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Carbon Adsorption Isotherm Evaluation for Perfluorooctanoic Acid (PFOA) In Samples From Chambers Works Wastewater Treatment Facility

Final Report

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Abstract : Carbon adsorption isotherms were determined for synthetic salt solution, primary clarifier effluent, primary clarifier underflow and mixed secondary/tertiary aerator solid samples taken from the Chambers Works wastewater treatment system. These tests show that the powdered activated carbon used by Chambers Works, primary clarifier and the combined aerator solids adsorb PFOA.

Keywords carbon adsorption isotherms, perflurooctanoic acid (PFOA)

Table of Contents

Carbon Adsorption Isotherm Evaluation for Perfluorooctanoic Acid (PFOA) In Samples From Chambers Works Wastewater Treatment Facility

Final report

Introduction and Objectives

Perfluorooctanoic Acid (PFOA) is a compound used for the production of fluoropolymers in DuPont. PFOA containing wastewaters are discharged to the Chambers Works (CW) site wastewater treatment system, which is operated by Secure Environmental Treatment (SET). To better understand the fate of PFOA in the CW treatment system, a series of carbon adsorption isotherm tests were performed. The tests used a sample of the same virgin powdered activated carbon (PAC, i.e.Calgon WPX-D) that SET uses in the site treatment system spiked into either synthetic wastewater effluent or an actual sample of SET primary clarifier effluent. In addition, isotherms were separately developed for the high solids containing primary clarifier underflow and mixed liquor suspended solids (MLSS) samples taken from CW secondary and tertiary aeration basins.

Summary and Conclusions

The isotherm tests showed that the virgin PAC used by the CW SET system is capable of adsorption of PFOA in primary clarifier effluent or in a synthetic wastewater simulating tertiary SET effluent. The SET MLSS and primary clarifier underflow samples also show similar behavior, though in these experiments they had a lower capacity on a unit dry weight basis for PFOA adsorption than virgin PAC.

Patent Situation

N/A

Program

The program is described below.

Publication Status

N/A

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Safety and Waste Disposal

N/A

Environmental Considerations

N/A

Acknowledgment

Signatures

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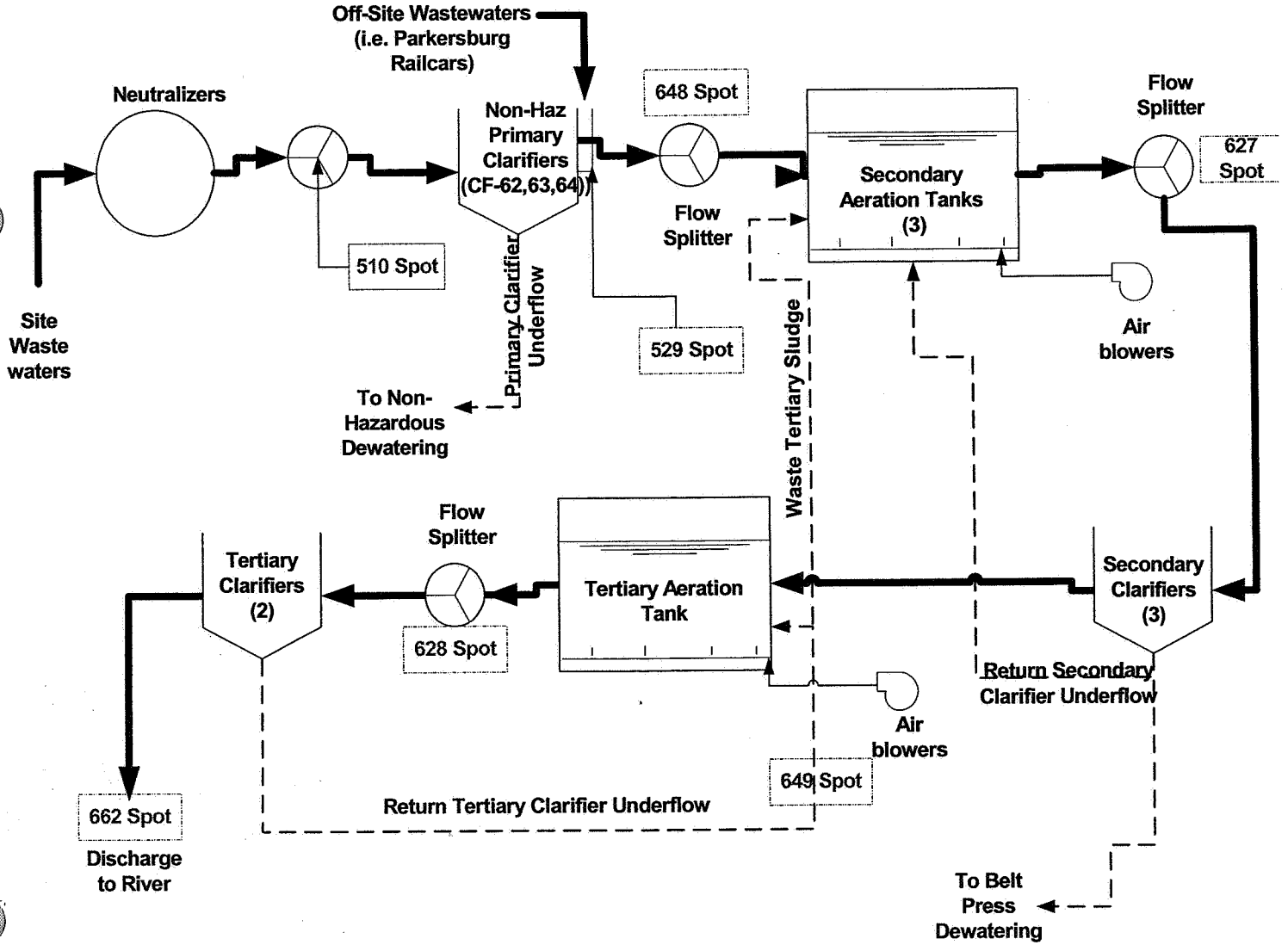
Experimental

