Study Title

ADSORPTION/DESORPTION OF AMMONIUM PERFLUOROOCTANOATE TO SOIL (OECD 106)

Test Guideline(s)

OECD 106 Guidelines for the Testing of Chemicals; Adsorption-Desorption Using a Batch Equilibrium Method (January 21, 2000)

Author

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Study Completion Date

17-April-2003

Test Facility

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EMSE Study / Project Number

EMSER T0111 / 14107

Report Number

EMSER 17-03

PAGE RESERVED FOR SPECIFIC COUNTRY REQUIREMENTS

GOOD LABORATORY PRACTICE COMPLIANCE STATEMENT

The study described in this report was conducted in compliance with the United States Environmental Protection Agency, (FIFRA), Title 40 Code of Federal Regulations Part 160 (effective October 16, 1989), and TSCA Title 40 Code of Federal Regulations Part 792 which are consistent with the OECD Principles on Good Laboratory Practice (ENV/MC/CHEM(98)17) (Paris, 1998).

The test substance is a commercially available material. The certificate of analysis (COA) was provided by the supplier and the accuracy of the data was considered sufficient for the purposes of this study.

Analysis to confirm concentration and uniformity of the stock solutions was not performed. This is believed not to affect the validity of the study because the test substance was accurately measured and added to the test vessels, and the concentration of test substance in the $CaCl_2$ controls (test solutions, no soil) was determined throughout the study.

Study Director

William R. Berti

17-April-2003

William R. Berti, Ph.D.
Senior Research Biologist
DuPont Central Research & Development

Date

Sponsor/Submitter

_____

Date

QUALITY ASSURANCE STATEMENT

Study Number
EMSER 17-03 / 14107

Study Title
Adsorption/Desorption of Ammonium Perfluorooctanoate to Soil (OECD 106)

The conduct of this study, or studies of the same type, was inspected periodically. Audit dates are given below:

Study Phase Inspected	Inspection/Audit Dates	Dates Findings Reported to Study Director	Dates Findings Reported to Management
Study Protocol	15-Jul-2002	15-Jul-2002	Not Applicable
Study Conduct	02-Jan-2003	02-Jan-2003	02-Jan-2003
Report	5,7,10-Feb-2003	10-Feb-2003	17-Apr-2003

These inspections confirm that the methods, procedures, and observations are accurately and completely described in this report, and the reported results accurately and completely reflect the raw data of this study.

Kimberly B. Brebner — 17-APR-2003

Kimberly B. Brebner
QA Auditor
DuPont Co.

Date

CERTIFICATION OF AUTHENTICITY

ADSORPTION/DESORPTION OF AMMONIUM PERFLUOROOCTANOATE TO SOIL (OECD 106)

We, the undersigned, declare that the work described in this report was performed under our supervision, and that this report provides an accurate record of the procedures and results.

Report by:

Lynn Ann Dekleva — 17-April-2003
Lynn Ann Dekleva
Staff Engineer
Date

Reviewed by:

William R. Berti — 17-April-2003
William R. Berti, Ph.D.
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John T. Gannon — 17-APRIL-2003
John T. Gannon, Ph.D.
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Date

Study Initiation Date:
26-July-2002

Date Study Completed:
17-Apr-2003

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ADSORPTION/DESORPTION OF AMMONIUM PERFLUOROOCTANOATE TO SOIL (OECD 106)

GENERAL STUDY INFORMATION

Study Purpose

- The purpose of this study was to test the adsorption behavior of the test substance on four soil samples and one activated sludge sample to determine a sorption value that can be used to predict partitioning of the test substance in the environment.

Study Objectives

- Study the sorption behavior of test substance in soils with varying soil characteristics.
- Provide data for determining the leaching and runoff potential of the test substance in soil including determinations of the following parameters:
    - adsorption coefficient, K_d
    - adsorption coefficient as a function of organic matter, K_{om}
    - adsorption coefficient as a function of organic carbon, K_{oc}
    - percent desorbed
    - Freundlich adsorption isotherms in all test soils with greater than 10% adsorption

Test System Justification

- The test system is outlined by the U.S. EPA and OECD and was requested by the sponsor.

Study Personnel

Management:	John T. Gannon, Ph.D.
Study Director:	William R. Berti, Ph.D.
Additional Study Personnel:	Stanley F. Bachmura, Jr.
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Study Execution Dates

Study Initiation Date:	26-July-2002
Experimental Start Date:	22-Aug-2002
Experimental Completion Date:	03-Feb-2003
Study Completion Date:	17-Apr-2003

ADSORPTION/DESORPTION OF AMMONIUM PERFLUOROOCTANOATE TO SOIL (OECD 106)

1.0 SUMMARY

The adsorption and desorption properties of ammonium perfluorooctanoate were investigated in four soil and one activated sludge samples. The adsorption coefficient (K_d), adsorption coefficient as a function of organic matter (K_{om}), adsorption coefficient as a function of organic carbon (K_{oc}), and Freundlich isotherm parameters (K_F and 1/n) were determined.

The adsorption of ammonium perfluorooctanoate was evaluated according to "OECD Guidelines for Testing of Chemicals 106" and was performed in two phases. Phase 1 consisted of screening studies to determine the optimal soil to solution ratio, the equilibrium time for adsorption, potential for adsorption on the surfaces of the test vessels, and the stability of the test substance during the test. Phase 2 utilized a batch equilibrium soil slurry method to determine the linear and Freundlich adsorption isotherm parameters and evaluate desorption of the test substance.

The table below summarizes the results from this study.

	Drummer	Hidalgo	Wilmington Sludge	Cape Fear	Keyport
Adsorption (%)	79.3 - 88.9	27.8 - 43.8	69.5 - 87.3	54.1 - 73.7	64.5 - 80.8
K_d (mL/g)	4.25 - 8.86	0.41 - 0.83	12.6 - 36.8	1.19 - 2.84	1.82 - 4.26
K_{oc} (mL/g)	73.8 - 111	53.0 - 108	20.5 - 59.6	95.9 - 229	48.9 - 115
K_{om} (mL/g)	42.8 - 89.2	30.8 - 62.6	11.9 - 34.6	55.6 - 133	28.4 - 66.5
K_F ($\mu g^{1-1/n}(mL)^{1/n} g^{-1}$)	5.64	0.59	3.90	3.23	1.64
1/n	0.994	1.00	1.36	0.885	1.11

Soils tested at 1:1 soil:solution ratio; Wilmington sludge tested at 1:5 solids:solution ratio

24 hour equilibration time

The average adsorption of ammonium perfluorooctanoate during a 24-hour equilibration time at a 1:1 soil:solution ratio ranged from 40.8% for the Hidalgo to 81.8% for the Drummer soil. The test soils yielded K_d values of 4.25 to 8.86 mL/g for the Drummer soil, 1.82 to 4.26 mL/g for the Keyport soil, 1.19 to 2.84 mL/g for the Cape Fear soil, and 0.41 to 0.83 mL/g for the Hidalgo soil. The Wilmington sludge sample had the highest average K_d value of 22.5 mL/g, with K_d values that ranged from 12.6 to 36.8 mL/g.

The K_{oc} values of the soils ranged from 48.8 mL/g in the Keyport soil to 229 mL/g in the Cape Fear soil and the K_{om} values ranged from 28.4 mL/g for the Keyport soil to 133 mL/g for the Cape Fear soil. The Wilmington sludge sample had an average K_{oc} value of 36.5 mL/g and average K_{om} value of 21.2 mL/g. There was a strong linear correlation (R^2= 0.9465) between the fraction of organic carbon and average K_d values (Figure 4).

The Freundlich adsorption coefficient (K_F) and the constant (1/n) were determined from the linear form of the Freundlich equation for all test materials. Freundlich adsorption coefficients ranged from 0.59 for the Hidalgo soil to 5.64 $\mu g^{1-1/n} (ml)^{1/n} g^{-1}$ for the Drummer soil. The K_{Foc} values ranged from 44.2 to 261 $\mu g^{1-1/n} (ml)^{1/n} g^{-1}$ and the K_{Fom} values ranged from 25.6 to 151 $\mu g^{1-1/n} (ml)^{1/n} g^{-1}$ for the Keyport and Cape Fear soils, respectively.

There was a strong inverse relationship (R^2=0.8665) between the fraction of organic carbon (foc) and the total % desorption of the test compound in the Drummer, Keyport and Cape Fear soils. The Drummer soil which had the highest foc of the soils used in this study (5.76%) had a 36.0% average total desorption. Cape Fear with a foc of 1.24% had an average desorption of 53.0%. The desorption results for the Hidalgo soil and the Wilmington Sludge sample were highly variable and ranged from 41.6 to 121% and 14.9 to 101%, respectively.

2.0 INTRODUCTION

2.1 Study Purpose

- The purpose of this study was to test the adsorption behavior of the test substance on four soil samples and one activated sludge sample to determine a sorption value that can be used to predict partitioning of the test substance in the environment.

2.2 Study Objectives

The major objectives of this study were to

- Study the sorptive behaviour of ammonium perfluorooctanoate in soils with varying soil characteristics
- Provide data for determining the leaching and runoff potential of the test substance in soil including determinations of the following parameters:
  - adsorption coefficient, K_d
  - adsorption coefficient as a function of organic matter, K_{om}
  - adsorption coefficient as a function of organic carbon, K_{oc}
  - percent desorbed
  - Freundlich adsorption isotherms in all test soils with greater than 10% adsorption

2.3 Test Guidelines

The study design met the data requirements specified in the OECD Guideline for Testing of Chemicals, "Adsorption-Desorption Using a Batch Equilibrium Method", Guideline 106, January 2000 and U.S. Environmental Protection Agency, Pesticide Assessment Guidelines (1982).

3.0 MATERIALS AND METHODS

3.1 Test Substance

Name:	Ammonium perfluorooctanoate
Synonyms:	Ammonium pentadecafluorooctanoate; Ammonium perfluorocaprylate; DS 101; Fluorad FC 143; Perflurorooctanoic acid ammonium salt; Unidyne DS 101; APFO
Active substance:	Octanoic acid, pentadecafluoro-, ammonium salt
CAS Name:	Octanoic acid, pentadecafluoro-, ammonium salt

CAS Number:	3825-26-1
Supplier:	Fluka Chemical Company 1001 West St. Paul Milwaukee, WI 53233 USA
Product Number:	77262
Lot Number:	421207/1
Molecular Formula:	$C_8H_4F_{15}NO_2$
Formula Weight:	431.1 g/mole
Concentration of a.s., nominal:	≥98.0%
Certificate of Analysis Date:	24-Jan-01
Solubility:	1 g/10 ml
Appearance:	White Powder
Date Received:	22-August-02

3.2 Reagents and Solvents

All chemicals and solvents were of reagent grade or purer and were purchased from the following suppliers: Calcium chloride dihydrate (Mallinckrodt); Methanol used for extractions (Burdick & Jackson), Methanol HPLC grade (EM Science), and Ammonium Acetate ACS grade (EM Science).

3.3 Application Information

The test substance was administered from a 1000 mg/L stock solution in 0.01M $CaCl_2$ prepared in a polypropylene volumetric flask (Nalgene 4000-0050). The stock solution was prepared the day of testing and stored at room temperature until use.

3.4 Test System

The test system employed in this study consisted of individually capped 50-mL polypropylene conical tubes (Falcon BD 35 2070), uniquely identified, containing 0.01M $CaCl_2$ solution with and without test soils or sludge. The tubes were mixed using an end-over-end rotator (Glas-Col Rotator Model 099A RD4512) at 30-35 RPM at an ambient temperature of 19-25°C. The temperature was monitored using a Dickson THDx Temperature recorder, which had a resolution of 0.5°C and accuracy of ±1°C. Following incubation, the samples were centrifuged for 30 minutes at 6000 RPM (Sorvall RC-5 HS-4 Rotor) and supernatants were transferred to 50-mL polypropylene tubes (Falcon BD 35 2070) using a disposable pipette (VWR 53283-706). Aliquots (5 mL) of the supernatants were filtered (Pall Gelman 4190) in 14-mL polypropylene tubes (Falcon 35 2059) using a 10-mL disposable syringe (BD 309695) and refrigerated or frozen until analysis. All experiments were conducted in duplicate.

