20) OECD 106-OPPTS 835.1220, Adsorption / Desorption, 023-048

21) OPPTS 835.1110, Activated sludge sorption isotherm (incorporated with OECD 106)

SANITIZED

FINAL REPORT

DEC 09 2003

STUDY TITLE

ADSORPTION AND DESORPTION STUDY TO DETERMINE THE MOBILITY AND DISTRIBUTION OF PERFLUOROBUTANESULFONIC ACID IN SOIL

DATA REQUIREMENTS

OECD Guideline for Testing of Chemicals, 106

STUDY DIRECTOR

Kevin Lloyd

STUDY COMPLETED ON

March 8, 2001

TESTING LABORATORY

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STUDY IDENTIFICATION NUMBER

Centre Study Number 023-048

Total pages 74

GOOD LABORATORY PRACTICE COMPLIANCE STATEMENT

Centre Study Number 023-048, entitled "Adsorption and Desorption Study to Determine the Mobility and Distribution of Perfluorobutanesulfonic Acid in Soil" conducted for 3M Environmental Laboratory, was performed in compliance with US EPA Good Laboratory Practice Standards (40 CFR Part 160) and the OECD Principles of Good Laboratory Practice (Monograph No. 45) by Centre Analytical Laboratories, Inc. with the following exceptions:

1. The test substance lacked full characterization per EPA 160.105 and OECD 1.1.2.p.
2. Test substance storage between receipt and login was not documented (EPA 160.107, OECD 6.1)
3. Occasionally data were not recorded promptly at the time of observation (EPA 160.130, OECD 8.3.3).
4. Computerized systems were not fully validated (OECD 1.2.2.g).
5. Computerized data lack a full audit trail (OECD 8.3.5).

3/8/01

Kevin Lloyd
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Date

3/15/01

Sponsor Representative
3M Environmental Technology and Safety Services (3METSS)

Date

QUALTITY ASSURANCE STATEMENT

Centre Study Number 023-048 entitled "Adsorption and Desorption Study to Determine the Mobility and Distribution of Perfluorobutanesulfonic Acid in Soil" was reviewed by Centre Analytical Laboratories' Quality Assurance Unit. All reviewed phases were reviewed for conduct according to Centre Analytical Laboratories' Standard Operating Procedures, the Study Protocol, and all applicable Good Laboratory Practice Standards. All findings were reported to the Study Director and to management.

Phase	Date Inspected	Date Reported to Study Director and Centre Management	Date Reported to Sponsor Management
1. Protocol Review	12/14/00	12/19/00,12/20/00	12/21/00
2. In-Phase Audit	12/27/00	1/11/01, 1/12/01	2/9/01
3. Raw Data Review Draft Report Review	1/22-25/01	3/8/01, 3/2/01	3/8/01
4. Final Report Review	2/28/01	3/8/01	3/8/01

Naomi Lovallo
Senior Quality Assurance Auditor

3/8/01
Date

CERTIFICATION OF AUTHENTICITY

This report, for Centre Study Number 023-048, is a true and complete representation of the raw data for the study.

Submitted by: Centre Analytical Laboratories, Inc.
3048 Research Drive
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William Spare, Technical Lead QAU

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Date

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President
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8-MAR-01
Date

STUDY IDENTIFICATION

ADSORPTION AND DESORPTION STUDY TO DETERMINE THE MOBILITY AND DISTRIBUTION OF PERFLUOROBUTANESULFONIC ACID IN SOIL

TYPE OF STUDY:	adsorption/desorption
TEST SYSTEM:	Domestic sludge (NIST #2781), river sediment, soils
TEST SUBSTANCE:	PFBS
CENTRE STUDY NUMBER:	023-048
STUDY PROTOCOL NUMBER:	00P-023-048
SPONSOR STUDY MONITOR:	3M Environmental Technology and Safety Services
STUDY DIRECTOR:	Kevin Lloyd Centre Analytical Laboratories, Inc. Phone: (814) 231-8032
TESTING FACILITIES:	Centre Analytical Laboratories, Inc. (Centre) 3048 Research Drive State College, PA 16801 Phone: 814-231-8032

STUDY TIMETABLE:

Study Initiation Date:	October 23, 2000
Experimental Start Date:	December 11, 2000
Experimental Termination Date:	January 9, 2001

STUDY PERSONNEL

The Study Director for this project was Kevin Lloyd at Centre Analytical Laboratories, Inc. The following personnel from Centre Analytical Laboratories, Inc., were associated with various phases of the study:

Name	Title
William Spare	Technical Lead QAU
Brent McCracken	Scientist
Matthew S. Yasovsky	Technician
Rick Keller	Sample Custodian
John Flaherty	Operations Manager

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Study Title

ADSORPTION AND DESORPTION STUDY TO DETERMINE THE MOBILITY AND DISTRIBUTION OF PERFLUOROBUTANESULFONIC ACID IN SOIL

1.0 SUMMARY

This study was performed to estimate the adsorption/desorption behavior of perfluorobutanesulfonic acid (PFBS) on soils, sediment and sludge to obtain a sorption value which can be used to predict partitioning under a variety of environmental conditions. The study was performed to meet the guideline requirements described in the OECD Guidelines for Testing of Chemicals 106.

The three tested soils and sediment demonstrated no adsorption of PFBS. The Don Uglem loam, Kittson clay, Broeren clay loam and Goose River sediment all showed no detectable PFBS remaining with the solids following adsorption. Detection of PFBS in desorption solutions occurred in only a few scattered samples.

No calculations using the Freundlich isotherm were possible for the Don Uglem loam, Kittson clay, Broeren clay loam and Goose River sediment.

The lack of sorption of PFBS to the three soils or the sediment placed PFBS in the very high mobility class based on ASTM E1195 (K_{oc} 0 - 50).

PFBS yielded a Freundlich K_f (adsorption) value of 0.3 with a 1/n value of 1.284 for activated sludge obtained from the NIST, Gaithersburg, MD 20899. The initial PFBS concentration in solution was independent of the determined sorption value. This value also placed PFBS in the very high mobility class.

2.0 INTRODUCTION

This report details the results of testing the adsorption and desorption of PFBS to soils, sediment and sludge supplied by 3M Environmental Technology and Safety Services (3METSS). The study was performed over a two-month period with analysis of the generated solutions and solids performed using an ion specific method of liquid chromatography/mass spectroscopy (LC/MS). All solutions and soils were extracted and analyzed for PFBS using the procedures detailed in Centre Analytical Labs SOP CAL-24FWL/0; "Extraction of Wastewater Samples for Fluorochemical Analyses by LC/MS" and SOP CAL-24FLM/1, "Analysis of Select Fluorochemicals by LC/MS'.

The study was initiated on October 23, 2000 when the study director signed protocol number 00P-023-048. The analytical start date was December 11, 2000, and the experimental termination date was January 9, 2001.

3.0 TEST SYSTEM

The test system for this study was each 50 mL plastic centrifuge tube containing soil, sediment or sludge to which PFBS fortified $CaCl_2$ solution was added. All test systems were established and maintained per the protocol and the test temperature ranged from 17.0 to 19.1°C (Tier 1), 19.5 to 22.7°C (Tier 2), and 18.2 to 19.3°C (Tier 3).

4.0 TEST SOILS, SEDIMENT AND SLUDGE

Soil, sediment, and sludge samples were obtained and transported to Centre by 3METSS. Source location (specified in geographical coordinates) and the depth of sampling (≤20 cm) were provided. Each sample was assigned a unique identification number at Centre, which was used for tracking and identification of the soil/sediment during the study. The soil/sediment/sludge were stored in a temperature-monitored refrigerator maintained at 2 to 6° C. The samples were kept isolated from the test substance during storage. AGVISE Laboratories, Northwood, ND, performed characterization of the test soils and sediment. See Table 1 for soil and sediment characteristics.

As specified by the OPPTS Guideline 835.1110, the activated sludge had been collected and prepared by settling, washing and centrifuging three times, lyophilization, powdering, and oven drying at 103°C for 3 hours or longer. The sludge used in this study was obtained from the National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899 and identified as Standard Reference Material 2781. The sludge was supplied to Centre by 3METSS. Each sludge sample was assigned a unique identification number at Centre, which was used for tracking and identification of the sludge during the study. The sludge was stored in a temperature-monitored refrigerator maintained at 2 to 6° C. The samples were kept isolated from the test substance during storage. The table below summarizes the characteristics of the sludge as provided by the NIST.

	Certified Values (mg/Kg)								
Sludge	**As**	**Cd**	**Cu**	**Pb**	**Hg**	**Mo**	**Ni**	**Se**	**Zn**
SRM 2781	7.82	12.78	627.4	202.1	3.64	46.7	80.2	16.0	1273

SRM = standard reference material (SRM #2781 used in this study)

5.0 TEST SUBSTANCE

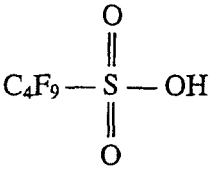
The following analytical standard was used:

Test Material	Lot Number	Purity (%)	Expiration Date
PFBS		TBD	07/06/2001

TBD = to be determined, under separate study protocol.

Chemical names and structures of the test substance are presented below.

Chemical Name: perfluorobutanesulfonic acid
Molecular Weight: 300



Test and Reference Substance Documentation

The methods of synthesis, fabrication and/or derivation of the test and reference substances are documented and retained by the Sponsor. The Sponsor, as required by US EPA FIFRA GLP Standard 40 CFR 160.105, is responsible for characterization of the test and reference substances, and the Sponsor retains these records. Archived samples of the test and reference substances are being retained by the Sponsor. The Sponsor is maintaining these records and archived samples at the 3M facilities in St. Paul, MN.

The test and reference substances containers were retained beyond the duration of the study. Any emptied containers at study completion were disposed of according to standard Centre procedures. Any remaining test and/or reference substances were retained by/at Centre, or authorization was obtained from the Sponsor to return any remaining substances. Records are maintained at Centre documenting use, disposal, or return of test and/or reference substances.

6.0 ANALYTICAL METHOD

All solutions and soils were extracted and analyzed for PFBS using the procedures detailed in Centre Analytical Labs SOP CAL-24FWL/0; "Extraction of Wastewater Samples for Fluorochemical Analyses by LC/MS" and SOP CAL-24FLM/1, "Analysis of Select Fluorochemicals by LC/MS'. The solution extraction procedure was changed to a filtration

of the samples through 0.45 micron filters followed by LC/MS analysis. This procedure provided more consistent results than the ion extraction method.

Sample/solution preparation, storage location and conditions during the study were documented in the study data. All samples and any soil/sediment extracts were identified with a unique label. Such identification was on the sample container.

During analytical runs calibration standards were interspersed throughout the run. No more than 5 samples were analyzed between standards. At least 8 standards were analyzed per run with a minimum of 6 used in the calibration curve. The r^2 value of the calibration curves were >0.99.

7.0 EXPERIMENTAL CONDITIONS

TIER 1 Preliminary Study

PFBS was dissolved in methanol (JT Baker Lot T34315) at 10.09 mg/mL. A 0.1 mL aliquot of this stock was brought to 1000 mL with 0.01M $CaCl_2$ solution (well below the water solubility of the test substance) to provide fortified (0.01 M Ca^{++}). The Don Uglem loam and the Kittson clay were used in the Tier 1 testing. The experiments were performed in individual disposable plastic 50 mL centrifuge tubes. Mixing of the soils and calcium chloride solution was accomplished using a tumbler which rotated the test tubes end-over-end at 32 rpm. Three different soil to solution ratios were tested: 1/1, 1/5 and 1/25. All experiments were performed in triplicate with individual analysis of each replicate. This included the controls and blanks. The pH of the blank and fortified 0.01M $CaCl_2$ solution as well as the aqueous phases recovered after contact with the sludge were measured and recorded.

The mixtures of soil and fortified 0.01M $CaCl_2$ solutions were placed on the tumbler and mixed until adsorption equilibrium was reached. Samples were collected over a 48-hour period of continuous mixing. At the specified sample intervals (4, 8, 24, and 48 hours) all test systems (centrifuge bottles with soil and solution) were centrifuged. Following this solid-liquid separation, an aliquot (1 mL) of the aqueous phase was removed for analysis. After removal of the sample, the soil was remixed with the aqueous phase and all centrifuge bottles were returned to the mixing apparatus until the subsequent sampling. Using a calibrated thermometer placed adjacent to the tumbler monitored temperature. Temperature ranged from 17.0 to 19.1°C during this phase of testing.

The percent adsorption (A_{ti}) was calculated at each time point (t_i) based on the average concentration of the three control replicates (fortified solution only) and the measured concentration at the sampling time (t_i). Plots of A_{ti} versus time were not generated since no apparent adsorption of PFBS was observed. The K_d value at 48 hours could likewise not be calculated. Based on the lack of adsorption the highest ratio was selected. The selected ratio used for all remaining work was 1g soil:1 mL of solution in an attempt to obtain adsorbed values between 20% and 80% of the original amount in solution.

Following the ratio-finding experiment and analysis of the last sample of the aqueous phase after 48 hours, the phases were separated by centrifugation. The aqueous phase was recovered and the soil was extracted with methanol for analysis of PBSF. The concentration of PFBS in solution and soil extracts was determined by LC/MS.

The mass balance was performed on all three soil/solution ratios for each soil type. The mass balance was determined as the total PFBS recovered in the soil plus the total PFBS in the aqueous phase at 48 hours. The mass balance was calculated as a percent of the applied PFBS based on analysis of the fortified 0.01M $CaCl_2$ solution (no soil).

TIER 2 -- Sorption Kinetics

The remaining soil, river sediment and sludge were next tested at a solids/solution ratio of 1/1 for the soil and sediment and 1/5 for the sludge (soil to solution -- 20 g to 20 mL; sludge 5g to 40 mL). The concentration of the PFBS in the solution (1000μg/L) was maintained based on the solubility of PFBS (>5000 mg/L). Analysis of aqueous solutions was performed at 2, 4, 6, 8, and 24 hours of contact time.

The soil, sediment and sludge were tested in triplicate with triplicate controls (test substance in 0.01M $CaCl_2$ solution with no solids) and triplicate blanks for each (solids and 0.01M $CaCl_2$ solution with no test substance). The test was performed as in the original preliminary work with tumbling of the soil, sediment and sludge with test solution, centrifugation of the samples, removal of aliquots following centrifugation, analysis of sampled aliquots, and reinitiating tumbling until the next sampling interval. The concentration of PFBS in the solutions was determined by LC/MS.

The percent adsorption was calculated at each time point (A_{ti}) and plotted versus time. The preliminary sorption coefficient K at equilibrium was also calculated.

TIER 3

Adsorption Isotherm

Five nominal test concentrations of PFBS (1000, 500, 250, 100, 50 μg/L) were used. Each test concentration was evaluated in triplicate with triplicate blanks (solids and 0.01M $CaCl_2$ solution with no PFBS). The concentration values were selected to stay well above the PFBS detection limit (limit of detection was 10 μg/L). The sludge/solution ratio used for the testing was 1/5 throughout this phase of the study. Soils and sediment were tested at a ratio of 1/1. The adsorption test was performed as described under Tiers 1 and 2, except that the aqueous phase was analyzed only once at the equilibrium time determined to be 24 hours in Tier 2. The equilibrium concentrations in the solutions were determined by LC/MS.

Desorption Isotherm

Following removal of the adsorption solutions from the solids, all remaining solids were next remixed with fresh 0.01M $CaCl_2$ solution without PFBS. The same volume of solution as used for the adsorption phase was used in the desorption phase. The desorption test was performed as described under Tiers 1 and 2, except that the aqueous phase was analyzed only once at 24 hours as for the adsorption phase. The equilibrium concentrations in the solutions were determined by LC/MS. Following desorption, solid samples for which the adsorption and desorption solutions did not account for >90% of the applied PFBS were subjected to methanol extraction and LC/MS analysis. The extraction was performed using a wrist action shaker with methanol for 30 minutes followed by 30 minute sonication. Samples were centrifuged to separate the solvent and solids and the supernatant was decanted. The extraction was performed twice and both extracts were combined, concentrated, and analyzed.

Mass balance was determined for all samples for all soils, sediment and sludge. The Freundlich adsorption and desorption isotherms were calculated only for the sludge since no soil or sediment demonstrated adsorbance of PFBS.

The pH of the blank and fortified 0.01M $CaCl_2$ solutions as well as the aqueous phases recovered after adsorption and desorption were measured and recorded.