Description of the Chambers Works Wastewater Treatment System and Rationale Behind Sample Matrices Used in This Study

The CW site treatment operations of interest to this work consist of influent neutralization using lime, primary gravity clarification and removal of solids and powder activated carbon (PAC) assisted biological treatment (PACT) in secondary and tertiary polishing units prior to discharge of treated effluent to the Delaware River (after mixing with other site waters). Figure 1 shows the unit operations and sampling spots of interest to the work discussed in this report.

Figure 1: Chambers Works Non-Hazardous Treatment System and Sampling Spots



Test Substance

Name:	Ammonium perfluorooctanoate
Synonyms:	Ammonium pentadecafluorooctanoate; Ammonium perfluorocaprylate; DS 101; Fluorad FC 143; Perflurorooctanoic acid ammonium salt; Unidyne DS 101
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 24501
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:	0.1 g/ml
Appearance:	White Powder

Reagents and Solvents

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

Test Materials

Lab experiments were devised to determine the adsorption behavior of PFOA according to the operational practices and in the wastewater matrices common to the SET system:

1. PAC is added to the SET system at both the primary clarifier effluent and in tertiary influent, with the split varying according to the seasons, treatment efficiency and other factors. Therefore, one isotherm test case used filtered primary clarifier effluent. Given that PFOA may be present in any effluent sample taken from the SET system and given that the PFOA concentration could not be determined prior to testing, a synthetic salt sample was prepared for isotherm testing so as to simulate the wastewater matrix found in the tertiary influent but without background PFOA present. This synthetic wastewater was prepared by spiking the major cations and anions found in the SET effluent into distilled water along with a known addition of PFOA.
2. The CW SET system is a complex treatment system, where PAC is co-mingled with activated sludge for enhanced removal. In order to gain some insights into PFOA fate in such a system, a series of isotherm tests were devised where PFOA was spiked to a mixture of secondary and tertiary solids. In addition, PFOA was spiked to primary solids to gain insights into PFOA partitioning in primary clarification. Distilled water was used to dilute some of the primary and secondary/tertiary samples so that a wide range of final solution PFOA concentrations could be obtained.

Samples of primary clarifier underflow, primary clarifier effluent, secondary aeration mixed liquor suspended solid (MLSS) and tertiary MLSS samples, and virgin powdered activated carbon (PAC Calgon WPX-D) were taken from the CW treatment plant system for use in the study. The primary clarifier underflow sample from primary clarifier CF-64 and the MLSS samples from Spot 627 (secondary treatment) and Spot 628 (tertiary treatment) were grab samples collected on May 27, 2003 and refrigerated until use. The Primary clarifier effluent (CF-64) was a 24-hr composite sample collected from 529 spot on May 29, 2003 and refrigerated until use. The virgin Powdered Activated Carbon (PAC) was obtained from DuPont Secure Environmental Treatment (SET) and was stored at room temperature. All samples were collected in accordance with the principles explained in Appendix A.

Test solutions were prepared as follows:

- The salt solution was prepared by dissolving calcium chloride (1400mg/L) and sodium sulfate (1250 mg/L) in deionized water. Hydrochloric acid and/or sodium hydroxide were used to adjust the final pH of the solution to 7-7.8

- The primary clarifier effluent was centrifuged for 10 minutes at 6000 RPM (Sorvall RC-5 HS-4 Rotor) and supernatants filtered (Pall Gelman 4190) prior to use.
- A mixed MLSS sample for isotherm testing was prepared by combining secondary and tertiary MLSS samples at a ratio of 3:1 in order to simulate the ratio of tertiary to secondary solids in the CW system (tertiary solids are wasted to secondary and

secondary is wasted to the belt presses for dewatering prior to landfilling dewatered cake on site).

Analytical protocols:

To determine soluble parameters, samples were centrifuged for 10 minutes at 6000 RPM (Sorvall RC-5 HS-4 Rotor) and supernatants filtered (Pall Gelman 4190) prior to analysis. Total PFOA was determined by sonicating the sample with equal parts methanol for 1-hr. Analytical samples were refrigerated or frozen until analysis.

