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Study Title

ADSORPTION-DESORPTION SCREENING STUDIES OF AMMONIUM PERFLUOROOCTANOATE

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Performing Laboratory

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CCER
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GENERAL INFORMATION

Material Tested: Ammonium perfluorooctanoate

Synonyms/Codes: APFO, C-8, FC-143

DuPont Notebook No.: E98312

Sponsor: Robert Pinchot
E. I. du Pont de Nemours and Company
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ADSORPTION-DESORPTION SCREENING STUDIES OF AMMONIUM PERFLUOROOCTANOATE

SUMMARY

Five of nine materials appeared to adsorb a significant amount (greater than 25% of APFO added) at one or more concentrations of APFO. For four of the five materials to which APFO significantly adsorbed, most of the adsorbed APFO appeared not to desorb after 2 washings at one or more concentrations of added APFO.

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INTRODUCTION AND PURPOSE

APFO adsorption/desorption screening studies were performed on several test materials, including two clays, a washed sand, peat moss, and an agricultural soil from Delaware, USA. The adsorption/desorption screening studies were also performed using two surface soils and two sediments from the Ohio River collected in the vicinity of the DuPont Washington Works plant near Parkersburg, West Virginia.

The adsorption/desorption procedure used in this study was adapted from a method developed by the Office of Prevention, Pesticides and Toxic Substances (OPPTS), United States Environmental Protection Agency for use in the testing of pesticides and toxic substances, and the development of test data (1). Our objectives were to develop an adsorption/desorption protocol and analytical procedure for APFO. As part of this objective, we screened a variety of test materials for their APFO adsorption/desorption characteristics.

MATERIALS AND METHODS

Test Materials

The Kaolin (KGa-2) and Montmorillonite (SAz-1) are Clay Mineral Society "Source Clays" and were obtained from the curator of the sample collection in the Department of Geology at the University of Missouri, Columbia. Additional information on these and other Source Clays has been published (2). The Quikrete® All-Purpose sand and Scotts® sphagnum peat moss were purchased locally at a builders' supply store (Home Depot®). The Sassafras soil is a surface (0 to 15 cm) soil collected from an agricultural field in Delaware, USA. The Garden Area soil and East Wood soil were surface soils collected from the DuPont Washington Works plant. The Upstream sediment was obtained from the bank of the Ohio River upstream of the DuPont Washington Works NPDES permitted outfall, and the Downstream sediment was from downstream of the outfall. The two soil and sediment sample from the vicinity Washington Works were collected in the fall of 1999.

Physical and chemical properties of the less than 2-mm size fractions of the soils, sediments, clays, sand, and peat moss used in this study are listed in Tables 1 and 2. Except for the clays, all samples were screened through a 2-mm (10 mesh) stainless steel sieve in preparation for the absorption/desorption screening test. Furthermore, the sand was washed using DI water through 2-mm and 50-um stainless steel sieves. Material retained on the 50 um sieve was used in the study. The sand, soils, and sediments used in the studies were air-dried prior to use in the studies. Data calculations, however, were based on oven-dry weights of the samples. Oven-dry weights were determined after drying a subsample of material in an oven at 105°C for a minimum of 24 h.

The pH of the sample were determined in a 1:1 test material to water. Percent organic matter was determined using the loss on ignition method.

Screening Test: Adsorption Studies

The adsorption test was performed in duplicate on each material. A blank containing 0.01M $CaCl_2$ solution with test materials and no APFO and a single control at each APFO concentration but no material were also included. Each material was equilibrated with the aqueous phase of a solution of the test chemical at 5.0, 0.5 and 0.05 mg L^{-1}. prepared in 0.01M $CaCl_2$

Sterile 50 mL Corning polypropylene centrifuge tubes were used as the test vessels. One part air-dried material (4.0 g) was weighed and 5 part test solution (20 mL) was decanted into a centrifuge tube, except the control tube. The centrifuge tubes were secured on an end-over-end mixer and agitated at about 30 rpm for 24 hours. Samples were centrifuged for 20 minutes using a RT6000B Sorvall centrifuge at 4000 x g and then filtered through a 0.2 µm nylon syringe filter into a new centrifuge tube. The volume of aqueous supernatant was measured and refrigerated at about 5°C until analyzed for the parent compound using an LC-MS. The blank and the control tubes were subjected to the same steps as the test systems, including filtering.