8.0 CALCULATIONS

Mass Balance

A mass balance was performed using the following formula to ensure that the test substance was adequately accounted for:

$$MB = \frac{(V_{rec} * C_e + m_E) * 100}{V_o * C_o}$$

Where:

MB = mass balance (%)
m_E = total mass of PFBS from solids (µg)
C_o = initial mass concentration of PFBS in contact with the solids (µg/mL)
C_e = equilibrium concentration of PFBS (µg/mL)
V_o = volume of the initial supernatant applied to the solids (mL).
V_{rec} = volume of the supernatant recovered after the adsorption equilibrium (mL).

Freundlich Isotherm (K_f)

The Freundlich equation was applicable to the adsorption/desorption of PFBS at intermediate concentrations and was used to evaluate the batch equilibrium data. The equation was an empirical relationship used in the form:

$$\log C_{ads} = 1/n \log C_e + \log K_f$$

Where:

C_{ads} = the adsorbed concentration (µg/g);
C_e = the solution equilibrium concentration (µg/mL);
K_f, n = constants.

The Tier 3 data was subjected to evaluation using the Freundlich equation. For calculation purposes, the concentration of PFBS in the solids following adsorption was determined as the sum of the desorption solution values plus the amount extracted from the solids. Where possible, the sorption coefficient K_f and the constant 1/n were calculated for adsorption and desorption.

9.0 RESULTS AND DISCUSSION

Tables 2 to 4 and Figures 1 to 4 present the preliminary testing performed in Tier 1 to determine any adsorption of the test substance to the test vessel, the ratio of soil to solution, and the equilibrium mixing time. Tables 5 to 7 and Figures 5 to 9 present the results of the Tier 2 testing.

The Tier 1 and 2 tests showed that adsorption of PFBS to the test vessel would not occur during the testing. Percent of applied material determined as percent of applied PFBS yielded recoveries of 70 to 100 percent (range 71.1 to 104.1%). See Tables 4 and 7.

Tier 1 testing using three soil to solution ratios and two soil types (loam and clay) was performed over a 48 hour period with solution sampling at 4, 8, 24, and 48 hours (Table 2). At 48 hours the soils were collected and analyzed for PFBS concentration (Table 3). No soil to solution ratio tested demonstrated adsorption of PFBS in the range of 20 to 80%. The 1/1 ratio was chosen because it represented the highest concentration of soil to solution ratio identified in the protocol. The estimated K values from Tier 1 approximated 0.0 (Table 4). With the lack of adsorption observed in Tier 1, no plots of percent adsorption versus time were generated.

Tier 2 testing (Tables 5-7) was performed over a 24 hour period with solution samplings at 2, 4, 6, 8, and 24 hours. At 24 hours the soil, sediment and sludge were collected and analyzed for PFBS concentration. The estimated K value (sludge only) was 0.5. The plots of percent adsorption versus time (bottom of Table 7) indicate that the equilibrium plateau was reached by 24 hours. Balance was good and averaged 102.1% for the river sediment, 100.3% for the clay loam soil, and 72.5% for the sludge.

The Tier 3 testing was performed in triplicate at a sludge to solution ratio of 1/5, the soils and sediment were tested at a ratio of 1/1. All testing used nominal PFBS concentrations of 50, 100, 250, 500, and 1000µg/L. Actual measured PFBS concentrations were 38, 79, 196, 391, and 758 µg/L. Analysis of adsorption solution samples was performed following a 24 hour mixing period. Following removal of the adsorption solutions, fresh unfortified calcium chloride solution was added and the samples tumbled for an additional 24 hour desorption period. The temperature during the Tier 3 testing was 18.2 to 19.3°C. The analytical results are presented in Tables 8 to 10. Table 8 presents the adsorption solution values, Table 9 the desorption solutions and Table 10 the residual soil, sediment and sludge values. If an average of greater than 90% of the applied PFBS was not recovered from the adsorption and desorption solutions the residual solids were extracted with methanol. Reproducibility between the three replicates at each concentration was obtained (Table 8). Except for the sludge detectable PFBS was recovered from only a scattered few desorption solutions (Table 9). The sludge residual values for PFBS are presented in Table 10. Representative chromatograms from the LC/MS analysis of PFBS during Tier 3 are presented in Figures 10 to 17.

Tables 11 to 15 present the obtained mass balance from all Tier 3 testing. Each soil, sediment or sludge is presented in a single table. Overall mass balances were good with the average recovery 90.3% for Don Uglem loam (range 77.2 - 105.1%), 105.9% for Kittson clay (range 89.5 - 126.8%), 101.7% for Broeren clay loam (range 91.5 - 116.8%), 117.4% for Goose River sediment (range 107.6 - 128.9%), and 79.1% for NIST sludge (range 68.9 - 93.5%).

PFBS was only detected in the sludge solids. Therefore, Freundlich isotherm calculations could only be performed for the sludge. The following K_f fit values were determined for adsorption $K_f = 0.3$ with 1/n of 1.2840; for desorption $K_f = 0.001$ with 1/n of 2.6055. The straight-line plots of the log C_e (solution equilibrium concentration ng/mL) versus log x/m (concentration sorbed to the sludge ng/g) are presented at the bottom of Tables 16 and 17 for adsorption and desorption, respectively.

The pH of the PFBS test solutions was approximately 6.0 at concentrations ranging from 50 to 1000 µg/L. Following contact with the soils, sediment or sludge the solution pH values were measured (Tables 18 and 19). The Don Uglem loam and the sludge increased solution pH to a range of approximately 6.3 to 6.5. The Kittson clay soil and Goose River sediment increased solution pH to a range of about 7.5 to 7.7. The Broeren clay loam increased the pH levels the least to approximately 6.0 to 6.2. There was no apparent effect of pH on the adsorption of PFBS in the tested soils, sediment or sludge.

The Don Uglem loam, Kittson clay, Broeren clay loam and Goose River sediment all showed no detectable PFBS remaining with the solids following adsorption ($K_f = 0.0$). The initial PFBS concentration in solution was independent of the determined sorption value. This value also placed PFBS in the very high mobility class based on ASTM E1195 (K_{oc} 0 - 50).

10.0 CIRCUMSTANCES THAT MAY HAVE AFFECTED THE DATA

Circumstances that may have affected the data are detailed in the SOP and Protocol deviations attached to the protocol in Appendix A.

11.0 RETENTION OF DATA AND SAMPLES

When the report is final, all original paper data generated by Centre Analytical Laboratories, Inc. will be shipped to the sponsor. This does not include facility-specific raw data such as instrument logs. Exact copies of all raw data, as well as a signed copy of the final report and all original facility-specific raw data, will be retained in the Centre Analytical Laboratories, Inc. archives for the period of time specified in 40 CFR Part 160.

12.0 REFERENCES

1. US Environmental Protection Agency, January 1998, Fate, Transport and Transformation Test Guidelines, OPPTS 835.1110 "Activated Sludge Sorption Isotherm", EPA 712-C-98-298.

2. OECD GUILDELINES FOR THE TESTING OF CHEMICALS: GUIDELINE 106, "Adsorption/Desorption" Adopted 21 January 2000.

3. Organisation for Economic Co-operation and Development, OECD "Principles of Good Laboratory Practice", ENV/MC(98)17, November 26, 1997.

4. US Environmental Protection Agency, August 17, 1989. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Good Laboratory Practice Standards; Final Rule (40 CFR: 160), Federal Register, Vol.54, No. 158: 34052-34074.

5. ASTM "Standard Test Method for Determining a Sorption Constant (Koc) for an Organic Chemical in Soil and Sediments," Designation E1195, 1994.Annual Book of ASTM Standards, Vol. 11.04.

TABLE 1: SOIL, SEDIMENT, AND SLUDGE CHARACTERIZATION

Source	Don Uglem Loam	Broeren Clay Loam	Kittson Co. Clay	Goose River Sediment	NIST Sludge
Date Collected	10/19/00	10/19/00	10/21/00	10/19/00	NA
Collection depth	0-6"	0-6"	0-6"	0-6"	NA
Centre #	0010916	0010917	0010919	0010918	0012493-0012499
Texture	loam	clay loam	clay	loam	NA
%sand	39	21	16	39	NA
%silt	50	46	22	42	NA
%clay	11	33	62	19	NA
Organic Carbon%	4.9	2.6	2.6	1.3	NA
Organic Matter %	8.4	4.4	4.5	2.3	100
pH in 0.01M $CaCl_2$	7.4	6.0	7.2	7.7	NA
Total Nitrogen (%)	0.358	0.216	0.223	0.101	4.78
Cation Exchange Capacity (meq/100g)	23.9	24.7	54.5	17.5	NA
Geographical Reference					Denver, CO
Latitude	47°44'	47°42'	48°62'	47°45'	NA
Longitude	97°48'	97°40'	96°89'	97°37'	NA

Soil and sediment characterization performed by AGVISE Laboratories, Northwood, North Dakota.
NA = not applicable or not performed.
Organic Carbon % = organic matter % / 1.724.

TABLE 2: SOLUTION VALUES FROM TIER 1 TESTING

Ratio	Analysis	PFBS from Aqueous Solution			
		4 hour (µg/mL)	8 hour (µg/mL)	24 hour (µg/mL)	48 hour* (µg/mL)
Don Uglem Loam (1000µg/L PFBS)					
20/20	1	0.282	0.325	0.250	0.642
	2	0.955	0.893	0.237	0.616
	3	0.986	0.675	0.221	0.606
	Average	0.741	0.631	0.236	0.621
	Avg %	95.8	81.6	30.5	80.3
5/25	1	0.296	0.552	0.770	0.749
	2	0.263	0.961	0.357	0.765
	3	0.462	1.286	0.220	0.737
	Average	0.340	0.933	0.449	0.750
	Avg %	44.0	120.6	58.1	97.0
1/25	1	0.584	0.645	0.889	0.789
	2	0.367	1.040	0.390	0.793
	3	0.637	0.228	0.930	0.801
	Average	0.529	0.638	0.736	0.794
	Avg %	68.4	82.5	95.2	102.7
Kittson Clay (1000µg/L PFBS)					
20/20	1	0.392	0.335	0.315	0.601
	2	1.151	1.030	0.464	0.582
	3	1.015	0.462	0.326	0.553
	Average	0.853	0.609	0.368	0.579
	Avg %	110.3	78.8	47.6	74.8
5/25	1	0.321	0.483	0.390	0.751
	2	0.992	0.353	0.319	0.726
	3	0.340	0.438	0.609	0.720
	Average	0.551	0.425	0.439	0.732
	Avg %	71.3	54.9	56.8	94.7
1/25	1	1.158	0.323	0.433	0.752
	2	1.016	0.361	0.256	0.722
	3	0.288	0.323	0.511	0.749
	Average	0.821	0.336	0.400	0.741
	Avg %	106.1	43.4	51.7	95.8
Avg. Fortified Control		0.305	0.773	0.675	0.773

Ratio = grams of soil per mL of $CaCl_2$ solution.

*48 Hour samples were filtered and analyzed versus other samples which were extracted.

Avg % = average percent of Fortified Control PFBS at 48 hours.

TABLE 3: SOIL VALUES FROM TIER 1 TESTING

Ratio	Replicate	PFBS Results From 48 Hour Soil (μg/mL methanol extract)	Total PFBS μg
Don Uglem Loam (1000μg/L PFBS)			
20/20	1	3.820	
	2	3.940	
	3	3.200	
	Average	3.653	0.00
5/25	1	2.710	
	2	2.810	
	3	2.690	
	Average	2.737	0.00
1/25	1	0.767	
	2	0.825	
	3	0.814	
	Average	0.802	0.00
Kittson Clay (1000μg/L PFBS)			
20/20	1	3.380	
	2	3.070	
	3	3.060	
	Average	3.170	0.00
5/25	1	2.950	
	2	2.430	
	3	2.500	
	Average	2.627	0.00
1/25	1	0.909	
	2	0.964	
	3	0.992	
	Average	0.955	0.01

Ratio = grams of soil per mL of $CaCl_2$ solution.
Total PFBS μg are corrected for μg in interstitial $CaCl_2$

TABLE 4: MASS BALANCE FROM TIER 1 TESTING

Ratio	Total PFBS μg			Percent of Applied		
	Solution	Soil	Total	Solution	Soil	Total
	(μg)	(μg)	(μg)			
Don Uglem Loam (1000mg/L PFBS)						
20/20	12.4	0.00	12.4	80.3%	0.0%	80.3%
	Estimated K = 0.0					
5/25	18.8	0.00	18.8	97.0%	0.0%	97.0%
	Estimated K = 0.0					
1/25	19.9	0.00	19.9	102.7%	0.0%	102.7%
	Estimated K = 0.0					
Kittson Clay (1000mg/L PFBS)						
20/20	11.6	0.00	11.6	74.8%	0.0%	74.8%
	Estimated K = 0.0					
5/25	18.3	0.00	18.3	94.7%	0.0%	94.7%
	Estimated K = 0.0					
1/25	18.5	0.01	18.5	95.8%	0.0%	95.8%
	Estimated K = 0.0				**Average**	**90.9%**

Total detected PFBS in control at 48 hours = 0.773μg/mL 0.01M $CaCl_2$ solution

Ratio = grams of soil per mL of $CaCl_2$ solution

TABLE 5: SOLUTION VALUES FROM TIER 2 TESTING

Ratio	Replicate	PFBS from Aqueous Solution				
		2 hour (μg/mL)	4 hour (μg/mL)	6 hour (μg/mL)	8 hour (μg/mL)	24 hour (μg/mL)
River Sediment (1000μg/L PFBS)						
20/20	1	0.955	0.851	0.882	0.778	0.776
	2	0.952	0.874	0.832	0.759	0.771
	3	0.959	0.860	0.859	0.797	0.796
	Average	0.955	0.862	0.858	0.778	0.781
	Avg %	105.5	107.4	105.1	109.1	102.1
Broeren Clay Loam (1000μg/L PFBS)						
20/20	1	1.004	0.852	0.876	0.758	0.795
	2	0.926	0.868	0.878	0.769	0.742
	3	0.997	0.878	0.887	0.768	0.765
	Average	0.976	0.866	0.880	0.765	0.767
	Avg %	107.7	107.9	107.8	107.3	100.3
NIST Sludge (1000μg/L PFBS)						
8/40	1	0.556	0.517	0.522	0.459	0.506
	2	0.553	0.526	0.509	0.454	0.508
	3	0.546	0.511	0.507	0.451	0.487
	Average	0.552	0.518	0.513	0.455	0.500
	Avg %	60.9	64.5	62.8	63.8	65.4
Avg. Fortified Control		0.906	0.803	0.816	0.713	0.765

Avg % = average percent of Avg. Fortified Control

Ratio = grams of soil or sludge per mL of $CaCl_2$ solution

TABLE 6: SOIL AND SLUDGE VALUES FROM TIER 2 TESTING

Ratio	Replicate	PFBS Results From 24 Hours (μg/mL methanol extract)	Total PFBS μg
Goose River Sediment (1000μg/L PFBS)			
20/20	1	6.110	0.000
	2	5.710	0.000
	3	5.650	0.000
	Average	5.823	
Broeren Clay Loam (1000μg/L PFBS)			
20/20	1	5.180	0.000
	2	5.000	0.000
	3	4.800	0.000
	Average	4.993	
NIST Sludge (1000μg/L PFBS)			
8/40	1	7.650	2.026
	2	7.900	2.268
	3	7.890	2.604
	Average	7.813	

Ratio = grams of soil or sludge per mL of $CaCl_2$ solution.
Total PFBS μg are corrected for μg in interstitial $CaCl_2$ solution (wet weight)

TABLE 7: TIER 2 MASS BALANCE

Ratio	Replicate	Total PFBS µg			Percent of Applied		
		Solution (µg)	Solids (µg)	Total (µg)	Solution	Solids	Total
Goose River Sediment (1000µg/L PFBS)							
20/20	1	15.5	0.0	15.5	101.4%	0.0%	101.4%
	2	15.4	0.0	15.4	100.8%	0.0%	100.8%
	3	15.9	0.0	15.9	104.1%	0.0%	104.1%
	Estimated K = 0.0					Average	102.1%
Broeren Clay Loam (1000µg/L PFBS)							
20/20	1	15.9	0.0	15.9	103.9%	0.0%	103.9%
	2	14.8	0.0	14.8	97.0%	0.0%	97.0%
	3	15.3	0.0	15.3	100.0%	0.0%	100.0%
	Estimated K = 0.0					Average	100.3%
NIST Sludge (1000µg/L PFBS)							
8/40	1	20.2	2.0	22.3	66.1%	6.6%	72.8%
	2	20.3	2.3	22.6	66.4%	7.4%	73.8%
	3	19.5	2.6	22.1	63.7%	8.5%	72.2%
	Estimated K = 0.6					Average	72.9%

Ratio = grams of soil or sludge per mL of $CaCl_2$ solution.