The total solids and total suspended solids of the primary underflow and MLSS samples were determined according to protocols outlined in Standard Methods for the Examination of Water and Wastewater, 20th Edition. (1998) American Public Health Association, Washington, DC. PFOA was analyzed per the procedures described in Appendix B.

Experimental Protocol:

Application Information

The test substance was administered from a 1000 mg/L stock solution in deionized water (Barnstead E-Pure Water Purification system) 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.

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 the salt solution, primary clarifier effluent, primary clarifier underflow or MLSS samples. 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 10 minutes at 6000 RPM (Sorvall RC-5 HS-4 Rotor) and supernatants were transferred to 50-mL polypropylene tubes using a disposable pipette (VWR 53283-706). Aliquots (5mL) of the supernatants were filtered (Pall Gelman 4190) in 14-mL polypropylene tubes (Falcon 35 2059) using a 10-mL disposable syringe (BD 309695). Samples were diluted (if required) and submitted for analysis in polypropylene vials (Agilent 5182-0567) sealed with a natural rubber crimp seal (Agilent 5182-1210). Analytical samples were refrigerated or frozen until analysis.

For determining total PFOA concentrations in select samples, PFOA was extracted by sonicating well mixed aliquots with methanol for one hour. Samples were filtered (Pall Gelman 4190), diluted (if required) and submitted for analysis.

Isotherm Round 1 Testing: Salt Solution and Primary Clarifier Effluent

PAC material was weighed directly into 50-ml polypropylene conical tubes, according to the study outline presented in Table 1, and 50-ml of salt solution or primary clarifier effluent was added. The test substance was added from a stock solution to the test vessels to achieve a target test concentration of 15 mg/L. Control tubes (test substance in salt solution or filtered effluent without PAC), solution blanks and PAC 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. After 48 hours at ambient temperature, the tubes were centrifuged for 15 minutes at 6000 RPM (Sorvall® RC-5B refrigerated centrifuge, HS-4 rotor). The supernatants were transferred to 50-mL polypropylene tubes, aliquots were filtered and submitted for determination of the test compound.

Table 1:
Salt Solution and Primary Clarifier Effluent
Isotherm Test Matrix

Sample Description	Target PAC Wt g	Target PFOA spike Conc mg/l
PAC addition Control	4.3	0
Control	0	0
Spiked PFOA PAC addition	0.025	15
Spiked PFOA PAC addition	0.28	15
Unspiked PFOA PAC addition / Desorb Control	0.28	0
Spiked PFOA PAC addition	0.55	15
Spiked PFOA PAC addition	0.75	15
Spiked PFOA PAC addition	1.7	15
Spiked PFOA PAC addition	4.3	15

Isotherm Repeat Testing: Salt Solution and Primary Clarifier Effluent

The PAC isotherm, as described the preceding section, was repeated for primary clarfier effluent and salt solution with the following modifications:

- A test solution was prepared by spiking the test compound (from a stock solution) to the desired test concentration of 15 mg/L into the salt solution or primary clarifier effluent. A 50-ml aliquot of the test solution was added to test system.
- The PAC test weights were expanded according to the study outline in Table 2.

Table 2:Salt solution and Primary clarifier effluent Isotherm Re-test Matrix

Sample Description	PAC (g)	PFOA (ppm)	Test Matrix
PAC addition Control	4.3	0	Salt Solution and Primary Clarifier Effluent
Control	0	0	Salt Solution and Primary Clarifier Effluent
Spiked PFOA Control	0	15	Salt Solution and Primary Clarifier Effluent
Spiked PFOA PAC addition	0.025	15	Salt Solution and Primary Clarifier Effluent
Spiked PFOA PAC addition	0.05	15	Salt Solution and Primary Clarifier Effluent
Spiked PFOA PAC addition	0.1	15	Salt Solution and Primary Clarifier Effluent
Spiked PFOA PAC addition	0.28	15	Salt Solution and Primary Clarifier Effluent
Unspiked PFOA PAC addition	0.28	0	Salt Solution and Primary Clarifier Effluent
Spiked PFOA PAC addition	0.55	15	Salt Solution and Primary Clarifier Effluent
Spiked PFOA PAC addition	0.75	15	Salt Solution and Primary Clarifier Effluent
Spiked PFOA PAC addition	1.7	15	Salt Solution and Primary Clarifier Effluent
Spiked PFOA PAC addition	4.3	15	Salt Solution and Primary Clarifier Effluent
Spiked PFOA PAC addition	0.005	15	Salt Solution only

Isotherm Round 1 Testing: Primary Solids

Aliquots (50-ml) of the primary clarifier underflow solids, primary clarifier underflow solids diluted with distilled water or distilled water alone were added to 50-ml polypropylene conical tubes and the test compound was added from a stock solution according to the study outline shown in Table 3. The test vessels were placed on the end-over-end rotator at 30-35 RPM at ambient room temperature. After 48 hours at ambient temperature, the tubes were centrifuged for 15 minutes at 6000 RPM (Sorvall® RC-5B refrigerated centrifuge, HS-4 rotor). The supernatants were transferred to 50-mL polypropylene tubes, aliquots were filtered and submitted for determination of the test compound.