Screening Test: Desorption Studies

To each solid phase (pellet) was added a fresh volume of 0.01M $CaCl_2$ solution without the test chemical equal to that added in the adsorption test, 20 mL. The sample was mixed, centrifuged, filtered, stored, and analyses as was done in the adsorption studies. This desorption step was repeated a second time, resulting in two washings that were analyzed separately.

Calculations

Data calculations included:

1. The percent of APFO adsorbed, A:
   $A = (G - Ce \times Vo)/G \times 100 = x/G \times 100$
2. The percent of APFO which is desorbed, D:
   $D = [(C1 + C2)V - (Vo - V)Ce]/x \times 100$
3. The percent of APFO which is not desorbed, R:
   $R = [G - (Ce + C1 + C2)V]/x \times 100$
4. The adsorption coefficient, K':
   $K' = (x/m)/Ce$
5. The adsorption coefficient calculated as a function of the organic carbon content of the test material, K'oc:
   $K'oc = K\ (100/\text{percent organic carbon})$

Where:

1. m = dry weight of soil employed (g)
2. Ce = concentration of APFO remaining in solution (V) in the adsorption step (µg L^{-1})
3. C1 = concentration of APFO in solution in the first wash (µg L^{-1})
4. C2 = concentration of APFO in solution in the second wash (µg L^{-1})
5. Vo = original volume of solution employed (mL)
6. V = volume of solution obtained after the adsorption step (mL)
7. G = quantity of material recovered from the soilless control (µg)

RESULTS AND DISCUSSION

Of the nine materials tested, five of them (peat moss, Upstream sediment, East Wood soil, Garden Area soil, and Kaolin Clay) exhibited significant adsorption (greater than 25% of APFO added) at one or more of the added concentrations of APFO. Peat moss alone, however, adsorbed a significant amount at all three concentrations of added APFO; 50, 500, and 5,000 µg APFO/L. Kaolin clay adsorbed a significant amount of APFO at 500 and 5,000 µg APFO/L. The Garden Area soil collected at Washington Works also adsorbed significant amounts of APFO at 500 µg APFO/L. Upstream sediments from the Ohio River and East Wood soil adsorbed a

significant amount of APFO at 50 µg APFO/L only. Sand, Montmorillonite clay, Downstream sediment, and Sassafras soil did not adsorb a significant amount of APFO at any concentration of the added APFO.

Once adsorbed on peat moss, most of the APFO (>76%) did not desorb after two washings with a solution of 0.01M $CaCl_2$. For the Kaolin clay, most the APFO adsorbed when added at 5,000 µg APFO/L desorbed with washing (>60%). At APFO added at 500 µg APFO/L, however, an average of 98% did not desorb from the Kaolin clay after two washings. The East Wood soil, which adsorbed 46% of the APFO added at 50 µg APFO/L desorbed only about 2%. For the Garden Area soil 57% of the APFO desorbed when adsorbed from the 500 µg APFO/L solution. No measurable desorption of APFO from the Upstream sediment after two washings was observed when the APFO was added at 50 µg APFO/L.

ADSORPTION-DESORPTION SCREENING STUDIES OF AMMONIUM PERFLUOROOCTANOATE

TABLE 1. Physical properties of test materials.

Test material	Moisture content†	Test Material Dry Wt., m	Sand	Silt	Clay	Organic Matter	Organic Carbon‡
	%	*g*	%	%	%	%	%
Sand	0.24	4.0	100	0	0	ND	ND
Peat moss	47	2.1	ND§	ND	ND	ND	ND
Kaolin clay	0.78	4.0	0	0	100	ND	ND
Montmorillonite	7.4	3.7	0	0	100	ND	ND
Sassafrass soil	1.4	3.9	71	19	10	1	0.58
East Wood soil	14	3.5	45	40	15	1.6	0.93
Garden Area soil	9.4	3.7	37	42	21	2.9	1.68
Upstream sediment	13	3.5	59	30	11	1.5	0.87
Downstream sediment	9.0	3.7	69	21	10	0.6	0.35

† Based on drying at 105C for a minimum of 24 h.
‡ Estimated from percent organic matter.
§ ND is not determined.

TABLE 2. Chemical properties of test materials.