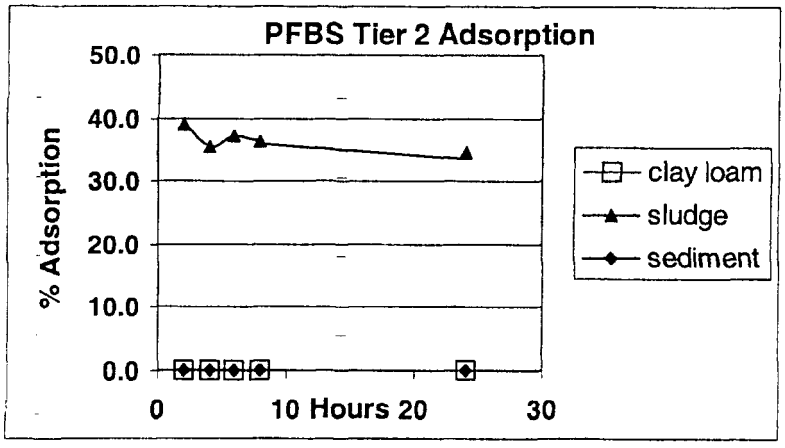


TABLE 8: ADSORPTION SOLUTION VALUES (C_e) FROM TIER 3 TESTING

Test Solution	Replicate	ng/ mL Solution From Adsorption Soil or Sludge				
		Don Uglem	Kittson	River	Broeren	NIST
ng/mL		Loam	Clay	Sediment	Clay loam	Sludge
758	1	789	932	977	852	526
	2	797	937	971	885	536
	3	776	961	975	884	532
391	1	377	450	493	416	260
	2	376	452	488	419	257
	3	378	463	492	421	254
196	1	162	201	222	190	115
	2	168	198	222	201	113
	3	165	201	229	195	113
79	1	61	75	87	75	46
	2	63	76	85	74	45
	3	61	75	86	73	46
38	1	33	35	41	36	23
	2	31	35	43	35	24
	3	34	34	41	34	31
Blank	1	0.0	0.0	0.0	0.0	0.0
	2	0.0	0.0	0.0	0.0	0.0
	3	0.0	0.0	0.0	0.0	0.0

Tier 3 Ratios =
all soils and sediment at 20g : 20 mL solution, sludge at 8g : 40 mL solution

TABLE 9: DESORPTION SOLUTION VALUES (C_e) FROM TIER 3 TESTING

Initial Solution	Replicate	ng/ mL Solution From Desorption Soil or Sludge				
		Don Uglem	Kittson	River	Broeren	NIST
ng/mL		Loam	Clay	Sediment	Clay loam	Sludge
758	1	0.0	0.0	0.0	0.0	117
	2	0.0	0.0	0.0	0.0	134
	3	1.4	0.0	0.0	0.0	88
391	1	0.0	0.0	0.0	0.0	73
	2	0.0	0.0	0.0	0.0	50
	3	0.0	0.0	0.0	0.0	54
196	1	0.0	0.0	0.0	0.0	28
	2	4.9	0.0	0.0	0.0	22
	3	4.9	0.0	0.0	0.0	25
79	1	3.1	0.0	0.0	0.0	10
	2	0.0	0.0	0.0	0.0	9
	3	0.0	0.0	0.0	0.0	13
38	1	0.0	0.0	0.0	0.0	3.2
	2	0.0	0.0	0.0	0.2	2.8
	3	0.0	0.0	0.0	0.8	1.9
Blank	1	0.0	0.0	0.0	0.0	0.0
	2	0.0	0.0	0.0	0.0	0.0
	3	0.0	0.0	0.0	0.0	0.0

Tier 3 Ratios =
all soils and sediment at 20g : 20 mL solution, sludge at 8g : 40 mL solution
All soils, sediment and sludge desorbed using $CaCl_2$ solution.

TABLE 10: SOIL AND SLUDGE VALUES (x/m) FROM TIER 3 TESTING

Initial Solution	Replicate	ng/ g Solids From Soil or Sludge Extraction				
		Don Uglem	Kittson	River	Broeren	NIST
ng/mL		Loam	Clay	Sediment	Clay loam	Sludge
758	1	NA	NA	NA	NA	248
	2	NA	NA	NA	NA	191
	3	NA	NA	NA	NA	278
391	1	NA	NA	NA	NA	91
	2	NA	NA	NA	NA	103
	3	NA	NA	NA	NA	102
196	1	NA	NA	NA	NA	4.9
	2	NA	NA	NA	NA	2.2
	3	NA	NA	NA	NA	0.0
79	1	NA	NA	NA	NA	0.0
	2	NA	NA	NA	NA	0.0
	3	NA	NA	NA	NA	0.0
38	1	NA	NA	NA	NA	0.0
	2	NA	NA	NA	NA	3.1
	3	NA	NA	NA	NA	0.0
Blank	1	NA	NA	NA	NA	0.0
	2	NA	NA	NA	NA	0.0
	3	NA	NA	NA	NA	0.0

Tier 3 Ratios =
all soils and sediment at 20g : 20 mL solution, sludge at 8g : 40 mL solution
NA = not analyzed, adsorption and desorption solutions were >90% of applied overall.

TABLE 11: MASS BALANCE FOR DON UGLEM LOAM - TIER 3 TESTING

Initial	Rep	ng PFBS				Percent of Applied			
		Solution			Total	Solution			Total
ng/mL		Ads	Des	Soil		Ads	Des	Soil	
758	1	15780	0.0	NA	15780	104.1%	0.0%	NA	104.1%
	2	15940	0.0	NA	15940	105.1%	0.0%	NA	105.1%
	3	15520	28.0	NA	15548	102.4%	0.2%	NA	102.6%
								Average	103.9%
391	1	7540	0.0	NA	7540	96.4%	0.0%	NA	96.4%
	2	7520	0.0	NA	7520	96.2%	0.0%	NA	96.2%
	3	7560	0.0	NA	7560	96.7%	0.0%	NA	96.7%
								Average	96.4%
196	1	3240	0.0	NA	3240	82.7%	0.0%	NA	82.7%
	2	3360	97.5	NA	3458	85.7%	2.5%	NA	88.2%
	3	3300	97.6	NA	3398	84.2%	2.5%	NA	86.7%
								Average	85.8%
79	1	1220	61.1	NA	1281	77.2%	3.9%	NA	81.1%
	2	1260	0.0	NA	1260	79.7%	0.0%	NA	79.7%
	3	1220	0.0	NA	1220	77.2%	0.0%	NA	77.2%
								Average	79.3%
38	1	660	0.0	NA	660	86.8%	0.0%	NA	86.8%
	2	620	0.0	NA	620	81.6%	0.0%	NA	81.6%
	3	680	0.0	NA	680	89.5%	0.0%	NA	89.5%
								Average	86.0%
								Overall Average	**90.3%**

Soil : solution ratio 1:1 (20g soil : 20 mL fortified 0.01M $CaCl_2$ solution)
Ads = adsorption
Des = desorption
NA = not analyzed, adsorption and desorption solutions were >75% of applied, >90% overall.

TABLE 12: MASS BALANCE FOR KITTSON CLAY - TIER 3 TESTING

Initial	Rep	ng PFBS				Percent of Applied			
		Solution			Total	Solution			Total
ng/mL		Ads	Des	Soil		Ads	Des	Soil	
758	1	18640	0.0	NA	18640	123.0%	0.0%	NA	123.0%
	2	18740	0.0	NA	18740	123.6%	0.0%	NA	123.6%
	3	19220	0.0	NA	19220	126.8%	0.0%	NA	126.8%
								Average	124.5%
391	1	9000	0.0	NA	9000	115.1%	0.0%	NA	115.1%
	2	9040	0.0	NA	9040	115.6%	0.0%	NA	115.6%
	3	9260	0.0	NA	9260	118.4%	0.0%	NA	118.4%
								Average	116.4%
196	1	4020	0.0	NA	4020	102.6%	0.0%	NA	102.6%
	2	3960	0.0	NA	3960	101.0%	0.0%	NA	101.0%
	3	4020	0.0	NA	4020	102.6%	0.0%	NA	102.6%
								Average	102.0%
79	1	1500	0.0	NA	1500	94.9%	0.0%	NA	94.9%
	2	1520	0.0	NA	1520	96.2%	0.0%	NA	96.2%
	3	1500	0.0	NA	1500	94.9%	0.0%	NA	94.9%
								Average	95.4%
38	1	700	0.0	NA	700	92.1%	0.0%	NA	92.1%
	2	700	0.0	NA	700	92.1%	0.0%	NA	92.1%
	3	680	0.0	NA	680	89.5%	0.0%	NA	89.5%
								Average	91.2%
								Overall Average	**105.9%**

Soil : solution ratio 1:1 (20g soil : 20 mL fortified 0.01M $CaCl_2$ solution)
Ads = adsorption
Des = desorption
NA = not analyzed, adsorption and desorption solutions were >90% of applied.

TABLE 13: MASS BALANCE FOR BROEREN CLAY LOAM - TIER 3 TESTING

Initial	Rep	ng PFBS				Percent of Applied			
		Solution			Total	Solution			Total
ng/mL		Ads	Des	Soil		Ads	Des	Soil	
758	1	17040	0.0	NA	17040	112.4%	0.0%	NA	112.4%
	2	17700	0.0	NA	17700	116.8%	0.0%	NA	116.8%
	3	17680	0.0	NA	17680	116.6%	0.0%	NA	116.6%
								Average	115.3%
391	1	8320	0.0	NA	8320	106.4%	0.0%	NA	106.4%
	2	8380	0.0	NA	8380	107.2%	0.0%	NA	107.2%
	3	8420	0.0	NA	8420	107.7%	0.0%	NA	107.7%
								Average	107.1%
196	1	3800	0.0	NA	3800	96.9%	0.0%	NA	96.9%
	2	4020	0.0	NA	4020	102.6%	0.0%	NA	102.6%
	3	3900	0.0	NA	3900	99.5%	0.0%	NA	99.5%
								Average	99.7%
79	1	1500	0.0	NA	1500	94.9%	0.0%	NA	94.9%
	2	1480	0.0	NA	1480	93.7%	0.0%	NA	93.7%
	3	1460	0.0	NA	1460	92.4%	0.0%	NA	92.4%
								Average	93.7%
38	1	720	0.0	NA	720	94.7%	0.0%	NA	94.7%
	2	700	3.6	NA	704	92.1%	0.5%	NA	92.6%
	3	680	15.6	NA	696	89.5%	2.1%	NA	91.6%
								Average	92.9%
								Overall Average	**101.7%**

Soil : solution ratio 1:1 (20g soil : 20 mL fortified 0.01M $CaCl_2$ solution)
Ads = adsorption
Des = desorption
NA = not analyzed, adsorption and desorption solutions were >90% of applied.

TABLE 14: MASS BALANCE RIVER SEDIMENT - TIER 3 TESTING

Initial	Rep	ng PFBS				Percent of Applied			
		Solution			Total	Solution			Total
ng/mL		Ads	Des	Sed		Ads	Des	Sed	
758	1	19540	0.0	NA	19540	128.9%	0.0%	NA	128.9%
	2	19420	0.0	NA	19420	128.1%	0.0%	NA	128.1%
	3	19500	0.0	NA	19500	128.6%	0.0%	NA	128.6%
								Average	128.5%
391	1	9860	0.0	NA	9860	126.1%	0.0%	NA	126.1%
	2	9760	0.0	NA	9760	124.8%	0.0%	NA	124.8%
	3	9840	0.0	NA	9840	125.8%	0.0%	NA	125.8%
								Average	125.6%
196	1	4440	0.0	NA	4440	113.3%	0.0%	NA	113.3%
	2	4440	0.0	NA	4440	113.3%	0.0%	NA	113.3%
	3	4580	0.0	NA	4580	116.8%	0.0%	NA	116.8%
								Average	114.5%
79	1	1740	0.0	NA	1740	110.1%	0.0%	NA	110.1%
	2	1700	0.0	NA	1700	107.6%	0.0%	NA	107.6%
	3	1720	0.0	NA	1720	108.9%	0.0%	NA	108.9%
								Average	108.9%
38	1	820	0.0	NA	820	107.9%	0.0%	NA	107.9%
	2	860	0.0	NA	860	113.2%	0.0%	NA	113.2%
	3	820	0.0	NA	820	107.9%	0.0%	NA	107.9%
								Average	109.6%
								Overall Average	**117.4%**

Sediment : solution ratio 1:1 (20g sediment : 20 mL fortified 0.01M $CaCl_2$ solution)
Ads = adsorption Des = desorption Sed = sediment
NA = not analyzed, adsorption and desorption solutions were >90% of applied.

TABLE 15: MASS BALANCE NIST SLUDGE - TIER 3 TESTING

Initial	Rep	ng PFBS				Percent of Applied			
		Solution			Total	Solution			Total
ng/mL		Ads	Des	Sludge*		Ads	Des	Sludge*	
758	1	21040	4666.0	1984.7	27691	69.4%	15.4%	6.5%	91.3%
	2	21440	5357.1	1539.9	28337	70.7%	17.7%	5.1%	93.5%
	3	21280	3512.7	2228.6	27021	70.2%	11.6%	7.4%	89.1%
								Average	91.3%
391	1	10400	2920.3	739.2	14060	66.5%	18.7%	4.7%	89.9%
	2	10280	1993.0	834.7	13108	65.7%	12.7%	5.3%	83.8%
	3	10160	2166.4	822.5	13149	65.0%	13.9%	5.3%	84.1%
								Average	85.9%
196	1	4600	1110.9	39.8	5751	58.7%	14.2%	0.5%	73.4%
	2	4520	870.8	18.3	5409	57.7%	11.1%	0.2%	69.0%
	3	4520	1004.3	0.0	5524	57.7%	12.8%	0.0%	70.5%
								Average	70.9%
79	1	1840	405.1	0.0	2245	58.2%	12.8%	0.0%	71.0%
	2	1800	378.2	0.0	2178	57.0%	12.0%	0.0%	68.9%
	3	1840	514.6	0.0	2355	58.2%	16.3%	0.0%	74.5%
								Average	71.5%
38	1	920	128.0	0.0	1048	60.5%	0.0%	5.3%	68.9%
	2	960	110.0	25.4	1095	63.2%	0.0%	8.6%	72.1%
	3	1240	77.1	0.0	1317	81.6%	0.0%	4.6%	86.7%
								Average	75.9%
								Overall Average	**79.1%**

Sludge : solution ratio 1:5 (8g sludge : 40 mL fortified 0.01M $CaCl_2$ solution)
Ads = adsorption
Des = desorption
*Sludge extracted with methanol.