3.5 Test Soils and Sludge

Four soil samples and one activated sludge sample were used in this study. The characterization of the soils and sludge was performed at MDS Harris Laboratories (Lincoln, Nebraska) and is presented in Table 1. The pH of the soils ranged from 5.4 to 7.8 and organic carbon ranged from 0.77 to 5.76 %. Prior to use, the test soils were air-dried and sieved though a 2-mm mesh sieve. The activated sludge sample was collected from the dewatering facility of the Wilmington Wastewater Treatment facility. Sludge samples were washed twice with distilled water, freeze-dried, pooled, and gamma irradiated. The moisture content of the test materials was determined on three aliquots (Ohaus AP 210-0) by heating at 100-105°C (Yamato drying oven DX 300) for a minimum of 12 hours. The moisture content was determined by the equation:

$$\% \text{ Moisture} = \frac{(\text{Wet Weight} - \text{Dry Weight})}{\text{Dry Weight}} \times 100$$

3.6 Analytical Methods

Ammonium perfluorooctanoate (APFO) was quantitated by liquid chromatography (LC) (Agilent 1090 Liquid Chromatograph) combined with tandem mass spectrometry (MS/MS) (Micromass Quatro). Negative ion electrospray was used to produce the molecular anion for the perfluorooctanoic acid, which was then subjected to collision-induced dissociation producing the decarboxylated anion. The MS/MS transition was specific to perfluorooctanoic acid and the area of the chromatogram was proportional to the concentration of APFO.

The standard operating conditions for the method are provided in Appendix 1. Samples were diluted (if required) with 0.01M $CaCl_2$ and submitted for analysis in polypropylene vials (Agilent 5182-0567) sealed with a natural rubber crimp seal (Agilent 5182-1210). Samples were refrigerated or frozen until analysis.

Samples were analysed by duplicate injections and quantified using a calibration curve generated the day of analysis. Sample concentrations were reported at or above the limit of quantitation (LOQ) for this study.

3.7 Experimental Design

3.7.1 Phase 1 Preliminary Studies

Validation of the Analytical Method

The solubility of the test substance was reported by the manufacturer to be 0.1 g/mL in H_2O. The solubility of the compound was not determined in this study because the highest test concentration used in this study, 2500 µg/L, was significantly below the solubility limit for the compound reported by the manufacturer.

The test substance was administered to the test systems by means of diluting a 1000 mg/L stock solution with 0.01M $CaCl_2$ solution (prepared using deionized water). Aliquots of the test substance were added to polypropylene tubes containing 0.01M $CaCl_2$ to achieve final test concentrations of 100, 500, 1000 and 2500 µg/L. Blank tubes were included and contained only the 0.01M $CaCl_2$ solution. Aliquots (5 mL) of the samples were filtered (Gelman Pall 4190) into 14 mL polypropylene tubes (Falcon 35 2059) using a 10 mL disposable syringe (BD 309695) and refrigerated or frozen until analysis. All experiments were conducted in duplicate. Analytical samples were diluted with 0.01M $CaCl_2$ solution prior to submission to achieve an analytical concentration in the range of 10 to 150 µg/L.

The analytical method was validated on two soils. Soil extracts from Drummer (5.76% organic carbon) and Cape Fear (1.24% organic carbon) soils were prepared by mixing 20 g of soil with 20 mL 0.01M $CaCl_2$ solution for 48 hours at 30-35 RPM at ambient temperature. The extracts were recovered after centrifugation (Sorvall RC-5B HS-4 rotor, 6000 RPM, 30 minutes). The test compound was added to the soil extracts, which were then filtered (Gelman Pall 4190) and submitted for analysis. Soil and $CaCl_2$ blanks and $CaCl_2$ controls at the four test concentrations (100, 500, 1000 and 2500 µg/L) were included in the study. Replicate concentration measurements were done on two separate days.

Adsorption to Test Vessel Containers

The potential for adsorption of the test substance to the test vessel was assessed by analyzing the test substance solutions containing the highest and lowest concentrations in the validation experiments (100 and 2500 µg/L). The test substance was added to 50 mL polypropylene centrifuge tubes containing 20 mL of 0.01M $CaCl_2$ solution. The tubes were placed on a rotator for 24 hours at 30 to 35 RPM at ambient room temperature. The concentration of the solution at 24 hours was compared to aliquots taken at set-up to determine the potential for adsorption of the test substance to the test vessel.

Determining the Soil:Solution Ratio and Equilibration Time

The Soil:Solution Ratio and Equilibration Time experiment was conducted with two soil types, Drummer and Hidalgo, and three soil:solution ratios (20 g soil:20 mL, 5 g soil:25 mL, and 1 g soil:25 mL).

Soil samples were pre-equilibrated with the 0.01M $CaCl_2$ solution using an end-over-end rotator at 30-35 RPM. Following pre-incubation (12 hr), the test substance was added to the test vessels to yield a final test concentration of 1000 µg/L. Control tubes (test substance in $CaCl_2$), $CaCl_2$ blanks and soil blanks were prepared and processed with the adsorption samples.

The test vessels were placed on the end-over-end rotator at 30-35 RPM at ambient room temperature. Duplicate test vessels for each soil:solution ratio, including control and blank tubes were collected at 2, 6, 24 and 72 hours and were centrifuged. The supernatants were transferred to 50 mL polypropylene tubes, aliquots were filtered and submitted for determination of the test compound. The percent adsorption was calculated at each time point on the basis of the nominal initial concentration and the measured concentration at the sampling time. Soil tubes and supernatants were frozen for approximately one month until the extraction procedure was performed for determination of test substance stability and mass balance calculations.

Determination of Test Substance Stability

A mass balance was performed after the soil:solution ratio experiment. The 1:1 soil solution ratio tubes from the 72-hour time point, were used for this experiment. Test and blank soil tubes were thawed at room temperature for approximately one hour before addition of 20 mL of methanol (Burdick & Jackson 232-1). The pellets were disrupted using a polystyrene weighing spoon (Bel Art H36940-000) and resuspended by vortexing. The tubes were mixed for a minimum of 2 hours before centrifugation (6000 RPM, 30 minutes) and recovery of the methanol. A second extraction was immediately performed.

Aliquots (5 mL) were filtered (Gelman Pall 4190) to remove any particulate material. Aliquots of the filtered methanol extracts (1 mL of the first and 3 mL of the second) were transferred to 5 mL polypropylene test tubes and evaporated completely using a Pierce Reacti-Vap Evaporating Unit (Model 18780) with a Nitrogen purge (1 psi). The residue in the tubes was resuspended in one mL 0.01M $CaCl_2$ and submitted for analysis.

3.7.2 Phase 2 Definitive Studies

Adsorption Experiments

The adsorption experiment was conducted on four soils and one sludge sample. The experiment was conducted, in duplicate, at a 1:1 soil: solution for the test soils and 1:5 soil:solution ratio for the sludge sample at 4 test concentrations (100, 500, 1000 and 2500 µg/L). The samples were pre-equilibrated with 0.01M $CaCl_2$ solution overnight (12 hours) before addition of the test substance. The tubes were mechanically agitated using an end-over-end rotator (30-35 RPM, ambient temperature) for 24 hours before the supernatants were recovered by centrifugation. Control tubes (test substance in $CaCl_2$), $CaCl_2$ blanks and soil blanks were prepared and processed with the adsorption samples.

An aliquot (5 mL) of the supernatants was filtered (Gelman Pall 4190), diluted (if required), and refrigerated or frozen until analysis. The percent adsorbed was determined by comparing the amount of test substance in the aqueous phase at equilibrium to the amount of test substance added to the system (based on calculated concentration).

Desorption Experiments

Desorption experiments were conducted on all test soils immediately following the adsorption study. The soil pellets from the adsorption study were resuspended in 20 mL of 0.01M $CaCl_2$ solution (sludge tubes received 25 mL). The pellets were disrupted via a polystyrene weighing spoon (Bel Art H36940-000) and vortexed to ensure complete mixing. The samples were agitated using an end-over-end rotator for 24 hours at ambient temperature, centrifuged and supernatants recovered. A second desorption step was conducted immediately.

Aliquots of the desorption supernatants were filtered and submitted for analysis. The percent test substance desorbed was determined by comparing the amount of test substance in the aqueous phase following a given desorption interval to the amount of test substance associated with the soil phases at the adsorption equilibrium. The total amount of test substance desorbed was obtained by summing the percent desorption at each desorption interval.

3.8 Data Analysis

3.8.1 Equilibration Time and Percent Adsorption

Equilibration time can be determined from plots of the concentration of the test substance in the aqueous phase versus time or from plots of percent adsorption (A) against time. The values of adsorption (A) were calculated according to the following equations.

$$A = \frac{m_{soil} \times 100}{m_0}$$

where $m_0 = C_0 \times V_0$

$$m_{soil} = m_0 - (C_W \times V_w)$$

Symbol	Definition	Unit
A	percent adsorption	%
m_{soil}	mass of test substance adsorbed to soil at equilibrium	µg
m_0	mass of test substance applied to test vessel	µg
C_0	initial concentration of test solution	µg/mL
V_0	volume of test solution added to test vessel	mL
C_w	concentration of test substance in aqueous phase at adsorption equilibrium	µg/mL
V_w	volume of aqueous phase in the adsorption test at equilibrium (test solution, V_o, plus water present in the soil)	mL

3.8.2 Adsorption

The adsorption coefficient, K_d, for each test solution concentration were calculated for each test soil using the following equation. The K_d value will also be used to calculate K_{om} and K_{oc} values.

$$K_d = \frac{C_s}{C_w}$$

$$K_{om} = \frac{K_d}{om}$$

$$K_{oc} = \frac{K_d}{oc}$$

Symbol	Definition	Unit
K_d	adsorption coefficient	mL/g
C_s	concentration of the test substance in the soil phase at adsorption equilibrium	µg/g
K_{om}	adsorption coefficient based on organic matter	mL/g
K_{oc}	adsorption coefficient based on organic carbon	mL/g
oc	fraction of organic carbon (foc) = % organic carbon/100	na
om	fraction of organic matter =fraction of organic carbon *1.724	na

3.8.3 Desorption

The percent desorbed, D, was calculated according to the following equations.

$$D_1 = \frac{m_{w,D1} \times 100}{m_{soil}}$$

$$D_2 = \frac{m_{w,D2} \times 100}{m_{soil}}$$

$$D_T = D_1 + D_2$$

where

$$m_{w,D1} = C_{w,D1} \times V_{w,D1} - (C_w \times V_{ret})$$

$$m_{w,D2} = C_{w,D2} \times V_{w,D2} - (C_{w,D1} \times V_{ret,D1})$$

Symbol	Definition	Units
D_1	percent of test substance desorbed after first desorption interval	%
D_2	percent of test substance desorbed after second desorption interval	%
D_T	total percent of test substance desorbed after both desorption intervals	%
m_{soil}	mass of test substance adsorbed to soil at equilibrium	µg
$m_{w,D1}$	mass of test substance in aqueous phase after first desorption interval	µg
$C_{w,D1}$	concentration of test substance in aqueous phase after first desorption interval	µg/mL
$V_{w,D1}$	total volume of aqueous phase (added solution plus volume of water retained in soil) after first desorption interval	mL
C_w	concentration of test substance in aqueous phase at adsorption equilibrium	µg/mL
V_{ret}	volume of water retained in soil at adsorption equilibrium	mL
$m_{w,D2}$	mass of test substance in aqueous phase after second desorption interval	µg
$C_{w,D2}$	concentration of test substance in aqueous phase after second desorption interval	µg/mL
$V_{w,D2}$	total volume of aqueous phase (added solution plus volume of water retained in soil) after second desorption interval	mL
$V_{ret,D1}$	volume of water retained after first desorption interval	mL

3.8.4 Material Balance from Adsorption/Desorption Experiments

$$MB = \frac{(C_w \times V_w) + m_{w,D1} + m_{w,D2}}{V_0 \times C_0} \times 100\%$$

Symbol	Definition	Units
MB	material balance	%
C_w	concentration of test substance in aqueous phase at adsorption equilibrium	µg/mL
V_w	total volume of the aqueous phase (added solution plus volume of water present in the soil)	mL

$m_{w,D1}$	mass of test substance in aqueous phase following first desorption interval	µg
$m_{w,D2}$	mass of test substance in aqueous phase following second desorption interval	µg
V_0	volume of solution added to test vessel	mL
C_0	concentration of test solution added to test vessel	µg/mL

3.8.5 Adsorption Isotherms

Linear and Freundlich adsorption isotherms were constructed for each soil in which adsorption exceeded >10%. Linear isotherms were constructed by plotting C_s (y-axis) and C_w (x-axis) for each soil tested. The Freundlich adsorption coefficient (K_F) and the exponential constant (1/n), were determined from linear regression analysis of the Freundlich equation:

$$C_s = K_F \times C_w^{1/n}$$

The linear form of this equation is shown below.

$$\log(C_s) = \log(K_F) + (1/n \times \log(C_w))$$

Plotting the linear form of the Freundlich equation with log (C_s) on the y-axis and log (C_w) on the x-axis will yield a line with a slope of 1/n and a y-intercept of log (K_F).