Table 3: Primary Clarifier Underflow

And Mixed MLSS Solids Isotherm Test Matrix

Aliquot #	Parts sludge	Parts distilled water	COI spike (ppm)
Control	0	1	none
Spiked Control	0	1	1
Lowest PFOA concentration Sludge	1	2	none
Low PFOA concentration Sludge	2	1	none
Sludge Only	1	0	none
Spiked Sludge	1	0	0.5
Spiked Sludge	1	0	0.75
Spiked Sludge	1	0	1

Isotherm Round 1 Testing: Mixed MLSS Isotherm testing

The secondary and tertiary MLSS samples were combined at a ratio of 3:1, respectively. Aliquots (50-ml) of the Mixed solids, mixed MLSS solids diluted with distilled water or distilled water alone were added to 50-ml polypropylene conical tubes and the test compound was added from a stock solution according to the study outline in Table 3. The test vessels were placed on the end-over-end rotator at 30-35 RPM at ambient room temperature. After 48 hours at ambient temperature, the tubes were centrifuged for 15 minutes at 6000 RPM (Sorvall® RC-5B refrigerated centrifuge, HS-4 rotor). The supernatants were transferred to 50-mL polypropylene tubes, aliquots were filtered and submitted for determination of the test compound.

Isotherm Repeat Testing: Primary Clarifier Underflow and Mixed Secondary/Tertiary Solids

Isotherm testing was repeated for the primary clarifier underflow and mixed secondary and tertiary MLSS samples according to the revised test conditions shown in Table 4 below:

Table 4: Primary Clarifier Underflow And Mixed MLSS Solids Isotherm Repeat Test Matrix

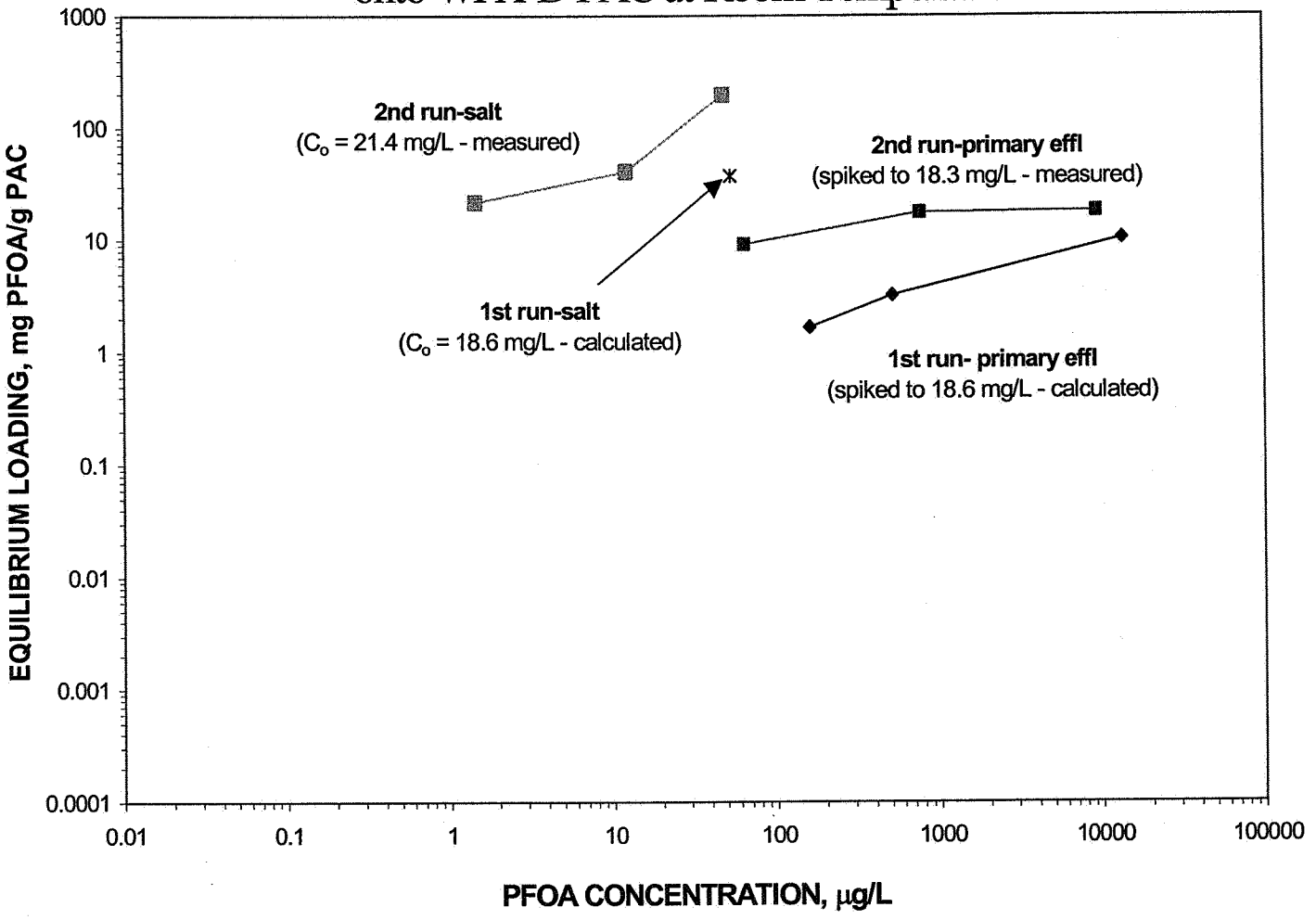
Sample Description	Parts Sludge	Parts DI H2O	Test Conc (ppm)
Spiked Control	0	1	1
Unspiked sludge Control	1	0	0
Spiked Sludge Test	1	0	0.1
Spiked Sludge Test	1	0	0.25
Spiked Sludge Test	1	0	0.5
Spiked Sludge Test	1	0	0.75
Spiked Sludge Test	1	0	1
Unspiked diluted Sludge Test	1	1	0