TABLE 16: FREUNDLICH ADSORPTION ISOTHERM

NIST Sludge 1/5 ratio (8g sludge/40 mL $CaCl_2$)

PFBS µg/L	Replicate	Sludge		$CaCl_2$ Solution		K	
		x/m (ng/g)	log x/m (log ng/g)	C_e (ng/mL)	log C_e (log ng/mL)	(x/m)/C_e n = 1	Average (x/m)/C_e
38	1	15.95	1.203	23.00	1.362	0.7	0.6
	2	16.65	1.222	24.00	1.380	0.7	
	3	9.50	0.978	31.00	1.491	0.3	
79	1	49.90	1.698	46.00	1.663	1.1	1.2
	2	46.46	1.667	45.00	1.653	1.0	
	3	63.58	1.803	46.00	1.663	1.4	
196	1	140.45	2.148	115.00	2.061	1.2	1.1
	2	109.09	2.038	113.00	2.053	1.0	
	3	124.96	2.097	113.00	2.053	1.1	
391	1	450.69	2.654	260.00	2.415	1.7	1.5
	2	347.48	2.541	257.00	2.410	1.4	
	3	371.98	2.571	254.00	2.405	1.5	
758	1	829.59	2.919	526.00	2.721	1.6	1.5
	2	854.92	2.932	536.00	2.729	1.6	
	3	715.78	2.855	532.00	2.726	1.3	

Linear Regression Analysis

Correlation = 0.9790
Slope (1/n) = 1.2840
Intercept = -0.5470

n = 0.779
K_f = 0.3

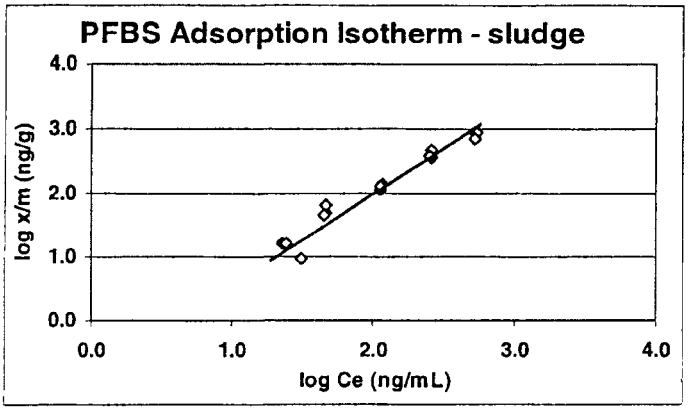


TABLE 17: FREUNDLICH DESORPTION ISOTHERM

NIST Sludge 1/5 ratio (8g sludge/40 mL $CaCl_2$)

PFBS µg/L	Replicate	Sludge		$CaCl_2$ Solution		K	
		x/m (ng/g)	log x/m (log ng/g)	C_e (ng/mL)	log C_e (log ng/mL)	(x/m)/C_e n = 1	Average (x/m)/C_e
196	1	4.86	0.687	27.77	1.444	0.2	0.1
	2	2.24	0.350	21.77	1.338	0.1	
	3	0.00	-------	25.11	1.400	0.0	
391	1	91.04	1.959	73.01	1.863	1.2	1.7
	2	102.58	2.011	49.82	1.697	2.1	
	3	102.36	2.010	54.16	1.734	1.9	
758	1	247.57	2.394	116.65	2.067	2.1	2.2
	2	190.88	2.281	133.93	2.127	1.4	
	3	277.84	2.444	87.82	1.944	3.2	

------ Not used in calculation

Linear Regression Analysis

Correlation = 0.9198
Slope (1/n) = 2.6055
Intercept = -2.8621

n = 0.3838
K_f = 0.001

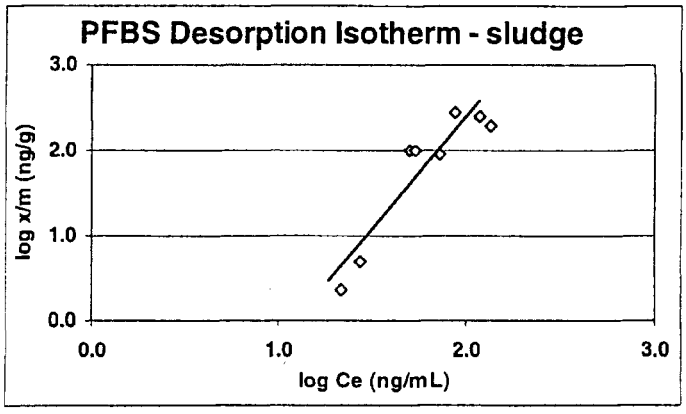


TABLE 18: pH READINGS DURING TIER 1 and 2 TESTING

TIER 1	Rep	pH at Ratio			
		1:1	1:5	1:25	Blank
Don Uglem Loam (1000µg/L PFBS)					
	1	6.25	6.03	5.99	6.62
	2	6.24	6.01	5.99	6.60
	3	6.31	6.01	5.98	6.68
Kittson Clay (1000µg/L PFBS)					
	1	7.57	6.95	7.00	7.70
	2	7.50	6.91	7.00	7.70
	3	7.50	6.93	7.00	7.65
Control (no soil)		5.99	5.85	5.89	
PFBS fortified $CaCl_2$			6.19		

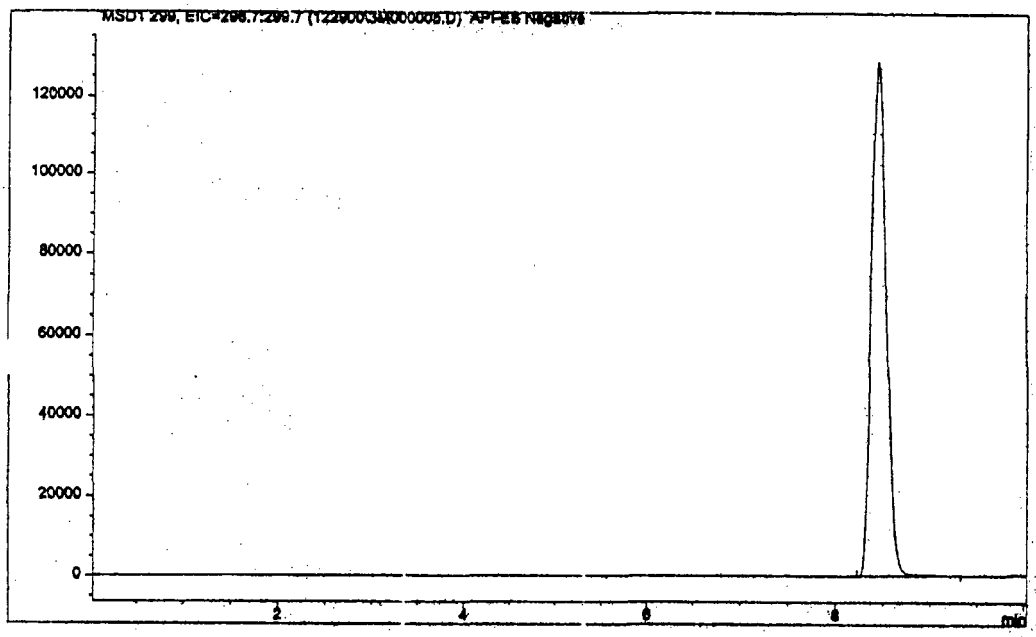
TIER 2	Rep	Broeren Clay Loam	River Sediment	NIST Sludge
PFBS	1	6.19	7.68	6.50
	2	6.16	7.68	6.50
	3	6.21	7.69	6.49
Blank	1	6.13	7.70	6.44
	2	6.17	7.71	6.44
	3	6.18	7.70	6.46
Control		6.10	6.00	5.75
PFBS fortified $CaCl_2$			5.80	

Blank contains soil, sediment or sludge with non-fortified $CaCl_2$ solution.
Control contains fortified CaCl2 solution with no soil, sediment or sludge.
PFBS nominal fortification = 1000 µg/L.

TABLE 19: pH READINGS DURING TIER 3 TESTING

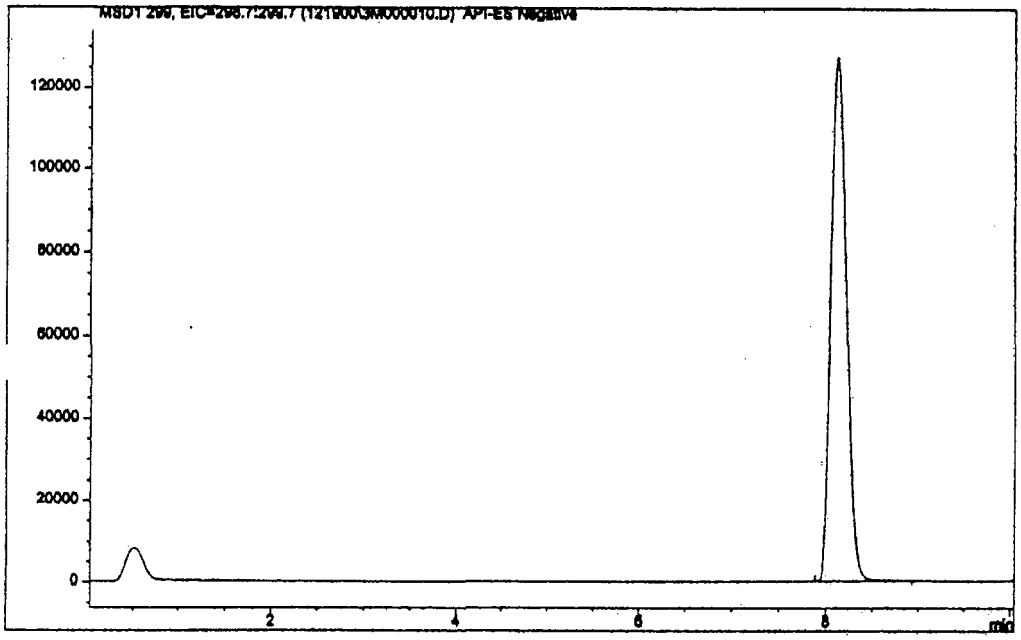
Initial ng/mL Solution	Rep	24 Hour Solution pH				
		Don Uglem	Kittson	River	Broeren	NIST
		Loam	Clay	Sediment	Clay loam	Sludge
758	1	6.31	7.48	7.58	6.20	6.45
	2	6.37	7.56	7.59	6.13	6.46
	3	6.31	7.58	7.56	6.10	6.47
391	1	6.27	7.57	7.66	5.99	6.48
	2	6.29	7.64	7.58	5.98	6.48
	3	6.30	7.75	7.64	5.96	6.47
196	1	6.39	7.77	7.64	6.09	6.46
	2	6.35	7.65	7.67	6.13	6.45
	3	6.26	7.74	7.57	6.06	6.46
79	1	6.21	7.61	7.62	6.07	6.46
	2	6.29	7.63	7.66	6.02	6.46
	3	6.24	7.64	7.66	6.05	6.45
38	1	6.34	7.71	7.70	6.17	6.48
	2	6.34	7.70	7.66	6.18	6.47
	3	6.30	7.72	7.70	6.17	6.48
0.0	1	6.26	7.69	7.65	6.10	6.50
	2	6.29	7.66	7.65	6.07	6.50
	3	6.30	7.71	7.67	6.10	6.47
Stock 758 ng/mL		6.05				
Stock 391 ng/mL		5.90				
Stock 196 ng/mL		5.89				
Stock 79 ng/mL		5.95				
Stock 38 ng/mL		5.96				
Stock 0 ng/mL		6.01				

FIGURE 1: REPRESENTATIVE STANDARD OF PFBS AT 500ppb



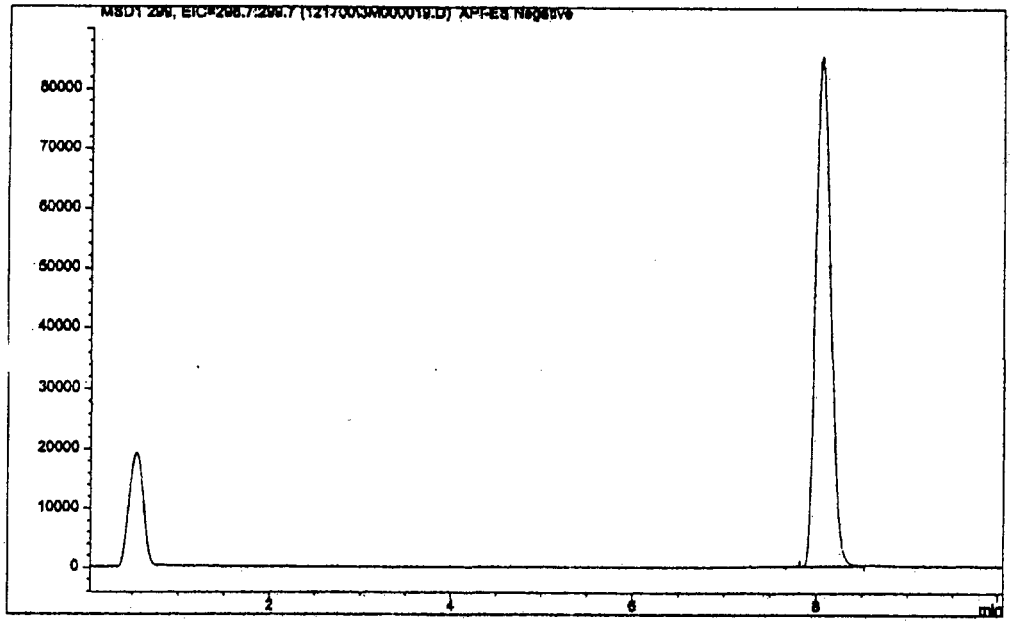
Compound Name	Amount	R.T.	Area	Signal
PFBS	487.2	8.44	1405842	MSD1 299, EIC=298.7:29

FIGURE 2: KITTSON CLAY 48 HOUR $CaCl_2$ SOLUTION AT THE 1/1 RATIO TIER 1



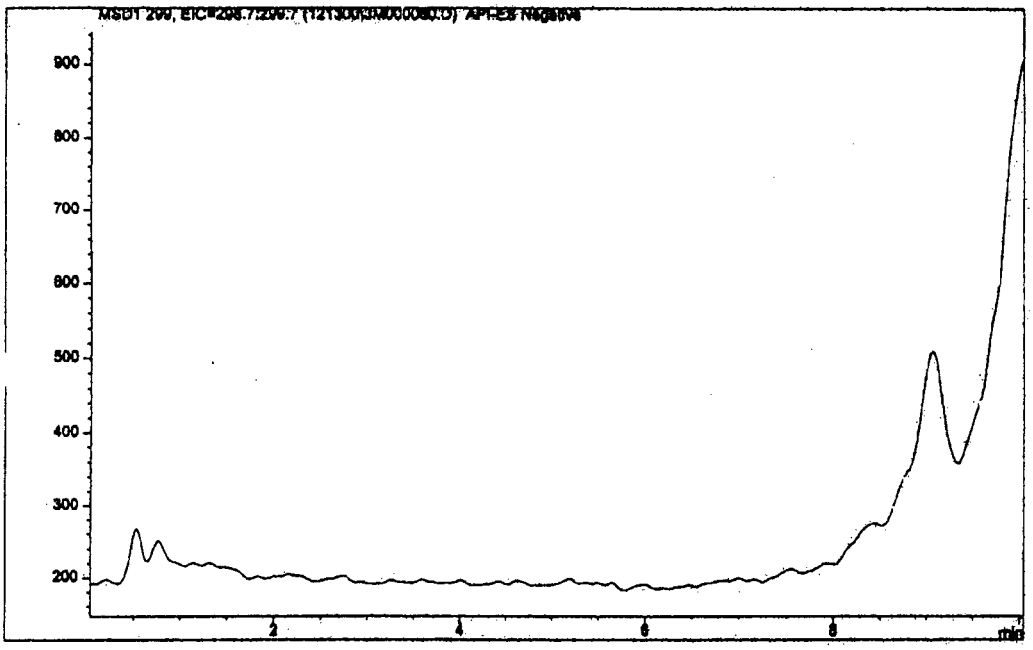
Compound Name	Amount	R.T.	Area	Signal
PFBS	582.1	8.12	1488816	MSD1 299, EIC=298.7:29

FIGURE 3: DON UGLEM LOAM 48 HOUR SOIL EXTRACT -- 1/1 RATIO TIER 1



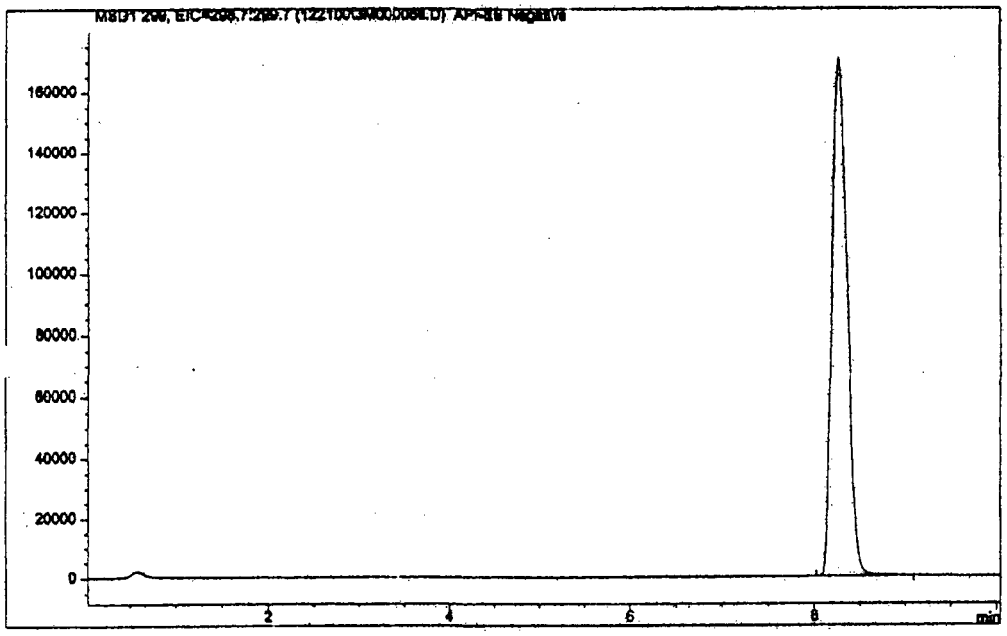
Compound Name	Amount	R.T.	Area	Signal
PFBS	382.0	8.05	969906	MSD1 299, EIC=298.7:29