The K_F value was used to calculate K_{Fom} and K_{Foc} values.

$$K_{Fom} = \frac{K_F}{om}$$

$$K_{Foc} = \frac{K_F}{oc}$$

3.9 Statistical Methods and Control of Bias

Statistical methods including means, standard deviations, and regression lines were used as appropriate. Bias was effectively controlled through duplicate sampling, replicate analysis, sample spiking, and maintenance of material balance. Microsoft Excel 2000 was used in all calculations and in the statistical t-Test.

3.10 Deviations from Test Protocol

The mass balance determinations from the preliminary study were not immediately performed after the completion of the soil:solution ratio and equilibrium time study. The analysis of the substance extracted from the solid phase (mass balance) studies was not completed until after the adsorption-desorption experiments were completed. This is not believed to have affected the definitive study and is discussed in more detail in the Results and Discussion section of this report.

One of the soil types for the soil:solution ratio was recommended to have an organic carbon content less than 2.0% and pH of less than 4.8. The measured pH from the original characterization of the Cape Fear soil (8-Dec-97) had a reported value of 4.9. The accuracy of the equipment utilized by Agvise laboratories for this analysis is unknown. The soil was re-characterized by Harris laboratories and had a reported pH of 5.4. The pH deviation is not believed to have affected the results from soil:solution ratio or definitive studies.

4.0 RESULTS AND DISCUSSION

4.1 Preliminary Studies

Validation of the Analytical Method

Ammonium perfluorooctanoate (APFO) in $CaCl_2$ solutions was quantified as the perfluorooctanoate anion using liquid chromatography (LC) combined with tandem mass spectrometry (MS/MS). Liquid chromatography was used to separate the analyte of interest using a linear gradient of Methanol (Appendix 1). The flow was diverted to waste for the first 3 minutes of the run and then directed to the mass spectrometer. The MS/MS transition 423 > 369 was specific to perfluorooctanoic acid and the area of the chromatogram was proportional to the concentration of ammonium perfluorooctanoate.

Calibration standards were prepared fresh each day by dilution of a refrigerated stock solution of 1000 mg/L APFO. The instrument was calibrated using a 5-point calibration ranging from 10 to 150 µg/L. The calibration standards were run in duplicate followed by a low (20 µg/L) check standard, high (100 µg/L) check standard, and a blank injection. The standard injection volume for the method was 25 µL. The calibrations curves had correlation coefficients (R^2) of greater than 0.985 and the check standards were ±10% the test concentration. The samples were analyzed from duplicate injections and the mean test concentration was reported.

The limit of quantitation (LOQ) (Reference 7) for this method was 10 µg/L with the method of detection limit (MDL) at 5 ppb. The coefficient of variation on 5 replicates was determined to be < ±15%. The accuracy was determined to be ±15% of the mean value of 5 replicates except at the LOQ where the accuracy was ±20%.

The analytical method was validated using filtered $CaCl_2$ solutions and extracts prepared from Drummer and Cape Fear soils. The measured concentration for the $CaCl_2$ tubes was < ±20% of the expected value except for one of the 2500 µg/L Control tubes, which had a deviation of 25.4% from the nominal test concentration (Table 2). This deviation from the expected concentration was not observed in subsequent testing of $CaCl_2$ control solutions, which had less than 20% difference from mean control tube measured values at all four test concentrations (Table 3). The $CaCl_2$ blanks in this preliminary study resulted in measured concentrations of 15.5 and 15.6 µg/L for the test compound (Table 2) and were isolated to this experiment. $CaCl_2$ in all subsequent testing resulted in measured concentrations of less than the limit of quantitation (LOQ) of 10 µg/L.

The soil extracts did not interfere with the detection of the test compound. The measured concentrations for the soil extracts were generally < ±15% that of the $CaCl_2$ controls (no soil) prepared during the study and had similar linear correlations (Table 3, Figure 1). One of the Cape Fear soil extracts prepared at a test concentration of 100 µg/L had a 33.1% difference from the mean value for the $CaCl_2$ 100 µg/L controls. Since this discrepancy was isolated to one tube and was detected in only one soil extract it was attributed to experimental error during the preparation of the sample.

Adsorption to Test Vessel

The test compound did not adsorb to the test vessel during the 24-hour study. The difference between the measured concentrations at the initial and 24-hour time point were not significant (p=0.05) and averaged 1.36% for the 100 µg/L tubes and 16.3% for the 2500 µg/L tubes (Table 4).

Soil Solution Ratio and Equilibration Time

The soil solution ratio and equilibration time investigation was conducted at a test concentration of 1000 µg/L on two soil types, Drummer and Hidalgo, and at three soil solution ratios. The adsorption was calculated (Table 5) based on the nominal test concentration and was plotted against incubation time for the both soils (Figures 2 and 3). At 24 hours, the adsorption ranged from 29.3% for the 1:25 soil:solution ratio to 83.9% for the 1:1 soil solution ratio with the Drummer soil, and 20.1% for the 1:25 soil:solution ratio to 42.2% for the 1:1 soil solution ratio with the Hidalgo soil. These values remained essentially unchanged or decreased slightly after 72 hours, and 24 hours was selected as the equilibration time for subsequent studies. To achieve adsorption values of greater than 20% and preferably greater than 50% for all test soils, a 1:1 soil:solution ratio was selected for adsorption studies for the test soils. The low density of the sludge sample required that the adsorption-desorption studies be performed at a 1:5 soil:solution ratio. However, this ratio met the desired adsorption of greater than 50% (Table 7).

Mass Balance Determinations

The mass balance for the Drummer and Hidalgo soil tubes was lower than the $CaCl_2$ control tubes (Table 6) based on the nominal test concentration from the soil:solution ratio study. The Hidalgo soil had an average mass balance of 84.4% and a range of 79.0 to 89.8%. The mass balance was 68.6% determined from the one Drummer soil tube available from the soil:solution ratio equilibrium time experiment. The $CaCl_2$ control tubes, which contained no soil, were included in the mass balance determinations. The supernatants recovered at the end of the soil:solution ratio equilibrium time experiment accounted for an average of 98.9% of the added test compound. The methanol extraction in the control tubes (no soil, with test substance) resulted in an average mass balance of 110% with a range of 100 to 119%.

The less than 90% recovery of the test substance from the soil pellets may be the result of the difficulty in resuspending the soil pellets in the extraction solvent. This disruption step required the mechanical manipulation of the soil pellets which inadvertently led to some soil loss. The pellets were vigorously vortexed after disruption but because of the soil matrix it was difficult to establish whether the slurry had a uniform particle dispersion or if there was some residual clumping. The Drummer soil pellet was extremely difficult to resuspend during the extraction phase and required more mechanical disruption than the Hidalgo soil pellets. This may account for the lower mass balance determinations between the two soils. The methanol extracts were not directly analyzed for the test compound but evaporated completely and resuspended in 0.01M $CaCl_2$ solution before analysis. The evaporation step may, however, not account for the lower recovery of the test compound in the soil extracts. The efficiency of methanol in extracting the test substance from the soils was not determined in this study, but was assumed to be a suitable extraction solvent for this compound. The effect of the time lag between the soil:solution ratio experiment and the extraction of the soil pellets on the recovery of the test compound is unknown.

The soil:solution ratio experiment was concluded approximately one month before the extraction of the soil pellets. This storage may have had some effect on the recovery of the test compound from the soil pellets or on the nature of the interaction between the test compound and the soil matrix. Although the recovery of the compound was < 90% in this experiment, the definitive adsorption desorption experiments are descriptive of the test compound's behavior in the presence of soil matricies. The difficulties in pellet resuspension during extraction and subsequent evaporation of the extraction solvent suggest that alternative experimental approaches may need to be developed and validated for subsequent mass balance studies.

4.2 Definitive Studies

Adsorption and Desorption Studies

The aqueous phase analysis of the adsorption experiment agreed well with the 24-hour results from the preliminary soil:solution ratio and equilibrium time phase of the study for the Drummer and Hidalgo soils. After 24 hours, the Drummer soil had adsorbed an average of 83.6% and Hidalgo soil had adsorbed an average of 38.1%, based on nominal initial concentrations, when tested at 1000 µg/L (Table 7).

Linear isotherms were constructed by plotting Cw (concentration of the aqueous solution at equilibrium) vs Cs (mass adsorbed to soil/test soil dry weight) for the four test soils and the activated sludge sample (Figures 7-11). The linear adsorption isotherms had correlation coefficients, which ranged from 0.926 for the Hidalgo soil to 0.977 for the Drummer soil. The values for the adsorption coefficient, K_d, were calculated for all four test soils and the one activated sludge sample (Table 7). The average K_d values ranged from an average of 0.61 mL/g for the Hidalgo soil to an average of 5.63 mL/g for the Drummer soil. The test soils yielded K_d values of 4.25 to 8.86 mL/g for the Drummer soil, 1.82 to 4.26 mL/g for the Keyport soil, 1.19 to 2.84 mL/g for the Cape Fear soil, and 0.41 to 0.83 mL/g for the Hidalgo soil. The Wilmington sludge sample had the highest average K_d value of 22.5 mL/g, with K_d values that ranged from 12.6 to 36.8 mL/g. There was a strong linear correlation (R^2= 0.947) between the fraction of organic carbon and average K_d values (Figure 4).

The adsorption coefficients were corrected for organic carbon and organic material content of the test materials to calculate the soil sorption coefficients K_{oc} and K_{om} (Table 7). The fraction of organic carbon (foc) of the test materials was determined by the Walkley-Black method and the fraction of organic matter was calculated based on the assumption that soil organic matter contains 58% carbon. The average K_{oc} values ranged from 79.0 mL/g in the Hidalgo soil to 148 mL/g in the Cape Fear soil and the average K_{om} values ranged from 45.8 mL/g for the Hidalgo soil to 56.7 mL/g for the Drummer soil. The Wilmington sludge sample had an average K_{oc} value of 36.5 mL/g and average K_{om} value of 21.2 mL/g.

The Freundlich adsorption coefficient (K_F) and the constant (1/n) were determined from the linear form of the Freundlich equation for all test materials. Adsorption isotherms were constructed for all test materials (Table 8, Figures 12-16) and resulted in Freundlich adsorption coefficients, which ranged from 0.59 for the Hidalgo soil to 5.64 $\mu g^{1-1/n} (ml)^{1/n} g^{-1}$ for the Drummer soil. The adsorption coefficients were corrected for organic carbon and organic material content for each test material (Table 8). The K_{Foc} values ranged from 44.2 to 261 $\mu g^{1-1/n} (ml)^{1/n} g^{-1}$ and the K_{Fom} values ranged from 25.6 to 151 $\mu g^{1-1/n} (ml)^{1/n} g^{-1}$ for the Keyport and Cape Fear soils, respectively.

There was a strong inverse relationship (R^2=0.8665) between the fraction of organic carbon (foc) in the Drummer, Keyport and Cape Fear soils and the total desorption of the test compound (Figure 17). The Drummer soil with a foc of 5.76% had an average of 36.0% total desorption while Cape Fear with a foc of 1.24% had an average desorption of 61.7%. The Keyport soil with an intermediate foc of 3.72% desorbed an average of 43.3% of the test compound, a result that is between the Drummer and Cape Fear soil. The amount of test compound recovered in the second stage of desorption is generally comparable to that recovered in the first stage. There was no evidence of "tailing off" which suggests that if further desorptions were performed more of the test compound would be recovered.

The desorption results for the Hidalgo soil and the Wilmington Sludge sample were highly variable and ranged from 41.6 to 141% and 14.9 to 101%, respectively. In addition, the amount of test substance recovered varied between desorption steps 1 and 2 with the Hidalgo and Wilmington Sludge samples while the test substance recovery was more uniform with the other test soils. The total desorption values were inversely related to the test concentration in the Wilmington Sludge samples and decreased from an average of 98.9% at 100 µg/L to 14.9% at the 2500 µg/L test concentration. This behavior was isolated to the sludge materials and remains unexplained in the current study.

The variability seen in both the desorption experiments and the mass balance experiments of this study may be attributed to the difficulty in resuspending the soil pellets. The desorption and extraction phases required two sequential steps that required the mechanical disruption of the pellet to ensure complete suspension. Although there were unquantifiable soils losses with this procedure the solid losses and variability were present in all test materials and did not affect the overall behaviour of the test compound.

5.0 CONCLUSIONS

- The adsorption of the test compound ranged from 36.0 to 83.0% for a soil:solution ratio of 1g/mL for the five test materials.
- The average adsorption coefficient values, K_d, ranged from 0.61 mL/g for the Hidalgo soil to 5.63 mL/g for the Drummer soil.
- The activated sludge sample had the highest average K_d of 22.5 mL/g.
- The Freundlich adsorption coefficients (K_F) ranged from 0.59 $\mu g^{1-1/n} (ml)^{1/n} g^{-1}$ for the Hidalgo soil to 5.64 $\mu g^{1-1/n} (ml)^{1/n} g^{-1}$ for the Drummer soil.
- The two sequential desorption steps, at a soil:solution ratio of 1 g/mL, recovered an average of 36.0 to 90.6% of the adsorbed test compound.

