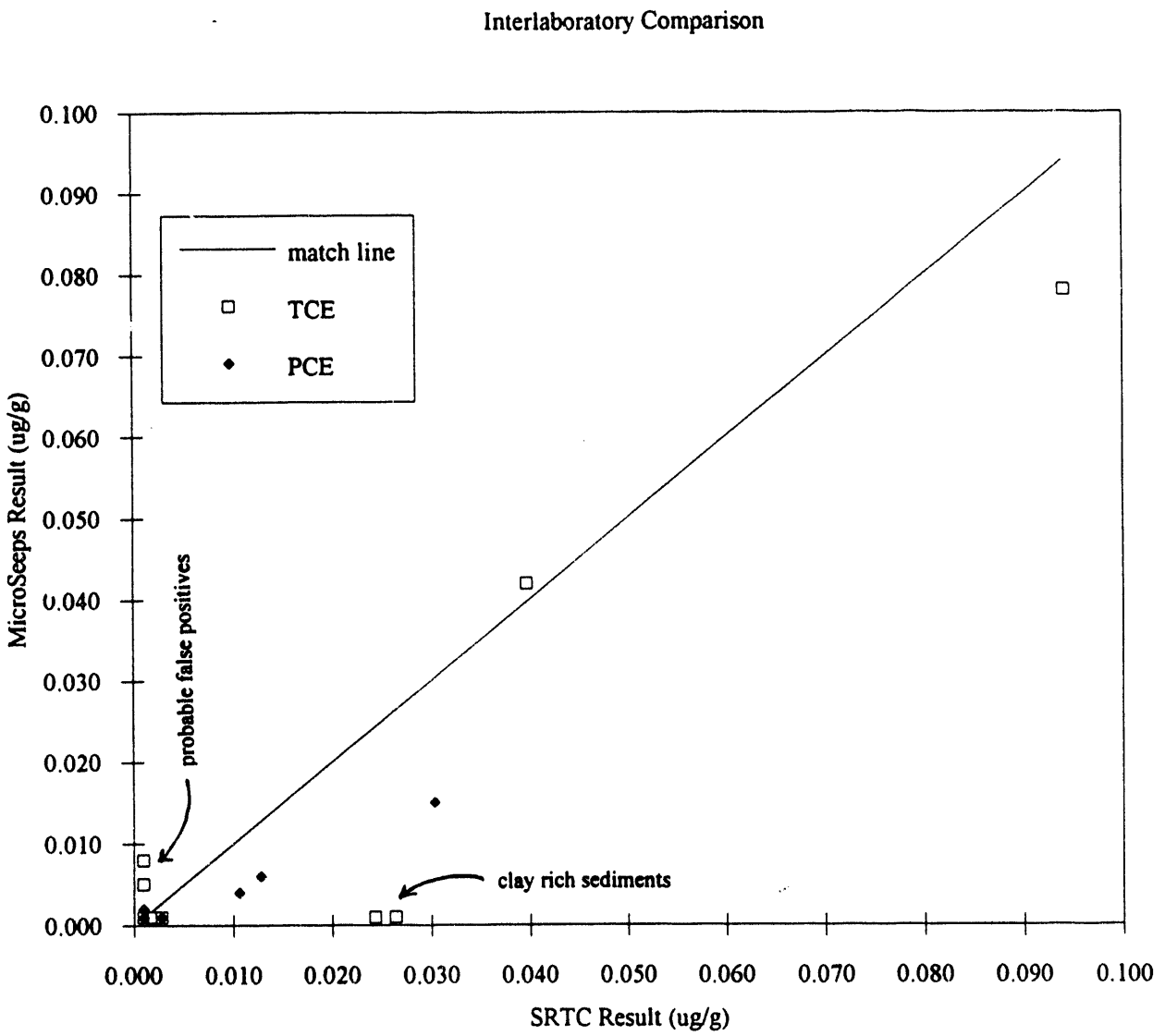

Figure 2. Evaluation of the concordance of the interlaboratory comparison samples.

Attachment A - Raw Data from the Headspace (SRTC) Analysis

Well ID	Depth feet	Vial Mass g	TCE counts	PCE counts	Sediment Mass g	TCE conc. ug/g	PCE conc. ug/g	TCE avg. conc. ug/g	PCE avg. conc. ug/g
MBCSB-1	200'	25.59	ND	1.571E+03	2.99	<0.001	<0.001	<0.001	<0.001
MBCSB-1	200'	25.94	ND	ND	3.34	<0.001	<0.001		
MBCSB-1	210'	24.71	ND	ND	2.11	<0.001	<0.001	<0.001	<0.001
MBCSB-1	210'	25.89	ND	ND	3.29	<0.001	<0.001		
MBCSB-1	220'	24.48	ND	ND	1.88	<0.001	<0.001	<0.001	<0.001
MBCSB-1	220'	24.53	ND	ND	1.93	<0.001	<0.001		
MBCSB-1	230'	26.13	ND	ND	3.53	<0.001	<0.001	<0.001	<0.001
MBCSB-1	230'	26.52	ND	ND	3.92	<0.001	<0.001		
MBCSB-1	240'	26.32	ND	ND	3.72	<0.001	<0.001	<0.001	<0.001
MBCSB-1	240'	25.82	ND	ND	3.22	<0.001	<0.001		
MBCSB-1	250'	25.96	ND	ND	3.36	<0.001	<0.001	<0.001	<0.001
MBCSB-1	250'	25.88	ND	ND	3.28	<0.001	<0.001		
MBCSB-1	260'	25.79	ND	ND	3.19	<0.001	<0.001	<0.001	<0.001
MBCSB-1	260'	25.99	ND	ND	3.39	<0.001	<0.001		
MBCSB-1	270'	25.83	ND	ND	3.23	<0.001	<0.001	<0.001	<0.001
MBCSB-1	270'	26.41	ND	ND	3.81	<0.001	<0.001		
MBCSB-1	280'	26.05	ND	ND	3.45	<0.001	<0.001	<0.001	<0.001
MBCSB-1	280'	25.46	ND	ND	2.86	<0.001	<0.001		
MBCSB-1	290'	26.48	ND	ND	3.88	<0.001	<0.001	<0.001	<0.001
MBCSB-1	290'	25.96	ND	ND	3.36	<0.001	<0.001		
MBCSB-1	300'	26.53	ND	ND	3.93	<0.001	<0.001	<0.001	<0.001
MBCSB-1	300'	26.31	ND	ND	3.71	<0.001	<0.001		
MBCSB-1	310'	25.39	ND	ND	2.79	<0.001	<0.001	<0.001	<0.001
MBCSB-1	310'	25.64	ND	ND	3.04	<0.001	<0.001		
MBCSB-1	320'	26.88	ND	3.125E+03	4.28	<0.001	<0.001	<0.001	<0.001
MBCSB-1	320'	26.35	ND	ND	3.75	<0.001	<0.001		
MBCSB-1	330'	27.62	ND	ND	5.02	<0.001	<0.001	<0.001	<0.001
MBCSB-1	330'	26.85	ND	ND	4.25	<0.001	<0.001		
MBCSB-1	340'	26.93	ND	ND	4.33	<0.001	<0.001	<0.001	<0.001
MBCSB-1	340'	26.08	ND	ND	3.48	<0.001	<0.001		
MBCSB-1	350'	27.39	ND	ND	4.79	<0.001	<0.001	<0.001	<0.001
MBCSB-1	350'	27.61	ND	ND	5.01	<0.001	<0.001		
MBCSB-1	360'	27.45	ND	4.798E+03	4.85	<0.001	<0.001	<0.001	<0.001
MBCSB-1	360'	27.77	ND	6.803E+04	5.17	<0.001	<0.001		

Well ID	Depth feet	Vial Mass g	TCE counts	PCE counts	Sediment Mass g	TCE conc. ug/g	PCE conc. ug/g	TCE avg. conc. ug/g	PCE avg. conc. ug/g
MBCSB-2	200'	25.35	4.511E+04	3.495E+03	2.75	0.001	<0.001	0.001	<0.001
MBCSB-2	200'	25.22	3.109E+04	4.057E+03	2.62	0.001	<0.001		
MBCSB-2	210'	26.08	9.485E+04	4.848E+03	3.48	0.002	<0.001	0.003	<0.001
MBCSB-2	210'	26.34	1.143E+05	4.069E+03	3.74	0.003	<0.001		
MBCSB-2	220'	25.61	1.099E+04	3.466E+03	3.01	<0.001	<0.001	<0.001	<0.001
MBCSB-2	220'	25.87	1.359E+04	2.348E+03	3.27	<0.001	<0.001		
MBCSB-2	230'	26.24	2.096E+03	3.018E+03	3.64	<0.001	<0.001	<0.001	<0.001
MBCSB-2	230'	25.80	1.738E+03	2.510E+03	3.20	<0.001	<0.001		
MBCSB-2	240'	26.02	3.505E+03	1.645E+03	3.42	<0.001	<0.001	<0.001	<0.001
MBCSB-2	240'	26.52	2.622E+03	2.344E+03	3.92	<0.001	<0.001		
MBCSB-2	250'	26.08	3.614E+03	2.037E+03	3.48	<0.001	<0.001	<0.001	<0.001
MBCSB-2	250'	25.98	3.879E+03	1.995E+03	3.38	<0.001	<0.001		
MBCSB-2	260'	26.43	1.683E+03	1.916E+03	3.83	<0.001	<0.001	<0.001	<0.001
MBCSB-2	260'	25.98	1.810E+03	N.D.	3.38	<0.001	<0.001		
MBCSB-2	270'	25.63	N.D.	1.556E+03	3.03	<0.001	<0.001	<0.001	<0.001
MBCSB-2	270'	26.31	N.D.	N.D.	3.71	<0.001	<0.001		
MBCSB-2	280'	27.01	N.D.	N.D.	4.41	<0.001	<0.001	<0.001	<0.001
MBCSB-2	280'	26.86	N.D.	1.583E+03	4.26	<0.001	<0.001		
MBCSB-2	290'	25.84	N.D.	1.513E+03	3.24	<0.001	<0.001	<0.001	<0.001
MBCSB-2	290'	25.60	N.D.	1.598E+03	3.00	<0.001	<0.001		
MBCSB-2	300'	25.33	N.D.	N.D.	2.73	<0.001	<0.001	<0.001	<0.001
MBCSB-2	300'	25.47	N.D.	N.D.	2.87	<0.001	<0.001		
MBCSB-2	310'	25.76	1.063E+04	N.D.	3.16	<0.001	<0.001	<0.001	<0.001
MBCSB-2	310'	26.27	9.116E+03	N.D.	3.67	<0.001	<0.001		
MBCSB-2	320'	25.41	5.273E+04	N.D.	2.81	0.002	<0.001	0.002	<0.001
MBCSB-2	320'	25.44	4.966E+04	N.D.	2.84	0.002	<0.001		
MBCSB-2	330'	26.55	N.D.	N.D.	3.95	<0.001	<0.001	<0.001	<0.001
MBCSB-2	330'	27.12	N.D.	1.394E+03	4.52	<0.001	<0.001		
MBCSB-2	340'	25.94	6.574E+04	N.D.	3.34	0.002	<0.001	0.002	<0.001
MBCSB-2	340'	26.18	1.022E+05	N.D.	3.58	0.002	<0.001		
MBCSB-2	350'	25.84	3.963E+03	N.D.	3.24	<0.001	<0.001	<0.001	<0.001
MBCSB-2	350'	25.74	4.610E+03	N.D.	3.14	<0.001	<0.001		
MBCSB-2	360'	25.91	5.740E+03	1.594E+03	3.31	<0.001	<0.001	<0.001	<0.001
MBCSB-2	360'	26.03	5.270E+03	N.D.	3.43	<0.001	<0.001		

Well ID	Depth feet	Vial Mass g	TCE counts	PCE counts	Sediment Mass g	TCE conc. ug/g	PCE conc. ug/g	TCE avg. conc. ug/g	PCE avg. conc. ug/g
MBCSB-3	200'	25.61	6.483E+05	7.031E+03	3.01	0.015	<0.001	0.015	<0.001
MBCSB-3	200'	25.72	6.910E+05	7.211E+03	3.12	0.015	<0.001		
MBCSB-3	210'	25.63	2.627E+05	2.756E+03	3.03	0.006	<0.001	0.007	<0.001
MBCSB-3	210'	25.25	3.032E+05	3.626E+03	2.65	0.008	<0.001		
MBCSB-3	220'	26.24	3.340E+05	3.405E+03	3.64	0.006	<0.001	0.006	<0.001
MBCSB-3	220'	26.50	3.495E+05	3.872E+03	3.90	0.006	<0.001		
MBCSB-3	230'	25.36	1.302E+05	1.632E+03	2.76	0.003	<0.001	0.003	<0.001
MBCSB-3	230'	24.63	6.394E+04	1.392E+03	2.03	0.002	<0.001		
MBCSB-3	240'	25.97	1.930E+05	2.069E+03	3.37	0.004	<0.001	0.003	<0.001
MBCSB-3	240'	25.07	9.929E+04	1.425E+03	2.47	0.003	<0.001		
MBCSB-3	250'	25.92	1.991E+06	5.196E+03	3.32	0.041	<0.001	0.051	<0.001
MBCSB-3	250'	26.62	3.545E+06	8.134E+03	4.02	0.060	<0.001		
MBCSB-3	260'	25.10	4.964E+05	2.136E+03	2.50	0.014	<0.001	0.011	<0.001
MBCSB-3	260'	24.77	2.549E+05	1.324E+03	2.17	0.008	<0.001		
MBCSB-3	270'	25.44	4.096E+05	3.930E+03	2.84	0.010	<0.001	0.009	<0.001
MBCSB-3	270'	25.44	3.338E+05	2.650E+03	2.84	0.008	<0.001		

Well ID	Depth feet	Vial Mass g	TCE counts	PCE counts	Sediment Mass g	TCE conc. ug/g	PCE conc. ug/g	TCE avg. conc. ug/g	PCE avg. conc. ug/g
MBCSB-4	200'	25.65	6.559E+04	1.153E+04	3.05	0.001	<0.001	<0.001	<0.001
MBCSB-4	200'	26.01	2.966E+04	5.551E+03	3.41	<0.001	<0.001		
MBCSB-4	210'	26.00	2.506E+04	1.174E+05	3.40	<0.001	<0.001	<0.001	<0.001
MBCSB-4	210'	25.89	2.704E+04	1.318E+05	3.29	<0.001	<0.001		
MBCSB-4	220'	25.34	4.242E+04	1.349E+04	2.74	<0.001	<0.001	0.001	<0.001
MBCSB-4	220'	26.15	7.630E+04	2.545E+04	3.55	0.001	<0.001		
MBCSB-4	230'	25.45	9.691E+05	8.861E+04	2.85	0.020	<0.001	0.024	<0.001
MBCSB-4	230'	25.58	1.408E+06	1.852E+05	2.98	0.028	0.001		
MBCSB-4	240'	25.75	1.476E+06	4.600E+05	3.15	0.028	0.003	0.026	0.003
MBCSB-4	240'	25.97	1.389E+06	4.378E+05	3.37	0.025	0.003		
MBCSB-4	250'	26.38	7.619E+04	1.040E+04	3.78	0.001	<0.001	0.001	<0.001
MBCSB-4	250'	26.33	6.091E+04	9.226E+03	3.73	<0.001	<0.001		
MBCSB-4	260'	25.73	1.757E+03	N.D.	3.13	<0.001	<0.001	<0.001	<0.001
MBCSB-4	260'	25.42	2.146E+03	1.336E+03	2.82	<0.001	<0.001		
MBCSB-4	270'	26.15	N.D.	N.D.	3.55	<0.001	<0.001	<0.001	<0.001
MBCSB-4	270'	26.26	N.D.	N.D.	3.66	<0.001	<0.001		
MBCSB-4	280'	26.10	N.D.	N.D.	3.50	<0.001	<0.001	<0.001	<0.001
MBCSB-4	280'	26.52	1.765E+03	N.D.	3.92	<0.001	<0.001		
MBCSB-4	290'	26.79	3.608E+03	1.445E+03	4.19	<0.001	<0.001	<0.001	<0.001
MBCSB-4	290'	26.72	3.038E+03	N.D.	4.12	<0.001	<0.001		
MBCSB-4	300'	25.83	N.D.	N.D.	3.23	<0.001	<0.001	<0.001	<0.001
MBCSB-4	300'	26.00	N.D.	1.310E+03	3.40	<0.001	<0.001		
MBCSB-4	310'	25.36	7.219E+04	3.099E+04	2.76	0.002	<0.001	0.002	<0.001
MBCSB-4	310'	25.65	1.250E+05	5.542E+04	3.05	0.002	<0.001		
MBCSB-4	320'	25.95	1.394E+05	1.893E+06	3.35	0.002	0.011	0.003	0.013
MBCSB-4	320'	26.07	1.848E+05	2.402E+06	3.47	0.003	0.014		
MBCSB-4	330'	25.43	1.232E+05	2.152E+06	2.83	0.003	0.015	0.003	0.016
MBCSB-4	330'	25.61	1.365E+05	2.373E+06	3.01	0.003	0.016		
MBCSB-4	340'	25.88	1.893E+06	4.294E+06	3.28	0.035	0.027	0.040	0.030
MBCSB-4	340'	25.37	2.082E+06	4.645E+06	2.77	0.045	0.034		
MBCSB-4	350'	25.47	2.292E+06	3.725E+06	2.87	0.048	0.026	0.054	0.030
MBCSB-4	350'	25.35	2.798E+06	4.590E+06	2.75	0.061	0.034		
MBCSB-4	360'	25.57	4.691E+06	1.546E+06	2.97	0.095	0.011	0.094	0.011
MBCSB-4	360'	25.68	4.813E+06	1.611E+06	3.08	0.094	0.011		