FIGURE 4: KITTSON CLAY BLANK SOLUTION AT 24 HOURS 1/1 RATIO TIER 1



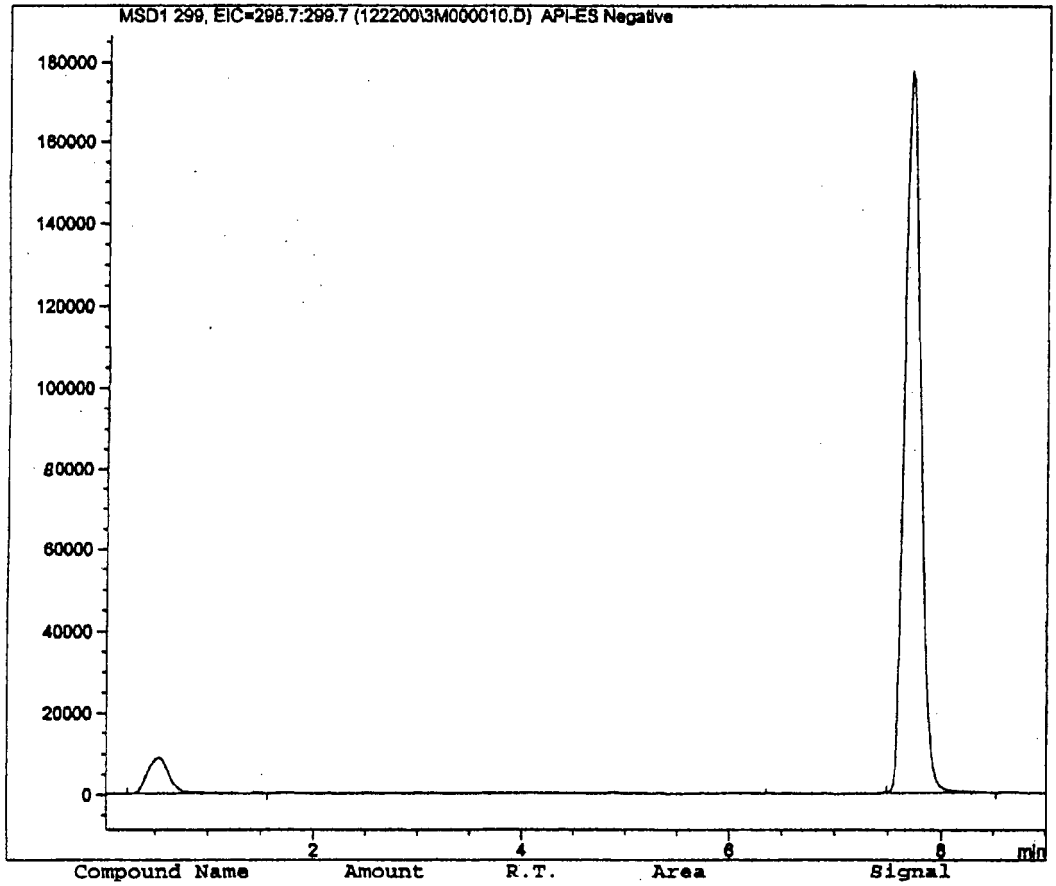
Compound Name	Amount	R.T.	Area	Signal
PFBS	0.0	0.00	0	MSD1 299, EIC=298.7:29

FIGURE 5: FORTIFIED CONTROL FROM TIER 2 TESTING NOMINAL 1000ppb



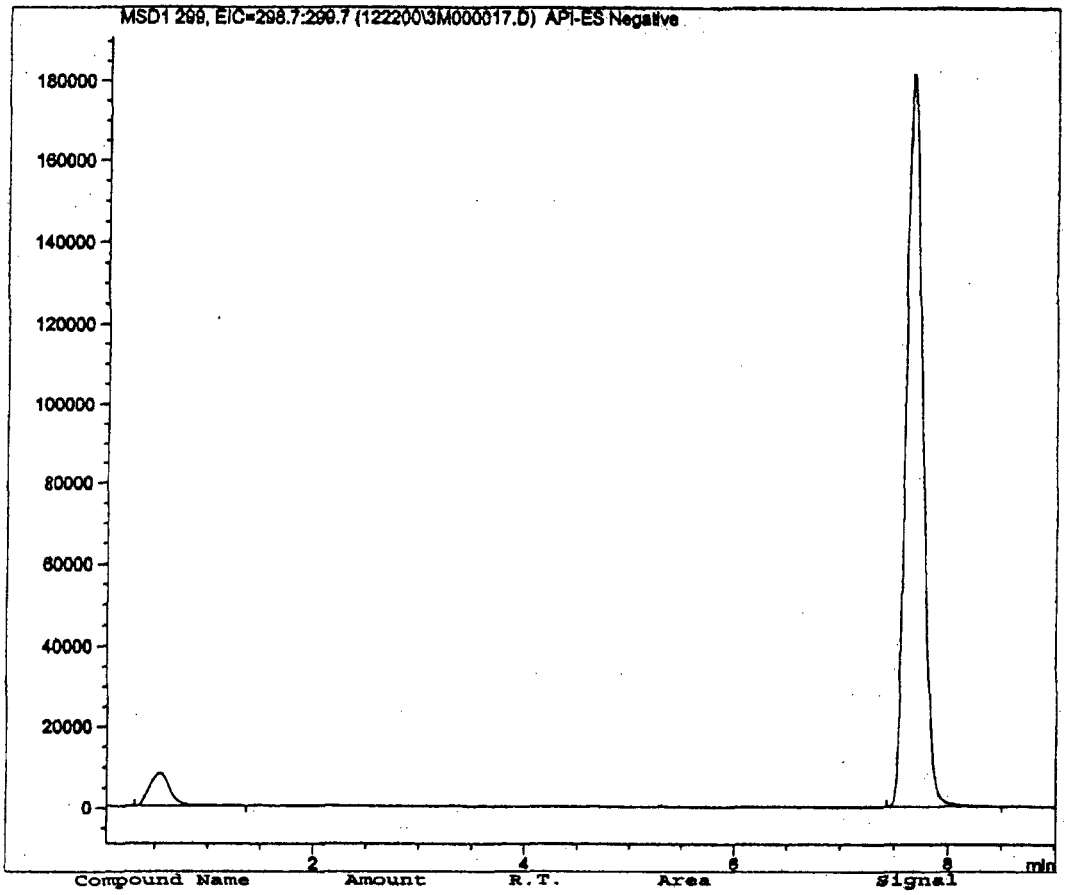
Compound Name	Amount	R.T.	Area	Signal
PFBS	735.0	8.26	1976410	MSD1 299, EIC=298.7:29

FIGURE 6 BROEREN CLAY LOAM 24 HOUR $CACL_2$ SOLUTION -- 1/1 RATIO TIER 2



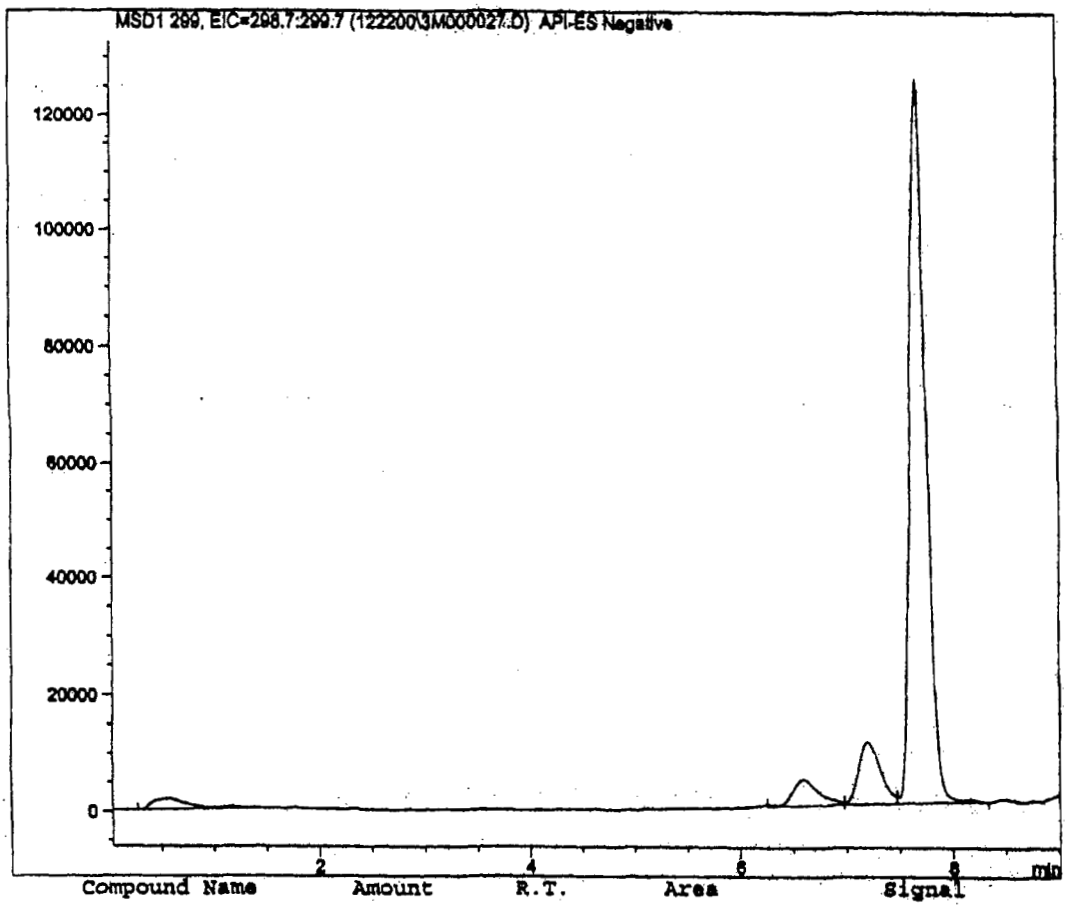
Compound Name	Amount	R.T.	Area	Signal
PFBS	742.3	7.71	1890871	MSD1 299, EIC=298.7:29

FIGURE 7: GOOSE RIVER SEDIMENT 24 HOUR $CACL_2$ SOLUTION -- 1/1 RATIO TIER 2



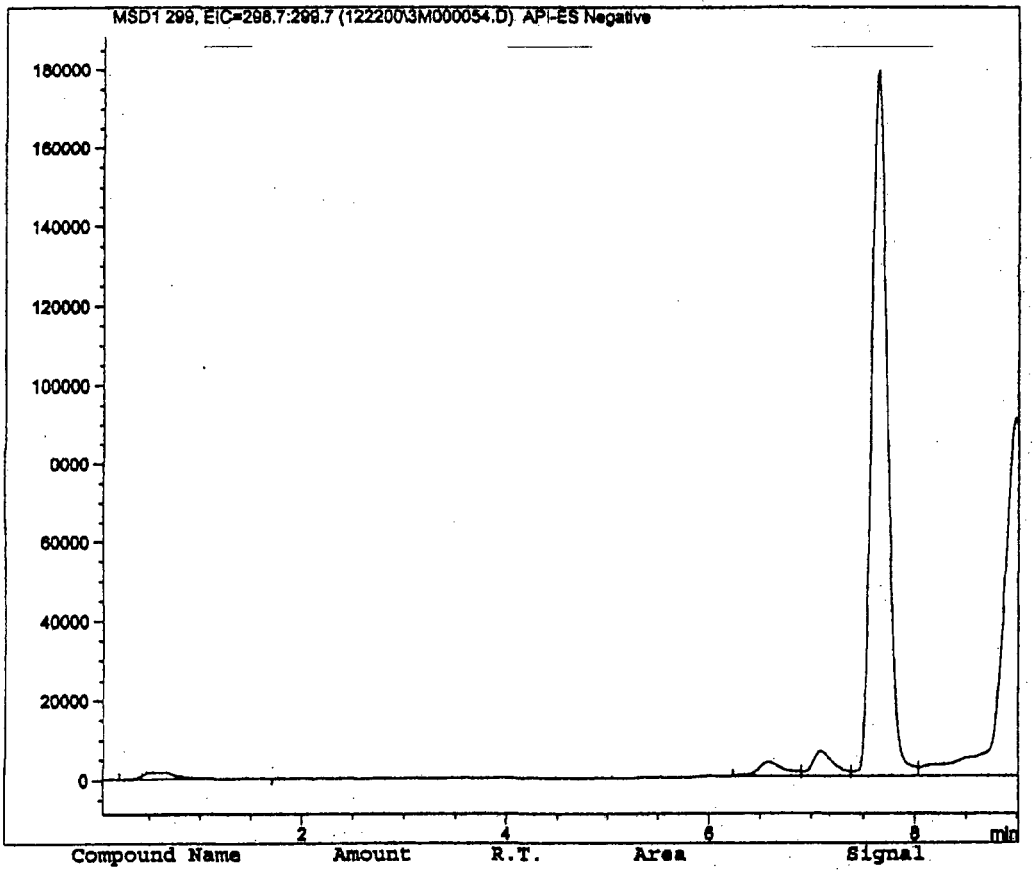
Compound Name	Amount	R.T.	Area	Signal
PFBS	775.8	7.66	1964200	MSD1 299, EIC=298.7:29

FIGURE 8: NIST SLUDGE 24 HOUR $CACL_2$ SOLUTION -- 1/5 RATIO TIER 2



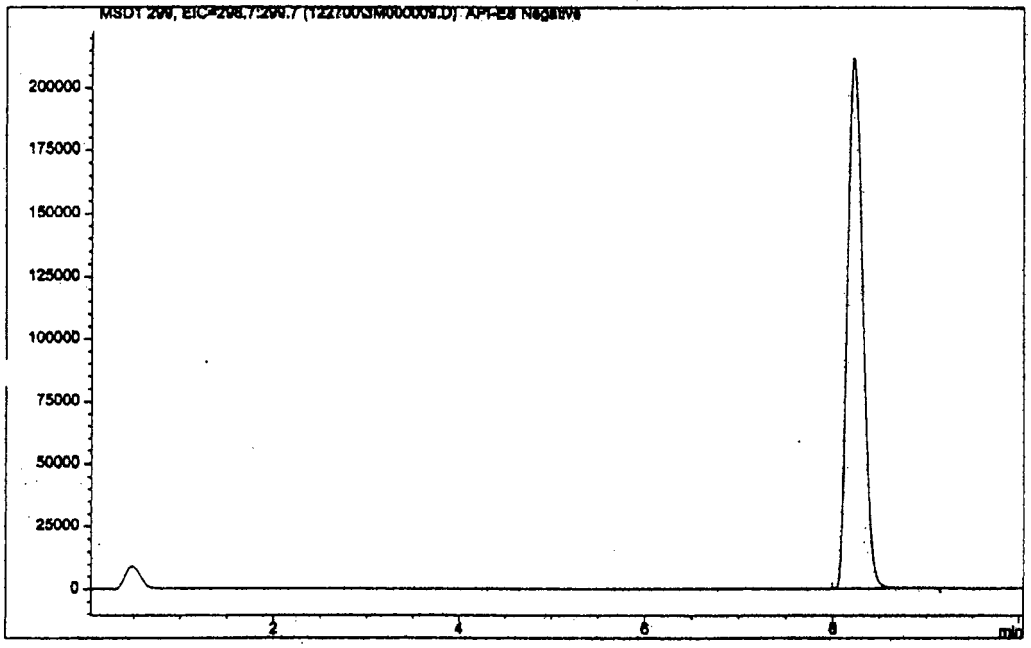
Compound Name	Amount	R.T.	Area	Signal
PFBS	486.6	7.68	1296605	MSD1 299, EIC=298.7:29