6.0 RETENTION OF RECORDS

For the periods required by GLP guidelines and specific country requirements, study documents and materials will be stored in the archives of DuPont CR&D Environmental & Microbiological Sciences and Engineering (EMSE) and/or Iron Mountain, Wilmington, Delaware USA, including but not limited to:

- study protocol;
- any protocol and/or report amendments or addenda or SOP deviations;
- all raw data;
- one original signed copy of the final report;
- laboratory-specific or site-specific raw data such as personnel files, instrument, equipment, refrigerator, and/or freezer raw data.

Documents and materials are archived according to the principles of Good Laboratory Practice in the organization of the testing facility.

7.0 DISPOSAL OF TEST SUBSTANCE

After issuance of the final report, the remaining test substance will be stored at the DuPont EMSE laboratory until its expiration date and then destroyed by burning, unless other arrangements are made between the facility supplying the test substance and the Test Facility.

8.0 REFERENCES

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3. U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances (OPPTS), Fate, Transport and Transformation Test Guidelines, OPPTS 835.1110 Activated Sludge Sorption Isotherm, EPA 712-C-98-298, January 1998.
4. U.S. Environmental Protection Agency. 1989. Good Laboratory Practice Standards, 40 CFR, Part 160, Final Rule. EPA, Washington, D.C.
5. OECD Principles of Good Laboratory Practice published in ENV/MC/CHEM(98)17, OECD, Paris, France.
6. DuPont Central Research & Development, Environmental and Microbiological Science and Engineering Standard Operating Procedure. Adsorption-Desorption Using a Batch Equilibrium Method: EMSE067-P (June 2002).
7. U.S. Department of Health and Human Services, Food and Drug Administration. Guidance for Industry Bioanalytical Method Validation, May 2001.

TABLE 1
CHEMICAL AND PHYSICAL PROPERTIES OF TEST MATERIALS

Soil	Location	Site Description	Depth	Texture Classification †	Particle Size Analysis 2mm-50µm (Sand) (%)	50-2µm (Silt) (%)	< 2 µm (Clay) (%)
Drummer	Rochelle, Illinois	Fallow	Top 20 cm	Silt Clay Loam	12.0	60.0	28.0
Hidalgo	Donna, Texas	Bedded Fallow	Top 20 cm	Sandy Clay Loam	52.0	20.0	28.0
Wilmington Sludge	Wilmington, Delaware			Sandy Loam	68.0	16.0	16.0
Cape Fear	Cooper River, South Carolina	Grass, walking path	20 - 30 cm	Sandy Loam	68.0	16.0	16.0
Keyport	Newark, Delaware	Fallow	Top 20 cm	Loam	48.0	36.0	16.0

Soil	Bulk Density (g/mL)	pH	foc Walkley-Black (%)	% Moisture (%)
Drummer	1.1	7.6	5.76	5.95
Hidalgo	1.3	7.8	0.77	3.32
Wilmington Sludge	0.4	6.7	61.7	8.14
Cape Fear	1.4	5.4	1.24	0.93
Keyport	1.2	5.5	3.72	1.91

Soil	Cation Exchange Capacity (meq/100g)	Hydrogen (% of CEC)	Potassium (% of CEC)	Magnesium (% of CEC)	Calcium (% of CEC)	Sodium (% of CEC)
Drummer	36.6	0	0.7	12.8	86.2	0.2
Hidalgo	25.7	0	3.8	10.2	83.4	2.6
Wilmington Sludge	10.2	0	3.4	22.7	69.5	4.4
Cape Fear	3.1	12.8	1.7	11.7	71.8	2.1
Keyport	9.5	31.5	2.2	10.5	55.2	0.6

† USDA system (sand: 2mm-50µm, silt: 50-2µm, clay: <2µm)

TABLE 2
DETERMINATION OF TEST SUBSTANCE IN $CaCl_2$ SOLUTIONS (NO SOIL)

Sample Description	Nominal Concentration	Measured Concentration †	Deviation from Expected Value ‡
	µg/L	µg/L	%
CaCl2 Blank	0	15.5	ND$^{\Phi}$
CaCl2 Blank	0	15.6	ND
100-1	100	96.7	-3.30
100-2	100	103	2.90
500-1	500	566	13.1
500-2	500	587	17.4
1000-1	1.00E+03	876	-12.4
1000-2	1.00E+03	972	-2.79
2500-1	2.50E+03	1.86E+03	-25.4
2500-2	2.50E+03	2.03E+03	-18.7

† Limit of Quantification (LOQ) = 10 µg/L

‡ Deviation from Expected Value = (Measured-Nominal)/ Nominal x 100

$^{\Phi}$ Not Determined

TABLE 3
DETERMINATION OF TEST SUBSTANCE IN $CaCL_2$ SOIL EXTRACTS

Sample Description	Measured Concentration	Deviation from Expected Value ‡	Deviation from Mean Control Tube Measured Value Φ
	µg/L	%	%
CaCl2 Blank	< LOQ†		
CaCl2 Blank	< LOQ		
Drummer Soil Blank 1	< LOQ		
Drummer Soil Blank 2	< LOQ		
Cape Fear Soil Blank 1	< LOQ		
Cape Fear Soil Blank 2	< LOQ		
$CaCl_2$ Controls (No Soil)			
100 ppb	104	4.44	
100 ppb	101	0.550	
500 ppb	521	4.20	
500 ppb	572	14.5	
1000 ppb	889	-11.1	
1000 ppb	826	-17.4	
2500 ppb	2.01E+03	-19.4	
2500 ppb	2.51E+03	0.516	
Drummer Soil Extract			
100 ppb	97.3	-2.69	-5.06
100 ppb	99.8	-0.200	-2.63
500 ppb	464	-7.16	-15.1
500 ppb	558	11.5	1.99
1000 ppb	874	-12.6	1.91
1000 ppb	951	-4.89	10.9
2500 ppb	2.22E+03	-11.3	-2.05
2500 ppb	2.19E+03	-12.5	-3.41
Cape Fear Soil Extract			
100 ppb	136	36.4	33.1
100 ppb	118	18.4	15.5
500 ppb	551	10.2	0.805
500 ppb	622	24.3	13.7
1000 ppb	985	-1.46	14.9
1000 ppb	943	-5.72	9.90
2500 ppb	1.97E+03	-21.1	-12.9
2500 ppb	2.34E+03	-6.50	3.26

† LOQ = 10 µg/L

‡ Deviation from Expected Value = (Measured-Nominal)/ Nominal x 100

Φ Deviation from CaCl2 Mean Control Tube Value =
(Measured-Mean CaCl2 Control)/Mean CaCl2 Control x 100

TABLE 4
ADSORPTION TO TEST VESSEL

Sample Description	Measured Concentration	Deviation from Initial Value ‡
	µg/L	%
CaCl2 Blank-1Start	< LOQ†	
CaCl2 Blank-2 Start	< LOQ	
CaCl2 Blank-1 24 hour	< LOQ	NDΦ
CaCl2 Blank-2 24 hour	< LOQ	ND
100 ppb-1 Initial	93.2	
100 ppb-2 Initial	98.1	
100 ppb-1 24hr	90.8	5.07
100 ppb-2 24 hr	98.3	-2.77
2500 ppb-1 Initial	1.64E+03	
2500 ppb-2 Initial	1.62E+03	
2500 ppb-1 24 hr	1.19E+03	26.9
2500 ppb-2 24 hr	1.54E+03	5.58

† LOQ Limit of Quantitation = 10 µg/L

‡ Deviation from Initial Value = (Average Initial Measured Concentration-Measured Concentration at 24hr)/ Average Initial Measured Concentration*100

Φ ND= Not Determined

TABLE 5
ADSORPTION IN PERCENT AS A FUNCTION OF SOIL:SOLUTION RATIO AND EQUILIBRATION TIME

Time, hours	Drummer 1:1	Drummer 1:5	Drummer 1:25	Hidalgo 1:1	Hidalgo 1:5	Hidalgo 1:25
2	65.3	29.9	24.8	21.1	7.84	-0.01
2	72.4	36.6	27.7	9.28	6.38	-1.61
6	75.7	32.9	4.11‡	30.5	16.6	6.84
6	73.3	37.7	25.4	22.5	16.5	18.7
24	83.9	39.3	33.0	42.2	24.4	20.1
24	79.8	51.2	29.3	39.3	24.2	25.9
72	78.8	48.1	23.4	27.7	29.7	12.3
72	ND†	ND	33.3	35.8	23.9	3.17

† ND = Not Determined; Sample was lost
‡ Result was an outlier and not reported in range of adsorption values

TABLE 6
MASS BALANCE CALCULATIONS OF DRUMMER AND HIDALGO SOILS PERFORMED AT 1:1 SOIL SOLUTION RATIO AFTER 24 MIXING

Sample Description	Soil Dry Wt	Measured Concentration of Aqueous Phase at Equilibrium (19-Dec-02)	Test Substance in Aqueous Phase at Equilibrium	Measured Concentration of MEOH Extraction 1 (01-Feb -03)	Test Substance in MEOH Extraction 1	Measured Concentration of MEOH Extraction 2 (01-Feb-03)	Test Substance in MEOH Extraction 2	Test Substance in Void Volume	Total Test Compound Recovered	Mass Balance
	g	µg/L	µg	µg/L	µg	µg/L	µg	µg	µg	%
MEOH Blank				<LOQ†		<LOQ	<LOQ	<LOQ	<LOQ	NC‡
MEOH Blank-2				<LOQ		<LOQ	<LOQ	<LOQ	<LOQ	NC
Control		1.14E+03	23.2	12.7	0.245	<LOQ	<LOQ	<LOQ	23.5	119
Control		972	19.6	11.4	0.223	<LOQ	<LOQ	<LOQ	19.8	100
Drummer Soil Blank 1	19.3	<LOQ	<LOQ	<LOQ		<LOQ	<LOQ	<LOQ	<LOQ	NC
Drummer Soil Blank 2	18.9	<LOQ	<LOQ	<LOQ		<LOQ	<LOQ	<LOQ	<LOQ	NC
Drummer 1000 ppb Test 1	19.1	224	2.92	323	6.69	146	2.83	1.11	13.6	68.6
Hidalgo Blank 1	19.8	<LOQ	<LOQ	<LOQ		<LOQ	<LOQ	<LOQ	<LOQ	NC
Hidalgo Blank 2	19.2	<LOQ	<LOQ	<LOQ		<LOQ	<LOQ	<LOQ	<LOQ	NC
Hidalgo 1000 ppb Test 1	19.6	763	10.4	262	5.45	72.3	1.41	0.451	17.7	89.8
Hidalgo 1000 ppb Test 2	19.5	678	9.29	218	4.52	70.0	1.38	0.430	15.6	79.0