Discussion of Results

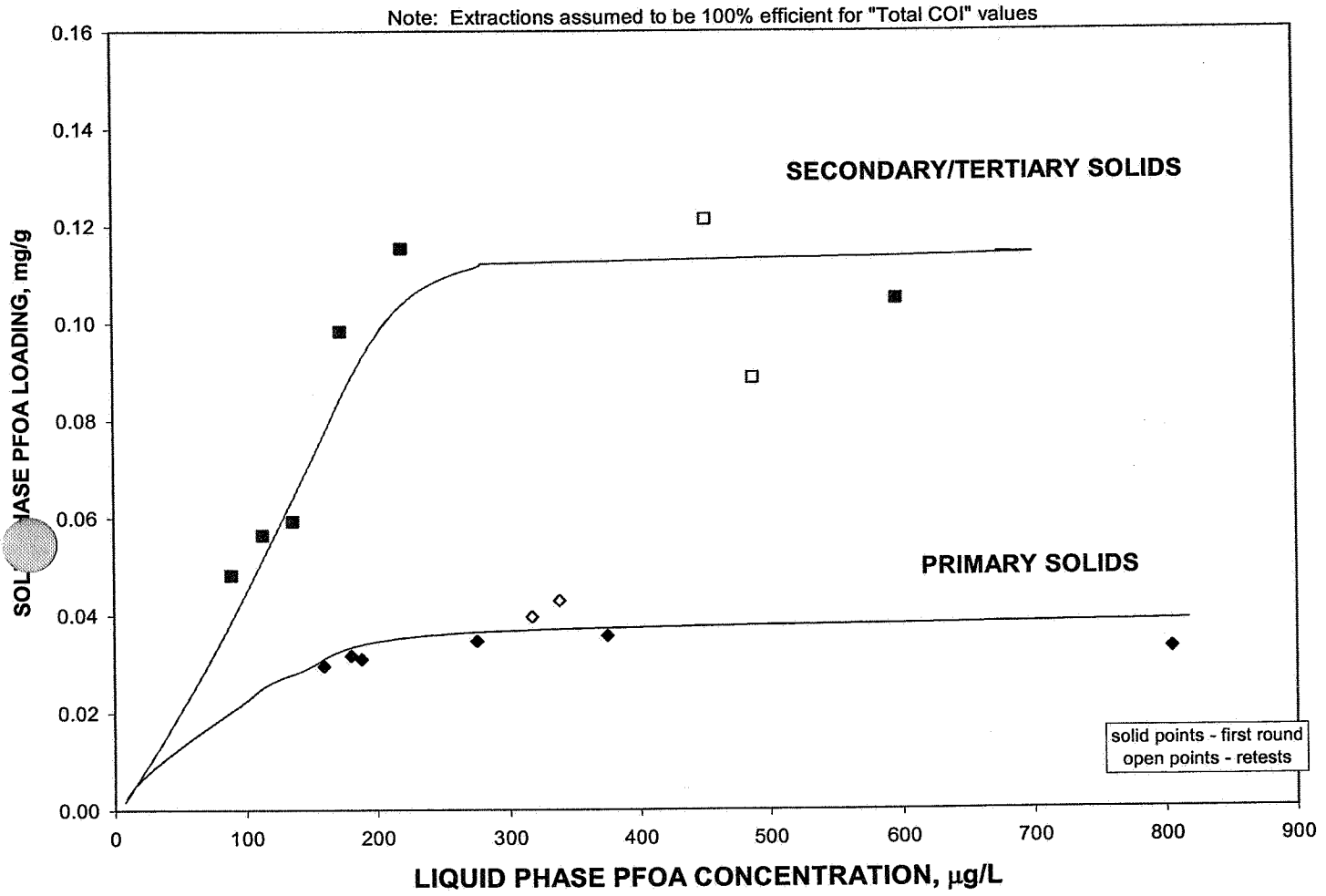
The analytical results of the isotherm testing for all matrices are included in Appendix C as Tables C1 and C2 for the synthetic salt and filtered primary clarifier effluent wastewater matrices, respectively. Analytical results for the primary clarifier underflow and mixed secondary/tertiary solids are included as Table C3. Table C4 shows the total and soluble PFOA results and computed extraction efficiencies for the high solids (i.e. primary clarifier underflow and secondary/tertiary solids) samples used in this study.