Test material	pH†	CEC‡	Exchangeable cations, meq/100g§				
		meq/100g	*Ca*	*Mg*	*Na*	*K*	*H*
Sand	6.6	ND¶	ND	ND	ND	ND	ND
Peat moss	3.7	ND	ND	ND	ND	ND	ND
Kaolin clay	3.8	3.3	ND	ND	ND	ND	ND
Montmorillonite	7.6	120	ND	ND	ND	ND	ND
Sassafrass soil	6.3	2.8	2.10	0.51	0.01	0.21	0.00
East Wood soil	5.6	10	4.19	0.61	0.04	0.15	5.01
Garden Area soil	4.7	17.2	5.85	1.15	0.01	0.18	10.01
Upstream sediment	7.1	7.4	6.08	0.86	0.27	0.15	0.04
Downstream sediment	6.9	5.9	4.54	1.09	0.20	0.09	0.00

† 1:1 test material to water.
‡ Cation Exchange Capacity.
§ Exchangeable cations in milliequivalents/100 g test material determined by a modified ammonium acetate method.
¶ ND is not determined.

TABLE 3. Absorption/desorption screening test data.

Test material	Nominal APFO concentration	Original solution volume, Vo	Volume of solution after adsorption step, V	APFO in solution after adsorption step, Ce	APFO in first wash, C1	APFO in second wash, C2
	$\mu g\ L^{-1}$	*mL*	*mL*	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$
Sand	0.00	20.0	18.0	2.79E+01	ND	ND
	0.05	20.0	18.0	1.39E+02	ND	ND
	0.5	20.0	18.0	4.98E+02	ND	ND
	5	20.0	18.0	3.80E+03	ND	ND
Peat moss	0.00	20.0	18.0	4.00E+01	0.00E+00	0.00E+00
	0.05	20.0	18.0	7.98E+00	0.00E+00	0.00E+00
	0.5	20.0	18.0	6.55E+01	4.07E+01	2.62E+01
	5	20.0	18.0	9.62E+02	5.87E+02	3.37E+02
Kaolin clay	0.00	20.0	18.0	1.65E+00	0.00E+00	0.00E+00
	0.05	20.0	18.0	3.83E+01	NA	NA
	0.5	20.0	18.0	3.27E+02	3.31E+01	7.15E+00
	5	20.0	18.0	3.02E+03	4.52E+02	3.82E+02
Montmorillonite	0.00	20.0	18.0	4.45E+01	0.00E+00	0.00E+00
	0.05	20.0	18.0	4.68E+01	ND	ND
	0.5	20.0	18.0	3.80E+02	6.25E+01	8.00E+00
	5	20.0	18.0	3.69E+03	ND	ND

TABLE 3 (cont'd)

Test material	Nominal APFO concentration	Original solution volume, Vo	Volume of solution after adsorption step, V	APFO in solution after adsorption step, Ce	APFO in first wash, C1	APFO in second wash, C2
	µg L^{-1}	mL	mL	µg L^{-1}	µg L^{-1}	µg L^{-1}
Sassafrass soil	0.00	20.0	18.0	0.00E+00	ND	ND
	0.05	20.0	18.0	4.33E+01	ND	ND
	0.5	20.0	18.0	4.35E+02	ND	ND
	5	20.0	18.0	3.63E+03	ND	ND
East Wood soil	0.00	20.0	18.0	7.50E-02	0.00E+00	0.00E+00
	0.05	20.0	18.0	1.18E+01	1.63E+00	0.00E+00
	0.5	20.0	17.8	3.98E+02	7.53E+01	1.98E+01
	5	20.0	18.0	4.78E+03	7.44E+02	1.43E+02
Garden Area soil	0.00	20.0	18.0	1.15E+01	6.93E+00	2.60E+00
	0.05	20.0	18.0	2.57E+01	1.24E+01	3.50E+00
	0.5	20.0	18.5	2.76E+02	1.19E+02	5.03E+01
	5	20.0	17.0	3.68E+03	1.09E+03	3.79E+02
Upstream sediment	0	20.0	18.0	0.00E+00	0.00E+00	0.00E+00
	50	20.0	18.0	1.59E+01	8.50E-01	0.00E+00
	500	20.0	18.5	4.12E+02	7.11E+01	2.10E+01
	5000	20.0	18.0	4.36E+03	7.71E+02	1.79E+02

TABLE 3 (cont'd)

Test material	Nominal APFO concentration	Original solution volume, Vo	Volume of solution after adsorption step, V	APFO in solution after adsorption step, Ce	APFO in first wash, C1	APFO in second wash, C2
	$\mu g\ L^{-1}$	*mL*	*mL*	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$
Downstream sediment	0	20.0	18.5	0.00E+00	0.00E+00	0.00E+00
	50	20.0	18.0	1.99E+01	0.00E+00	0.00E+00
	500	20.0	18.0	4.58E+02	4.63E+01	9.83E+00
	5000	20.0	17.8	5.54E+03	5.72E+02	6.64E+01
Sassafrass soil	0.00	20.0	18.5	0.00E+00	0.00E+00	0.00E+00
	0.05	20.0	18.5	2.04E+01	4.50E-01	0.00E+00
	0.5	20.0	19.0	4.94E+02	5.32E+01	1.10E+01
	5	20.0	16.3	5.25E+03	8.40E+02	9.64E+01

TABLE 4. Adsorption/desorption screening test calculations.