Well ID	Depth feet	Vial Mass g	TCE counts	PCE counts	Sediment Mass g	TCE conc. ug/g	PCE conc. ug/g	TCE avg. conc. ug/g	PCE avg. conc. ug/g
MBCSB-5	200'	25.70	1.217E+05	1.785E+04	3.10	0.003	<0.001	0.003	<0.001
MBCSB-5	200'	25.42	1.015E+05	1.493E+04	2.82	0.003	<0.001		
MBCSB-5	210'	25.54	6.335E+03	1.855E+03	2.94	<0.001	<0.001	<0.001	<0.001
MBCSB-5	210'	25.29	9.356E+03	3.534E+03	2.69	<0.001	<0.001		
MBCSB-5	220'	27.02	2.809E+04	1.868E+03	4.42	<0.001	<0.001	<0.001	<0.001
MBCSB-5	220'	26.21	1.816E+04	1.925E+03	3.61	<0.001	<0.001		
MBCSB-5	230'	25.83	N.D.	1.416E+03	3.23	<0.001	<0.001	<0.001	<0.001
MBCSB-5	230'	25.88	1.768E+03	2.432E+03	3.28	<0.001	<0.001		
MBCSB-5	240'	24.42	N.D.	N.D.	1.82	<0.001	<0.001	<0.001	<0.001
MBCSB-5	240'	23.85	N.D.	N.D.	1.25	<0.001	<0.001		
MBCSB-5	250'	27.44	1.060E+06	1.606E+05	4.84	0.018	<0.001	0.013	<0.001
MBCSB-5	250'	28.11	4.828E+05	5.197E+04	5.51	0.007	<0.001		
MBCSB-5	260'	28.22	1.095E+06	3.554E+04	5.62	0.016	<0.001	0.017	<0.001
MBCSB-5	260'	28.00	1.137E+06	3.098E+04	5.40	0.017	<0.001		
MBCSB-5	270'	25.44	2.276E+03	N.D.	2.84	<0.001	<0.001	<0.001	<0.001
MBCSB-5	270'	25.61	2.525E+03	N.D.	3.01	<0.001	<0.001		
MBCSB-5	280'	25.70	N.D.	1.517E+03	3.10	<0.001	<0.001	<0.001	<0.001
MBCSB-5	280'	26.66	N.D.	9.750E+03	4.06	<0.001	<0.001		
MBCSB-5	290'	26.02	N.D.	1.370E+03	3.42	<0.001	<0.001	<0.001	<0.001
MBCSB-5	290'	26.79	N.D.	N.D.	4.19	<0.001	<0.001		
MBCSB-5	300'	26.81	N.D.	5.027E+04	4.21	<0.001	<0.001	<0.001	<0.001
MBCSB-5	300'	26.77	N.D.	N.D.	4.17	<0.001	<0.001		
MBCSB-5	310'	26.61	7.312E+03	3.703E+04	4.01	<0.001	<0.001	<0.001	<0.001
MBCSB-5	310'	27.30	7.628E+03	3.851E+04	4.70	<0.001	<0.001		
MBCSB-5	320'	26.06	9.853E+03	4.542E+04	3.46	<0.001	<0.001	<0.001	<0.001
MBCSB-5	320'	25.68	1.466E+04	1.077E+05	3.08	<0.001	<0.001		
MBCSB-5	330'	26.58	2.192E+03	1.554E+03	3.98	<0.001	<0.001	<0.001	<0.001
MBCSB-5	330'	26.27	2.283E+03	1.654E+03	3.67	<0.001	<0.001		
MBCSB-5	340'	25.85	1.646E+04	1.027E+05	3.25	<0.001	<0.001	<0.001	<0.001
MBCSB-5	340'	25.91	1.629E+04	4.676E+04	3.31	<0.001	<0.001		
MBCSB-5	350'	25.91	7.867E+05	4.755E+05	3.31	0.020	0.003	0.020	0.004
MBCSB-5	350'	26.22	9.409E+05	6.699E+05	3.62	0.021	0.004		
MBCSB-5	360'	25.87	1.939E+06	2.032E+06	3.27	0.049	0.015	0.046	0.013
MBCSB-5	360'	25.90	1.734E+06	1.582E+06	3.30	0.043	0.011		
MBCSB-5	365'	25.91	2.834E+05	9.472E+05	3.31	0.007	0.007	0.015	0.007
MBCSB-5	365'	27.03	1.199E+06	1.374E+06	4.43	0.022	0.007		

Well ID	Depth feet	Vial Mass g	TCE counts	PCE counts	Sediment Mass g	TCE conc. ug/g	PCE conc. ug/g	TCE avg. conc. ug/g	PCE avg. conc. ug/g
MBCSB-6	200'	25.70	2.301E+03	2.539E+03	3.10	<0.001	<0.001	<0.001	<0.001
MBCSB-6	200'	26.43	2.596E+03	2.097E+03	3.83	<0.001	<0.001		
MBCSB-6	210'	28.98	1.318E+04	2.150E+03	6.38	<0.001	<0.001	<0.001	<0.001
MBCSB-6	210'	28.45	6.583E+03	1.957E+03	5.85	<0.001	<0.001		
MBCSB-6	220'	27.00	2.648E+03	1.585E+03	4.40	<0.001	<0.001	<0.001	<0.001
MBCSB-6	220'	27.24	3.324E+03	1.712E+03	4.64	<0.001	<0.001		
MBCSB-6	230'	25.97	N.D.	N.D.	3.37	<0.001	<0.001	<0.001	<0.001
MBCSB-6	230'	26.22	N.D.	N.D.	3.62	<0.001	<0.001		
MBCSB-6	240'	26.17	N.D.	N.D.	3.57	<0.001	<0.001	<0.001	<0.001
MBCSB-6	240'	25.91	N.D.	N.D.	3.31	<0.001	<0.001		
MBCSB-6	250'	26.26	N.D.	N.D.	3.66	<0.001	<0.001	<0.001	<0.001
MBCSB-6	250'	27.01	N.D.	N.D.	4.41	<0.001	<0.001		
MBCSB-6	260'	26.21	N.D.	N.D.	3.61	<0.001	<0.001	<0.001	<0.001
MBCSB-6	260'	27.20	N.D.	N.D.	4.60	<0.001	<0.001		
MBCSB-6	270'	26.32	N.D.	N.D.	3.72	<0.001	<0.001	<0.001	<0.001
MBCSB-6	270'	26.39	N.D.	N.D.	3.79	<0.001	<0.001		
MBCSB-6	280'	26.39	N.D.	N.D.	3.79	<0.001	<0.001	<0.001	<0.001
MBCSB-6	280'	26.36	N.D.	N.D.	3.76	<0.001	<0.001		
MBCSB-6	290'	26.35	N.D.	N.D.	3.75	<0.001	<0.001	<0.001	<0.001
MBCSB-6	290'	25.83	N.D.	N.D.	3.23	<0.001	<0.001		
MBCSB-6	300'	26.60	N.D.	N.D.	4.00	<0.001	<0.001	<0.001	<0.001
MBCSB-6	300'	26.03	N.D.	N.D.	3.43	<0.001	<0.001		
MBCSB-6	310'	26.19	N.D.	N.D.	3.59	<0.001	<0.001	<0.001	<0.001
MBCSB-6	310'	26.08	N.D.	N.D.	3.48	<0.001	<0.001		
MBCSB-6	320'	26.03	N.D.	1.426E+03	3.43	<0.001	<0.001	<0.001	<0.001
MBCSB-6	320'	26.53	N.D.	N.D.	3.93	<0.001	<0.001		
MBCSB-6	330'	25.11	N.D.	N.D.	2.51	<0.001	<0.001	<0.001	<0.001
MBCSB-6	330'	25.24	N.D.	N.D.	2.64	<0.001	<0.001		
MBCSB-6	340'	25.43	N.D.	N.D.	2.83	<0.001	<0.001	<0.001	<0.001
MBCSB-6	340'	26.90	N.D.	N.D.	4.30	<0.001	<0.001		
MBCSB-6	350'	25.97	N.D.	N.D.	3.37	<0.001	<0.001	<0.001	<0.001
MBCSB-6	350'	26.45	N.D.	N.D.	3.85	<0.001	<0.001		
MBCSB-6	360'	26.78	N.D.	N.D.	4.18	<0.001	<0.001	<0.001	<0.001
MBCSB-6	360'	26.50	N.D.	N.D.	3.90	<0.001	<0.001		

Well ID	Depth feet	Vial Mass g	TCE counts	PCE counts	Sediment Mass g	TCE conc. ug/g	PCE conc. ug/g	TCE avg. conc. ug/g	PCE avg. conc. ug/g
MBCSB-7	200'	25.56	2.328E+03	2.334E+03	2.96	<0.001	<0.001	<0.001	<0.001
MBCSB-7	200'	26.20	1.721E+03	1.548E+03	3.60	<0.001	<0.001		
MBCSB-7	205'	25.55	N.D.	N.D.	2.95	<0.001	<0.001	<0.001	<0.001
MBCSB-7	205'	25.19	N.D.	N.D.	2.59	<0.001	<0.001		
MBCSB-7	210'	25.58	1.549E+03	N.D.	2.98	<0.001	<0.001	<0.001	<0.001
MBCSB-7	210'	25.80	2.170E+03	N.D.	3.20	<0.001	<0.001		
MBCSB-7	220'	26.07	N.D.	N.D.	3.47	<0.001	<0.001	<0.001	<0.001
MBCSB-7	220'	25.82	N.D.	N.D.	3.22	<0.001	<0.001		
MBCSB-7	230'	26.64	1.496E+03	N.D.	4.04	<0.001	<0.001	<0.001	<0.001
MBCSB-7	230'	25.61	2.153E+03	N.D.	3.01	<0.001	<0.001		
MBCSB-7	240'	25.67	2.104E+03	N.D.	3.07	<0.001	<0.001	<0.001	<0.001
MBCSB-7	240'	25.74	1.900E+03	N.D.	3.14	<0.001	<0.001		
MBCSB-7	250'	25.44	1.654E+03	N.D.	2.84	<0.001	<0.001	<0.001	<0.001
MBCSB-7	250'	26.25	1.709E+03	N.D.	3.65	<0.001	<0.001		
MBCSB-7	260'	27.03	N.D.	N.D.	4.43	<0.001	<0.001	<0.001	<0.001
MBCSB-7	260'	26.65	N.D.	N.D.	4.05	<0.001	<0.001		
MBCSB-7	270'	25.93	2.057E+03	1.375E+03	3.33	<0.001	<0.001	<0.001	<0.001
MBCSB-7	270'	25.98	2.477E+03	1.753E+03	3.38	<0.001	<0.001		
MBCSB-7	280'	26.75	N.D.	N.D.	4.15	<0.001	<0.001	<0.001	<0.001
MBCSB-7	280'	26.14	N.D.	N.D.	3.54	<0.001	<0.001		
MBCSB-7	290'	26.21	N.D.	N.D.	3.61	<0.001	<0.001	<0.001	<0.001
MBCSB-7	290'	25.88	N.D.	N.D.	3.28	<0.001	<0.001		
MBCSB-7	300'	26.07	1.786E+03	N.D.	3.47	<0.001	<0.001	<0.001	<0.001
MBCSB-7	300'	26.26	N.D.	2.992E+03	3.66	<0.001	<0.001		
MBCSB-7	310'	26.21	N.D.	N.D.	3.61	<0.001	<0.001	<0.001	<0.001
MBCSB-7	310'	26.37	N.D.	N.D.	3.77	<0.001	<0.001		
MBCSB-7	320'	25.55	N.D.	N.D.	2.95	<0.001	<0.001	<0.001	<0.001
MBCSB-7	320'	25.92	N.D.	N.D.	3.32	<0.001	<0.001		
MBCSB-7	330'	26.05	2.213E+03	N.D.	3.45	<0.001	<0.001	<0.001	<0.001
MBCSB-7	330'	25.78	2.088E+03	N.D.	3.18	<0.001	<0.001		
MBCSB-7	340'	25.53	N.D.	N.D.	2.93	<0.001	<0.001	<0.001	<0.001
MBCSB-7	340'	25.67	N.D.	N.D.	3.07	<0.001	<0.001		
MBCSB-7	350'	26.20	N.D.	N.D.	3.60	<0.001	<0.001	<0.001	<0.001
MBCSB-7	350'	26.49	N.D.	N.D.	3.89	<0.001	<0.001		
MBCSB-7	360'	25.47	N.D.	N.D.	2.87	<0.001	<0.001	<0.001	<0.001
MBCSB-7	360'	25.69	N.D.	N.D.	3.09	<0.001	<0.001		
MBCSB-7	365'	26.07	N.D.	N.D.	3.47	<0.001	<0.001	<0.001	<0.001
MBCSB-7	365'	25.74	N.D.	N.D.	3.14	<0.001	<0.001		

Attachment B - Raw Data from the Purge and Trap (MicroSeeps Ltd) Analysis

MICROSEEPS

----- SAVANNAH RIVER SITE -----
----- CRETACEOUS AQUIFER STUDY -----
----- A/M AREA WELL CORE SAMPLES -----
----- DYNASOILS PURGE & TRAP -----

SAMPLE NAME	VINYL CHLORIDE (ug/g)	METHYLENE CHLORIDE (ng/g)	TRANS 1,2 DICHLORO ETHYLENE (ng/g)	CHLORO FORM (ng/g)	111 TRI CHLORO ETHANE (ng/g)	CARBON TETRA CHLORIDE (ng/g)	TRI CHLORO ETHYLENE (ng/g)	TETRA CHLORO ETHYLENE (ng/g)	FILE #
MB-SCB-1-1	<1	<20	<20	<1	25	<1	8	2	T2 104
MB-SCB-1-2	<1	<20	<20	<1	<1	<1	<1	<1	T2 105
MB-SCB-1-3	<1	<20	<20	<1	<1	<1	<1	<1	T2 106
MB-SCB-1-4	<1	<20	<20	<1	<1	<1	<1	<1	T2 107
MB-SCB-1-5	<1	<20	<20	<1	14	<1	5	1	T2 108
MB-SCB-1-6	<1	<20	<20	<1	<1	<1	<1	<1	T2 109
MB-SCB-1-6A	<1	<20	<20	<1	<1	<1	<1	<1	T2 110
MB-SCB-2-1	<1	<20	<20	<1	<1	<1	<1	<1	T2 111
MB-SCB-2-1A	<1	<20	<20	<1	<1	<1	<1	<1	T2 112
MB-SCB-2-2	<1	<20	<20	<1	<1	<1	<1	<1	T2 113
MB-SCB-2-3	<1	<20	<20	<1	<1	<1	<1	<1	T2 114
MB-SCB-2-4	<1	<20	<20	<1	<1	<1	<1	<1	T2 118
MB-SCB-2-5	<1	<20	<20	<1	<1	<1	<1	<1	T2 119
MB-SCB-2-6	<1	<20	<20	<1	<1	<1	<1	<1	T2 120
MB-SCB-2-7	<1	<20	<20	<1	<1	<1	<1	<1	T2 121
MB-SCB-2-8	<1	<20	<20	<1	<1	<1	<1	<1	T2 122
MB-SCB-2-9	<1	<20	<20	<1	<1	<1	<1	<1	T2 123
MB-SCB-2-10	<1	<20	<20	<1	<1	<1	<1	<1	T2 124
MB-SCB-2-11	<1	<20	<20	<1	14	<1	<1	<1	T2 125
MB-SCB-2-11A	<1	<20	<20	<1	<1	<1	<1	<1	T2 126
MB-SCB-2-12	<1	<20	<20	<1	<1	<1	<1	<1	T2 127
MB-SCB-2-13	<1	<20	<20	<1	<1	<1	<1	<1	T2 128
MB-SCB-2-14	<1	<20	<20	<1	<1	<1	<1	<1	T2 133
MB-SCB-2-15	<1	<20	<20	<1	<1	<1	1	<1	T2 134
MB-SCB-2-16	<1	<20	<20	<1	<1	<1	<1	<1	T2 135
MB-SCB-4-1	<1	<20	<20	4	<1	<1	<1	<1	T2 142
MB-SCB-4-1A	<1	<20	<20	3	<1	<1	<1	<1	T2 143
MB-SCB-4-2	<1	<20	<20	2	<1	<1	<1	<1	T2 144
MB-SCB-4-3	<1	<20	<20	2	<1	<1	<1	<1	T2 145
MB-SCB-4-6	<1	<20	<20	2	<1	<1	<1	<1	T2 149
MB-SCB-4-8	<1	<20	<20	<1	<1	<1	<1	<1	T2 151
MB-SCB-4-9	<1	<20	<20	<1	<1	<1	<1	<1	T2 152
MB-SCB-4-10	<1	<20	<20	<1	<1	<1	<1	<1	T2 153
MB-SCB-4-11	<1	<20	<20	<1	<1	<1	<1	<1	T2 154
MB-SCB-4-11A	<1	<20	<20	<1	<1	<1	<1	<1	T2 155
MB-SCB-4-12	<1	<20	<20	<1	1	<1	1	<1	T2 159
MB-SCB-4-13	<1	<20	<20	<1	1	<1	1	6	T2 160
MB-SCB-4-15	<1	<20	<20	1	<1	<1	42	15	T2 162
MB-SCB-4-17	<1	<20	<20	<1	<1	<1	78	4	T2 164
MB-SCB-1-SB1	<1	<20	<20	<1	26	<1	9	2	T2 103
MB-SCB-2-SB1	<1	<20	<20	<1	<1	<1	<1	<1	T2 115
MB-SCB-2-SB2	<1	<20	<20	<1	<1	<1	<1	<1	T2 129
MB-SCB-4-SB1	<1	<20	<20	<1	1	<1	<1	<1	T2 141
MB-SCB-4-SB2	<1	<20	<20	<1	<1	<1	<1	<1	T2 158

MICROSEEPS LTD.

CLIENT: SRS / John Hazlet
LOCATION: M Area
PROJECT(#): AM Cretaceous Aquifer
PAGE: ____ OF: ____

SAMPLE COLLECTION LOG

SAMPLER NAME(S): Kab

Soil Boring MB SCB-1

SAMPLE ID#	DATE	TIME	SEQ.#	SAMPLE DEPTH	SAMPLE TYPE G	S	W	SAMPLE SIZE	COMMENTS
MB-SCB-1 SB-1	7/27/93	~~1105~~	1	~~310'~~		·		40	5.0 H2O ~~5.0 Soil~~
MB-SCB-1-1		1105	2	310'					" " 5.0 Soil
MB-SCB-1-2		1122	3	320'					" " 5.0
MB-SCB-1-3		1140	4	330'					" " 5.1
MB-SCB-1-4		1155	5	340'					" " 5.3 Soil
MB-SCB-1-5		1210	6	350'					" " 5.0
MB-SCB-1-6		1235	7	360'					" " 5.4
MB-SCB-1-6A		1236	8	360'					" " 5.0

USE A NEW SHEET WHEN RESTARTING SEQUENCE #

MICROSEEPS LTD.