FIGURE 9: NIST SLUDGE 24 HOUR SOLIDS EXTRACT -- 1/5 RATIO TIER 2



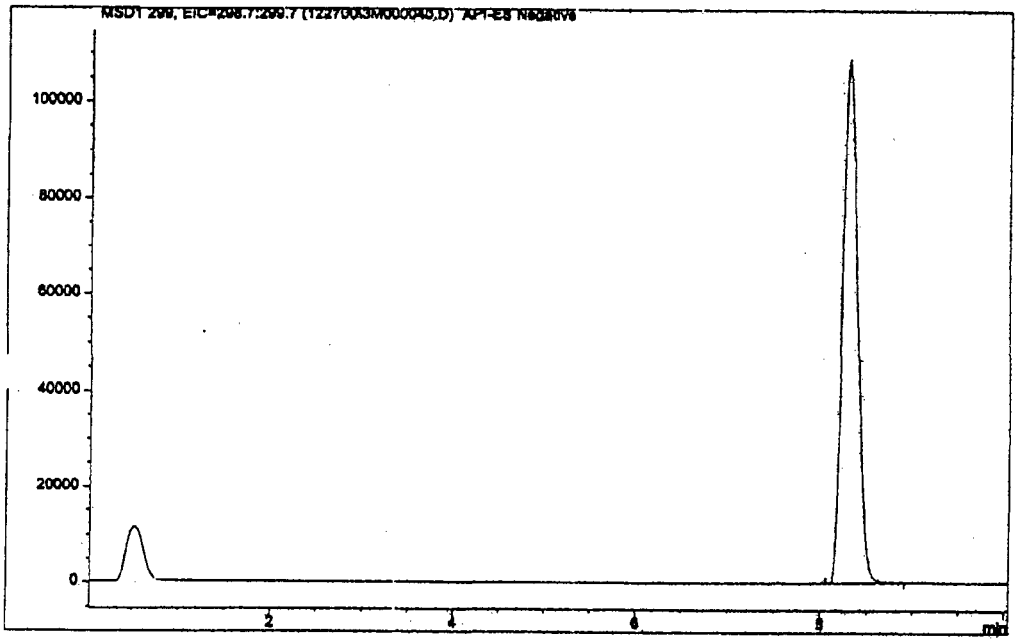
Compound Name	Amount	R.T.	Area	Signal
PFBS	765.4	7.64	1941468	MSD1 299, EIC=298.7:29

FIGURE 10: TIER 3 KITTSON CLAY ADSORPTION SOLUTION NOMINAL 1000ppb



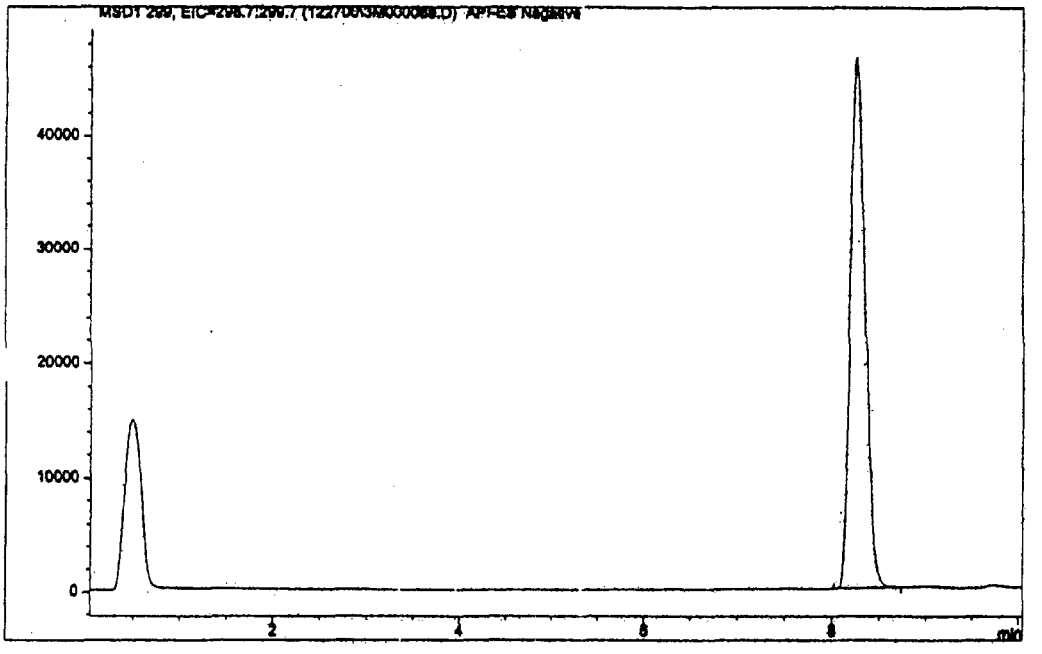
Compound Name	Amount	R.T.	Area	Signal
PFBS	932.4	8.22	2408791	MSD1 299, EIC=298.7:29

FIGURE 11: TIER 3 BROEREN CLAY LOAM ADSORPTION SOLUTION NOMINAL 500ppb



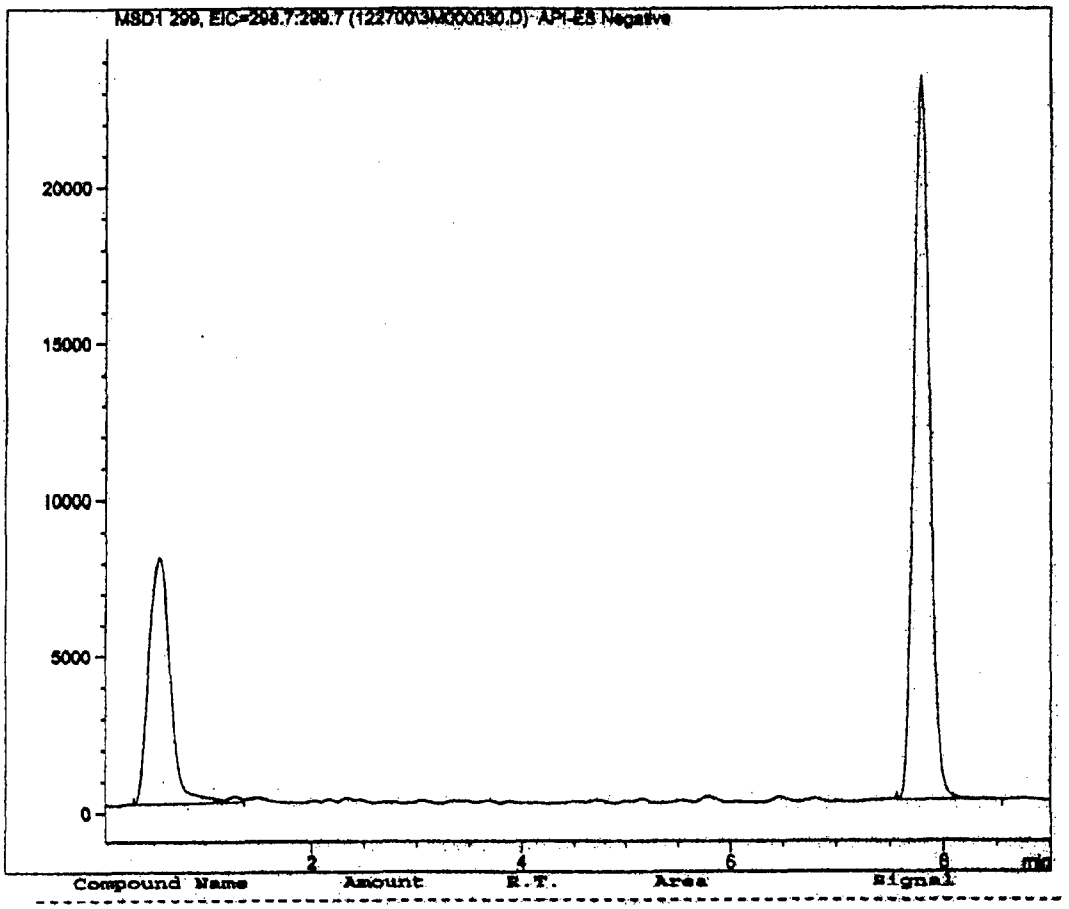
Compound Name	Amount	R.T.	Area	Signal
PFBS	420.9	8.29	1211916	MSD1 299, EIC=298.7:29

FIGURE 12: TIER 3 DON UGLEM LOAM ADSORPTION SOLUTION NOMINAL 250ppb



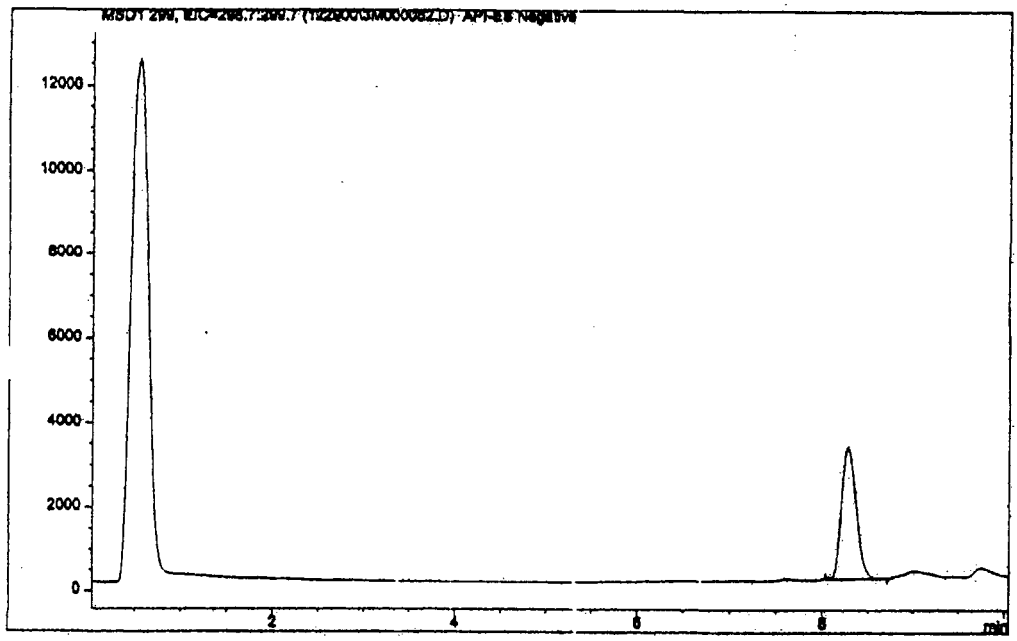
Compound Name	Amount	R.T.	Area	Signal
PFBS	167.5	8.26	506997	MSD1 299, EIC=298.7:29

FIGURE 13: TIER 3 GOOSE RIVER SEDIMENT ADSORPTION SOLUTION NOMINAL 100ppb



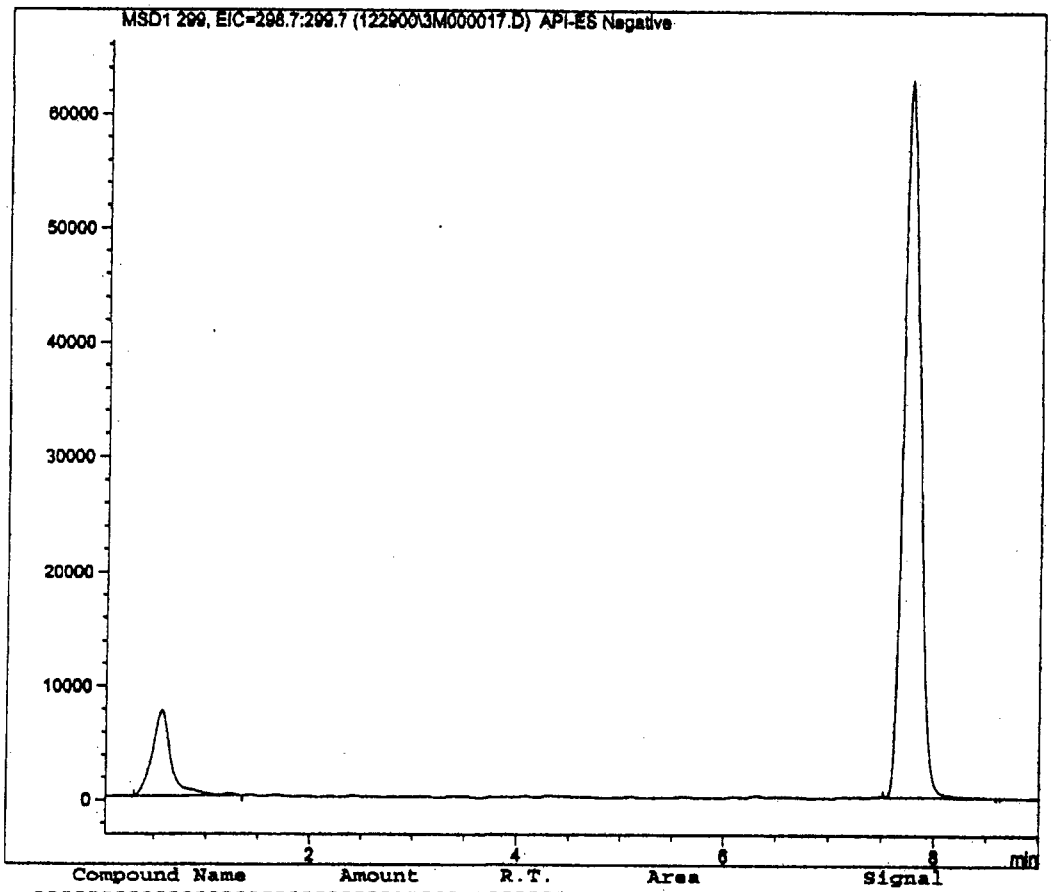
Compound Name	Amount	R.T.	Area	Signal
PFBS	86.9	7.79	238067	MSD1 299, EIC=298.7:29

FIGURE 14: TIER 3 BROEREN CLAY LOAM DESORPTION SOLUTION NOMINAL 50ppb



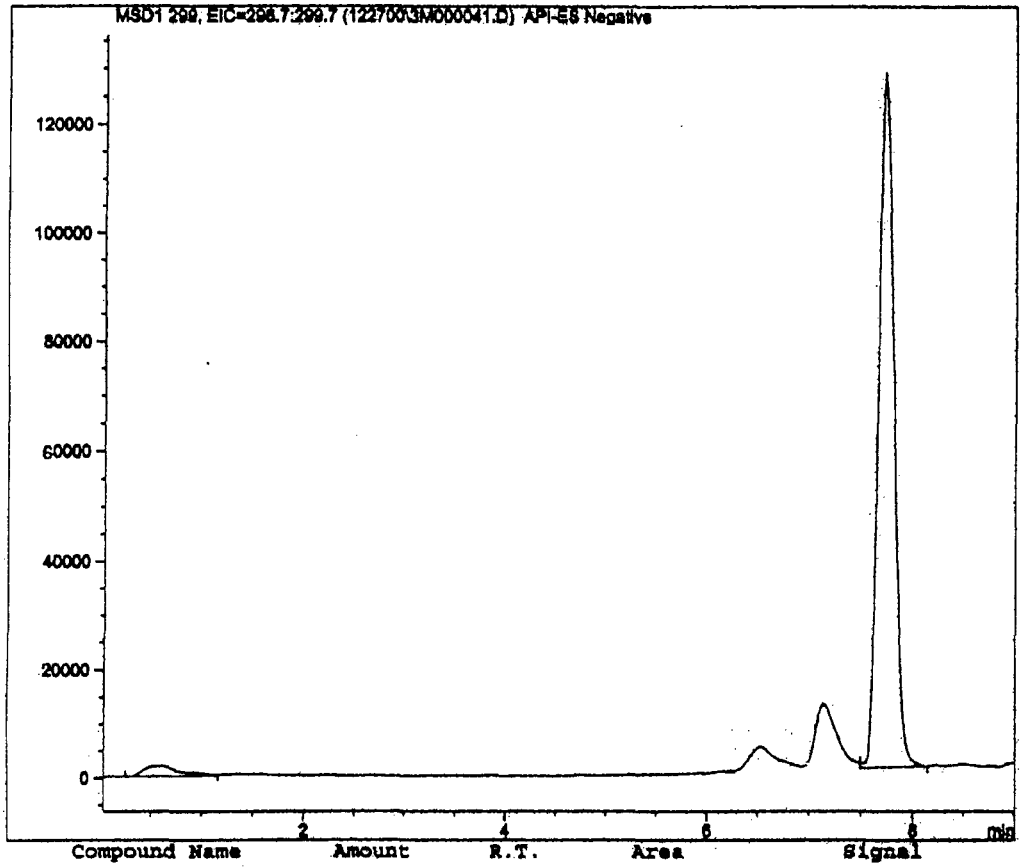
Compound Name	Amount	R.T.	Area	Signal
PFBS	11.5	8.27	35658	MSD1 299, EIC=298.7:29