† LOQ Limit of Quantitation = 10 µg/L

‡ NC = Not Calculated, Mass Balance could not be determined because samples <LOQ

TABLE 7
DEFINITIVE ADSORPTION STUDY; PERCENT ADSORPTION AND LINEAR ADSORPTION ISOTHERM PARAMETERS

Sample ID	Test Soil	% Adsorption †	Cs	Cw	log Cs	log Cw	Kd	Koc	Kom
			µg/g	µg/L	µg/g	µg/L	mL/g	mL/g	mL/g
Soil 1 100 ppb	Drummer	82.2	0.08	16.4	-1.07	1.21	5.17	89.7	52.0
Soil 1 100 ppb	Drummer	79.3	0.08	18.9	-1.09	1.28	4.25	73.8	42.8
Soil 1 500 ppb	Drummer	82.7	0.39	73.4	-0.41	1.87	5.35	92.9	53.9
Soil 1 500 ppb	Drummer	88.9	0.45	50.3	-0.35	1.70	8.86	154	89.2
Soil 1 1000 ppb	Drummer	82.0	0.83	164	-0.08	2.22	5.04	87.6	50.8
Soil 1 1000 ppb	Drummer	85.3	0.86	135	-0.07	2.13	6.39	111	64.3
Soil 1 2500 ppb	Drummer	82.9	2.01	374	0.30	2.57	5.38	93.5	54.2
Soil 1 2500 ppb	Drummer	80.6	1.95	425	0.29	2.63	4.60	79.8	46.3
	Mean	83.0					5.63	97.7	56.7
Soil 2 100 ppb	Hidalgo	33.4	0.03	60.4	-1.49	1.78	0.53	68.9	40.0
Soil 2 100 ppb	Hidalgo	29.5	0.03	64.3	-1.54	1.81	0.45	58.2	33.8
Soil 2 500 ppb	Hidalgo	41.2	0.20	267	-0.70	2.43	0.75	97.1	56.3
Soil 2 500 ppb	Hidalgo	43.8	0.21	253	-0.68	2.40	0.83	108	62.6
Soil 2 1000 ppb	Hidalgo	39.7	0.38	545	-0.42	2.74	0.70	90.4	52.5
Soil 2 1000 ppb	Hidalgo	36.6	0.35	574	-0.46	2.76	0.61	79.0	45.8
Soil 2 2500 ppb	Hidalgo	27.8	0.65	1.60E+03	-0.18	3.21	0.41	53.0	30.8
Soil 2 2500 ppb	Hidalgo	36.0	0.84	1.42E+03	-0.07	3.15	0.59	77.2	44.8
	Mean	36.0					0.61	79.0	45.8
Soil 3 100 ppb	Wilmington Sludge	69.5	0.35	28.1	-0.45	1.45	12.6	20.5	11.9
Soil 3 100 ppb	Wilmington Sludge	70.8	0.37	26.8	-0.44	1.43	13.7	22.2	12.9
Soil 3 500 ppb	Wilmington Sludge	74.6	1.95	119	0.29	2.08	16.3	26.5	15.4
Soil 3 500 ppb	Wilmington Sludge	77.7	1.91	106	0.28	2.02	18.1	29.3	17.0
Soil 3 1000 ppb	Wilmington Sludge	83.4	4.40	155	0.64	2.19	28.3	45.9	26.7
Soil 3 1000 ppb	Wilmington Sludge	82.7	4.27	161	0.63	2.21	26.4	42.9	24.9
Soil 3 2500 ppb	Wilmington Sludge	87.3	10.7	291	1.03	2.46	36.8	59.6	34.6
Soil 3 2500 ppb	Wilmington Sludge	83.4	10.9	390	1.04	2.59	27.9	45.3	26.3
	Mean	78.7					22.53	36.5	21.2
Soil 4 100 ppb	Cape Fear	64.8	0.06	32.5	-1.22	1.51	1.87	151	87.5
Soil 4 100 ppb	Cape Fear	63.3	0.06	33.7	-1.23	1.53	1.73	140	80.9
Soil 4 500 ppb	Cape Fear	70.8	0.33	134	-0.49	2.13	2.43	196	114
Soil 4 500 ppb	Cape Fear	73.7	0.34	121	-0.46	2.08	2.84	229	133
Soil 4 1000 ppb	Cape Fear	60.3	0.52	348	-0.28	2.54	1.51	121	70.4
Soil 4 1000 ppb	Cape Fear	59.3	0.55	372	-0.26	2.57	1.48	119	69.1
Soil 4 2500 ppb	Cape Fear	54.1	1.22	1.02E+03	0.09	3.01	1.19	95.9	55.6
Soil 4 2500 ppb	Cape Fear	61.4	1.36	847	0.13	2.93	1.61	130	75.3
	Mean	63.5					1.83	147.8	85.7
Soil 5 100 ppb	Keyport	64.5	0.06	33.7	-1.21	1.53	1.82	48.9	28.4
Soil 5 100 ppb	Keyport	68.9	0.07	28.7	-1.19	1.46	2.27	61.1	35.4
Soil 5 500 ppb	Keyport	77.2	0.37	107	-0.43	2.03	3.48	93.4	54.2
Soil 5 500 ppb	Keyport	73.7	0.30	105	-0.52	2.02	2.90	77.9	45.2
Soil 5 1000 ppb	Keyport	76.7	0.73	215	-0.14	2.33	3.39	91.0	52.8
Soil 5 1000 ppb	Keyport	80.8	0.75	175	-0.13	2.24	4.26	115	66.5
Soil 5 2500 ppb	Keyport	75.8	1.74	550	0.24	2.74	3.17	85.1	49.4
Soil 5 2500 ppb	Keyport	70.6	1.64	655	0.21	2.82	2.50	67.2	39.0
	Mean	63.1					2.85	90.7	52.6

† Adsorption determined on 1:1 (soils) and 1:5 (sludge) soil:solution ratio 24 hr equilibration time

TABLE 8
DEFINITIVE ADSORPTION STUDY; FREUNDLICH ADSORPTION ISOTHERM PARAMETERS

Test Soil	Slope (1/n)	Intercept ($\log K_F$)	R^2	K_F ($\mu g^{1-1/n} (mL)^{1/n} g^{-1}$)	K_{Foc} ($\mu g^{1-1/n} (mL)^{1/n} g^{-1}$)	K_{Fom} ($\mu g^{1-1/n} (mL)^{1/n} g^{-1}$)
Drummer	0.994	-2.25	0.97	5.64	98.0	56.8
Hidalgo	1.00	-3.23	0.96	0.59	76.2	44.2
Cape Fear	0.885	-2.49	0.96	3.23	261	151
Keyport	1.11	-2.78	0.97	1.64	44.2	25.6
Wilmington Sludge	1.36	-2.41	0.98	3.90	6.3	3.7

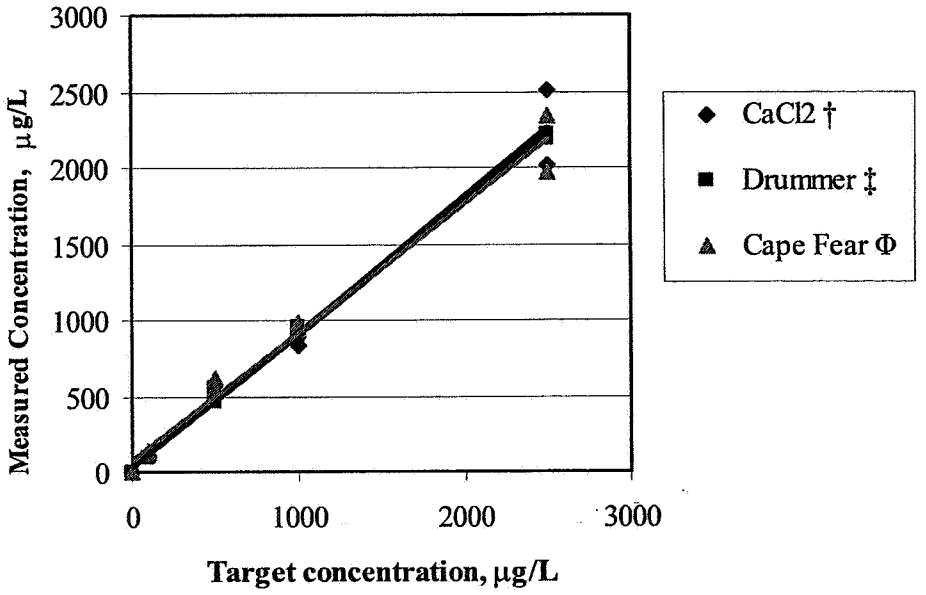
TABLE 9
DESORPTION OF TEST SUBSTANCE FROM TEST SOILS

Sample Description	Measured Concentration Desorp 1 Soln	Cpd Recovered in Desorp 1	Desorbed Stage 1	Measured Concentration Desorp 2 Soln	Cpd Recovered in Desorp 2	Desorbed Stage 2	Total Cpd Recovered	Desorption Total
	µg/L	µg	%	µg/L	µg	%	µg	%
Drummer 100 ppb	13.3	0.26	16.0	9.53	0.27	16.8	0.53	32.9
Drummer 100 ppb	12.9	0.24	15.4	11.6	0.33	21.4	0.56	36.7
Drummer 500 ppb	73.9	1.39	18.9	53.8	1.51	20.4	2.90	39.3
Drummer 500 ppb	93.0	1.77	20.7	48.0	1.33	15.6	3.09	36.3
Drummer 1000 ppb	211.5	3.97	25.2	113	3.09	19.6	7.06	44.7
Drummer 1000 ppb	166.8	3.17	19.2	75.8	2.11	12.8	5.27	32.0
Drummer 2500 ppb	397.8	7.68	20.0	182	5.10	13.3	12.8	33.3
Drummer 2500 ppb	367.4	6.96	18.7	190	5.27	14.2	12.2	32.9
Hidalgo 100 ppb	28.3	0.53	85.5	7.99	0.22	35.3	0.75	121
Hidalgo 100 ppb	29.7	0.57	102.2	7.86	0.21	38.8	0.78	141
Hidalgo 500 ppb	124.3	2.33	60.6	45.1	1.24	32.3	3.57	92.9
Hidalgo 500 ppb	125.1	2.31	57.0	43.3	1.18	29.1	3.49	86.0
Hidalgo 1000 ppb	148.9	2.79	37.7	89.6	2.47	33.4	5.26	71.2
Hidalgo 1000 ppb	138.3	2.62	38.5	102	2.81	41.2	5.43	79.7
Hidalgo 2500 ppb	426.4	7.99	62.4	137	3.74	29.2	11.7	91.6
Hidago 2500 ppb	158.5	3.02	18.4	141	3.84	23.5	6.86	41.9
Wilmington Sludge 100 ppb	52.7	1.27	78.1	11.4	0.37	22.6	1.64	101
Wilmington Sludge 100 ppb	49.4	1.19	72.3	12.6	0.40	24.5	1.60	96.8
Wilmington Sludge 500 ppb	142.2	3.45	38.8	53.2	1.71	19.2	5.16	58.0
Wilmington Sludge 500 ppb	139.1	3.25	35.0	29.3	0.96	10.4	4.21	45.4†
Wilmington Sludge 1000 ppb	112.9	2.70	13.6	70.7	2.24	11.3	4.94	25.0
Wilmington Sludge 1000 ppb	121.5	2.90	14.9	45.9	1.48	7.60	4.39	22.5
Wilmington Sludge 2500 ppb	129.7	4.03	8.0	66.8	2.17	4.30	6.20	12.3‡
Wilmington Sludge 2500 ppb	174.7	4.25	8.6	96.8	3.12	6.33	7.37	14.9
Cape Fear 100 ppb	18.4	0.36	29.8	10.2	0.28	23.2	0.64	53.0
Cape Fear 100 ppb	20.8	0.40	34.1	10.4	0.28	23.9	0.68	57.9
Cape Fear 500 ppb	162.1	3.04	46.5	70.6	1.93	29.6	4.97	76.1
Cape Fear 500 ppb	113.3	2.16	31.7	64.6	1.76	25.8	3.92	57.5
Cape Fear 1000 ppb	173.9	3.26	31.0	161	4.45	42.2	7.71	73.2
Cape Fear 1000 ppb	169.4	3.23	29.7	145	3.99	36.7	7.22	66.5
Cape Fear 2500 ppb	439.0	8.19	33.8	221	6.09	25.1	14.3	58.9
Cape Fear 2500 ppb	447.2	8.25	30.5	197	5.41	20.0	13.7	50.5
Keyport 100 ppb	23.5	0.44	37.1	7.66	0.21	17.5	0.65	54.7
Keyport 100 ppb	22.0	0.41	31.8	10.2	0.29	22.4	0.69	54.2
Keyport 500 ppb	35.5	0.66	9.1	61.7	1.71	23.6	2.37	32.7
Keyport 500 ppb	30.5	0.58	9.8	68.0	1.92	32.4	2.50	42.2
Keyport 1000 ppb	162.8	3.10	21.8	152	4.28	30.1	7.38	51.9
Keyport 1000 ppb	100.5	1.90	12.8	143	3.97	26.7	5.87	39.5
Keyport 2500 ppb	227.5	4.15	11.8	221	6.28	17.9	10.4	29.8†
Keyport 2500 ppb	412.2	7.76	24.3	201	5.64	17.7	13.4	41.9