CLIENT: SAS / John Hazlow
LOCATION: M Area
PROJECT(S): A/M Cretaceous Aquifer
PAGE: ____ OF: ____ (MB-SCB-2)

########## SAMPLE COLLECTION LOG ##########

SAMPLER NAME(S): Kgh

SAMPLE ID#	DATE	TIME	SEQ.#	SAMPLE DEPTH	SAMPLE TYPE G	S	W	SAMPLE SIZE	COMMENTS Each Vial
MB-SCB-2-SB-1	7-29-93	0800	1	0		✓		40mL	5mL DI H2O — gm Soil
MB-SCB-2-1		1359	2	200'					5.0
MB-SCB-2-1A		1400	3	200'					5.0
MB-SCB-2-2		1410	4	210'					5.2
MB-SCB-2-3	↓	1433	5	220'		↓		↓	6.5 Rolled out Limit found
MB-SCB-2-4	8-2-93	1305	6	230'					5.0
MB-SCB-2-5		1310	7	240					5.0
MB-SCB-2-6		1330	8	250'					5.0
MB-SCB-2-7		1440	9	260'					5.0
MB-SCB-2-8		1450	10	270'					5.0
MB-SCB-2-9		1515	11	280'					5.0
MB-SCB-2-10		1530	12	290'					5.0
MB-SCB-2-11		1550	13	300'					5.0
MB-SCB-2-11A	↓	1551	14	300'					6.5 Full out
MB-SCB-2-SB-2	8-3-93	700	15	-0-					5.0 H2O only
B-SCB-2-12		920	16	310'					5.0 Soil
MB-SCB-2-13		935	17	320'					5.1 " "
MB-SCB-2-14		1045	18	330'					5.2
MB-SCB-2-15		1100	19	340'					5.0
MB-SCB-2-16		1125	20	350'					5.0
MB-SCB-2-17	↓	1150	21	360		↓		↓	5.1

USE A NEW SHEET WHEN RESTARTING SEQUENCE # .

MICROSEEPS LTD.

CLIENT: SRS / John Hazlow
LOCATION: M. AREA
PROJECT(#): Soil Core Boring
PAGE: ____ OF: ____

########## SAMPLE COLLECTION LOG ##########

SAMPLER NAME(S): KAB

SAMPLE ID#	DATE	TIME	SEQ.#	SAMPLE DEPTH	SAMPLE TYPE G	S	W	SAMPLE SIZE	COMMENTS All vials include 5mL H2O
MB-SCB-4-SB-1	8.5.93	730	1	-0-		✓		40mL	5.0 H2O only
MB-SCB-4-1		1234	2	200'					5.0 Soil
MB-SCB-4-1A		1235	3	200'					5.3 Soil
MB-SCB-4-2		1250	4	210'					5.0 Soil
MB-SCB-4-3		1400	5	220'					5.0
MB-SCB-4-4		1415	6	230'					5.1
MB-SCB-4-5		1425	7	240'					5.0
MB-SCB-4-6		1445	8	250'					5.0
MB-SCB-4-7		1505	9	260'					5.0
MB-SCB-4-8		1520	10	270'					5.3
MB-SCB-4-9		1535	11	280'					5.2
MB-SCB-4-10	↓	1550	12	290'					5.1
MB-SCB-4-11	8.6.93	915	13	300'					5.1
MB-SCB-4-11A		916	14	306'					5.1
MB-SCB-4-SB-2		917	15	-0-					5.0 H2O
MB-SCB-4-12		935	16	310'					5.0
MB-SCB-4-13		950	17	320'					5.0
MB-SCB-4-14		1015	18	330'					5.0
MB-SCB-4-15		1030	19	340'					6.5 (ooze!)
MB-SCB-4-16		1100	20	350'					5.0
MB-SCB-4-17	↓	1130	21	360'		↓		↓	5.0
MB-SCB-4-18									

USE A NEW SHEET WHEN RESTARTING SEQUENCE #.

Attachment C - Headspace (SRTC) Analysis Method
Looney et al. (1993)

EVALUATION OF HEADSPACE METHOD FOR VOLATILE CONSTITUENTS IN SOILS AND SEDIMENTS

B. B. Looney, C. A. Eddy, and W. R. Sims

Westinghouse Savannah River Company
Aiken, SC 29808

Summary

Detection and delineation of volatile organic contaminants (VOCs) in sediments and soils underlying a hazardous waste site is often a complex problem. The number and quality of analyses used in characterization studies can be compromised by the difficulties and costs associated with quantitative analysis of volatile analytes. A headspace analysis method was developed to facilitate the accurate and rapid delineation of the vertical and horizontal distribution of VOCs in the subsurface, and to reduce the sample handling, laboratory preparation, and analytical complexity associated with most existent sampling and analysis schemes. The headspace method consists of the following four steps:

- Subsample the core immediately after retrieval using a small tube/plunger system.
- Place the subsample into a 22.5 mL headspace vial.
- Add 5 mL of suspending solution and cap with a teflon lined septum.
- Analyze an aliquot of the headspace using a gas chromatograph.

This method was developed and modified as a result of multiple site investigations and has been applied to over 2000 samples from both saturated and unsaturated sediments. Data collected during these studies indicated that distilled water suspending solution is similar to an ionic (Na_2SO_4/H_2PO_4) solution and that sonication of the samples does not enhance the recovery of VOCs. Sealed samples exhibited stable concentrations for more than 20 days. To further evaluate the headspace method, 92 pairs of samples were analyzed to allow direct comparison of the headspace method to a modified EPA solvent extraction method typically applied to environmental samples. Despite the precautions incorporated into the solvent extraction method, the results indicated that sample transfers in the field and laboratory resulted in substantial volatilization of VOCs. The headspace method minimized these losses and generated results rapidly, facilitating informed decision making during site characterization.

Background

Barcelona (1989) suggests that sample collection and handling activities can contribute to systematic errors in environmental data. These errors are often relatively large compared to the random and systematic errors typically associated with the instrumental analysis. Perhaps the most difficult sample collection and handling error to delineate and control is negative bias (measured value less than true value). In the case of VOCs, this error is principally caused by volatilization of the analyte during sample collection, storage, and handling. In samples from the saturated zone, displacement of pore water by drilling fluids

or drainage of the core can contribute to negative bias. Recent research (Seigrist and Jenssen, 1990; Urban et al., 1989) indicates that the typical methods (containerization of disturbed samples, followed by refrigerated storage and solvent extraction) may lead to substantial volatilization loss; the investigators recommended controlled research and development of alternate procedures.

Analytical methods for VOCs in water samples can logically be grouped into the following three categories:

- solvent extraction
- static headspace methods
- dynamic headspace methods (purge and trap)

Each of these categories relies on a partitioning of the contaminant from the water into an alternate phase prior to instrumental analysis. In the case of solvent extraction, the alternate phase is typically a liquid organic solvent, while in the headspace categories, the alternate phase is a volume of gas. The success of an analytical method depends on the relative affinity of the VOC for the alternate phase, the compatibility of the extracting phase with the analytical instrumentation, and the ability to reproducibly contact the phases and handle the extract. For solvent extraction and static headspace methods, an aliquot of the extract is generally introduced into a gas chromatograph (GC) equipped with an appropriate detector or mass spectrometer. In purge and trap analysis, gas is bubbled through the sample at a constant rate for a specified time. Contaminant vapors are collected on an adsorbent trap; following the purge, the contaminants are thermally desorbed into the GC.

Existing analysis methods for soil and sediments are predominantly in the solvent extraction class; however, both static headspace and purge and trap methods are documented in the literature (McNally and Grob, 1985). Successful application of the gas phase extraction methods to soils and sediments relies on effective and reproducible partitioning from the solid to the gas phase for dry samples, and from the solid and liquid phases to the gas phase for wet samples.

The relative simplicity and minimal sample handling suggest that the static headspace method may be a relatively attractive technique for analysis of volatile constituents in soil and sediment samples. Static headspace methods are most applicable to samples with mineral or low organic matrices. Additionally, these methods require relatively constant conditions for reliable proportionality between original sample concentration and the mass of each VOC introduced into the GC. In particular, the properties of any suspending solution (e.g., ionic strength, pH, etc.) and the physical conditions in the vial (e.g., temperature, pressure, phase volumes, etc.) should be selected to minimize sorption and maximize the conditional Henry's Law partitioning from the solution to the gas phase.

Reports in the literature document successful application of static headspace methods to water, wastewater, industrial effluents, soil, sediments, and sewage (McNally and Grob, 1985). In cases where reproducible results are documented, headspace methods are often preferred because they are simpler and faster, and therefore less expensive than either solvent extraction or purge and trap methods. Since sample handling can be minimized and analyses are generated rapidly, results of this screening approach can be incorporated during the site characterization process.

Methods and Study Design

The sediments for the headspace sampling and analysis studies were collected from borings at sites in the vicinity of the metallurgical manufacturing facility in M-Area at the Savannah River Site (SRS). Solvents -- trichloroethylene (TCE) and tetrachloroethylene (PCE) -- were used in this facility during the late 1950s to the early 1980s to degrease the fuel and target tubes prior to use in other facilities at SRS. Concentrations of VOCs in the partially saturated and saturated sediments vary vertically and horizontally beneath the site. Proper site characterization and long term remediation system design requires adequate delineation of this variation.

The boring locations in M Area were selected based on results from a shallow soil gas survey, combined with process records, groundwater data and past core data. The overall method development study consisted of two parts. First, following an initial period of method development, a series of samples was collected and analyzed to optimize the conditions for sampling and analysis. Second, a series of paired samples was collected to compare the headspace method to a solvent extraction method typically used for soil-sediment analysis. A brief discussion of the headspace method is provided below, followed by specific details associated with each phase of the study.

Drilling and Coring

Continuous borings were drilled to an approximate depth of 200 feet at each location using two drilling methods. Within the vadose zone (130 - 140 foot depth), samples were collected using 4.25-inch inside diameter hollow-stem augers and a standard 2-inch inside diameter, split-spoon sampler. Below the water table, the boreholes were stabilized using a (bentonite-based) mud rotary system, and continuous samples were collected ahead of the borehole using a CP wireline system and Christensen Core Barrel. All subsamples for VOC analysis were collected as quickly as possible after the core was retrieved.

Headspace Sampling-Analysis Procedure

The headspace sediment subsample (3-5 grams) was collected immediately from the open split-spoon using an open-ended plastic disposable syringe and extruded into a 22.5 mL borosilicate vial. Using as pipet, 5 mL of suspending solution were added to the subsample and the vial was sealed by crimping an aluminum cap around a teflon-lined butyl rubber septum. The sample vial was labeled and placed in an ice chest cooled to approximately 4° C for later analysis at an onsite laboratory. The subsample corer (syringe) was decontaminated between sampling events by brushing and rinsing with isopropanol followed by a distilled water wash.

The onsite laboratory consisted of a headspace analyzer connected to a Hewlett Packard (HP) 5890A Gas Chromatograph (GC). Details of the headspace analysis procedure used are given below. Prior to field sampling, we determined the average weight of a sealed headspace vial containing five milliliters of suspending solution. Upon receipt of the headspace sample vials from the field, the capped vials containing the sediment samples were weighed. The amount of sediment in each vial was determined by subtracting the average weight from the sample weight. Each vial with the sediment subsample was analyzed using the HP GC equipped with an electron capture detector, an HP 19395 headspace sampler, an HP 3392 networking integrator, and a 60 m widebore capillary

column coated with a nonpolar silicone phase. The flow and oven temperature conditions recommended by the manufacturers were used. The instrument was calibrated using vials containing known quantities of VOCs, suspending solution, and (in some cases) clean representative sediments. The conditions in the vials (headspace volume, suspending solution volume, and temperature) were standardized as much as possible to maintain the proportionality between the sample concentration and VOC mass in the headspace aliquot. The heated (70 °C) bath in the headspace sampler maximizes the transfer into the vapor phase. The data for each peak was entered into a spreadsheet and the concentration of contaminant in the original sample was estimated using the response factors from the calibration. All values were reported in units of micrograms of VOC per gram of bulk sediment (μg/g). Approximately 30 to 50 samples were analyzed each day.

Headspace Method Optimization Study

The purpose of this phase of the project was to identify the most effective operating conditions for the three phase static headspace procedure. Specifically, the nature of the suspending solution and the need for physical agitation were analyzed. In each case, a reference condition was identified and the relationship between the reference and alternate conditions were evaluated by comparing the relative recoveries for a large number of sample pairs. Because of documented superiority of adding salt when analyzing water samples (Gottauf, 1966), a Na_2SO_4/H_2PO_4 buffer solution was selected for the reference suspending solution (200 mL distilled water, 10 g sodium sulfate, and 0.3 mL concentrated phosphoric acid) and was compared with the distilled water. The reference physical agitation method was sonication, which was compared with the alternate method of no agitation (i.e., the vials were placed directly into heated headspace bath). Additionally, a time-series study was performed to determine the stability of the sediment samples sealed in headspace vials.

Comparison of Headspace Method to Solvent Extraction

The two separate laboratories utilized in the study to analyze the sediment subsamples were an onsite laboratory operated by Savannah River Laboratory personnel and a close support laboratory (CSL) operated by independent subcontract personnel. The onsite laboratory analyzed the headspace sediment subsamples and the CSL analyzed the sediment subsamples collected by the independent subcontractor. Both laboratories used standard chain-of-custody procedures and collected quality assurance/quality control (QA/QC) sediment subsamples to comply with the SRS QA requirements. These requirements included the analysis of duplicate samples, matrix spikes, and trip blanks. All analyses were performed within the required holding time. The method selected by the subcontractor for the CSL was typical of those applied at waste sites in the United States (EPA method 3550). The method generally consisted of containerization of disturbed samples followed by refrigerated storage, sample transfer, and solvent extraction.

During this study, water was used for the headspace suspending solution and the headspace samples were not sonicated. The results from the headspace analysis and CLS were used to determine screen intervals for vapor extraction wells installed as part of a vadose zone remediation program.

Results and Discussion

The data suggest that a headspace analysis approach provides rapid and reproducible analytical results for analysis of VOCs in many common soils and sediments. The parameter optimization phase of the study indicated that a distilled water suspending solution is similar to a Na_2SO_4/H_2PO_4 suspending solution and that sonication of the sample does not improve the transfer of contaminant into the headspace from the solid/liquid phases. The time-series data suggested that samples are relatively stable following collection; the replicate vials generated similar concentrations for the entire time-series period of 20 days. Elimination of the buffer solution and sonication step, based on the parameter optimization phase, yields a sampling/analytical scheme that is rapid and simple to implement.

In a second phase of the study, the headspace method was directly compared to a modified EPA solvent extraction method. Despite the precautions incorporated into the solvent extraction method, the analytical results indicated that sample transfers in the field and laboratory resulted in significant volatilization of VOCs from the sediment samples prior to analysis. The headspace method appears to provide more representative data on the samples. The headspace analysis method generally resulted in a higher value for the measured concentration of both TCE and PCE. The two primary exceptions to this general trend are samples with very high concentrations of contaminants and samples where both methods were below detection limits. For example, in the samples from one of the cores, there are five examples where the two methods are the same for TCE. All of these examples are found where the analytical results are below detection limits for both methods. Similarly, in this core, the results from the solvent extraction method are greater in only 4 of 33 examples. All 4 examples result from overloading of the GC during the headspace analysis (the samples can not be diluted). These same trends may be observed in all of the other cores. In the comparison study, the headspace method indicated the presence of contamination in each of the silty, clayey, and poorly graded layers throughout the vadose zone. The solvent extraction method generated below detection results for most of these zones. Additionally, the headspace method indicated low (but measurable) concentrations in the well-graded sands, while the solvent extraction method indicates below detection results in almost all of these layers.

The paired data were ranked and ordered for statistical analysis. In this form, a Wilcoxon Signed Rank Test was applied to determine if the two methods yielded statistically similar results. This hypothesis was rejected at greater than the 99% confidence level, signifying that the two populations are different. Thus, the statistical test indicated that there is greater than a 99% probability that the two methods are statistically different (i.e., the headspace method generates higher values).

As discussed above, one limitation of the headspace method is that the sample can not be diluted; thus, very high concentrations are truncated by an upper limit of detection. In most cases, this truncation may not be of practical significance because it occurs at relatively high concentrations (e.g., 100,000 ng/g). This truncation can be essentially eliminated by splitting the column effluent to a flame ionization detector (FID) in parallel with a halogen specific detector. In this configuration, the less sensitive FID extends the range of the analysis by several orders of magnitude.

Conclusions

The results indicate that the headspace method minimized loss of volatiles associated with sample handling and provided large amounts of closely spaced data. From an analytical standpoint, at sites with low sediment organic carbon and relatively volatile constituents, there are several advantages of the headspace method over solvent extraction methods. Some of these advantages include the following:

- reduced sample handling effort and time in the field
- no solvent extraction required (the Henry's Law mass transfer in the headspace vial requires no operator effort)
- elimination of multiple sample transfers and minimization of the opportunities for volatilization of analyte

The headspace sediment sample is sealed in its final form ready for analysis within a few seconds of collection and is never directly handled again during weighings or transfers. Once in the laboratory, approximately 50 samples can be analyzed in a normal working day on a single instrument. Headspace analysis is cost effective; we have calculated the fully loaded costs of the analysis to be $50 - $100 per sample. In addition, the headspace results can be generated rapidly and transferred to the field so that informed decisions can be made during site characterization.

The information contained in this article was developed during the course of work under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy.

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Attachment D - Purge and Trap (MicroSeeps Ltd) Analysis Method
EPA Method 5035 (draft)

METHOD 5035

MODIFIED PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a modified purge-and-trap process for the analysis of low concentrations of volatile organic compounds (VOCs) in soils/sediments and solid waste. Guidance is also provided for sample preparation of soils, solid waste and non-aqueous liquids with high concentrations of volatile organics. The gas chromatographic determinative steps are found in Methods 8010, 8015, 8020, 8021 and 8030 (Table 1). The method is also applicable to GC/MS Methods 8240, 8260, and 8266.

1.2 The low soil method differs from the low soil/sediment method in the original Method 5030 because the hermetic seal of the sample vial is never broken from time of sampling to time of analysis. Since the sample is never exposed to the atmosphere after sampling, the loss of VOCs is negligible. Therefore, concentration data obtained using Method 5035 would be expected to be higher and more representative of the soil contamination at time of sampling, than that obtained using the original low soil method (after subsampling a portion of sample from the sample vial in the laboratory). The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 5 to 200 g/kg range. The estimated quantitation limit range for high concentration analysis of soil and waste samples will be in the 20 mg/kg range. However, this is highly dependent on interferences.