FIGURE 15: TIER 3 GOOSE RIVER SEDIMENT DESORPTION SOLUTION NOMINAL 1000ppb



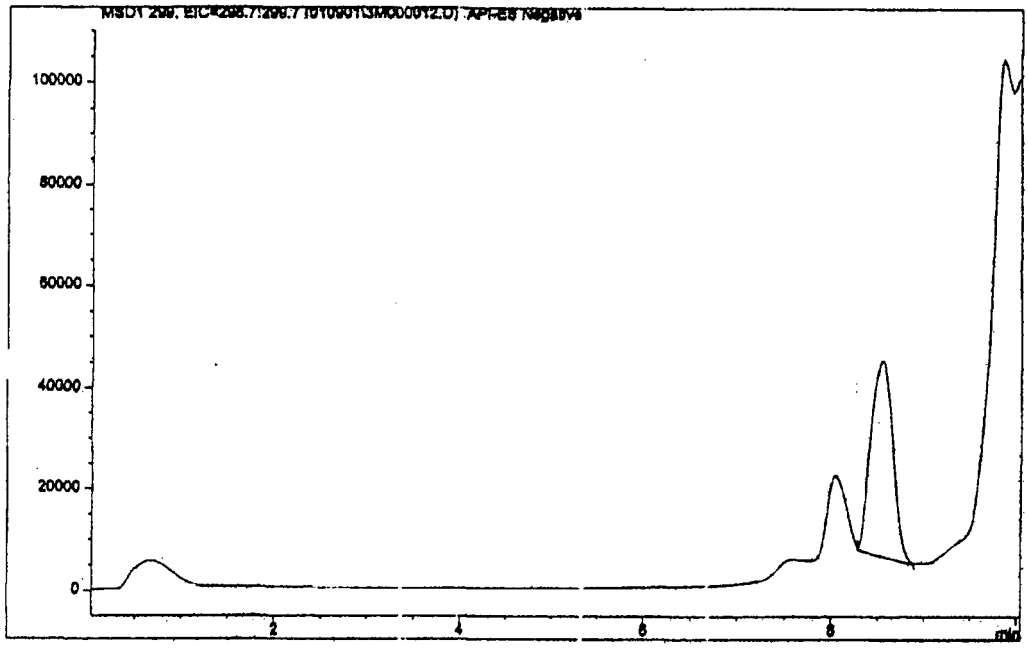
Compound Name	Amount	R.T.	Area	Signal
PFBS	241.7	7.75	691031	MSD1 299, EIC=298.7:29

FIGURE 16: TIER 3 NIST SLUDGE ADSORPTION SOLUTION NOMINAL 1000ppb



Compound Name	Amount	R.T.	Area	Signal
PFBS	525.6	7.72	1339074	MSD1 299, EIC=298.7:29

FIGURE 17: TIER 3 NIST SLUDGE SOLIDS EXTRACT NOMINAL 500ppb



Compound Name	Amount	R.T.	Area	Signal
PFBS	230.5	8.54	634020	MSD1 299, EIC=298.7:29

APPENDIX A

Study Protocol 00P-023-048
Adsorption and Desorption Study to Determine the Mobility and Distribution of Perfluorobutanesulfonic Acid in Soil
Protocol and SOP Deviations

STUDY PROTOCOL

STUDY TITLE

ADSORPTION AND DESORPTION STUDY TO DETERMINE THE MOBILITY AND DISTRIBUTION OF PERFLUOROBUTANESULFONIC ACID IN SOIL.

SPONSOR

3M Environmental Technology and Safety Services
Building 2-3E-09
PO Box 33331
St. Paul, MN 55133-3331

DATA REQUIREMENTS

OECD Guideline for Testing of Chemicals, 106
OECD Guidelines for the Testing of Chemicals Proposal for Updating Guideline 106

TESTING LABORATORY

Centre Analytical Laboratories, Inc. (Centre)
3048 Research Drive
State College, PA 16801
Phone 814-231-8032

PROTOCOL IDENTIFICATION NUMBER

00P-023-048

TABLE OF CONTENTS

Study Title
Adsorption and Desorption Study to Determine the Mobility and Distribution of Perfluorobutanesulfonic Acid in Soil

1. PURPOSE

The purpose of this study is to estimate the adsorption/desorption behavior of perfluorobutanesulfonic acid on soils to obtain a sorption value which can be used to predict partitioning under a variety of environmental conditions. The study will be performed to meet the guideline requirements described in the OECD Guidelines for Testing of Chemicals 106 and the Proposal for Updating Guideline 106.

Sorption studies estimate the availability of a chemical for: degradation; transformation and uptake by organisms; leaching through soil; volatility from soil; and run-off into natural waters. This study is designed on three tiers: Tier 1, a determination of soil/solution ratio, equilibration time for adsorption, potential for adsorption on the surfaces of the test vessels and stability of the test substance(s) during the test period; Tier 2, screening varied soil types at a single concentration; and Tier 3, determination of Freundlich isotherms.

2. JUSTIFICATION FOR THE SELECTION OF THE TEST SYSTEM

Chemical residues may move through the soil profile by leaching or be transported to aquatic environments by movement in surface water. This study is designed to predict the potential for leaching and movement of chemicals in terrestrial and aquatic systems by the use of the batch equilibrium technique with three soil types, one sediment, and one sludge. The test systems (soils, sediment, and sludge) were chosen as recommended in the "OECD Guideline For Testing of Chemicals 106".

As specified by the OECD Guidelines (106 and Proposal for updating Guideline 106), soil types will be selected such that they will vary significantly in cation exchange capacity, clay content, organic matter content, exchangeable cations and pH.

3. SUMMARY

Perfluorobutanesulfonic acid (PFBS) will be evaluated in each matrix for adsorption/desorption isotherms. Perfluorobutanesulfonic acid prepared in aqueous 0.01M calcium chloride ($CaCl_2$) solution is mixed with representative soils, sediment and sludge and allowed to equilibrate at a constant temperature between 20 and 25°C. The soil/test solution phases are separated by centrifugation and the concentration of perfluorobutanesulfonic acid in solution is determined. The adsorbed concentration is determined by difference or extraction and analysis. In Tier 1 two soil types and three soil/solution ratios are used. The

solution concentrations are determined at selected intervals over a 48-hour mixing period (for example 4, 8, 24, 48 hours). By analyzing the control samples, adsorption to the test vessels and stability of the test substance will be evaluated. Data are reduced and the appropriate soil/solution ratio and equilibration time determined for use in Tier 2. Tier 2 screening uses all soils, sediment, and sludge samples except those from Tier 1. The solution values of perfluorobutanesulfonic acid are determined after 2, 4, 6, 8, and 24 hour contact times. The advanced test, Tier 3, is performed to determine Freundlich isotherms. All soils and sediment are evaluated using five concentrations of perfluorobutanesulfonic acid covering two orders of magnitude (if possible). The soil/solution ratio and the equilibrium time determined in Tiers 1 and 2 are used in performing Tier 3 testing. The adsorption test is performed once, the equilibrium concentrations in the solution are determined and the amount adsorbed is calculated from the depletion of the test substance. Desorption is next performed by replacing the volume of solution with an equal volume of 0.01M $CaCl_2$ without test substance. Desorption continues until equilibrium is reached. Data are evaluated for percent desorption, the percent desorption (D_{ti}) and adsorption (A_{ti}) $_{versus}$ time are plotted, and the Freundlich adsorption and desorption isotherms are determined.

4. SPONSOR

3M Environmental Technology and Safety Services
Building 2-3E-09
PO Box 33331
St. Paul, MN 55133-3331

SPONSOR STUDY MONITOR:

5. TESTING FACILITY AND PERFORMING LABORATORY

Centre Analytical Laboratories, Inc. (Centre)
3048 Research Drive
State College, PA 16801

STUDY DIRECTOR:
Kevin Lloyd, Centre
TELEPHONE: 814-231-8032
FAX NUMBER: 814-231-1253

6. PROPOSED EXPERIMENTAL TIME-FRAME

Experimental Start Date	October 23, 2000
Experimental Termination Date	December 31, 2000
Report Issued	January 31, 2001

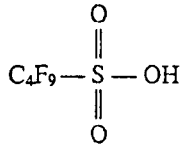
7. TEST SUBSTANCE

The following analytical standards will be used:

Test Material	Lot Number	Purity (%)	Expiration Date
PFBS		TBD	Oct 2001

TBD = to be determined.
Chemical names and structures of the test substance are presented below.

Chemical Name: perfluorobutanesulfonic acid
Molecular Weight: 300



From time to time the following reference compounds will be used to calibrate the method. These reference compounds will be naphthalene (providing K_{oc} values from 1000-30,000), 2,4-dichlorophenoxy acetic acid (providing K_{oc} values from 100-400), and p-chloroaniline (providing K_{oc} values <100).

A record of test and reference substance receipt, storage conditions, and a record of use will be maintained at Centre Analytical Laboratories, Inc. Forms documenting chain-of-custody and shipping records for tracking of the test substances will be included as part of the raw data package.

All standards/test substances and any prepared solutions will be identified with a unique label or number on the container or cross-referenced to the container. All samples submitted for analysis are identified using a unique designation.

Hazard Information
A current MSDS for the chemical(s) used in this study will be maintained at the testing facility.

Test and Reference Substance Documentation
The methods of synthesis, fabrication and/or derivatization of the test and reference substances are documented and retained by the Sponsor. The Sponsor, as required by US EPA FIFRA GLP Standard 40 CFR 160.105, conducted characterization of the test and reference substances, and the Sponsor retains these records. Archived samples of the test and reference substances are being retained by the Sponsor. The Sponsor is maintaining these records and archived samples at the 3M facilities in St. Paul, MN.

The test and reference substances containers will be retained for at least the duration of the study. If the containers are emptied, and the study is completed, discontinued, or terminated, the containers will be disposed of according to standard Centre procedures. Any remaining test and/or reference substances will be retained by/at Centre, or authorization will be obtained from the Sponsor to return any remaining substances. Records will be maintained at Centre documenting use and disposal, if any, of test and/or reference substances.

8. SOIL/SEDIMENT/SLUDGE RECEIPT, PROCESSING, STORAGE AND IDENTIFICATION

Soil, sediment, and sludge samples will be obtained and transported so as not to alter their initial properties. Source location (specified in geographical coordinates), depth of sampling (≤20 cm), amount and type of vegetation cover, treatment(s) with chemical pesticides or fertilizers and/or biological additions, and/or accidental contamination will be documented for each soil sample. Each sample will be assigned a unique identification number at Centre, which will be used for tracking and identification of the soil/sediment during analysis. The soil/sediment/sludge will be stored in a temperature-monitored refrigerator maintained at 1 to 6° C. The samples will be kept isolated from the test substance during storage.

The sludge sample was obtained from the US NIST Laboratories in Gaithersburg, MD and has been fully characterized. Soil and sediment will be collected, sieved (retaining the fraction ≤ 2 mm), homogenized, and characterized by 3M Environmental Technology and Safety Services. Soil/sediment will be analyzed for percent sand/silt/clay content, bulk density (disturbed), field moisture capacity (FMC) at 1/3 bar, pH value in 0.01M $CaCl_2$ (1:1 soil:solution), organic carbon content, organic matter content (%OM), nitrogen content, C/N ratio, cation exchange capacity and extractable cations (meq/100g of Ca, Mg, Na, K, H), carbonate as $CaCO_3$, and clay fraction mineralogy.

9. BIAS/CONTAMINANTS

No experimental bias is expected in this study. Measures to control bias will include the use of replicate test systems with separate analysis and arbitrary sampling of the replicates. No contaminants are expected during the studies that are known to be capable of interfering with the purpose and conduct of the study.

10. SILYLATION OF GLASSWARE

All glassware used in this study (e.g., volumetric flasks, graduated cylinders, pipettes, HPLC vials, centrifuge tubes, etc.) will be silylated before use according to the pertinent Centre standard operating procedure.

11. ANALYTICAL METHOD

All solutions and soils will be extracted and analyzed for PFBS using the procedures detailed in Centre Analytical Labs SOP CAL-24FWL/0; "Extraction of Wastewater Samples for Fluorochemical Analyses by LC/MS" and SOP CAL-24FLM/1, "Analysis of Select Fluorochemicals by LC/MS'.

Sample/solution preparation, storage location and conditions during the study will be documented. All samples and any soil/sediment extracts will be identified with a unique label or sample number. Such identification will be either on the container or cross-referenced to the container.

During analytical runs calibration standards will be interspersed throughout the run. No more than 5 samples will be analyzed between standards. At least 8 standards will be analyzed per run with a minimum of 6 used in the calibration curve (up to 2 may be rejected). The r^2 value of the calibration curve will be >0.99. The run is acceptable with the final acceptable standard, provided that sufficient standards have been analyzed to create a calibration curve.

12. EXPERIMENTAL DESIGN

TIER 1 - Preliminary Study

The test substance is dissolved in 0.01M $CaCl_2$ in deionized water (CAL Type I); the $CaCl_2$ solution is used to improve centrifugation and minimize cation exchange. The concentration of the stock solution will be three orders of magnitude (if possible) higher than the detection limit of the analytical method. Additionally, the stock solution concentration will be below the water solubility of the test substance. If the stock solution is stored, it will be held in the dark under refrigeration at ~4°C. If the test substance is poorly soluble in water, an organic co-solvent may be used at no more than 0.1% by volume of the aqueous phase.

Two soil types and three soil/solution ratios are used. One soil will be the highest in organic carbon with low clay content and the second soil will be the highest in clay content with low organic carbon content. The following soil (dry weight basis) to solution ratios will be used:

- 20 g soil and 20 mL aqueous solution of the test substance (1/1 ratio),

- 5 g soil and 25 mL aqueous solution of the test substance (1/5 ratio),
- 1 g soil and 25 mL aqueous solution of the test substance (1/25 ratio).

All experiments are performed in triplicate. This includes the controls and blanks as described below.

In order to check for stability and adsorption to the test vessel, controls (triplicates) with only the test substance in 0.01M $CaCl_2$ solution (no soil) are subjected to the same steps as the test systems. Triplicate blanks per soil type will be run at 10 g soil and 10 mL 0.01M $CaCl_2$ solution (without test substance) to serve as a background control to detect any interfering compounds or contaminated soils.

If soil samples have been air-dried, the soil will be equilibrated with 0.01M $CaCl_2$ solution overnight (12 hours) the day prior to the test. The minimum volume of 0.01M $CaCl_2$ solution will be 10mL for 1, 5 or 10 g of soil. Following overnight mixing the samples will be centrifuged and the aqueous phase decanted. The weight of the hydrated soils will be recorded.

The pH of the blank and fortified 0.01M $CaCl_2$ solution as well as the aqueous phases recovered after contact with the soil will be measured and recorded.

The mixtures of soil and fortified 0.01M $CaCl_2$ solutions are mixed until adsorption equilibrium is reached. The equilibrium time depends on the chemical and the soil and will vary considerably from one study to the next. Samples will be collected over a 48-hour period of mixing. At the specified sample interval (approximately, 4, 8, 24, and 48 hours) all test systems (centrifuge tubes with soil and solution) will be centrifuged and an aliquot (1 mL) of the aqueous phase removed for analysis. The same quantity of fresh 0.01M $CaCl_2$ solution is added to the mixture to maintain the soil to solution ratio. After removal of the sample the soil is remixed with the aqueous phase and all centrifuge tubes returned to the mixing apparatus until the subsequent sampling.

The percentage adsorption (A_{ti}) is calculated at each time point (t_i) on the basis of the nominal initial concentration and the measured concentration at the sampling time (t_i). Plots of A_{ti} versus time are generated to estimate the equilibrium plateau. The K_d value at equilibrium is also calculated. Based on this K_d value, appropriate soil/solution ratios are selected from Figure 1 (from ENV/EPOC(99)24), so that adsorption is >20%<80%.

The mass balance is performed on both soils and for one soil/solution ratio per soil that gives a depletion above 20% and preferably > 50% at equilibrium. Following the ratio-finding experiment and analysis of the last sample of the aqueous phase after 48 hours, the phases are separated by centrifugation. The aqueous phase is recovered and a suitable extraction solvent added to the soil to extract the test substance. At least two successive extractions are performed. The amount of test substance in the soil and test vessel extracts is determined and the

mass balance is calculated (see calculations). If balance is less than 90%, the test substance is considered unstable in the time scale of the test. If the study is continued this instability will be considered and both phases (aqueous and soil) analyzed in the main study.