† Soil tube spilled during processing; not included in average calculations

‡ Adsorption supernatant added to soil tube during processing; not included

FIGURE 1
ANALYTICAL METHOD VALIDATION OF $CaCl_2$ CONTROLS (NO SOIL) AND EXTRACTS FROM DRUMMER AND CAPE FEAR SOILS



† $y = 0.8928x + 23.403$, $R^2 = 0.978$

‡ $y = 0.8749x + 27.432$, $R^2 = 0.998$

Φ $y = 0.8463x + 73.34$, $R^2 = 0.983$

FIGURE 2
ADSORPTION OF TEST SUBSTANCE AS A FUNCTION OF SOIL:SOLUTION RATIO AND EQUILIBRATION TIME WITH DRUMMER SOIL

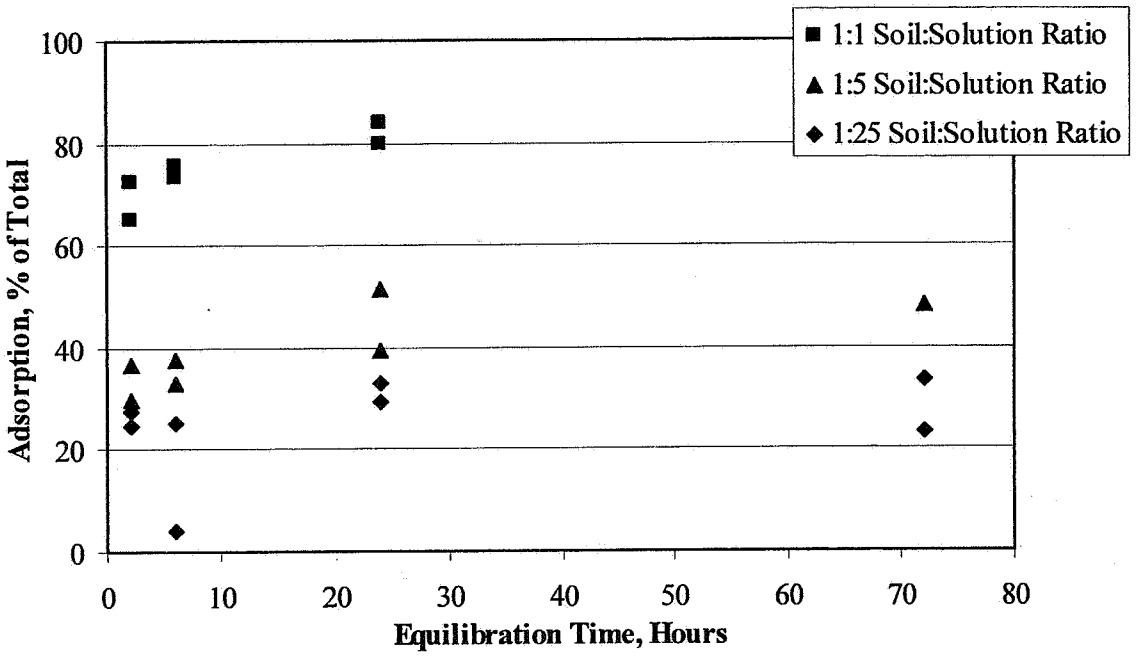


FIGURE 3
ADSORPTION OF TEST SUBSTANCE AS A FUNCTION OF SOIL:SOLUTION RATIO AND EQUILIBRATION TIME WITH HIDALGO SOIL

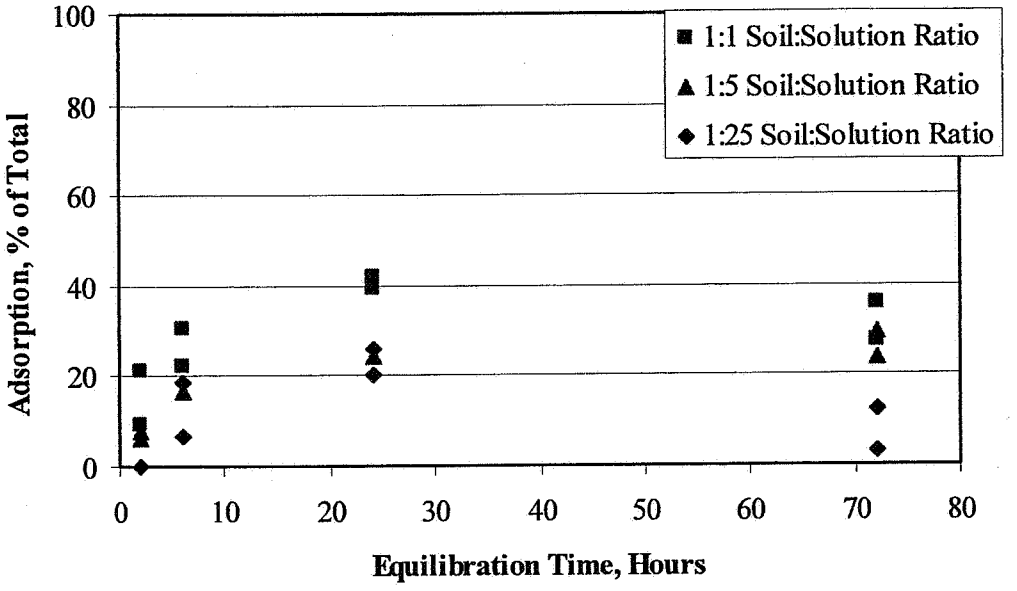


FIGURE 4
AVERAGE K_D VS FRACTION OF ORGANIC CARBON FOR DRUMMER, HIDALGO, CAPE FEAR AND KEYPORT SOILS

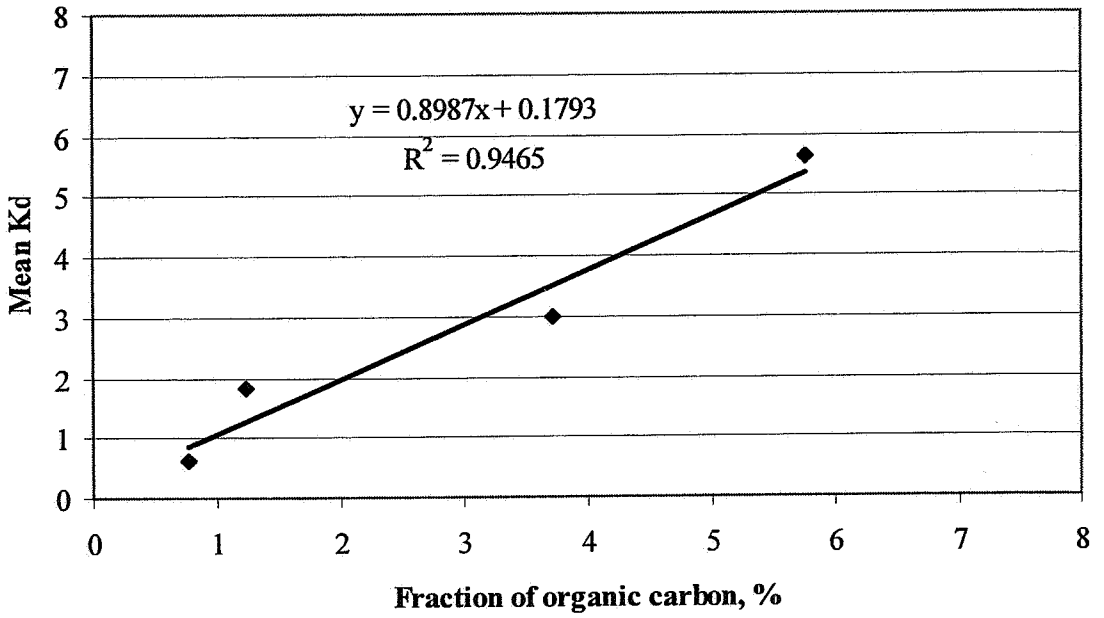


FIGURE 5
AVERAGE K_{OM} VS FRACTION OF ORGANIC CARBON FOR DRUMMER, HIDALGO, CAPE FEAR AND KEYPORT SOILS

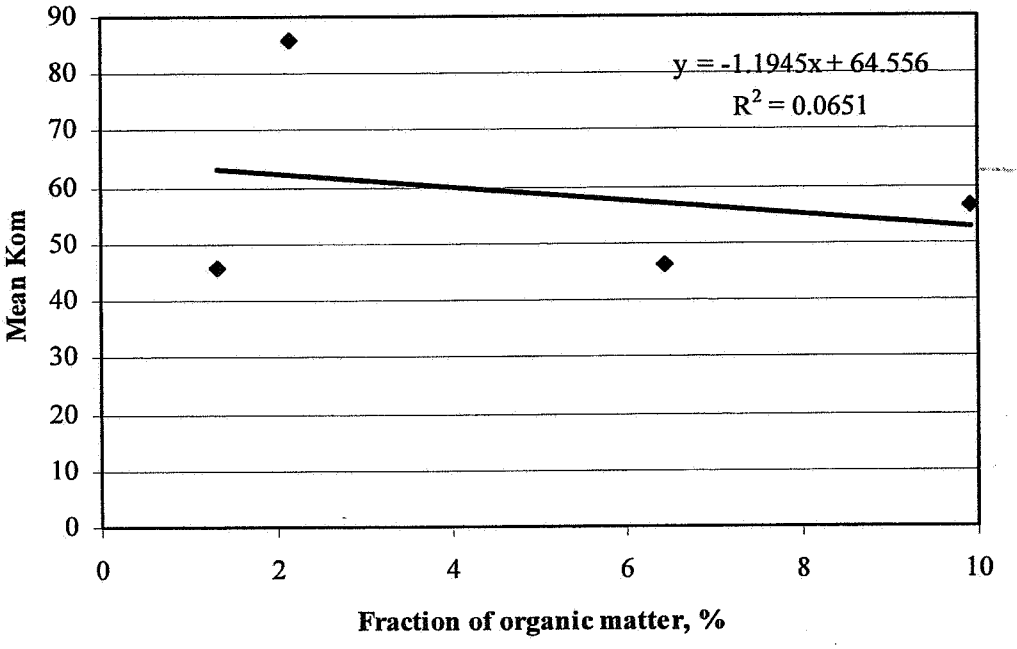


FIGURE 6
AVERAGE K_{OC} VS FRACTION OF ORGANIC CARBON FOR DRUMMER, HIDALGO, CAPE FEAR AND KEYPORT SOILS

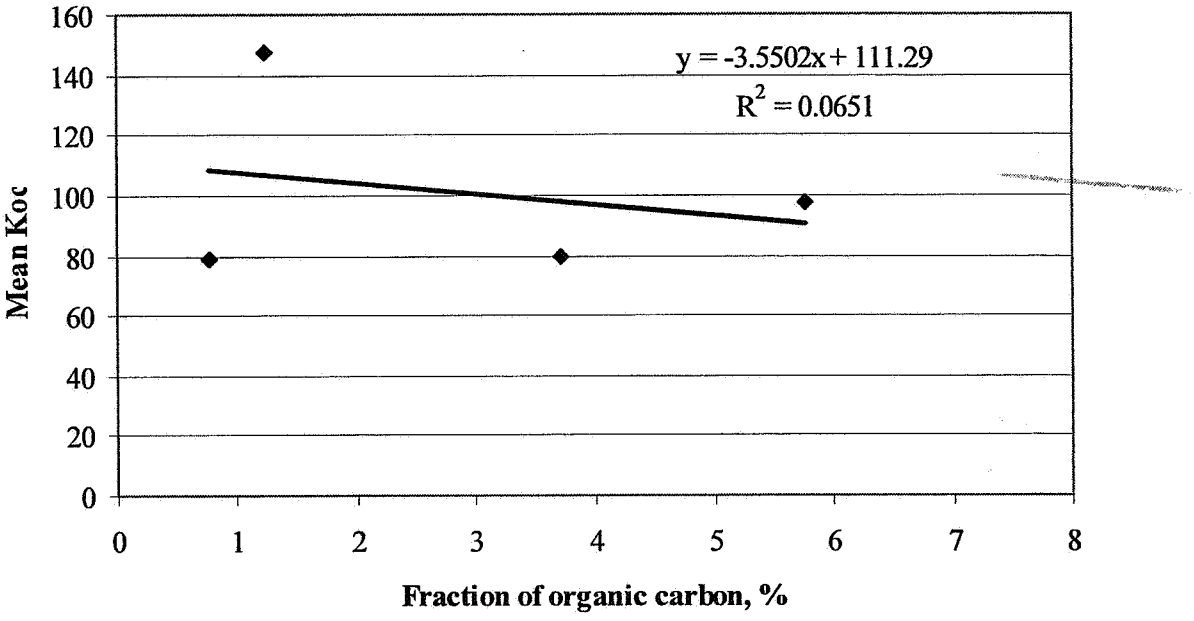


FIGURE 7
LINEAR ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN DRUMMER SOIL

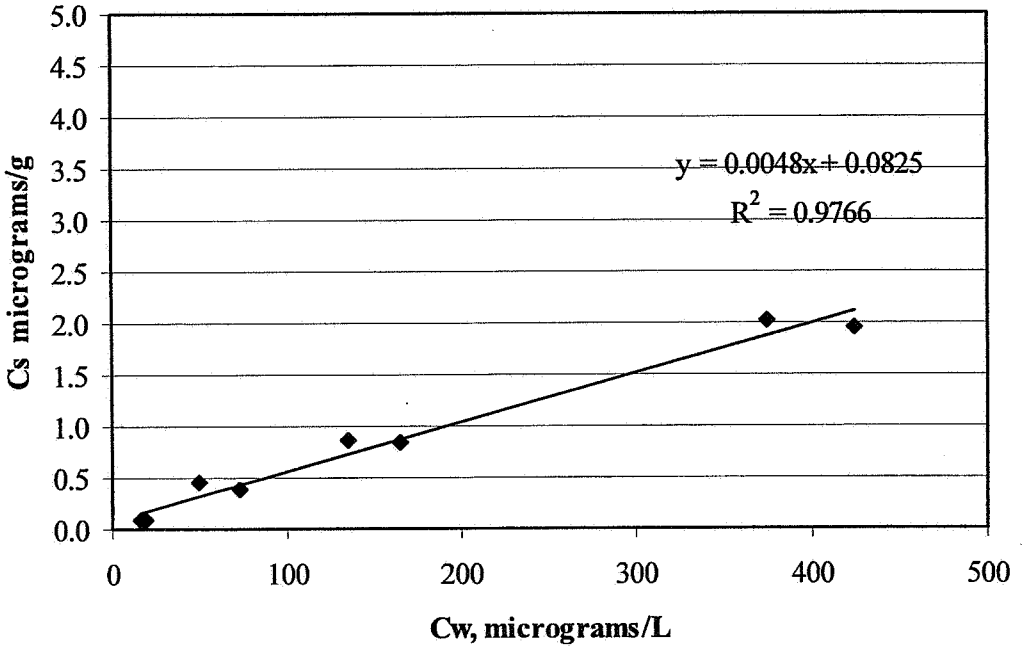


FIGURE 8
LINEAR ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN HIDALGO SOIL