1.3 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with Carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, sulfides.

1.4 Method 8015 in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5035 and Method 8020 or 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Methods 8020 or 8021 in series with Method 8015.

1.5 Samples should be screened, prior to application of this method, to avoid contamination of the purge-and-trap system by samples that fall beyond the concentration range of the low concentration method.

2.0 SUMMARY OF METHOD

2.1 Low Concentration Method: Volatile organic compounds (VOCs) are determined from a 5 g soil sample by placing the sample, at time of collection, into a specially designed, fritted, 40-mL vial. A stirring bar is added and, if desired, preservative may be added as well. The vial is then sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, water, surrogate standards and internal standards are automatically added without breaking the hermetic seal on the sample vial. The slurry is preheated to 40°C, then purged by passing an inert gas through the bottom of the vial while mechanical agitation is being provided by the magnetic stirring bar. Purged components then travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatographic (GC) column interfaced to a mass spectrometer (MS) or a specific detector, depending on the determinative method selected.

2.2 High Concentration Method: If the sample introduction technique in Section 2.1 is not applicable, a portion of the sample is dispersed in a water miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is combined with water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC following the water purge-and-trap method (Method 5030).

3.0 INTERFERENCES

3.1 Impurities in the purge gas [illegible] organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealant, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Sample Containers/Purge Device - 40-mL clear glass vials with a special frit (Figure 1) available from Dynatech Precision Sampling Corporation (or equivalent). Each vial must be equipped with a PTFE-faced silicone septa which demonstrate minimal bleed at elevated temperatures. Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics. Be sure the PTFE side of each septum is toward the sample.

4.2 Purge-and-Trap System - The system used for purging and trapping consists of two pieces of equipment linked together to form a hybrid system. The first piece of equipment performs as the automated sample preparation and purging device while the other piece of equipment contains the trap and functions as the desorber. Systems are commercially available from several sources that meet all of the following specifications.

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler (Dynatech Precision Sampling Corporation, 8275 West El Cajon, Baton Rouge, LA 70815).

4.2.1 The purging device must be capable of accepting the 40-mL soil vials, maintaining the vial at 40°C while the inert gas is allowed to pass through the sample effectively purging it. The device must also be capable of introducing 5 mL of organic-free reagent water into the purging device without venting the headspace of the vial. It must also be capable of stirring the sample during purging. The analytes being purged must be allowed to escape the vial through an inert transfer line maintained at an elevated temperature. After passing through the transfer line, the analytes are then allowed to concentrate on a trap.

4.2.2 The trap used to develop this method was 25 centimeters long, had an inside diameter of 0.105 inches and was packed with Carbopack/Carbosieve (Supelco, Inc.). Traps that demonstrate similar hydrophobic and retention properties may be used. The trap must demonstrate sufficient adsorption and desorption characteristics to meet the method MDLs of all the target analytes for a given Project and the QC requirements in Method 8000 and the Determinative Method. The most difficult are the gases and especially dichlorodifluoromethane. Also,

demonstrate that the trap is capable of desorbing the late eluting target analytes.

NOTE: Check the response of the brominated compounds when using these alternative charcoal traps (especially Vocarb 4000), as some degradation has been noted relating to the higher desorption temperatures (especially temperatures above 240 - 250°C). 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 is used. The primary criteria, as stated above, is that all target analytes meet the MDL requirements for a given project.

4.2.2.1 The desorber for the above trap must be capable of rapidly heating the trap to 245°C prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.2.3 The standard trap used in previous EPA purge-and-trap methods is also acceptable. This trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap. If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before first use, this trap should be conditioned overnight at 180°C by backflushing with inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.2.3.1 Trap Packing Materials

4.2.3.1.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.2.3.1.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.3.1.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.2.3.1.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.3.2 The desorber for the trap must be capable of rapidly heating the trap to 180°C for desorption. The polymer

section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during the bake-out mode.

4.2.3.3 Prior to initial use, condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to daily use, condition the trap for 10 min while backflushing at 180°C with the GC column at 220°C.

4.3 Syringe and Syringe Valves

4.3.1 Two 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 Three 2-way syringe valves with Luer ends.

4.3.3 One 25- L micro syringe with a 2 inch x 0.0 inch ID, 22 bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10, 100 L.

4.3.5 Syringes - 0.5, 1.0, and mL, gas tight with shut-off valve.

4.4 Miscellaneous

4.4.1 Glass vials - 60 mL, septum sealed, to collect samples for screening, dry weight determination, and high concentration analysis (if needed).

4.4.2 Top-loading balance -

4.4.3 Glass scintillation vials - 20 mL, with screw-caps and Teflon liners or glass culture tubes with screw-caps and Teflon liners.

4.4.4 Volumetric flasks, Class A - 10 mL and 100 mL, with ground glass stoppers.

4. Vial for GC autosampler.

4.4.6 Spatula - Stainless steel.

4.4.7 Disposable pipets - Pasteur.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5. Methanol, CH_3OH - Pesticide quality or equivalent. Store away from other solvents.

5.3 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.4 See the determinative method and Method 3500 for guidance on internal and surrogate standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample Collection

6.1.1 Weigh the assembled soil sample vial containing the stirring bar to 0.1 g. Ship the tared sampling vial to the sampling site with the seals intact. Open the large chamber containing the stirring bar, and add about 5 grams (2 - 3 centimeters) of soil on top of the stirring bar (wear gloves whenever handling the tared containers). Immediately seal and store at 4°C. (Samples may be weighed in the field if a means is available to weigh to 0.1 g.) Do not interchange seals and stirring bars with other soil vials. It is advisable to collect duplicate samples in the initial tared sample/purge vials in case reanalysis of the sample is required.

6.1.2 Collect additional duplicate aliquots of each sample in 60 mL glass vials (septum sealed) for screening, dry weight determination, and high concentration analysis (if needed).

6.2 Sample Storage

6.2.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

6.2.2 All samples should be analyzed within 14 days of collection. Samples not analyzed within this period must be noted and data are considered minimum values.

7.0 PROCEDURE

7.1 The Low Concentration Method utilizing a modified purge-and-trap technique is found in Section 7.2 and sample preparation for the High Concentration Method is found in Section 7.3. The gas chromatographic determinative steps are found in Methods 8010, 8015, 8020, 8021 and 8030 (Table 1). The method is also applicable to GC/MS Methods 8240, 8260 and 8266. For the analysis of gasoline, use Method 8020 or 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons.

7.2 Low Concentration Method for Soil/Sediment and Solid Waste Amenable to the Modified Purge-and-Trap Method (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.2.1 Initial calibration: Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the

determinative methods and Method 3500 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods because of possible interference problems with internal standards. If interferences are not a problem, based on historical data, internal standard calibration is acceptable. The GC/MS methods normally utilize internal standard calibration. The GC/MS methods require instrument tuning prior to proceeding with calibration.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Section 4.2 and is interfaced to a gas chromatograph or a gas chromatograph/mass spectrometer system. Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing with an inert gas flow of at least 20 mL/minute. (If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. See Section 4.2.2 for guidance on conditioning the trap.) Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.2 To prepare a calibration standard, inject an appropriate volume of a primary dilution standard (containing analytes and surrogates) to an aliquot of organic-free reagent water in a volumetric flask or a gas tight syringe, or to 10 mL of this solution in a soil vial and inject an appropriate amount of internal standards to the organic-free reagent water. Be sure that the same amount of internal standards are added to each standard and sample. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 10 mL). The surrogate and internal standard solutions must be added with a syringe needle long enough to ensure addition below the surface of the water. Prior to purging, heat the sample equal to 40°C for 1.5 minutes (the analytes in Method 8030 normally require an 85°C purge temperature).

NOTE: The device on the autosampler that introduces the internal standard solution containing the internal standards and surrogates must be disabled during calibration. Aqueous standards are not stable and should be discarded after one hour unless transferred to a sample bottle (or gas tight syringe) with no headspace and sealed immediately.

7.2.1.3 Carry out the purge-and-trap procedure as outlined in Section 7.2.4.4.

7.2.1.4 Calculate response factors (RF) or calibration factors (CF) for each analyte of interest using the procedure described in Method 8000.

7.2.1.5 The average CF (external standards) or RF (internal standards must be calculated for each compound. For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Methods 8240/8260/8266). If the purge-and-trap procedure is used with Method 8010/8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.5.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.1.5.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.5.3 Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.6 The analytes in Method 8020 normally are not as negatively affected by small changes in purge flow or system contamination. When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross contamination and memory effects from a high concentration sample or even standard are a common problem. Extra rinsing of the purge chamber after analysis normally corrects this. Moisture effects are often a problem with Method 8030 because of the high temperature purge. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification: Refer to Method 8000 for details on calibration verification.

7.2.2 To prepare a calibration standard, inject an appropriate volume of a primary dilution standard (containing analytes and surrogates) to an aliquot of organic-free reagent water in a volumetric flask, a gas tight syringe, or to 10 mL of this solution in a soil vial, and inject an appropriate amount of internal standards to the organic-free reagent water. Be sure the same amount of internal standards are added to each standard and sample. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 10 mL). The surrogate and internal standard solutions must be added with a syringe needle long enough to ensure addition below the surface of the water. Assemble the purge-and-trap device as outlined in 7.2.4.2. Prior to purging, heat the sample vial to 40°C for 1.5 minutes (the analytes in Method 8030 normally require

an 85°C purge temperature). Follow the guidance for the purge-and-trap procedure in Section 7.2.4.4. GC or GC/MS calibration verification criteria must be met as specified in Method 8000 before analyzing samples.

NOTE: The device on the autosampler that introduces the solution containing the internal standards and surrogates must be disabled during calibration. Aqueous standards are not stable and should be discarded after one hour unless transferred to a sample bottle (or gas tight syringe) with no headspace and sealed immediately.

7.2.3 Sample screening

7.2.3.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system thereby requiring extensive cleanup and instrument downtime. See Section 4.2.2 for suggested screening techniques. Use the screening data to determine whether to use the Low Concentration modified purge-and-trap or to prepare samples by the High Concentration method.

7.2.3.2 Two suggested screening techniques are: the use of an automated headspace sampler interfaced to a gas chromatograph (GC) equipped with a photo ionization detector (PID) and an electrolytic conductivity detector (HECD) in series; or, extraction of the sample with methylene chloride (Method 3510) and analysis of the extract on a GC equipped with a FID and/or an ECD. Use the Low Concentration modified purge-and-trap if the estimated concentration falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range, then prepare the samples by the High Concentration method (Section 7.3).

7.2.4 Sample purge-and-trap

7.2.4.1 This method is designed for a 5-g sample size, but other sizes (e.g., 10 g) may be used. The soil vial is hermetically sealed at the sampling site, and MUST remain so to guarantee the validity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.1 g unless the sample weight is determined in the field.

7.2.4.2 Assemble a purge-and-trap device that meets the specification in Section 4.2. Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing with an inert gas flow of at least 20 mL/minute. (If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. See Section 4.2.3.3 for guidance on conditioning the trap.) Vent the trap effluent to the room, not to the analytical

column. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.4.3 Without disturbing the hermetic seal on the sample vial, add 10 mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used. However, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. For the sample selected for matrix spiking, add 10 L of the matrix spike solution specified in Section 5 of Method 3500. The concentration for a sample would be equivalent to 50 g/kg of each matrix spike analyte. Prior to purging, heat the sample vial to 40°C for 5 minutes (the analytes in Method 8030 normally require an 85°C purge temperature).

7.2.4.4 Purge the sample at a flow rate of 40 mL/minute (the flow rate may vary from 20 mL/min depending in the target analyte group) with helium or another inert gas for 11 minutes while the sample is being agitated. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

7.2.5 Sample Desorption

7.2.5.1 Non-cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow of desorption gas. Then, simultaneously, start the flow of desorption gas at 10 mL/minute for about 4 minutes (1.5 minutes is normally adequate for analytes in Methods 8015 and 8030); begin the temperature program of the gas chromatograph and, start data acquisition.

7.2.5.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure the cryogenic interface is -150°C or lower, and rapidly heat the trap to 250°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 minutes is normally adequate for analytes in Methods 8015 and 8030). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C; simultaneously begin the temperature program of the gas chromatograph, and, start the data acquisition.

7.2.6 Trap Reconditioning

7.2.6.1 After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (dependent on trap packing materials). After approximately 10 minutes, turn off

the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

7.2.7 Data Interpretation

7.2.7.1 Perform qualitative and quantitative analysis on the data following the guidance given in the determinative method and Method 8000. If concentrations of any target analyte exceeds the calibration range of the analyte, it will be necessary to reanalyze the sample by the High Concentration Method.

7.2.8 Determination of % Dry Weight

7.2.8.1 Weigh 5-10 g of the sample from the 60 mL VOA vial into a tared crucible.

NOTE: It is highly recommended that a separate sample for dry weight determination be withdrawn from the 60 mL vial until it is certain that no analytical samples will be needed for High Concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere.

7.2.8.2 Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.3 High Concentration Method for Soil, Solid Waste and Nonaqueous Liquid Waste with Concentration Generally >200 µg/kg.

7.3.1 The [illegible] is based on a methanol extraction. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with hexadecane (Section 7.3.1.6) or possibly polyethylene glycol (PEG). (Perform a solubility test with about one gram of sample and 10 mL of each solvent if the solubility is unknown, before proceeding. Discard this test solution.) An aliquot of the extract is added to organic-free reagent water containing surrogate and, if applicable, internal and matrix spiking standards. This is analyzed as per Method 5030, the purge-and-trap method for aqueous samples.

7.3.1.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula.

7.3.1.2 For soil and solid waste that is insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20 mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent dry weight of the sample using the procedure in Section 7.1.8. Quickly add 9.0 mL of methanol; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 min.

7.3.1.3 For waste that is soluble in methanol or PEG weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of methanol into the vial and mark the bottom of the meniscus. Discard this solvent.) Quickly add 1.0 mL of surrogate spiking solution to the vial or flask and dilute to 10.0 mL with the appropriate solvent. Shake the vial to mix the contents. For certain oily liquids, the following methanol dilution/extraction has proven effective. Dilute 1 g of oily liquid with 10 mL of methanol (2 minute shake) which results in the target analytes being extracted into the methanol along with the majority of the oily waste (some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial. Add 10 - 100 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis. Prior to using this technique, test it by spiking a 1 g aliquot of the oily waste with a matrix spike mixture of the analytes of concern (10 - 50 µL of the matrix spike standard dissolved in methanol). Shake the vial to disperse the matrix spike throughout the oil prior to adding the 9 mL of methanol extraction solvent. Compare the data with single-lab data for oily waste presented in Method 8260. If recovery is not within the limits presented for the majority of compounds, use the hexadecane dilution technique in Section 7.3.1.6.

NOTE: Sections 7.3.1.1 through 7.3.1.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a location free from solvent fumes.

7.3.1.4 Pipet approximately 1 mL of the extract into a GC vial for storage, using a disposable pipet. The remainder may be discarded. Also transfer approximately 1 mL of solvent used for extraction or dissolution to a separate GC vial for use as the method blank for each set of samples.

7.3.1.5 The extracts must be stored at 4°C in the dark, prior to analysis. An appropriate aliquot of the extract (see Table 2) will be added to 5 mL of organic-free reagent water and analyzed as per Method 5030. Proceed to Section 7.0 in Method 5030 and follow the guidance for the analysis of high concentration samples.

7.3.1.6 For waste, soil or solids, where methanol or PEG are not effective solvents (e.g., those samples consisting primarily

of petroleum or coking waste) dilute or extract with hexadecane following the guidance in Method 3585 (Waste Dilution for Volatiles).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Each analysis batch of 20 or less samples must contain: a reagent blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis; and a laboratory control sample, unless the determinative method provides other guidance.

8.4 Surrogate standards should be added to all samples when specified in the appropriate determinative method.

9.0 METHOD PERFORMANCE

9.1 Single laboratory accuracy and precision data were obtained for the method analytes in three soil matrices: sand, a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon, and a surface garden soil. Each sample was fortified with the analytes at a concentration of 20 ng/5 g, which is equivalent to 4 g/kg. These data are listed in tables found in Method 8260.

9.2 Single laboratory accuracy and precision data were obtained for certain method analytes extracting oily liquid using methanol as the extraction solvent. The data is presented in a table in Method 8260. The compounds were spiked into three portions of an oily liquid (taken from a waste site) following the procedure for matrix spiking described in Section 7.3.1.3. This represents a worst case set of data based on recovery data from many sources of oily liquid.

9.3 Method detection limits (MDL) for soil were calculated by analyzing sand, the matrix with the least matrix effect. Replicate 5 g samples were fortified with 20 ng of each of the method analytes. After an equilibration period each sample was analyzed according to Section 11, and quantitated using fluorobenzene as the internal standard. The results, in nanograms recovered from each 5 g sample, are listed in Table 6. Using these data, MDLs were calculated

according to the formula (2):

$$MDL = S\ t_{(n-1,1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom,

n = number of replicates

S = the standard deviation of the replicate analyses.

10.0 REFERENCES

1. Bellar, Tom, "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" Environmental Monitoring Systems Laboratory, U.S Environmental Protection Agency, Cincinnati, Ohio, November 1991.

2. Strattan, Larry, Private communication, methanol extraction of oil, US EPA, National Enforcement Investigation Center, Denver, CO, October, 1992.