Isotherm graphs were developed by determining the total amount of PFOA adsorbed to the solids per unit dry weight of solid (PAC, primary clarifier underflow or secondary/tertiary solid) for each test condition's equilibrium soluble PFOA concentration. Graph 1 shows the isotherms for the filtered primary clarifier effluent and synthetic salt solutions while Graph 2 shows the isotherms for the primary clarifier underflow and mixed secondary/tertiary solids, respectively. Graph 3 shows the isotherms for the primary clarifier underflow and mixed secondary/tertiary solids after correcting for extraction efficiency. Graph 4 shows the results for all tested matrices. On a unit dry solids basis, PFOA adsorption appears to be highest in synthetic salt, followed closely by primary clarifier effluent; it is less well adsorbed by PACT and least well adsorbed by primary clarifier solids in these tests.

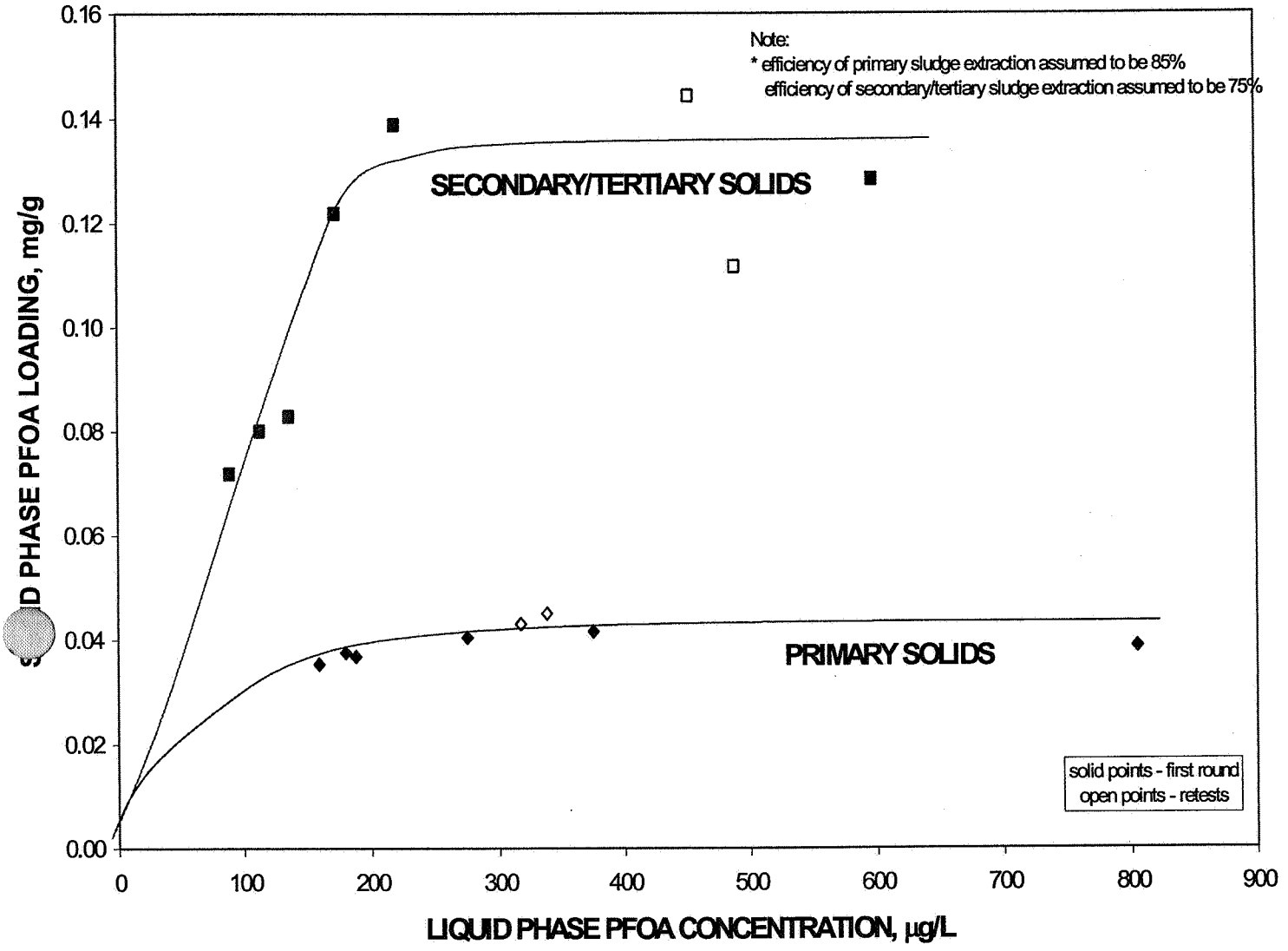
Graph 1:
Sorption of PFOA from Spiked Filtered Primary Effluent onto WPX-D PAC at Room Temperature