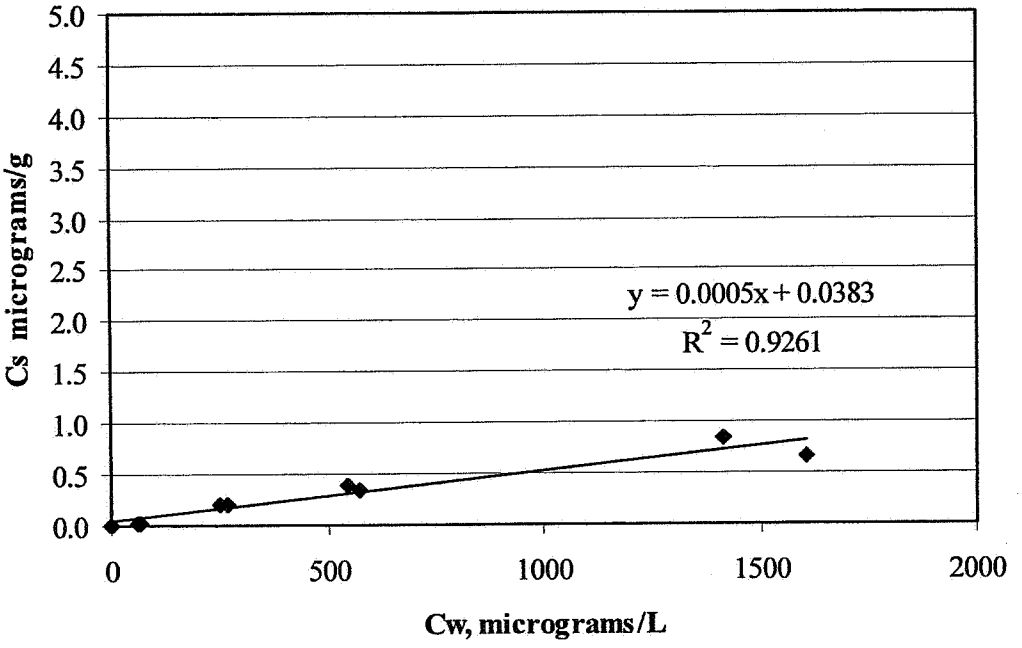


FIGURE 9
LINEAR ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN CAPE FEAR SOIL

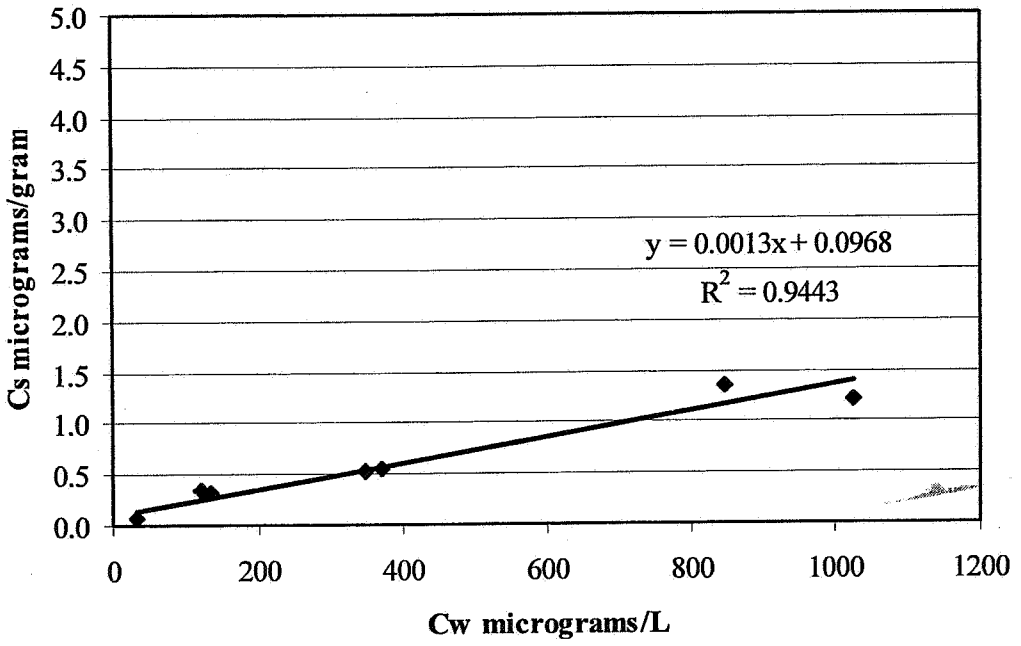


FIGURE 10
LINEAR ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN KEYPORT SOIL

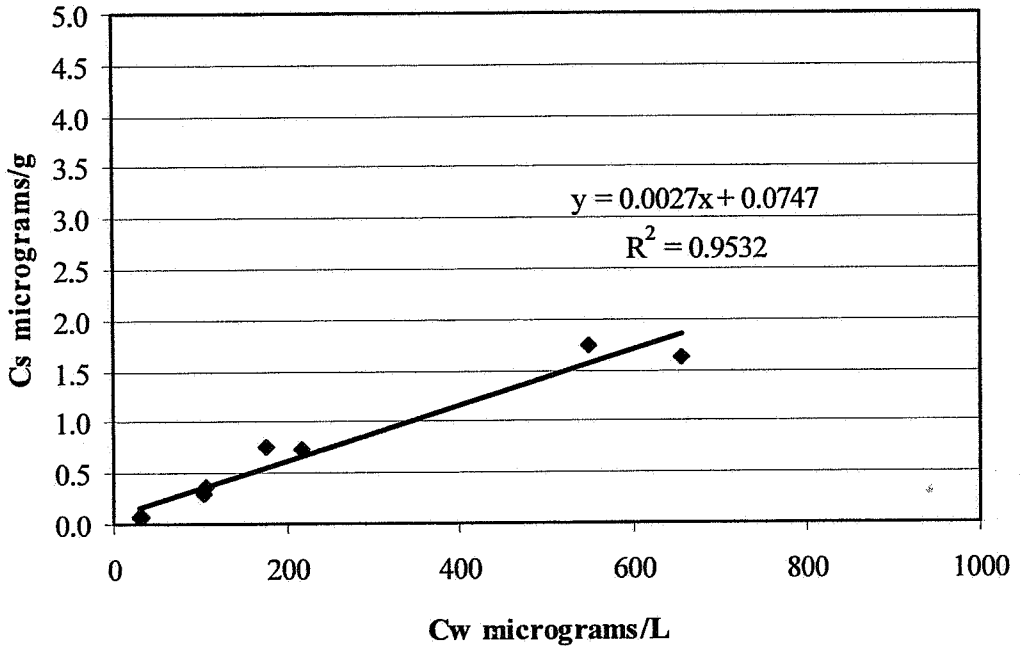


FIGURE 11
LINEAR ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN WILMINGTON SLUDGE

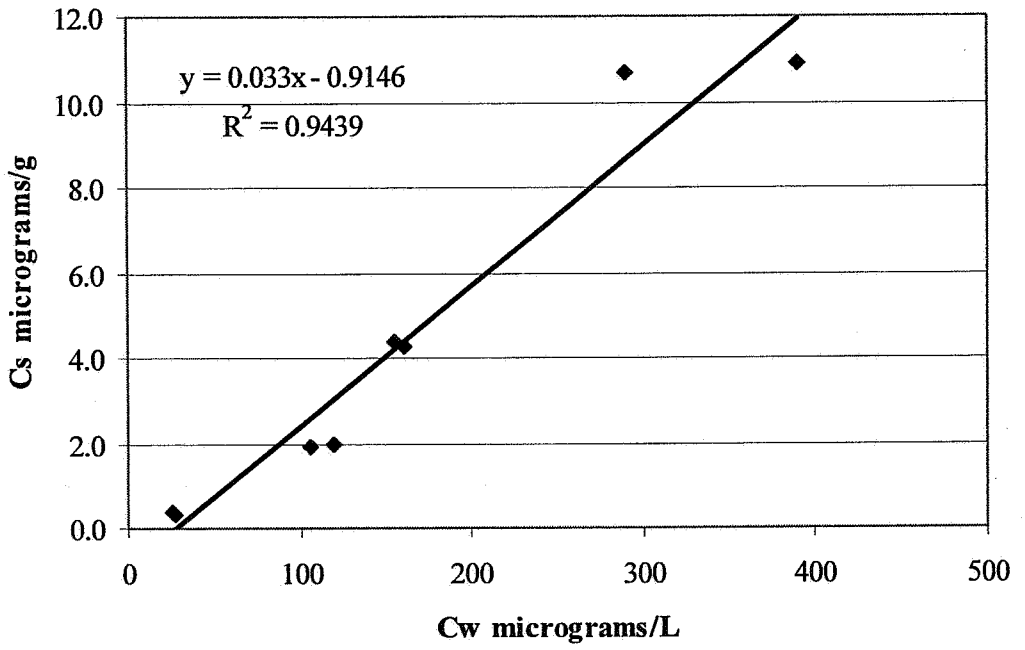


FIGURE 12
FREUNDLICH ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN DRUMMER SOIL

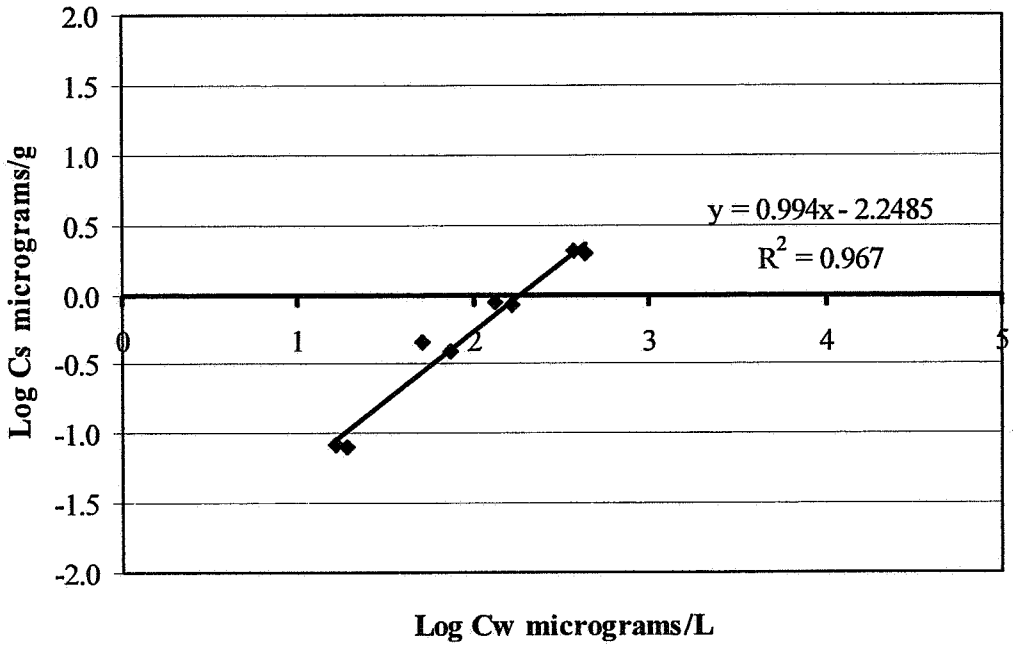


FIGURE 13
FREUNDLICH ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN HIDALGO SOIL