TIER 2 – Adsorption Kinetics

All soils, sediment, and sludge selected for the study (except those used in Tier 1) will be tested in Tier 2. The equilibrium time, soil/solution ratio, weight of soil sample, the volume of the aqueous phase, and the concentration of the test substance in the solution are chosen based on the Tier 1 results. Analysis of aqueous solutions will be done at approximately 2, 4, 6, 8, and 24 hours of contact time. The same quantity of fresh 0.01M $CaCl_2$ solution is added to the mixture to maintain the soil to solution ratio and the agitation continues until the next time interval. The mixing time may be extended to a maximum of 48 hours if the test substance requires longer equilibration time with respect to ratio-finding results.

Each soil/sediment/sludge is tested in triplicate at one concentration with triplicate controls (sample of test substance with no soil) and triplicate blanks (soil and 0.01M $CaCl_2$ solution with no test chemical). The test is performed as in Tier 1 with mixing of soil/sediment with test solution, centrifugation, remixing until the next sampling interval.

The percent adsorption is calculated at each time point (A_{ti}) and plotted versus time. The distribution coefficient K_d at equilibrium, as well as organic carbon normalized adsorption coefficient K_{oc} are also calculated.

TIER 3

Adsorption Isotherms

Five test substance concentrations are used covering two orders of magnitude, if possible. All soils, sediment, and sludge selected for the study will be tested in Tier 3. The same soil/solution ratio per soil/sediment will be used throughout the study. The adsorption test is performed as described under Tier 1 except that the aqueous phase is analyzed only once at the equilibrium time as determined in Tier 2. The equilibrium concentrations in the solution are determined and the amount adsorbed is calculated either directly (no desorption to be performed) or by difference (desorption isotherm to be determined). The adsorbed mass per unit mass of soil/sediment/sludge is plotted as a function of the equilibrium concentration of the test substance. The Freundlich isotherm is calculated (see calculations below).

Desorption Kinetics

Using the remaining samples from the adsorption kinetics determination (Tier 2), the aqueous phase of the centrifuged test systems is removed as much as possible. The volume of aqueous solution removed is replaced with an equal volume of 0.01M $CaCl_2$ solution with no test substance. The new mixture is mixed until the

desorption equilibrium is reached. During this time period, at defined time intervals (such as 2, 4, 6, 8, and 24 hours), the centrifuge tubes are centrifuged to separate the phases. A small aliquot of the aqueous phase is immediately analyzed for the test substance. If possible, the volume of each aliquot should be < 1% of the total volume. The same quantity of fresh 0.01M $CaCl_2$ solution is added to the mixture to maintain the soil to solution ratio and the agitation continues until the next time interval.

The percent desorption is calculated at each time point (D_{ti}) and is plotted versus time. The desorption coefficient as K_{des} at equilibrium is also calculated. See Calculations.

Desorption Isotherms

Freundlich desorption isotherms are determined on the soils used for the adsorption isotherm determination. The desorption test is performed as described above under 'desorption kinetics' except that the aqueous phase is analyzed only once, at desorption equilibrium. The amount of test substance desorbed is calculated. The content of test substance remaining adsorbed on soil at desorption equilibrium is determined directly (extraction) and plotted as a function of the equilibrium concentration of the test substance in solution.

13. CALCULATIONS

Mass Balance

Determination of the mass balance over time: Study must have reached adsorption equilibrium.

$$MB = \frac{(V_{rec} * C_{ads}(eq) + m_E) * 100}{V_o * C_o}$$

Where:

- MB = mass balance (%)
- m_E = total mass of test chemical extracted from soil and walls of test vessel (µg)
- C_o = initial mass concentration of test chemical in contact with the soil (µg cm^{-3})
- C_{ads} = equilibrium concentration of test chemical (µg cm^{-3})
- V_o = volume of the initial supernatant applied to the soil (cm^3).
- V_{rec} = volume of the supernatant recovered after the adsorption equilibrium (cm^3).

Adsorption/Desorption Freundlich Isotherms

The Freundlich equation is applicable to the adsorption/desorption of chemicals at intermediate concentrations and is commonly used to evaluate batch equilibrium data. The equation is an empirical relationship which may be expressed as:

$$C_{ads} = KC_e^{1/n}$$

Where:

C_{ads} = the adsorbed concentration (µg);
C_e = the solution equilibrium concentration (µg/mL);
K,n = constants.

Another relationship that assumes that n equals one is the simple proportionality:

$$x/m = K_dC_e$$

Where:

x/m = the adsorbed concentration (µg/g);
C_e = the solution equilibrium concentration (µg/mL);
K_d = the sorption constant.

Both adsorption and desorption are subjected to evaluation using the Freundlich equation. The adsorption coefficient K_d and the constant 1/n are calculated for each soil type. Additionally, K_{oc} (sorption coefficient based on organic carbon) is determined from the following equation:

$$K_{oc} = (K_d * 100) / \%OC$$

Where:

%OC = % organic carbon = % organic matter / 1.724.

14. STATISTICAL METHODS TO BE USED

Mathematical methods of linear regression, means, sums, and logs will be used for data reduction. Standard (linear) curves used to determine the concentration of the compound being analyzed will be constructed from a minimum of five concentrations. Correlation coefficients of the standard curve will be determined.

Other than these descriptive statistics, no other statistical methods will be used during the course of this study.

If necessary, a standard test for outliers, e.g., Dixon's test will apply. If an outlier exists, then it may be excluded from the statistical analysis.

15. PROTOCOL DEVIATIONS AND AMENDMENTS

Any deviations from the protocol or from the analytical method as provided will be documented and reported promptly to the Sponsor Representative. Planned changes to this protocol or to the analytical method will be made in writing as an amendment or modification, and approved by the Study Director and the Sponsor

Representative. Any amendments will be appended to this protocol and included in the final report.

1. Protocol amendments: Planned changes to the approved protocol shall be documented by amendments that clearly describe the change, justification for the change, and impact on the study. Amendments will be signed and dated by the Study Director and Sponsor Representative. Copies of amendments will be sent to the quality assurance unit.

2. Protocol deviations: Protocol deviations, which are one time and unplanned deviations from the protocol, shall be documented in the study records, noting the nature of the deviation, potential effect or impact on the study, and corrective action if required. Protocol deviations are signed or initialed by the Study Director and Sponsor Representative.

16. RECORDS

Records to be maintained include the following (as appropriate):

1. Sample tracking sheet(s)
2. Sample records*, storage history, and chains of custody
3. History and preparation of standards (stock, fortification, calibration)
4. Description of any modifications to the method
5. Instrument run sheets, bench-sheets or logs
6. Analytical data tables
7. All chromatographic and instrumental conditions
8. Sample analysis dates
9. A complete listing of study personnel, signatures and initials
10. Chronological presentation of all study correspondence
11. Any other data necessary for the reconstruction of the study

* Sample records will include soil characterization as specified in OECD Guideline 106.

17. QUALITY ASSURANCE

The Quality Assurance Unit of Centre Analytical Laboratories, Inc. (QAU) will audit the study for compliance with OECD GLP's and EPA FIFRA Good Laboratory Practice standards 40 CFR Part 160. The QAU will review the protocol; audit the study conduct and the study documentation (including raw data and final report) to ascertain that all QA/GLP procedures are adhered to. Centre QAU will inspect the study at intervals adequate to assure compliance to GLP's, and will report the findings of the audits to the Study Director, Centre Management, and the Sponsor Representative.

18. DATA AND REPORT

All raw data and the original signed protocol will be maintained in the study file. This data includes (as appropriate) the protocol amendments, protocol deviations, laboratory notebooks, analytical standard solution preparation, sample chain of custody sheets, sample work sheets, chromatograms, calibration curves, and any other appropriate data generated. Raw data not used will be stored in the study file. The reason for exclusion will be documented.

A final report following the guidelines of United States Environmental Protection Agency PR Notice 86-5, approved and signed by the Study Director and sufficient for submission to EPA, will be prepared.

Centre will send a copy of the draft report to the Sponsor Representative, who will return the report with comments. Centre Analytical will make revisions and finalize the report with the approval of the Sponsor Representative. The Centre QAU will conduct an audit of the final draft report and data files to assure accuracy and GLP compliance. Prior to signature, the Sponsor Representative must approve the final report and copies of the raw data. A QAU statement of inspections and a GLP statement of compliance by the Study Director will be included in the final report.

Any corrections or additions to the final report shall be in the form of an amendment by the Study Director. The amendment shall clearly identify the part of the final report that is being corrected and the justification for correction. The amendment shall be signed and dated by the Study Director and the Sponsor Representative.

REPORT DISTRIBUTION: Original to Sponsor Representative, Copy to Centre Archives.

19. ARCHIVE STATEMENT

When the final report is complete, all original paper data generated by Centre Analytical Laboratories, Inc. will be shipped to the sponsor. This does not include facility-specific raw data such as instrument logs, however exact copies of temperature logs will be submitted. Exact copies of all raw data, as well as a signed copy of the final analytical report and all original facility-specific raw data, will be retained in the Centre Analytical Laboratories, Inc. archives for the period of time specified in 40 CFR Part 160. Retained samples of reference substances are archived by the sponsor.

Upon completion of the study (acceptance of the final report by 3M), all remaining samples and unused soil, sediment, and sludge will be returned to 3M Environmental Technology and Safety Services. 3M will be responsible for the archiving or disposal of all samples and unused soil/sediment/sludge.

20. REFERENCES

1. OECD GUILDELINES FOR THE TESTING OF CHEMICALS: GUIDELINE 106, "Adsorption/Desorption" Adopted 12 May 1981.

2. OECD GUILDELINES FOR THE TESTING OF CHEMICALS: "PROPOSAL FOR UPDATING GUIDELINE 106" ENV/EPOC(99)24

3. US Environmental Protection Agency, August 17, 1989. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Good Laboratory Practice Standards; Final Rule (40 CFR: 160), Federal Register, Vol.54, No. 158: 34052-34074.

4. The OECD Principles of Good Laboratory Practice, Environment Monograph No. 45, OECD/GD(92)32, Paris 1992.

10/20/00 DEC 0 9 2003 Centre Protocol No. 00P-023-048

21. PROTOCOL REVIEW/APPROVAL

The Quality Assurance Unit of Centre Analytical Laboratories, Inc, reviewed this protocol.

REVIEW

Lisa Manning, Centre Quality Assurance Officer — Date: 23-OCT-00

APPROVAL

Centre

Kevin Lloyd, Study Director
Vice President — Date: 10/23/00

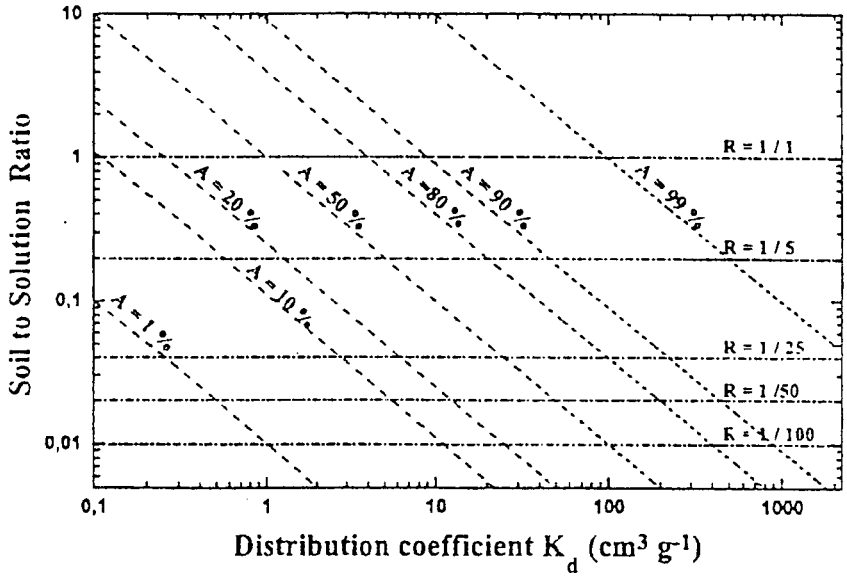
John Flaherty, Facility Management Group/Team Leader – Operations — Date: 10/23/00

Richard A. Grazzini, Ph.D., Facility Management
President — Date: 23-OCT-00

3M

Date: 10/20/00

FIGURE 1: RELATIONSHIP BETWEEN SOIL TO SOLUTION RATIOS AND K_d AT VARIOUS PERCENTAGES OF ADSORBED TEST SUBSTANCE



DEC 09 2003

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Page 1

PROTOCOL DEVIATION

Deviation Number: 1
Date of Occurrence: 12/26-27/00

Centre Study Number: 023-048 Sponsor Study Number: 00P-023-048

DESCRIPTION OF DEVIATION

Tier 3 testing did not meet the protocol specified temperature range of 20-25°C but was 18.0 to 19.3°C.

ACTIONS TAKEN

i.e.. amendment issued. SOP revision. etc...

Deviation issued.

Recorded By/Date: Bill Agnew 1/24/01

IMPACT ON THE STUDY

No known impact on the study.

Study Director Signature — Date 2/1/01

Sponsor Management Signature — Date 1/31/01

Centre QAU Review MLL 1/25/01

January 5, 2001/3

SANITIZED

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PROTOCOL DEVIATION

Deviation Number: 2
Date of Occurrence: 12/15/00

Centre Study Number: 023-048 Sponsor Study Number: 00P-023-048

DESCRIPTION OF DEVIATION

Extraction of water samples per SOP CAL-24FWL was not performed for Tier 2 or 3. Water samples for Tier 2 and 3 and at 48 hours for Tier 1 were filtered through a 0.45 micron filter followed by direct LC/MS analysis.

ACTIONS TAKEN

i.e., amendment issued, SOP revision, etc...

Deviation issued.

Recorded By/Date: Bill Apan 2/28/01

IMPACT ON THE STUDY

The change in procedure yielded more consistent analytical results between replicates of the same sample than the SOP specified ion paired extraction of water samples.

Study Director Signature _____ Date 3/8/01

Sponsor Management Signature _____ Date 3/8/01

Centre QAU Review _____ 2/28/01

January 5, 2001/3

RECEIVED TIME MAR. 8. 2:16PM

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Page 1 of 1

SOP DEVIATION

Deviation Number: 1
Date of Occurrence: 12/27,28/00

CAL Study Number: 023-048 Sponsor Study Number: 00P-023-048

DESCRIPTION OF DEVIATION

SOP CAL-11P/8 Section 3.0 requires that the pH meter be calibrated prior to daily use. On the following dates the calibration was not performed prior to use:

Dec. 27, 2000
Dec. 28, 2000

ACTIONS TAKEN

i.e., amendment issued, SOP revision, etc...

SOP deviation issued.

Recorded By/Date: Bill Apan 1/24/01

IMPACT ON THE STUDY

No negative impact on the study. The instrument successfully calibrated on Dec 22, 2000 and Jan. 2, 2001.

Study Director Signature — Date: 1/26/01

CAL QAU Review: MEW 1/25/01

February 12, 1998/2

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SOP DEVIATION

Deviation Number: 2
Date of Occurrence: entire study

CAL Study Number: 023-048 Sponsor Study Number: 00P-023-048

DESCRIPTION OF DEVIATION

1. SOP CAL-24FLM describes the use of an internal standard in sample analysis. No internal standard was used in this study
2. SOP CAL-24FWL ion paired extraction procedure was not used in the study.
3. Several solutions from Tier 1 testing (4 hr clay1:1-2 and clay1:25-1; 8 hr clay1:1-2, control 2, loam1:5-3 and loam1:25-2; 24 hr control 1) had LC responses greater than the highest standard and should have been diluted and reinjected per SOP CAL24FLM/1-9.3.1d.

ACTIONS TAKEN

i.e., amendment issued, SOP revision, etc...

SOP deviation issued.

Recorded By/Date: Bill Agee 1/25/01

IMPACT ON THE STUDY

No negative impact on the study.
1. An internal standard was not necessary for analysis of PFBS.
2. The selected method of filtration prior to analysis rather than ion paired extraction yielded more reporducible results.
3. The over curve responses were only from the range finding work in Tier 1 testing and had no impact on the final results from Tier 3 testing.

Study Director Signature 1/26/01 Date

CAL QAU Review 1/25/01

February 12, 1998/2