TABLE 1
DETERMINATIVE METHODS INTERFACED TO METHOD 5035

METHOD #	METHOD NAME
8010	Halogenated Volatile Organics
8015	Nonhalogenated Volatile Organics Using GC/FID
8020	Aromatic Volatile Organics by Gas Chromatography
8021	Halogenated and Aromatic Volatiles by GC with Detectors in Series: Capillary Column
8030	Acrolein and Acrylonitrile by Gas Chromatography
8240	Volatile Organics by GC/MS: Packed Column
8260	Volatile Organics by GC/MS: Capillary Column
8266	Volatile Organics by GC/MS: Capillary Column with Isotope Dilution

TABLE 2
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-CONCENTRATION SOILS/SEDIMENTS

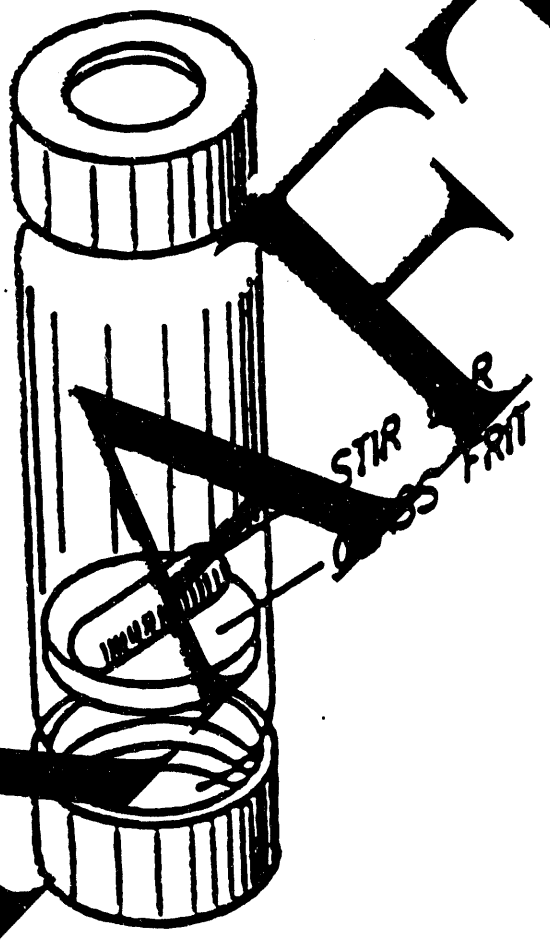
Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 g/kg	100 L
1,000-20,000 g/kg	50 L
5,000-100,000 g/kg	10 L
25,000-500,000 g/kg	100 L of 1/50 dilution [b]

Calculate appropriate dilution factor for concentrations exceeding this table.

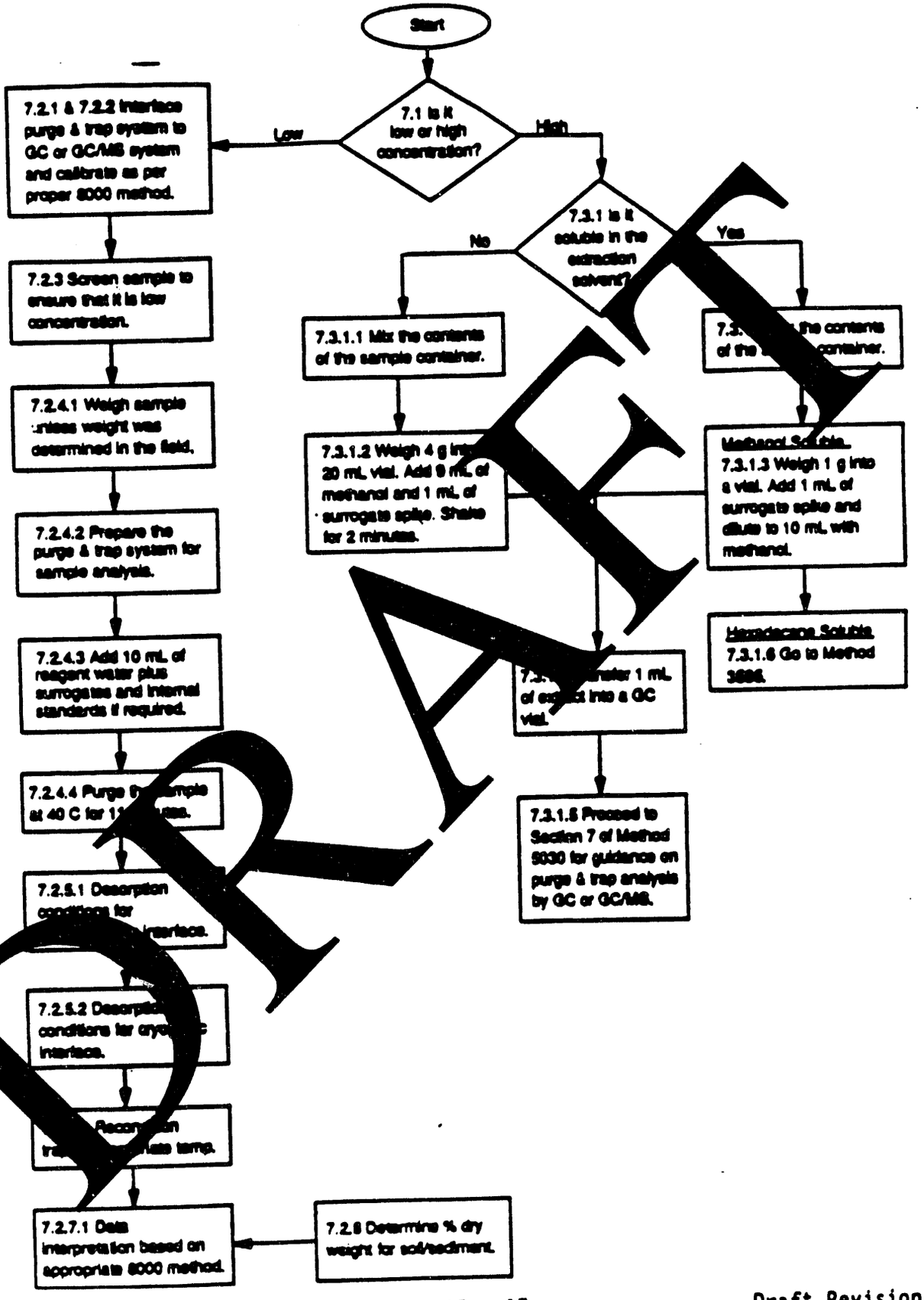
[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 L added to the syringe.

[b] Dilute an aliquot of the methanol extract and then take 100 L for analysis.

Figure 1
Dynatech Soil Vial



METHOD 5035
PURGE-AND-TRAP



Attachment E - SRTC Calibration Curves and Response Data

Calibration Data for Depth Discrete Samples Collected from MBCSB-1

Sample (sediment) concentrations are related to calibration concentrations using the equation:

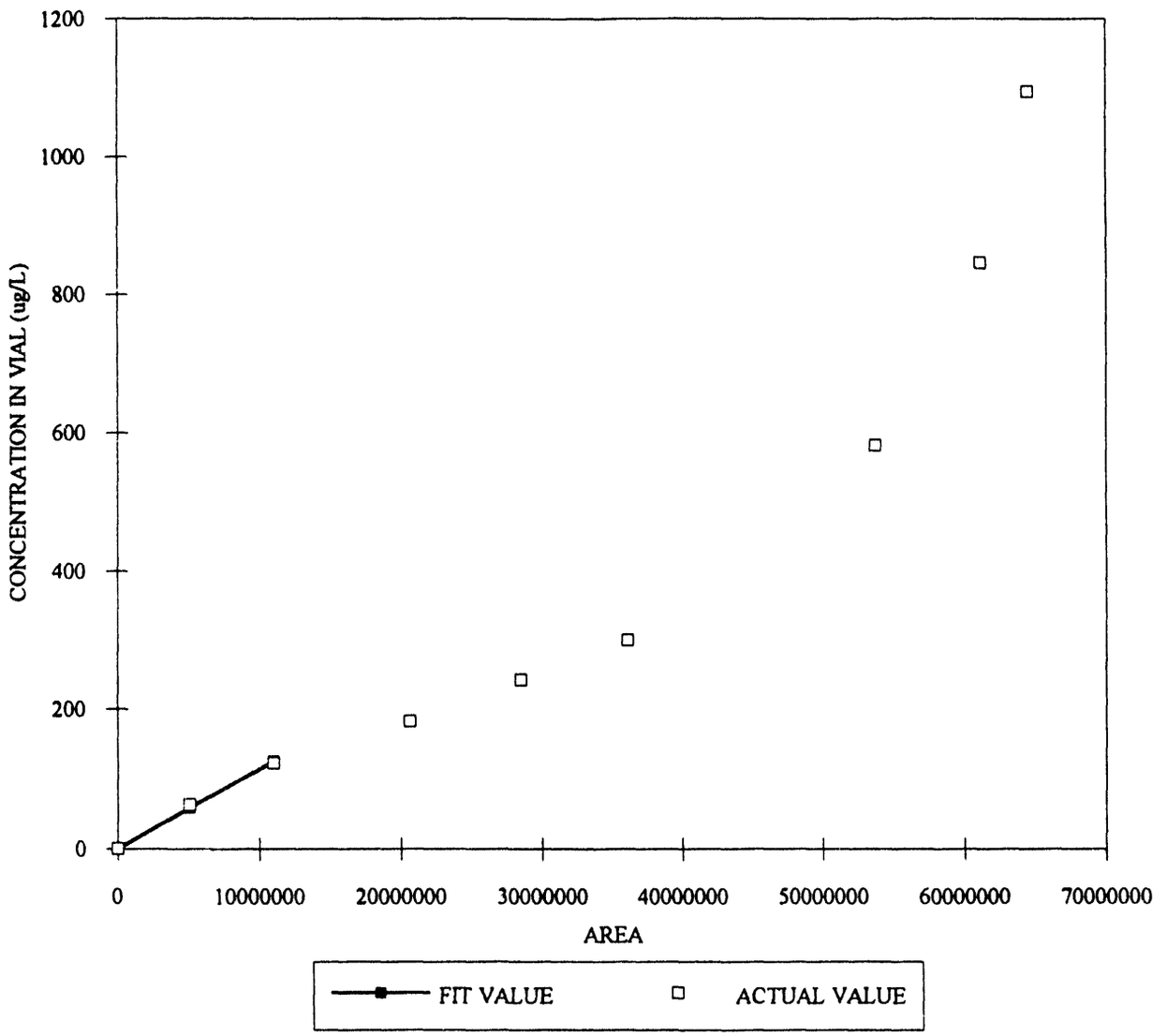
Sediment concentration [ug/g] =
(Standard concentration [ug/L] x 0.0075 [L]) / sediment mass [g].

MSBCB1E.CAL

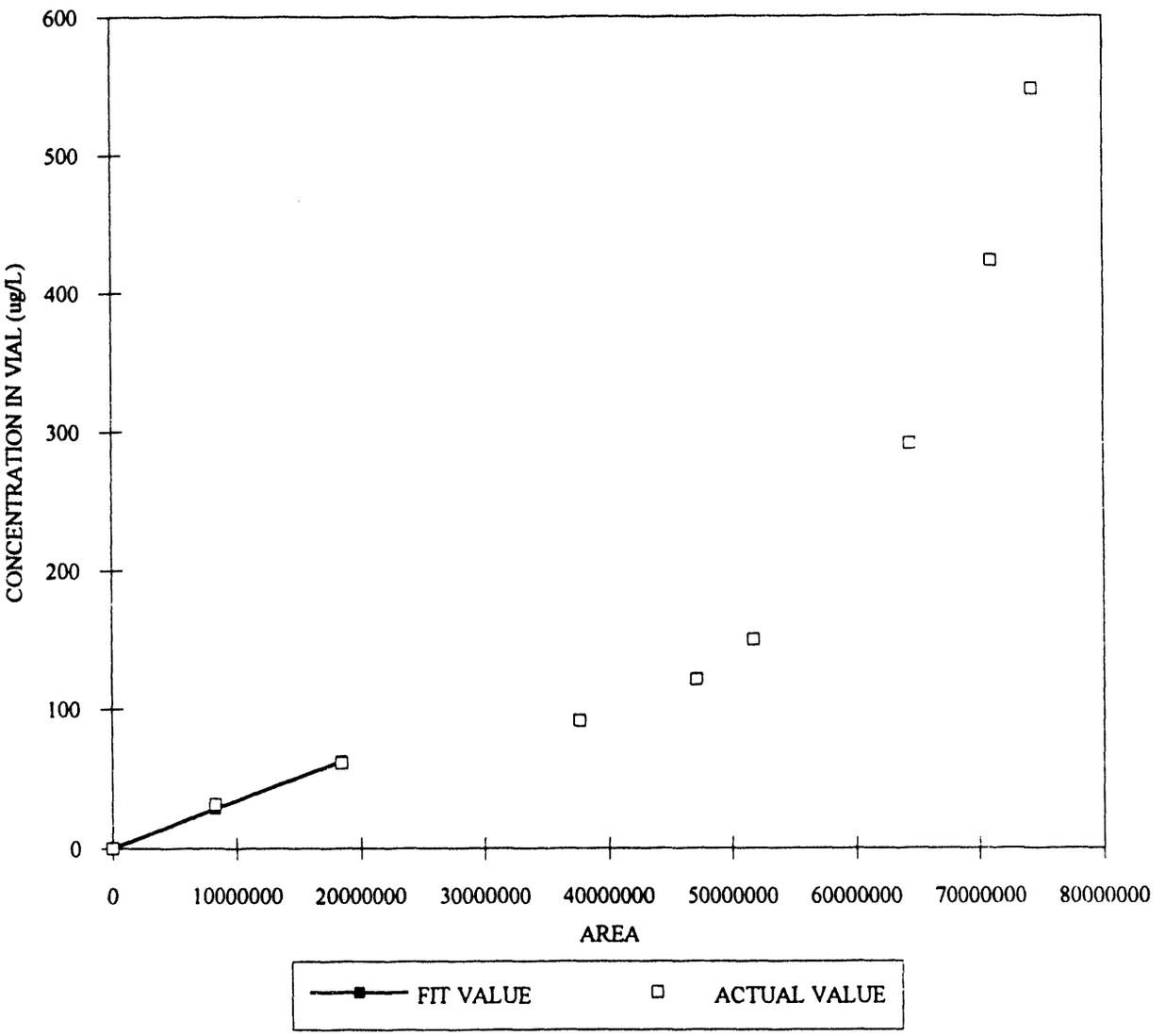
Samples	TCE area	PCE area	Samp. Info	TCE µg/L	PCE µg/L
0	0.000E+00	0.000E+00	0	0.0	0.0
50	5.091E+06	8.276E+06	STANDARD TCE/PCE MIX	62.0	31.0
100	1.101E+07	1.844E+07	STANDARD TCE/PCE MIX	122.0	61.0
150	2.063E+07	3.771E+07	STANDARD TCE/PCE MIX	182.0	91.0
200	2.849E+07	4.715E+07	STANDARD TCE/PCE MIX	242.0	121.0
250	3.608E+07	5.177E+07	STANDARD TCE/PCE MIX	300.0	150.0
500	5.375E+07	6.441E+07	STANDARD TCE/PCE MIX	581.0	291.0
750	6.114E+07	7.102E+07	STANDARD TCE/PCE MIX	845.0	423.0
1000	6.449E+07	7.431E+07	STANDARD TCE/PCE MIX	1094.0	547.0

	TCE			PCE	
slope	1.127E-05		slope	3.382E-06	
y intercept	0.000E+00		y intercept	0.000E+00	
r2	0.99653		r2	0.96573	
AREA	FIT VALUES	ACTUAL VALUES	AREA	FIT VALUES	ACTUAL VALUES
0.000E+00	0.0	0.0	0.000E+00	0.0	0.0
5.091E+06	57.4	62.0	8.276E+06	28.0	31.0
1.101E+07	124.1	122.0	1.844E+07	62.4	61.0
2.063E+07		182.0	3.771E+07		91.0
2.849E+07		242.0	4.715E+07		121.0
3.608E+07		300.0	5.177E+07		150.0
5.375E+07		581.0	6.441E+07		291.0
6.114E+07		845.0	7.102E+07		423.0
6.449E+07		1094.0	7.431E+07		547.0

MSB-CB1 ECD/TCE



MSB-CB1 ECD/PCE



Calibration Data for Depth Discrete Samples Collected from MBCSB-2

Sample (sediment) concentrations are related to calibration concentrations using the equation:

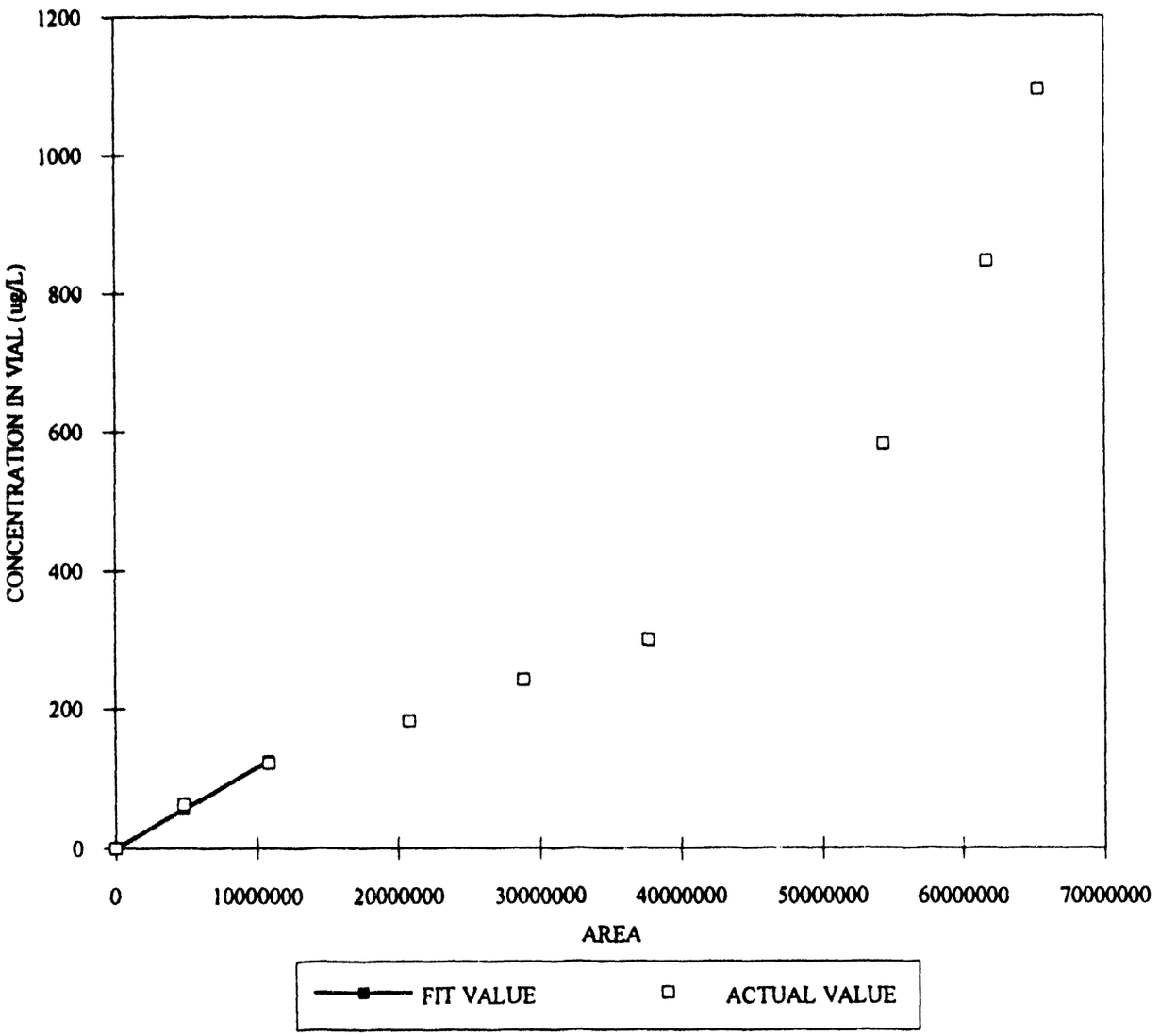
Sediment concentration [ug/g] =
(Standard concentration [ug/L] x 0.0075 [L]) / sediment mass [g].