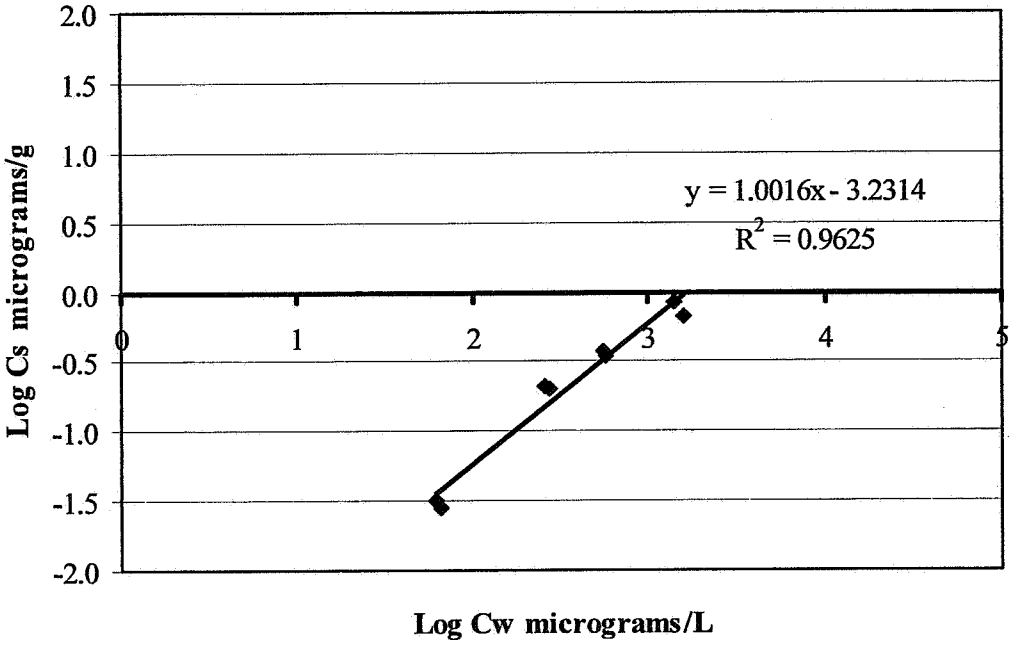


FIGURE 14
FREUNDLICH ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN CAPE FEAR SOIL

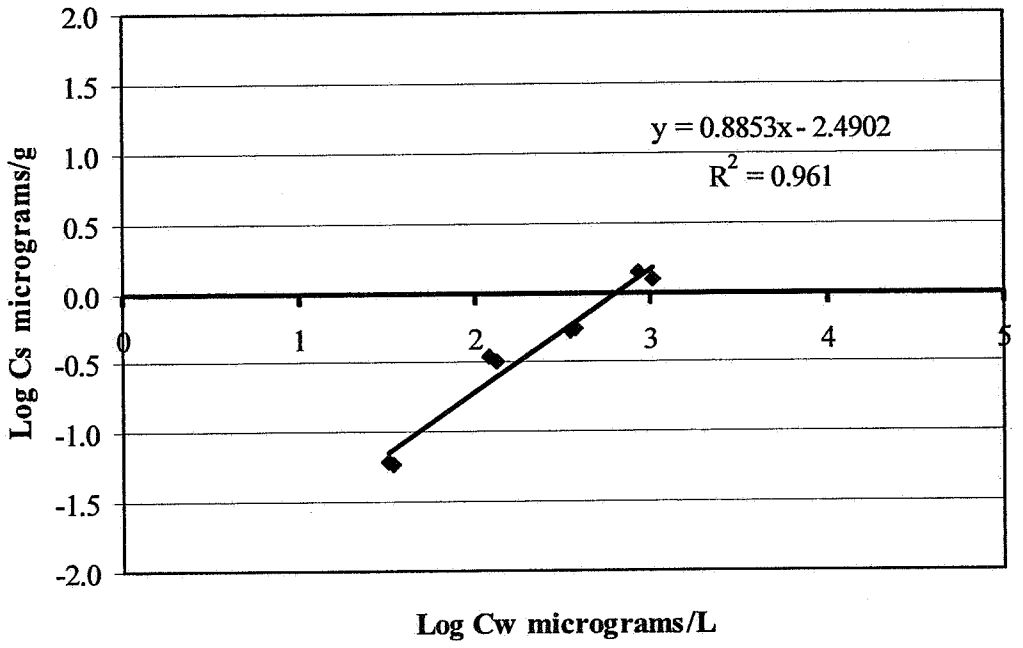


FIGURE 15
FREUNDLICH ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN KEYPORT SOIL

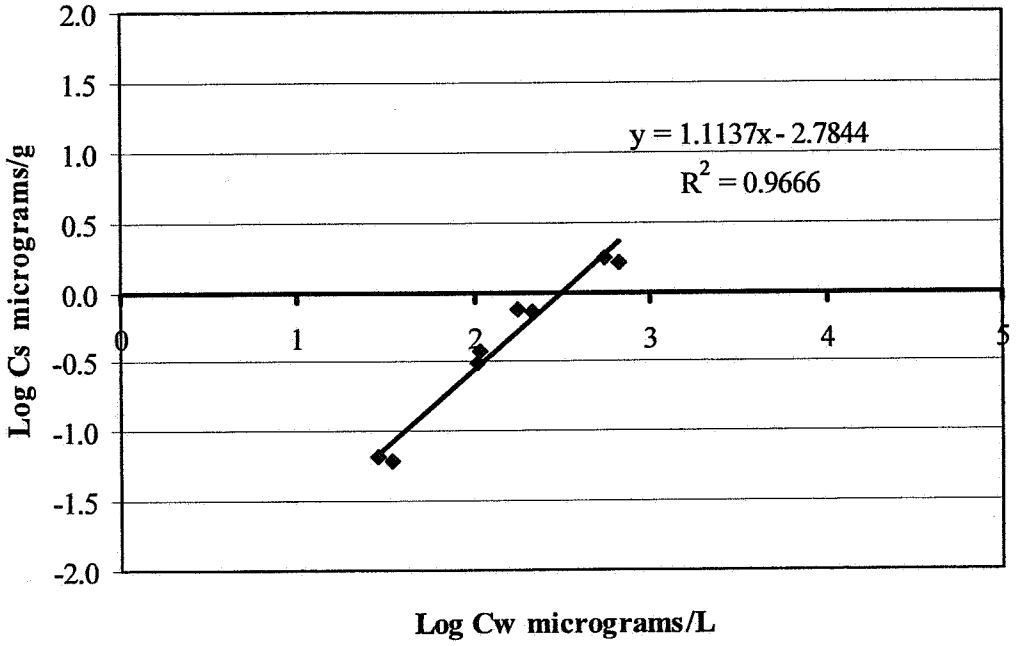


FIGURE 16
FREUNDLICH ADSORPTION ISOTHERM OF THE TEST SUBSTANCE IN WILMINGTON SLUDGE

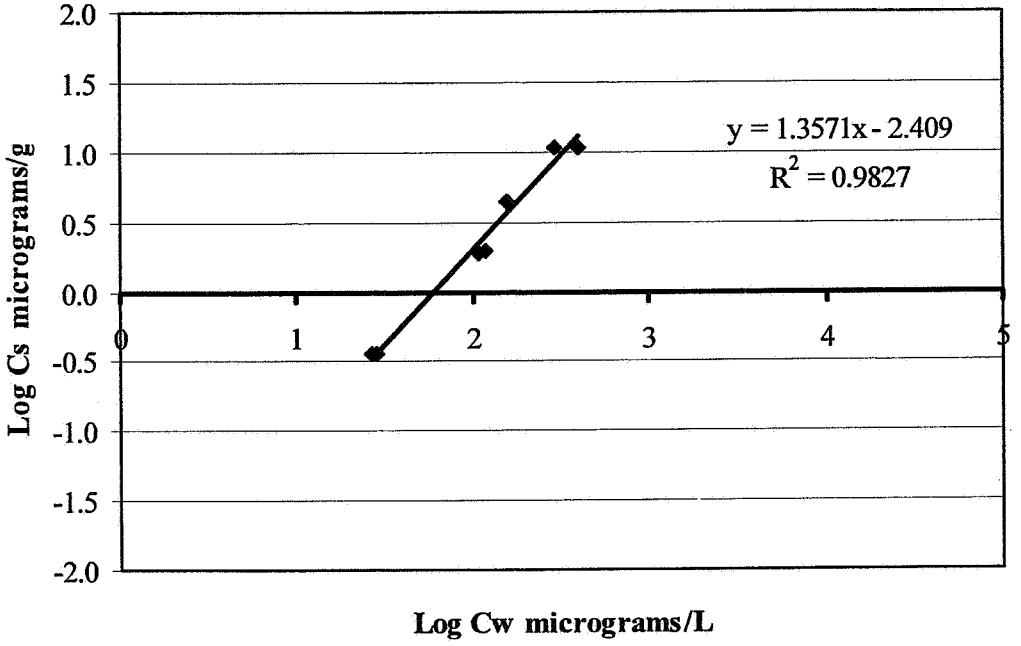
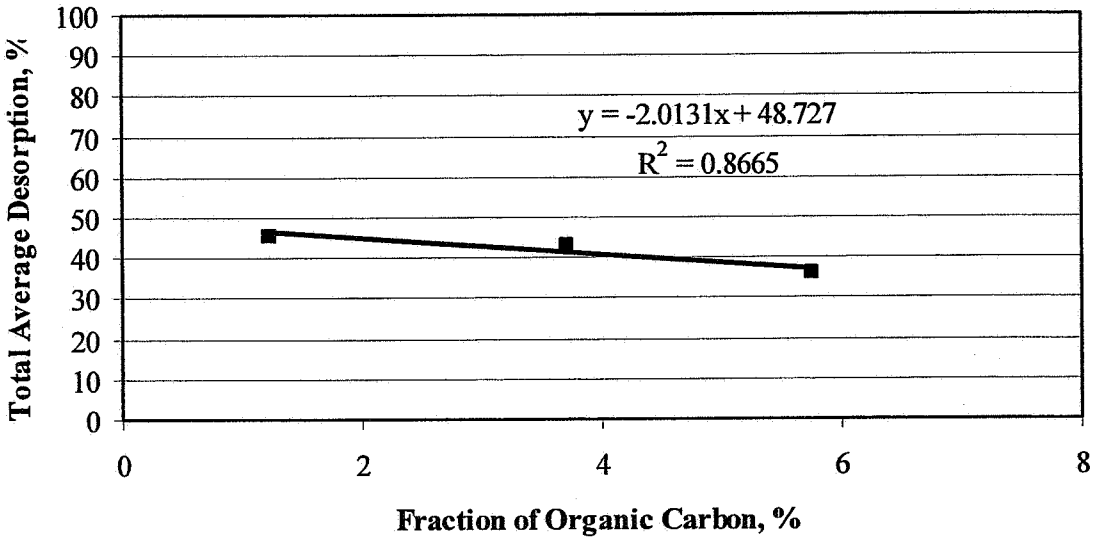


FIGURE 17
TOTAL DESORPTION VS FRACTION OF ORGANIC CARBON FOR DRUMMER, KEYPORT AND CAPE FEAR SOILS



APPENDIX 1
AMMONIUM PERFLUOROOCTANOATE ANALYTICAL METHOD

Operating Conditions

The LC column is equilibrated with 95% Solvent A (5% Methanol in 2mM Ammonium Acetate) and Solvent B (100% Methanol). The method utilizes a linear gradient with the following conditions:

Time (min)	Solvent B %	Flow (ml/min)
0	5	0.25
1	5	0.25
6	100	0.25
8	100	0.25
9	5	0.25
13	5	0.25

The flow is diverted to waste between 0-3 minutes and directed to the mass spectrometer between 3 to 12.5 minutes. The injection volume is 25 microliters.

The mass spectrometer is optimized for the molecular anion at 413 m/z with the Capillary Voltage set at 3.0kV, Cone Voltage set at 10V, the source block temperature is set at 150°C and desolvation temperature is set at 200°C. The collision cell is maintained at a pressure of argon 1.0 E-3 and nitrogen flow is maintained at 100 psi. The mass spectrometer monitors the transition 423 > 369.

APPENDIX 2
CERTIFICATE OF ANALYSIS OF TEST SUBSTANCE

Sigma-Aldrich Certificate of Analysis

Fluka

Certificate of Analysis

TEST	LOT (421207/1) RESULTS
Product Name	Pentadecafluorooctanoic acid ammonium salt
Product Number	77262
CAS Number	3825261
Formula	$C_8H_4F_{15}NO_2$
Formula Weight	431.1
TITRATION (NT) HCLO4 0.1N	100.0 %
APPEARANCE	WHITE POWDER
SOLUBILITY (COLOUR)	COLOURLESS
SOLUBILITY (TURBIDITY)	CLEAR (<3.5 TE(F))
SOLUBILITY (METHOD)	1 G IN 10 ML H2O
WATER	< 0.1 %
RESIDUE ON IGNITION	< 0.1 %
INFRARED SPECTRUM	CORRESPONDS
DATE OF QC-RELEASE	24/JAN/01

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Dr. G. van Look