Test material	Nominal APFO concentration	APFO recovered from the soilless control, G	x	x/m or Cs	Material Adsorbed, A	Adsorbed material desorbed, D	Adsorbed material not desorbed, R	Adsorption coefficient, K'	Adsorption coefficient as a function of organic carbon, K'oc
	$\mu g\ L^{-1}$	μg	μg	$\mu g/g$	%	%	%		
Sand	0.00	0	-5.57E-01	-1.40E-01	0	ND	ND	-5.01E-03	ND†
	0.05	0.896	-1.88E+00	-4.71E-01	-210	ND	ND	-2.93E-03	ND
	0.5	9.99	3.50E-02	8.77E-03	0	ND	ND	2.36E-05	ND
	5	83	6.96E+00	1.55E+00	7	ND	ND	4.04E-04	ND
Peat moss	0.00	0	-7.99E-01	-3.77E-01	#VALUE!	#VALUE!	#VALUE!	#VALUE!	ND
	0.05	0.896	7.37E-01	3.47E-01	82	-2	102	4.36E-02	ND
	0.5	9.99	8.68E+00	4.09E+00	87	12	88	6.91E-02	ND
	5	83	6.38E+01	3.01E+01	77	23	77	3.28E-02	ND
Kaolin Clay	0.00	0	-3.30E-02	-8.31E-03	#VALUE!	0	#VALUE!	#VALUE!	ND
	0.05	0.896	1.30E-01	3.26E-02	15	ND	#VALUE!	8.61E-04	ND
	0.5	9.99	3.45E+00	8.68E-01	35	2	98	2.71E-03	ND
	5	83	2.26E+01	5.70E+00	27	61	39	1.90E-03	ND
Montmorillonite	0.00	0	-8.90E-01	-2.40E-01	#VALUE!	#VALUE!	#VALUE!	#VALUE!	ND
	0.05	0.896	-3.90E-02	-1.05E-02	-4	#VALUE!	#VALUE!	-2.10E-04	ND
	0.5	9.99	2.38E+00	6.44E-01	24	21	79	1.70E-03	ND
	5	83	9.15E+00	2.47E+00	11	#VALUE!	#VALUE!	6.75E-04	ND
Sassafrass Soil	0.00	0	0.00E+00	0.00E+00	#VALUE!	ND	ND	#DIV/0!	#DIV/0!
	0.05	0.896	2.95E-02	7.48E-03	3	ND	ND	1.76E-04	3.03E-02
	0.5	9.99	1.30E+00	3.28E-01	13	ND	ND	7.70E-04	1.33E-01
	5	83	1.04E+01	2.63E+00	12	ND	ND	7.26E-04	1.25E-01

TABLE 4 (cont'd)