MSBCB2E.CAL

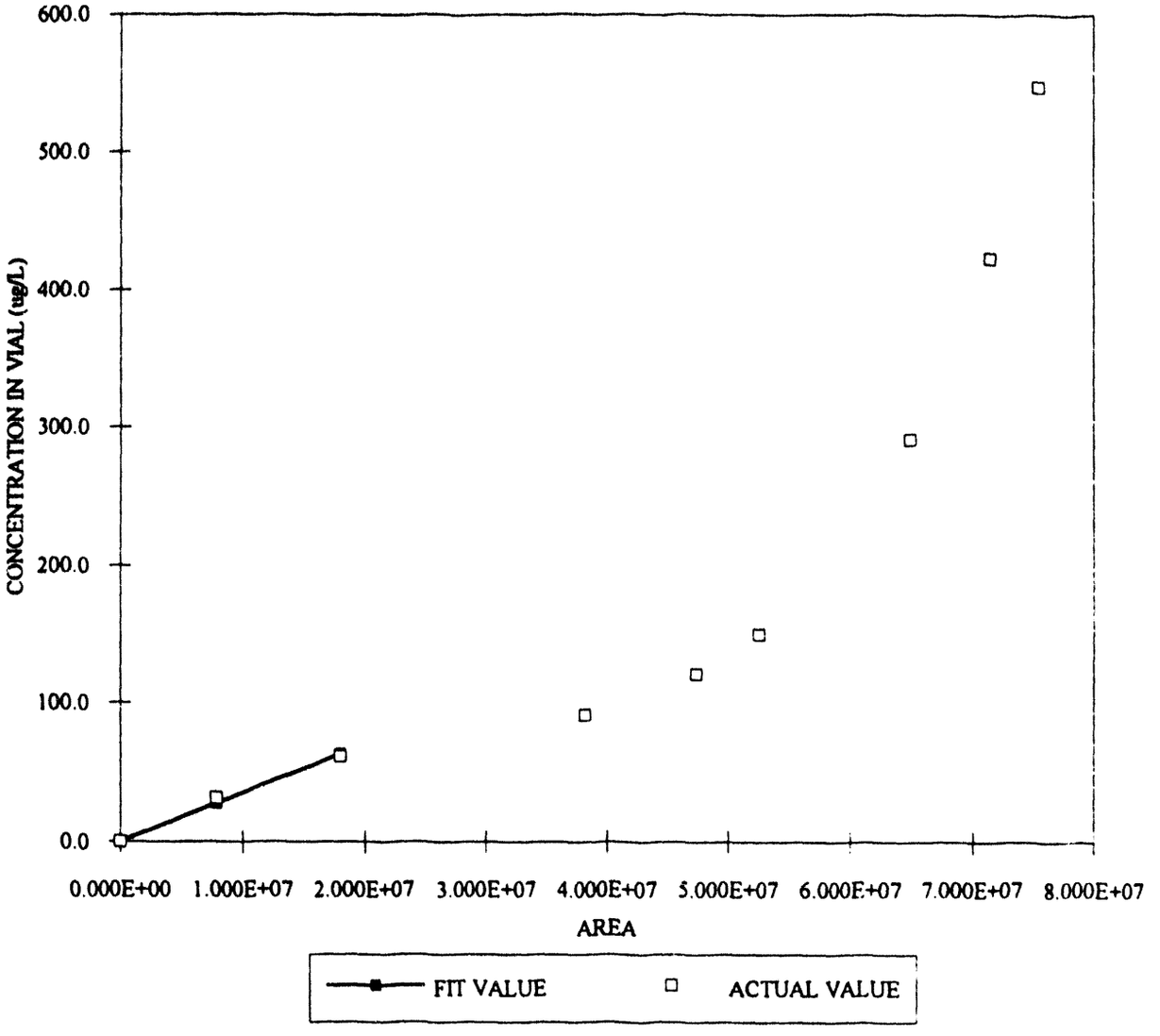
Samples	TCE area	PCE area	Samp. Info	TCE µg/L	PCE µg/L
0	3.196E+03	5.846E+03	0	0.0	0.0
50	4.822E+06	7.795E+06	STANDARD TCE/PCE MIX	62.0	31.0
100	1.080E+07	1.803E+07	STANDARD TCE/PCE MIX	122.0	61.0
150	2.081E+07	3.819E+07	STANDARD TCE/PCE MIX	182.0	91.0
200	2.886E+07	4.741E+07	STANDARD TCE/PCE MIX	242.0	121.0
250	3.769E+07	5.249E+07	STANDARD TCE/PCE MIX	300.0	150.0
500	5.438E+07	6.491E+07	STANDARD TCE/PCE MIX	581.0	291.0
750	6.169E+07	7.146E+07	STANDARD TCE/PCE MIX	845.0	423.0
1000	6.539E+07	7.547E+07	STANDARD TCE/PCE MIX	1094.0	547.0

	TCE			PCE	
slope	1.155E-05		slope	3.477E-06	
y intercept	0.000E+00		y intercept	0.000E+00	
r2	0.97357		r2	0.99030	
AREA	FIT VALUES	ACTUAL VALUES	AREA	FIT VALUES	ACTUAL VALUES
3.196E+03	0.0	0.0	5.846E+03	0.0	0.0
4.822E+06	55.7	62.0	7.795E+06	27.1	31.0
1.080E+07	124.8	122.0	1.803E+07	62.7	61.0
2.081E+07		182.0	3.819E+07	132.8	
2.886E+07		242.0	4.741E+07	164.8	
3.769E+07		300.0	5.249E+07	182.5	
5.438E+07		581.0	6.491E+07	225.7	
6.169E+07		845.0	7.146E+07	248.4	
6.539E+07		1094.0	7.547E+07	262.4	

MSB-CB2 ECD/TCE



MSB-CB2 ECD/PCE



Calibration Data for Depth Discrete Samples Collected from MBCSB-3

Sample (sediment) concentrations are related to calibration concentrations using the equation:

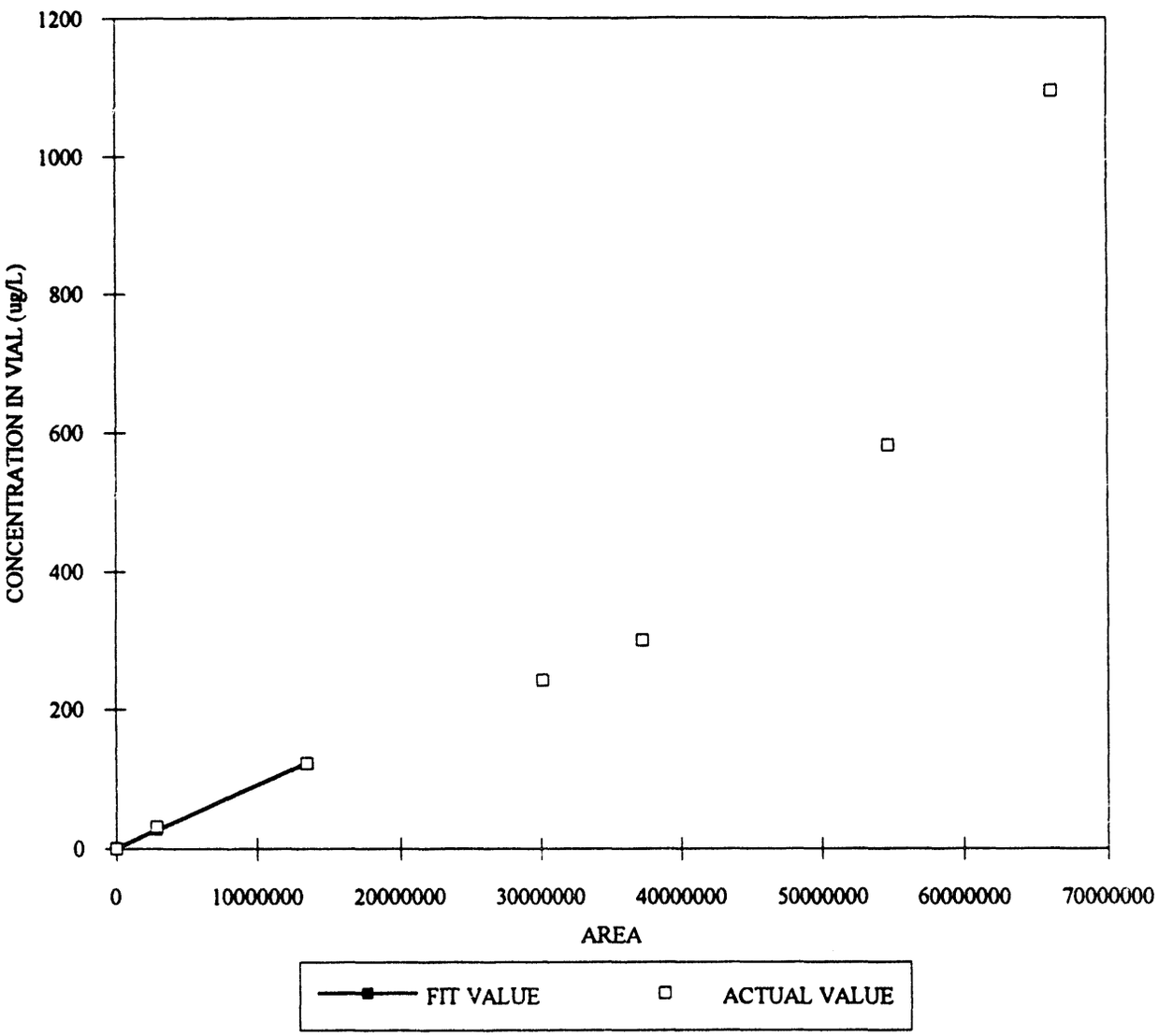
Sediment concentration [ug/g] =
(Standard concentration [ug/L] x 0.0075 [L]) / sediment mass [g].

MSBCB3E.CAL

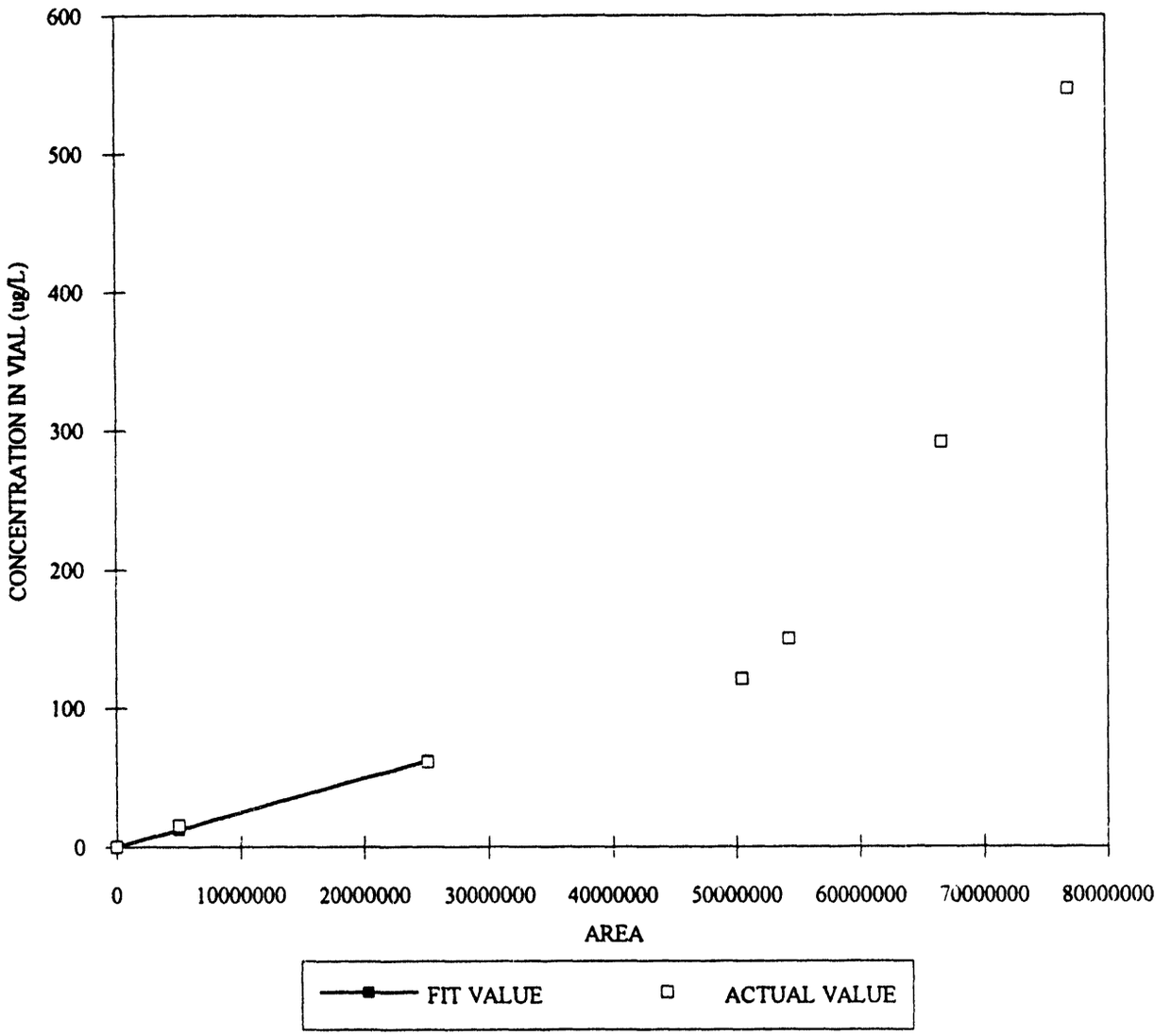
Samples	TCE area	PCE area	Samp. Info	TCE µg/L	PCE µg/L
0	3.005E+03	2.195E+03	0	0.0	0.0
25	2.941E+06	4.995E+06	STANDARD TCE/PCE MIX	31.0	15.0
100	1.347E+07	2.508E+07	STANDARD TCE/PCE MIX	122.0	61.0
200	3.011E+07	5.053E+07	STANDARD TCE/PCE MIX	242.0	121.0
250	3.728E+07	5.429E+07	STANDARD TCE/PCE MIX	300.0	150.0
500	5.470E+07	6.666E+07	STANDARD TCE/PCE MIX	581.0	291.0
1000	6.621E+07	7.706E+07	STANDARD TCE/PCE MIX	1094.0	547.0

	TCE			PCE	
slope	9.122E-06		slope	2.454E-06	
y intercept	0.000E+00		y intercept	0.000E+00	
r2	0.99773		r2	0.99613	
AREA	FIT VALUES	ACTUAL VALUES	AREA	FIT VALUES	ACTUAL VALUES
3.005E+03	0.0	0.0	2.195E+03	0.0	0.0
2.941E+06	26.8	31.0	4.995E+06	12.3	15.0
1.347E+07	122.9	122.0	2.508E+07	61.5	61.0
3.011E+07		242.0	5.053E+07		121.0
3.728E+07		300.0	5.429E+07		150.0
5.470E+07		581.0	6.666E+07		291.0
6.621E+07		1094.0	7.706E+07		547.0

MSB-CB3 ECD/TCE



MSB-CB3 ECD/PCE



Calibration Data for Depth Discrete Samples Collected from MBCSB-4

Sample (sediment) concentrations are related to calibration concentrations using the equation:

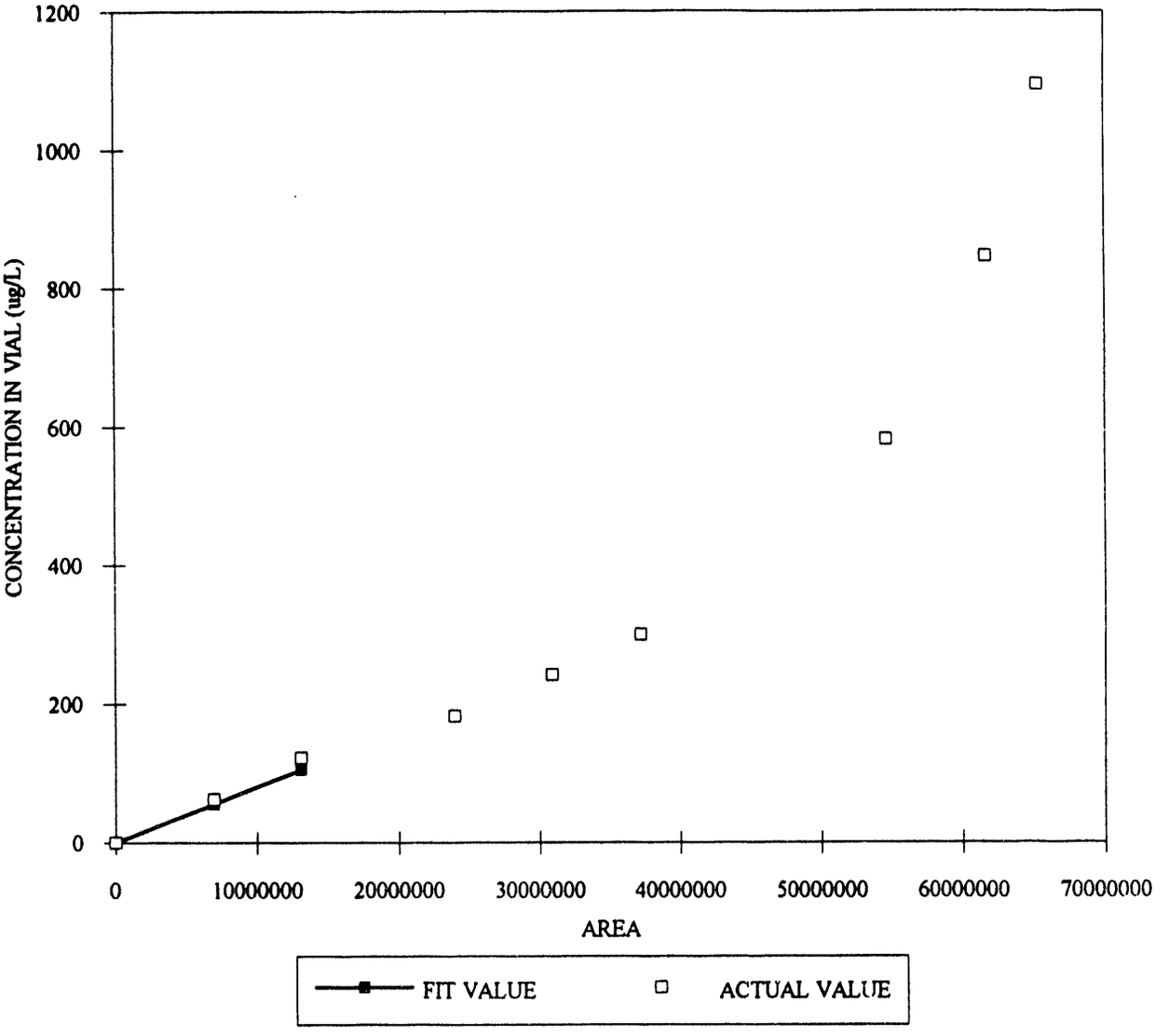
Sediment concentration [ug/g] =
(Standard concentration [ug/L] x 0.0075 [L]) / sediment mass [g].