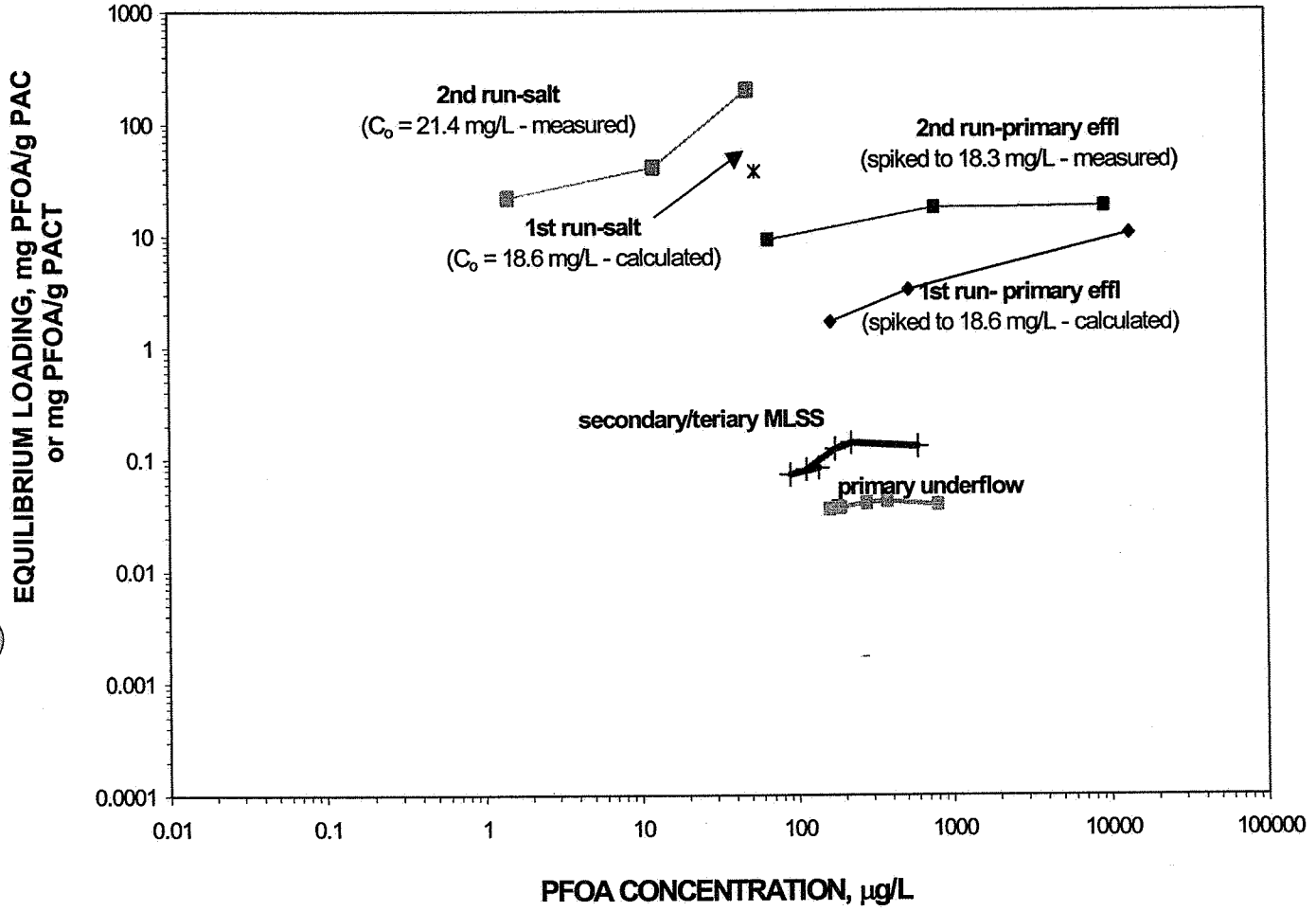
Graph 2:
Sorption of PFOA onto Primary and Combined Secondary/Tertiary Solids



Graph 3:
Sorption of PFOA onto Primary and Combined Secondary/Tertiary Solids



Graph 4:
Sorption of PFOA on WPX-D PAC for Filtered Primary Effluent and , Synthetic Salt Solution and on 2/3 MLSS or Primary Clarifier Underflow



References

N/A

Appendices

Appendix A: Suggested Protocol For Sampling

Appendix B: Liquid Chromatography and Liquid Chromatography Tandem Mass Spectrometry for Perfluorooctanoic Acid (PFOA) Quantitation

Appendix C: Isotherm Test Results for Round 1 and Retesting

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Appendix C: Isotherm Test Results for Round 1 and Retesting