Test material	Nominal APFO concentration	APFO recovered from the soilless control, G	x	x/m or Cs	Material Adsorbed, A	Adsorbed material desorbed, D	Adsorbed material not desorbed, R	Adsorption coefficient, K'	Adsorption coefficient as a function of organic carbon, K'oc
	$\mu g\ L^{-1}$	μg	μg	$\mu g/g$	%	%	%		
East Wood Soil	0.00	0	-1.50E-03	-4.26E-04	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
	0.05	0.422	1.86E-01	6.35E-02	46	2	87	5.39E-03	5.81E-01
	0.5	10.1	2.14E+00	7.93E-01	19	29	39	2.00E-03	2.15E-01
	5	96.8	1.17E+00	1.12E+00	-6	162	-315	2.34E-04	2.52E-02
Garden Area Soil	0.00	0	-2.31E-01	-6.30E-02	#DIV/0!	-64	164	-5.47E-03	-3.25E-01
	0.05	0.422	-9.15E-02	-7.15E-03	-18	-2142	2726	-2.70E-04	-1.60E-02
	0.5	10.1	4.58E+00	1.30E+00	44	57	34	4.72E-03	2.81E-01
	5	96.8	2.32E+01	7.50E+00	18	51	9	2.04E-03	1.21E-01
Upstream Sediment	0	0	0.00E+00	0.00E+00	#VALUE!	#VALUE!	#VALUE!	#VALUE!	#VALUE!
	50	0.422	1.05E-01	4.25E-02	27	-11	90	0.00E+00	0.00E+00
	500	10.1	1.86E+00	6.27E-01	16	56	17	0.00E+00	0.00E+00
	5000	96.8	9.52E+00	3.23E+00	3	84	-82	7.64E-04	8.78E-02
Downstream Sediment	0	0	0.00E+00	0.00E+00	#VALUE!	#VALUE!	#VALUE!	#VALUE!	#VALUE!
	50	0.422	2.35E-02	2.11E-02	9	-81	100	1.15E-03	3.30E-01
	500	10.1	9.36E-01	4.40E-01	7	5	34	9.75E-04	2.80E-01
	5000	96.8	-1.40E+01	-2.29E+00	-23	13	259	-4.11E-04	-1.18E-01
Sassafrass Soil	0.00	0	0.00E+00	0.00E+00	#VALUE!	#VALUE!	#VALUE!	#VALUE!	#VALUE!
	0.05	0.422	1.35E-02	1.46E-02	6	-44	84	7.35E-04	1.27E-01
	0.5	10.1	2.17E-01	1.19E-01	0	180	-201	2.43E-04	4.19E-02
	5	96.8	-8.28E+00	1.20E+00	-17	-107	-2450	2.24E-04	3.86E-02

† ND = Not determined.

FIGURE 1. Adsorption isoline of APFO onto Sand, Peat moss, Kaolin clay, Montmorillonite clay, and Sassafras soil.