MSBCB4E.CAL

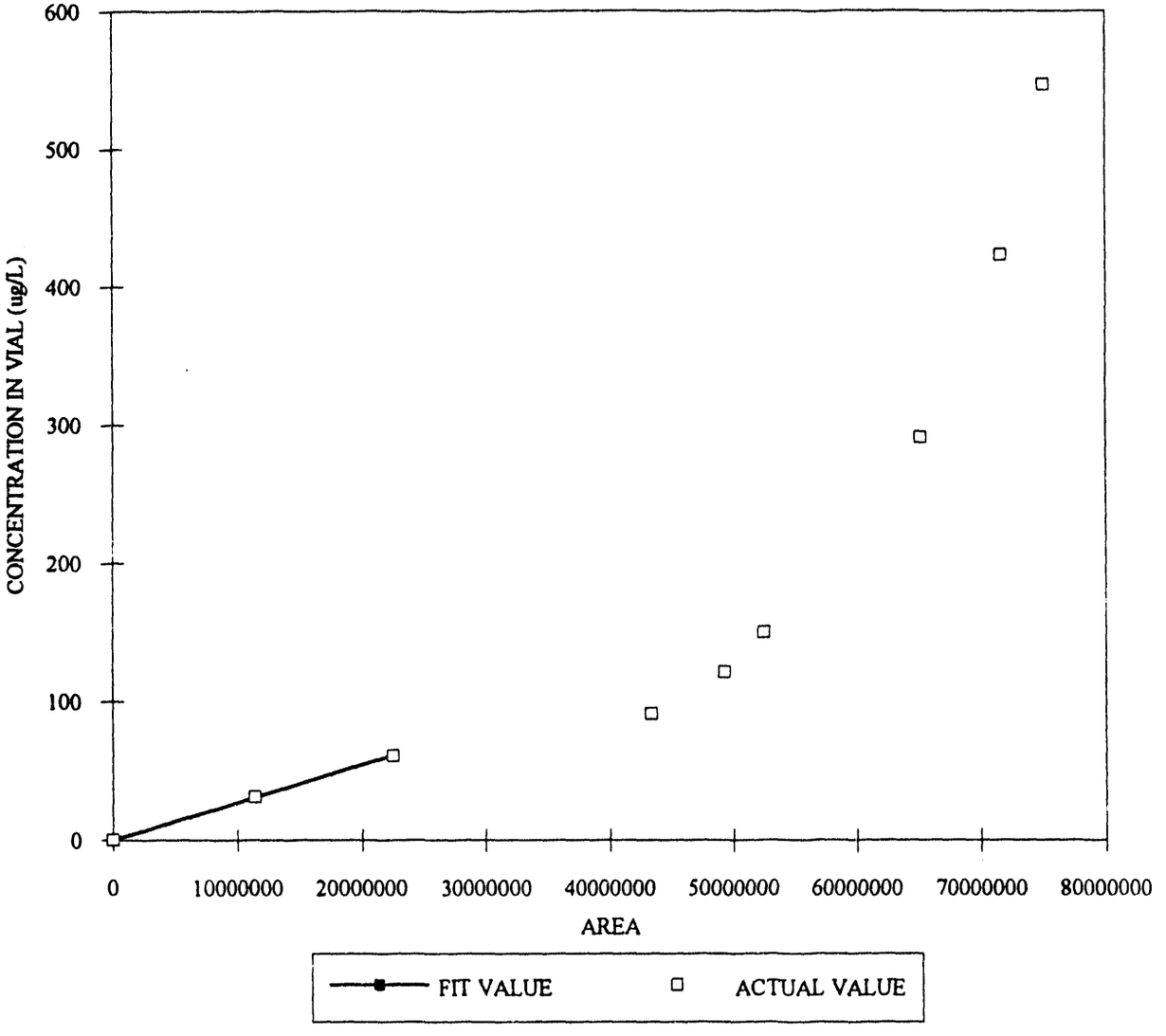
Samples	TCE area	PCE area	Samp. Info	TCE µg/L	PCE µg/L
0	4.282E+03	1.877E+03	0	0.0	0.0
50	6.930E+06	1.138E+07	STANDARD TCE/PCE MIX	62.0	31.0
100	1.308E+07	2.253E+07	STANDARD TCE/PCE MIX	122.0	61.0
150	2.395E+07	4.335E+07	STANDARD TCE/PCE MIX	182.0	91.0
200	3.089E+07	4.930E+07	STANDARD TCE/PCE MIX	242.0	121.0
250	3.723E+07	5.252E+07	STANDARD TCE/PCE MIX	300.0	150.0
500	5.460E+07	6.518E+07	STANDARD TCE/PCE MIX	581.0	291.0
750	6.166E+07	7.160E+07	STANDARD TCE/PCE MIX	845.0	423.0
1000	6.532E+07	7.507E+07	STANDARD TCE/PCE MIX	1094.0	547.0

	TCE			PCE	
slope	7.995E-06		slope	2.711E-06	
y intercept	0.000E+00		y intercept	0.000E+00	
r2	0.99928		r2	0.99998	
AREA	FIT VALUES	ACTUAL VALUES	AREA	FIT VALUES	ACTUAL VALUES
4.282E+03	0.0	0.0	1.877E+03	0.0	0.0
6.930E+06	55.4	62.0	1.138E+07	30.8	31.0
1.308E+07	104.6	122.0	2.253E+07	61.1	61.0
2.395E+07		182.0	4.335E+07		91.0
3.089E+07		242.0	4.930E+07		121.0
3.723E+07		300.0	5.252E+07		150.0
5.460E+07		581.0	6.518E+07		291.0
6.166E+07		845.0	7.160E+07		423.0
6.532E+07		1094.0	7.507E+07		547.0

MSB-CB4 ECD/TCE



MSB-CB4 ECD/PCE



Calibration Data for Depth Discrete Samples Collected from MBCSB-5

Sample (sediment) concentrations are related to calibration concentrations using the equation:

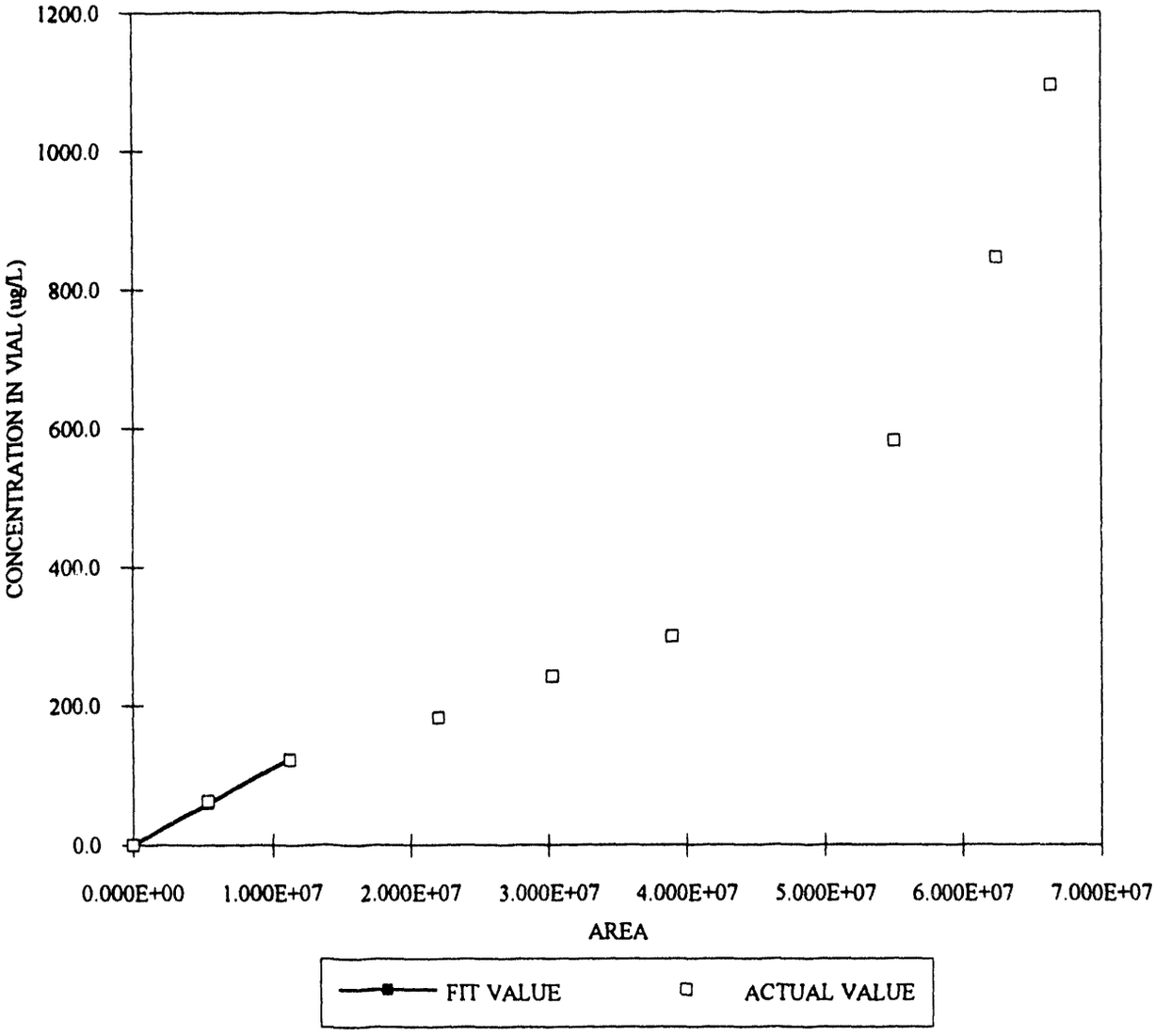
Sediment concentration [ug/g] =
(Standard concentration [ug/L] x 0.0075 [[L])/ sediment mass [g].

MSBCB5E.CAL

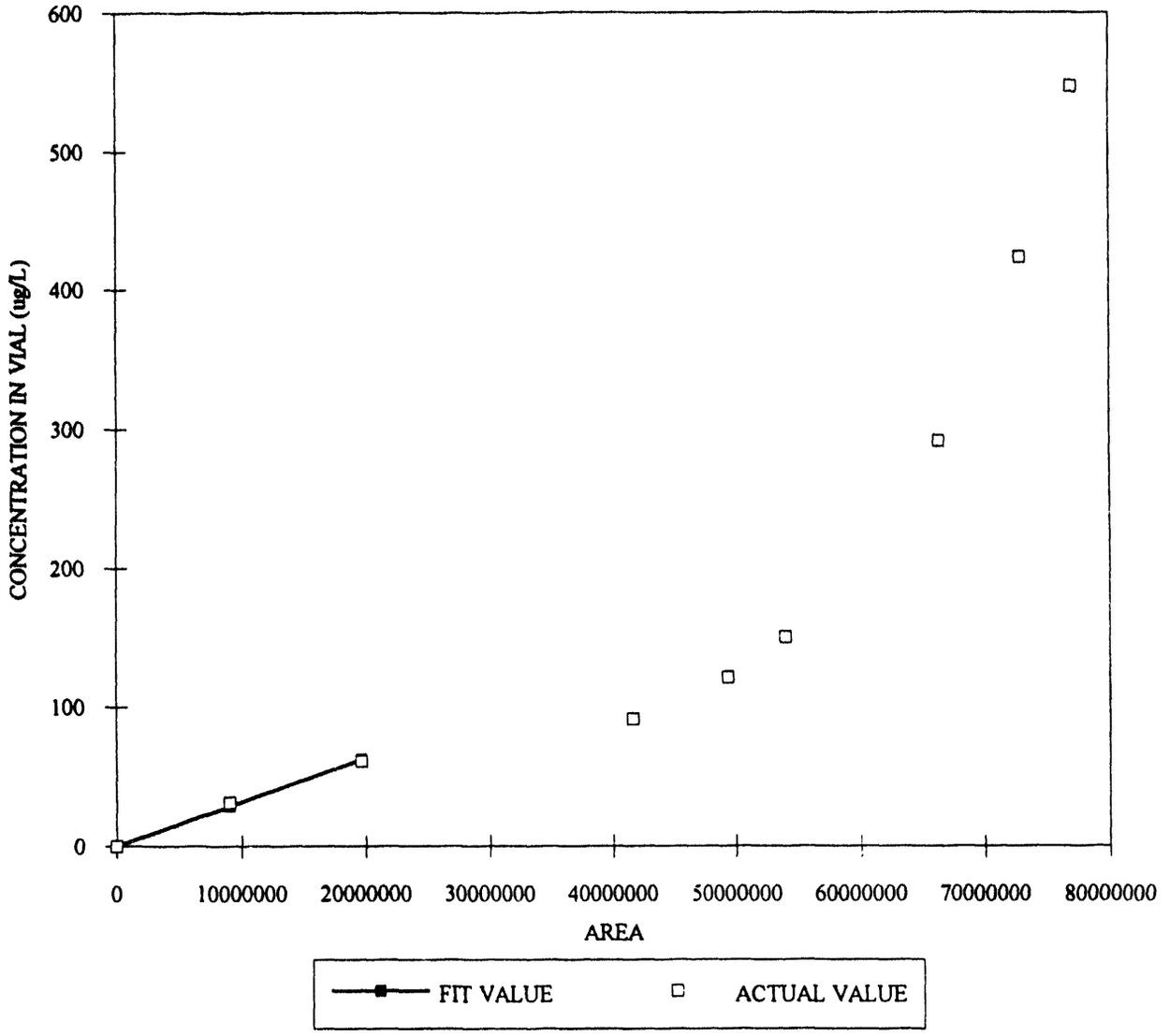
Samples	TCE area	PCE area	Samp. Info	TCE µg/L	PCE µg/L
0	4.034E+03	2.640E+03	0	0.0	0.0
50	5.340E+06	9.033E+06	STANDARD TCE/PCE MIX	62.0	31.0
100	1.124E+07	1.965E+07	STANDARD TCE/PCE MIX	122.0	61.0
150	2.201E+07	4.161E+07	STANDARD TCE/PCE MIX	182.0	91.0
200	3.029E+07	4.940E+07	STANDARD TCE/PCE MIX	242.0	121.0
250	3.895E+07	5.400E+07	STANDARD TCE/PCE MIX	300.0	150.0
500	5.508E+07	6.633E+07	STANDARD TCE/PCE MIX	581.0	291.0
750	6.248E+07	7.287E+07	STANDARD TCE/PCE MIX	845.0	423.0
1000	6.646E+07	7.698E+07	STANDARD TCE/PCE MIX	1094.0	547.0

	TCE			PCE	
slope	1.099E-05		slope	3.162E-06	
y intercept	0.000E+00		y intercept	0.000E+00	
r2	0.99821		r2	0.99613	
AREA	FIT VALUES	ACTUAL VALUES	AREA	FIT VALUES	ACTUAL VALUES
4.034E+03	0.0	0.0	2.640E+03	0.0	0.0
5.340E+06	58.7	62.0	9.033E+06	28.6	31.0
1.124E+07	123.6	122.0	1.965E+07	62.1	61.0
2.201E+07		182.0	4.161E+07		91.0
3.029E+07		242.0	4.940E+07		121.0
3.895E+07		300.0	5.400E+07		150.0
5.508E+07		581.0	6.633E+07		291.0
6.248E+07		845.0	7.287E+07		423.0
6.646E+07		1094.0	7.698E+07		547.0

MSB-CB5 ECD/TCE



MSB-CB5 ECD/PCE



Calibration Data for Depth Discrete Samples Collected from MBCSB-6

Sample (sediment) concentrations are related to calibration concentrations using the equation:

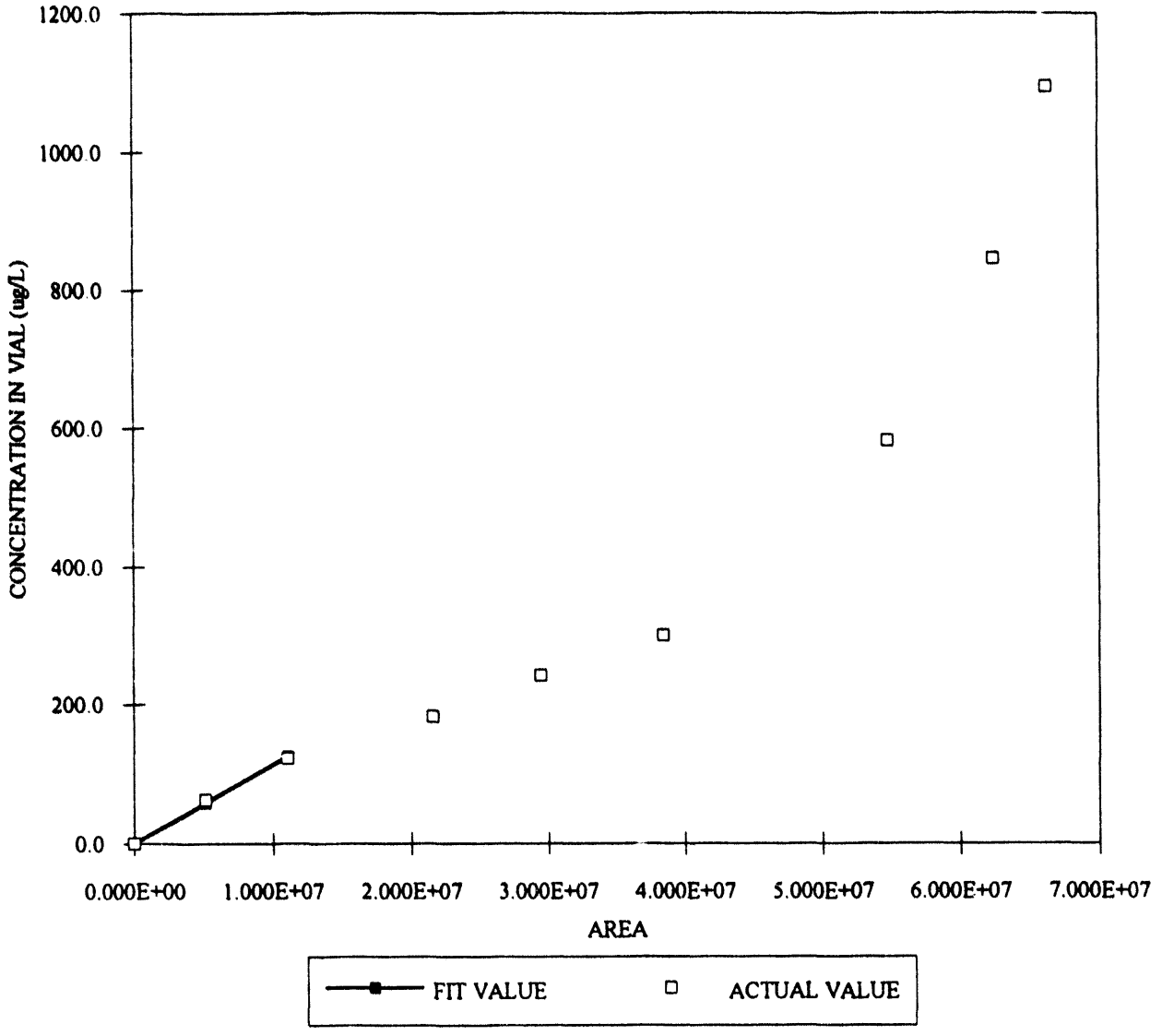
Sediment concentration [ug/g] =
(Standard concentration [ug/L] x 0.0075 [L]) / sediment mass [g].

MSBCB6E.CAL

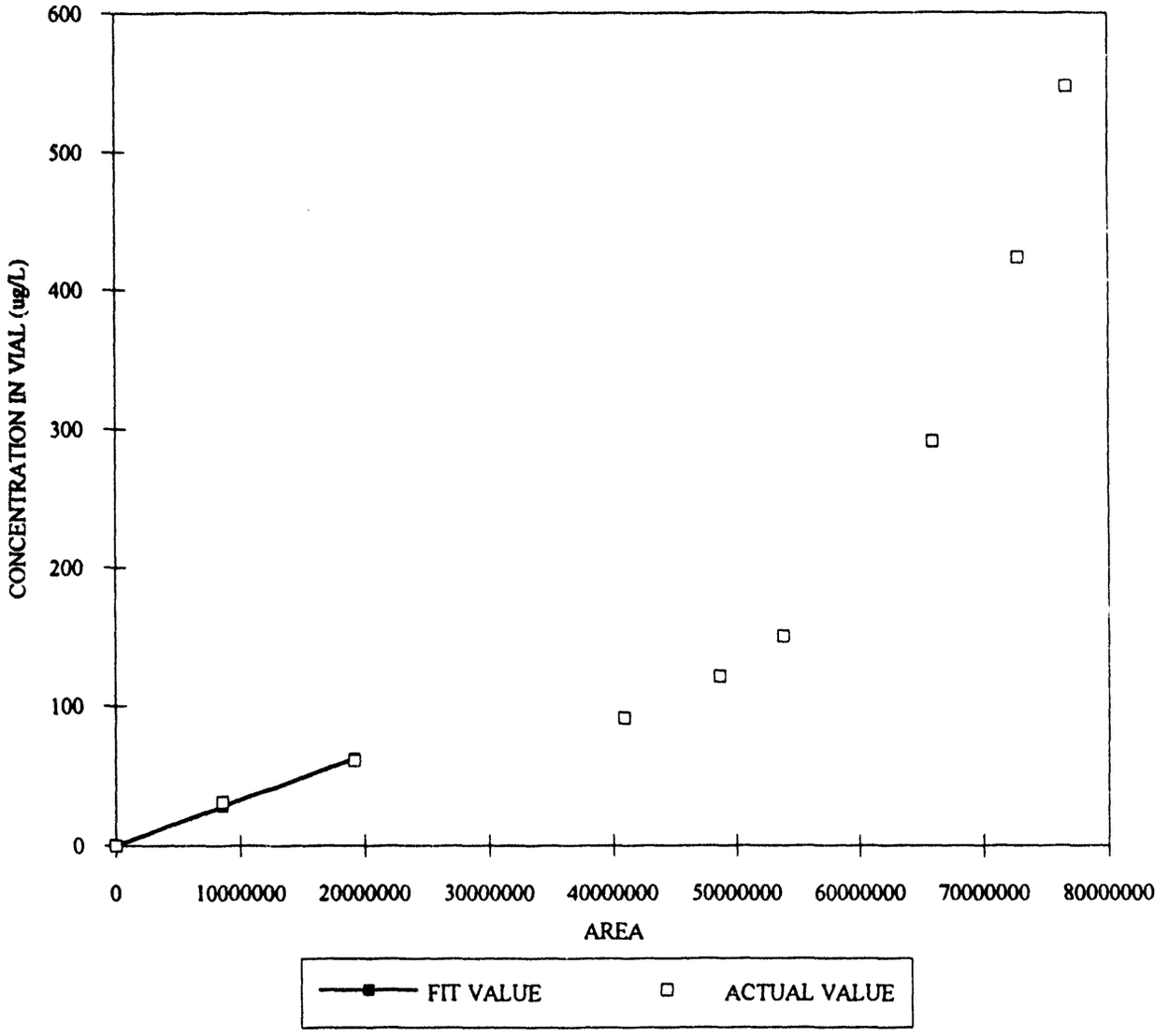
Samples	TCE area	PCE area	Samp. Info	TCE µg/L	PCE µg/L
0	3.220E+03	4.047E+03	0	0.0	0.0
50	5.117E+06	8.581E+06	STANDARD TCE/PCE MIX	62.0	31.0
100	1.105E+07	1.916E+07	STANDARD TCE/PCE MIX	122.0	61.0
150	2.159E+07	4.093E+07	STANDARD TCE/PCE MIX	182.0	91.0
200	2.941E+07	4.872E+07	STANDARD TCE/PCE MIX	242.0	121.0
250	3.842E+07	5.383E+07	STANDARD TCE/PCE MIX	300.0	150.0
500	5.475E+07	6.598E+07	STANDARD TCE/PCE MIX	581.0	291.0
750	6.249E+07	7.283E+07	STANDARD TCE/PCE MIX	845.0	423.0
1000	6.628E+07	7.674E+07	STANDARD TCE/PCE MIX	1094.0	547.0

	TCE			PCE	
slope	1.123E-05		slope	3.256E-06	
y intercept	0.000E+00		y intercept	0.000E+00	
r2	0.99666		r2	0.99395	
AREA	FIT VALUES	ACTUAL VALUES	AREA	FIT VALUES	ACTUAL VALUES
3.220E+03	0.0	0.0	4.047E+03	0.0	0.0
5.117E+06	57.5	62.0	8.581E+06	27.9	31.0
1.105E+07	124.1	122.0	1.916E+07	62.4	61.0
2.159E+07		182.0	4.093E+07		91.0
2.941E+07		242.0	4.872E+07		121.0
3.842E+07		300.0	5.383E+07		150.0
5.475E+07		581.0	6.598E+07		291.0
6.249E+07		845.0	7.283E+07		423.0
6.628E+07		1094.0	7.674E+07		547.0

MSB-CB6 ECD/TCE



MSB-CB6 ECD/PCE



Calibration Data for Depth Discrete Samples Collected from MBCSB-7

Sample (sediment) concentrations are related to calibration concentrations using the equation:

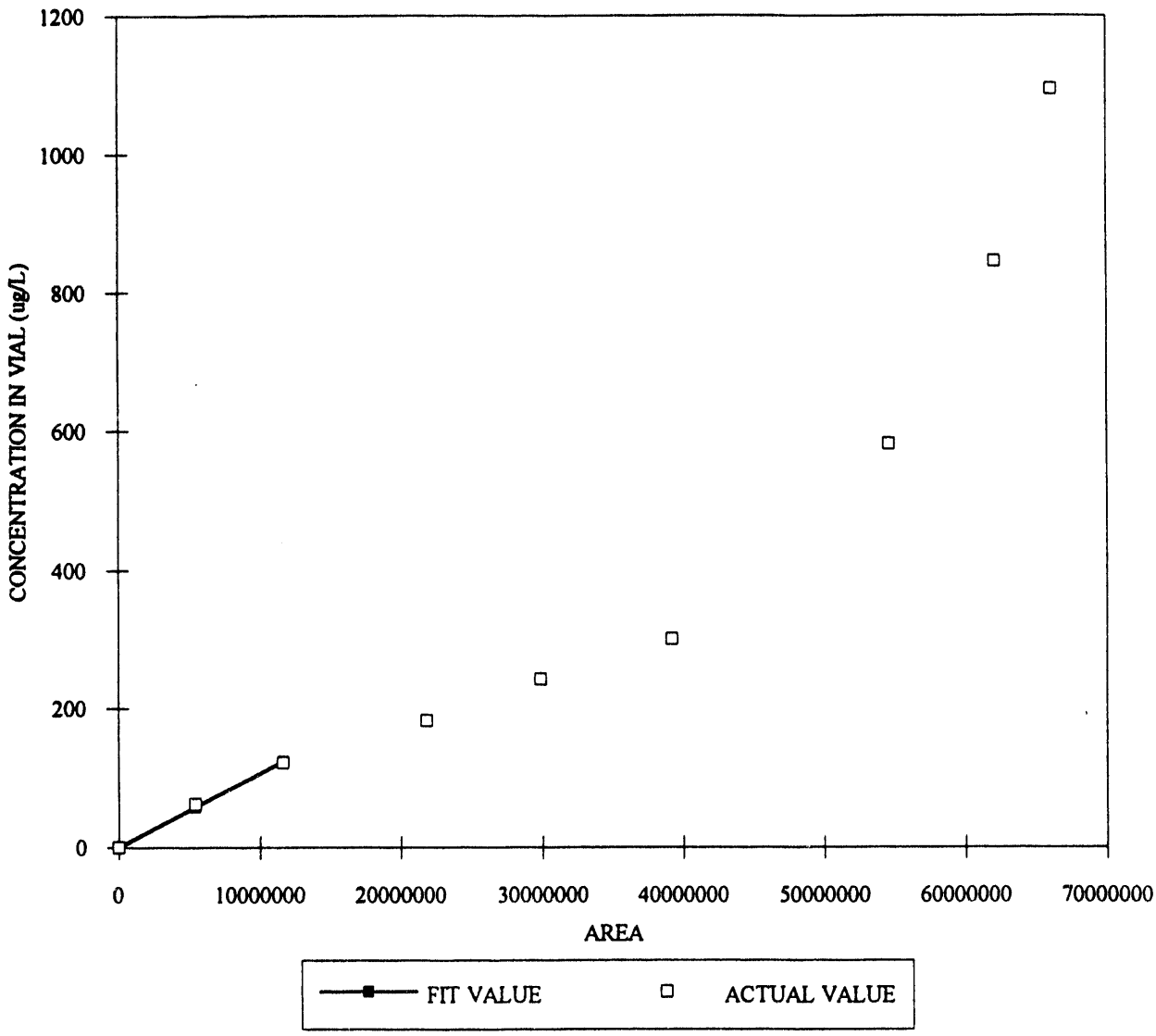
Sediment concentration [ug/g] =
(Standard concentration [ug/L] x 0.0075 [L]) / sediment mass [g].

MSBCB7E.CAL

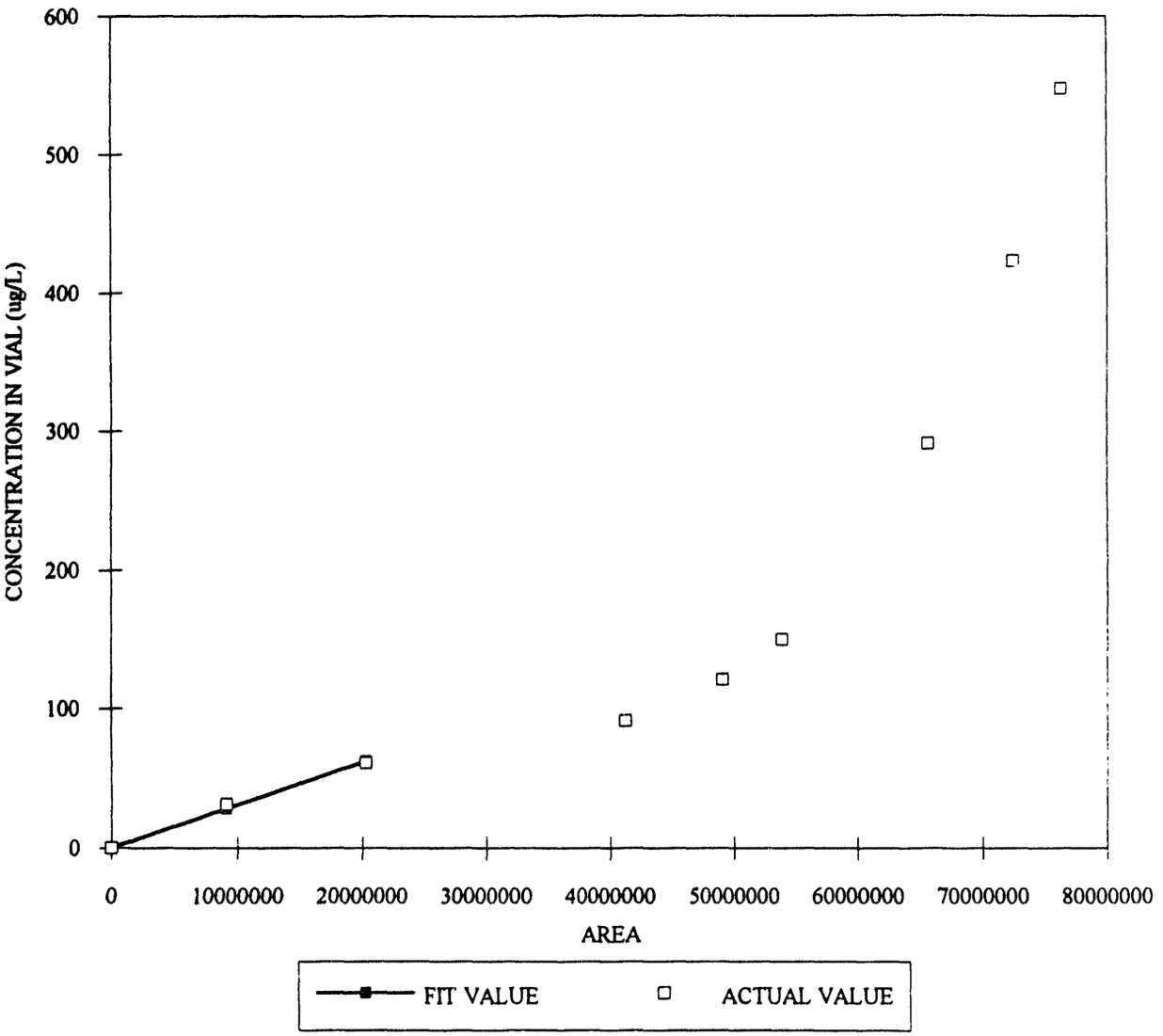
Samples	TCE area	PCE area	Samp. Info	TCE µg/L	PCE µg/L
0	3.640E+03	1.732E+03	0	0.0	0.0
50	5.433E+06	9.131E+06	STANDARD TCE/PCE MIX	62.0	31.0
100	1.164E+07	2.026E+07	STANDARD TCE/PCE MIX	122.0	61.0
150	2.184E+07	4.123E+07	STANDARD TCE/PCE MIX	182.0	91.0
200	2.987E+07	4.912E+07	STANDARD TCE/PCE MIX	242.0	121.0
250	3.916E+07	5.390E+07	STANDARD TCE/PCE MIX	300.0	150.0
500	5.460E+07	6.569E+07	STANDARD TCE/PCE MIX	581.0	291.0
750	6.210E+07	7.248E+07	STANDARD TCE/PCE MIX	845.0	423.0
1000	6.611E+07	7.634E+07	STANDARD TCE/PCE MIX	1094.0	547.0

	TCE			PCE	
slope	1.065E-05		slope	3.075E-06	
y intercept	0.000E+00		y intercept	0.000E+00	
r2	0.99720		r2	0.99449	
AREA	FIT VALUES	ACTUAL VALUES	AREA	FIT VALUES	ACTUAL VALUES
3.640E+03	0.0	0.0	1.732E+03	0.0	0.0
5.433E+06	57.9	62.0	9.131E+06	28.1	31.0
1.164E+07	123.9	122.0	2.026E+07	62.3	61.0
2.184E+07		182.0	4.123E+07		91.0
2.987E+07		242.0	4.912E+07		121.0
3.916E+07		300.0	5.390E+07		150.0
5.460E+07		581.0	6.569E+07		291.0
6.210E+07		845.0	7.248E+07		423.0
6.611E+07		1094.0	7.634E+07		547.0

MSB-CB7 ECD/TCE



MSB-CB7 ECD/PCE



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