Table C1: PFOA and Total Suspended Solids Test Results for the Synthetic Salt Solution

Sample Description	*PAC dose (g)*	*Soluble PFOA-1st Test ug/l*	*Soluble PFOA Repeat Test Result ug/l*	*Soluble PFOA Repeat Test Desorb ug/l*
Unspiked Salt Solution Control 1	4.3	<LOQ		
Unspiked Salt Solution Control 2	0	<LOQ		
Salt Solution Control w/ 15 ppm Nominal spike	0		21388	
Salt Solution PAC addition Desorb Control	0.28	<LOQ		
Salt Solution PAC addition Control	0.005		48.5	
15 ppm Spiked Salt Solution PAC addition	0.025	53.9	12.26	
15 ppm Spiked Salt Solution PAC addition	0.05		1.44	
15 ppm Spiked Salt Solution PAC addition	0.1		<LOQ	
15 ppm Spiked Salt Solution PAC addition	0.28	<LOQ	<LOQ	0.9
Unspiked Salt Solution PAC addition Control	0.28	<LOQ		0.8
15 ppm Spiked Salt Solution PAC addition	0.55	<LOQ		
15 ppm Spiked Salt Solution PAC addition	0.75	<LOQ		
15 ppm Spiked Salt Solution PAC addition	1.7	<LOQ		
15 ppm Spiked Salt Solution PAC addition	4.3	<LOQ		

Table C2:
PFOA and Total Suspended Solids Test Results for the Primary Clarifier Effluent

Sample Description	PAC Dose (g)	Soluble PFOA-1st Test ug/l	Soluble PFOA Repeat Test Result ug/l	Soluble PFOA Repeat Test Desorb ug/l
Unspiked PAC addition Filtered Primary Effluent Control	4.3	<LOQ		
Unspiked Filtered Primary Effluent Control	0	69		
15 ppm spiked Filtered Primary Effluent Control	0		18345	
Unspiked PAC addition Filtered Primary Effluent Desorb Control	0.28	<LOQ		
15 ppm spiked PAC addition Filtered Primary Effluent Control	0.025	13400	9282	
15 ppm spiked PAC addition Filtered Primary Effluent Control	0.05		770	
15 ppm spiked PAC addition Filtered Primary Effluent Control	0.1		65	
15 ppm spiked PAC addition Filtered Primary Effluent Control	0.28	522	<LOQ	2.5
Unspiked PAC addition Filtered Primary Effluent Control	0.28	<LOQ		
15 ppm spiked PAC addition Filtered Primary Effluent Control	0.55	163		
15 ppm spiked PAC addition Filtered Primary Effluent Control	0.75	<LOQ		
15 ppm spiked PAC addition Filtered Primary Effluent Control	1.7	<LOQ		
15 ppm spiked PAC addition Filtered Primary Effluent Control	4.3	<LOQ		0.9

Table C3
PFOA and Total Suspended Solids Test Results for the Primary Clarifier Underflow and Mixed Secondary/Tertiary MLSS Samples

Sample Description	Total Suspended Solids-1st Test g/l	Soluble COI-1st Test ug/l	Total Suspended Solids-Repeat Test g/l	Soluble COI Repeat Test Result ug/l	Total COI Test ug/l
Primary Solids Control 1		<LOQ			
Primary Solids 1 ppm Spiked Control		<LOQ		1841	
1:2 Primary Solids: water dilution		159			
1:2 Primary Solids: water dilution		188			
Primary Solids only	140	180	132		4607
Primary Solids w/ 0.5 ppm nominal spike		275		317	
Primary Solids w/ 0.75 ppm nominal spike		375		338	
Primary Solids w/ 1 ppm nominal spike		805			
Mixed Secondary/Tertiary Solids Control		**<LOQ**			
Mixed Secondary/Tertiary Solids Control w/ 1 ppm nominal spike		**<LOQ**		**1451**	
1:2 Mixed Secondary/Tertiary Solids:water dilution		**89**			
1:2 Mixed Secondary/Tertiary Solids:water dilution		**113**			
Mixed Secondary/Tertiary Solids only	**11.9**	**136**	**12.2**		**841**
Mixed Secondary/Tertiary Solids w/ 0.5 ppm nominal spike		**173**		**488**	
Mixed Secondary/Tertiary Solids w/ 0.75 ppm nominal spike		**220**		**452**	
Mixed Secondary/Tertiary Solids w/ 1 ppm nominal spike		**597**			

Table C4: Analytical Results For High Solids Samples				
Sample	**Soluble PFOA µg/L**	**Total PFOA µg/L**	**Spike recovered PFOA µg/L**	**Extraction Efficiency**
H2O Control	2342	2461		
Primary Undeflow	1110	4607		
Primary Spike	1251	6688	2081	85%
Secondary MLSS	380	843		
Secondary Spike	1347	2829	1987	81%
Tertiary MLSS	408	848		
Tertiary Spike	2002	2834	1986	81%
Mixed MLSS	398	841		
Mixed Spike	1447	2679	1838	75%