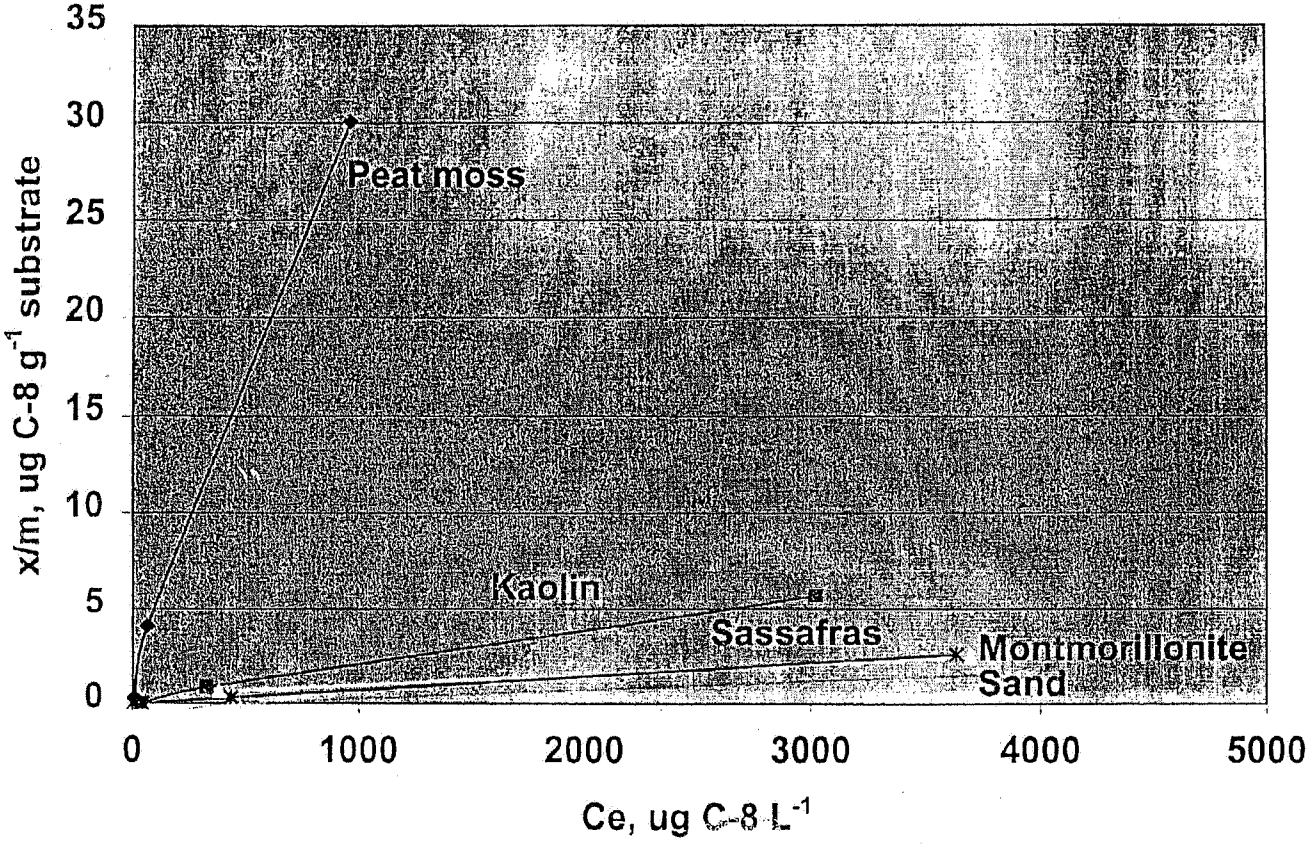
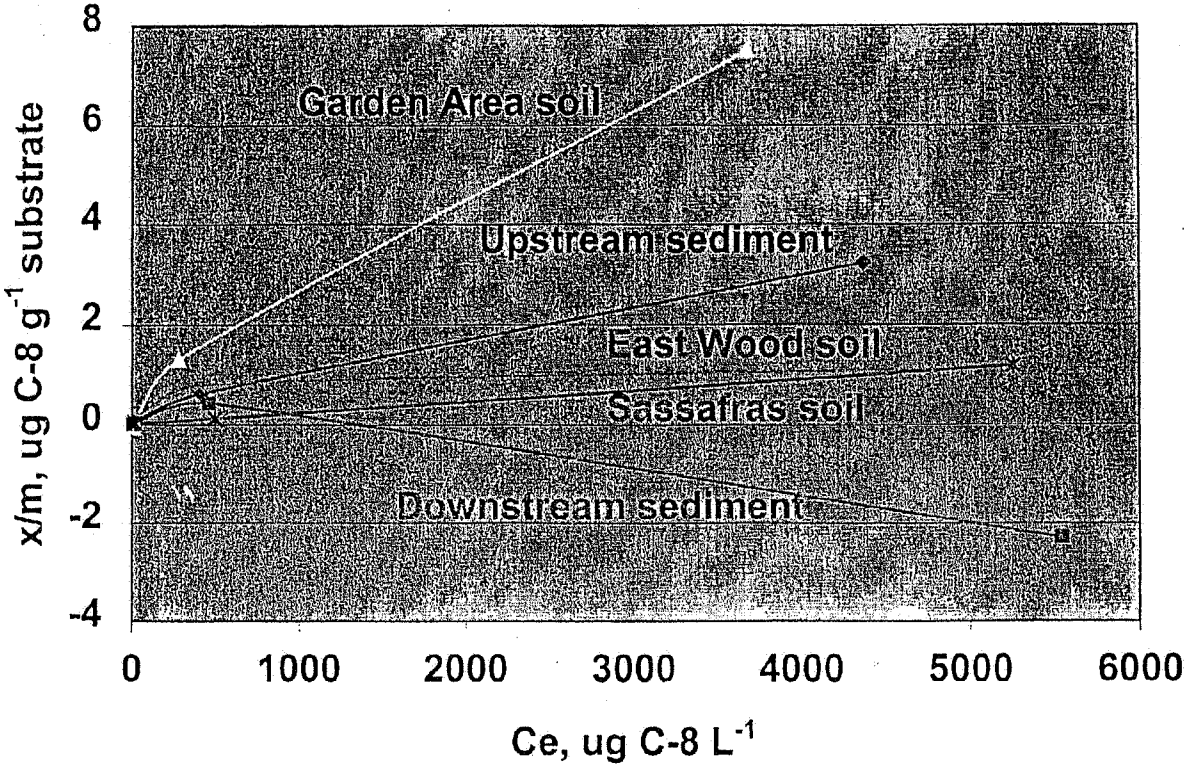


FIGURE 2: Adsorption isoline of APFO onto East Wood soil, Garden Area soil, Upstream sediment, and downstream sediments.



Reference:

1 US EPA. 1998. Fate, transport and transformation test guidelines: OPPTS 835.1220 sediment and soil adsorption/desorption isotherm. United State Environmental Protection Agency Office of Prevention, Pesticides, and Toxic Substances. EPA712-C-98-048. January 1998

2 Olphen, H.V., and J.J. Fripiat (eds.). 1979. Data handbook for clay materials and other non-metallic minerals Pergamon Press. New York 346 pp.