DETECTION OF PERFLUORO-ALKYL COMPOUNDS (PFCs) IN SEWAGE TREATMENT PLANT EFFLUENTS AND BIOSOLIDS BY LIQUID CHROMATOGRAPHY – TANDEM MASS SPECTROMETRY

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BACKGROUND

- Fluorocarbon specialty chemicals having a polar head and non-polar tail composed principally of C-F bonds
- Used in industrial polymers (Teflon™), paper coatings, stain repellents (ScotchGard™) and fire fighting foams (AFFF)

- Exhibit both acute and chronic toxicity to animals
- Bioconcentration in the blood, liver and gall bladder not fat
- Bind to proteins affecting hormonal feedback systems
- Disrupt reproductive cycles, increase stress response hormones, reduce serum lipid/cholesterol levels, change cell membrane permeability and cause liver/bladder/thyroid cancer
- PFOS ½ life – 4 to 8 years in humans and > 1000 years in the environment
- European Chemicals Bureau (ECB) Maximum Permissible Concentrations (iMAC) in surface water (calculated) :
  PFOS ~ 5 ug/L and PFOA ~ 300 ug/L
- USEPA Drinking Water Health Advisory Level (calculated) :
  PFOS ~ 1 ug/L

- Detected in humans and the environment world-wide
- Detected in Sewage Treatment Plant (STP) sludge

Matrix	PFOS	PFOSA	PFOA	Reference
Human Serum/Blood ng/mL	<1 – 164	<0.4 - 26	<1 – 256	Kannan, 2004
Arctic Wildlife ng/g wwt	<1 - >4000	<0.5 - 110	<2 – 13	Martin, 2004
Surface Water ng/L	<4 – 2,200,000	<0.3 - 18	11 – 11,000	Boulanger, 2004
Ocean Water ng/L	0.17 – 730	<0.005 – 0.007	0.24 - 320	So, 2004
Sediment ng/g dwt	<0.08 – 0.804	<0.08 – 0.516	<0.8 – 1.75	3M, 2001
WWTP Sludge ng/g dwt	**14.4 - 2610**		**< 6 – 29.4**	**Higgins, 2005**
Household Dust ng/g dwt	11 - 2500		69 – 3700	Moriwaki, 2003

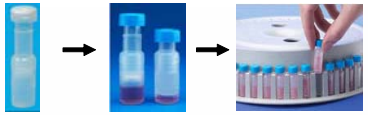
SAMPLE PREPARATION

- Only polyethylene or polypropylene labware used
- Extracts stored at 4ºC in dark until LC-MS/MS analysis

EFFLUENTS

- Samples processed entirely in Whatman polypropylene Mini-UniPrep™ syringeless filter devices
- 250uL sample added to Mini-UniPrep™ filter vial
- $^{13}C_2$-PFOS & $^{13}C_2$-PFDA (IS) added to sample in filter vial
- Solution forced through 0.2 um polypropylene filter
- Mini-UniPrep™ assembly placed directly in autosampler

Whatman Mini-UniPrep™ Syringeless Filter Device



BIOSOLIDS

- Modified Hansen Method (Environ. Sci. Technol., 2001)
- 5g sample - air dried, weighed and reconstituted with dH_2O
- Blank & Spike (~10 ng) sample processed with each set
- 0.25M sodium carbonate (Na_2CO_3) solution + 0.5M tetrabutylammonium hydrogen sulfate (TBAS) ion pairing agent solution (pH 10) added to each sample
- Slurries extracted with methyl tert-butyl ether (MTBE)
- 7H-dodecafluoroheptanoic acid (surrogate) added to extract
- Extracts evaporated to dryness under stream of nitrogen
- Extracts reconstituted in 0.5 mL methanol
- Final extracts filtered through 0.2 um nylon syringe filter

INSTRUMENTAL ANALYSIS

- Agilent 1100™ LC – ABS/Sciex 4000QTrap™ MS/MS (Effluents)
- Waters 700™ LC – Quattro Micro™ MS/MS (Biosolids)

LIQUID CHROMATOGRAPH (LC) CONDITIONS

- LC guard and analytical column
  4 mm x 2.0 mm, Phenomenex SecurityGuard™ C18
  50 mm x 2.1 mm, 4 um, Jones Genesis™ C18
- Water/Methanol (10mM ammonium acetate) mobile phase

Agilent 1100™ LC (Effluents)
- 100 uL injection volume
- 250 uL/minute flow rate
- 20:80 Water/Methanol isocratic gradient (5 minute run)

Waters 700™ LC (Biosolids)
- 20 uL injection volume
- 200 uL/minute flow rate
- 60:40 to 5:95 Water/Methanol gradient (20 minute run)

MASS SPECTROMETER (MS/MS) CONDITIONS

- Negative electrospray ionization (ESI)
- Q1 & Q3 Resolution – 0.7 amu FWHM
- Optimized MRM Transitions – see Table

ABS/Sciex 4000QTrap™ MS/MS (Effluents)
- Nebulizer Gas – 45 (Nitrogen)
- Desolvation Gas – 60 (Nitrogen) at 400 ºC
- Curtain Gas – 10 (Nitrogen)
- Interface Heater Temperature – 100 ºC
- Needle Voltage – -4.5 kV
- Entrance Potential – -10
- Collision Gas – 7 (Nitrogen)

Waters Quattro Micro™ MS/MS (Biosolids)
- Nebulizer Gas – 600 L/hour (Nitrogen) at 210 ºC
- Ion Source Temperature – 150 ºC
- Capillary Voltage – 2.75 kV
- Collision Gas – 5 x10^{-3} mBar (Argon)

QUANTIFICATION

- Effluents – Internal Standard ($^{13}C_2$-PFOA) & standard addition
- Biosolids – External Standard with surrogate monitored

Mass Spectrometer - Optimized Acquisition Parameters

Compound (Acronym)	MRM Transition Ions (m/z)		Waters Quattro Micro MS/MS		ABS/MDS Sciex 4000QTrap MS/MS		
	Parent	Product	Cone Voltage (V)	Collision Energy (eV)	Declustering Potential	Collision Energy	Collision Cell Exit Potential
Perfluorohexane sulphonate (PFHxS)	399	99	45	35	- 87	- 57	- 10
Perfluorooctane sulphonate (PFOS)	499	99	55	45	- 103	- 75	- 9
Perfluorooctane suphonamide (PFOSA)	498	78			- 84	- 79	- 11
Perfluoroheptanoic acid (PFHpA)	363	319	14	12	- 43	- 14	- 8
Perfluorooctanoic acid (PFOA)	413	369	15	12	- 44	- 14	- 9
Perfluorononanoic acid (PFNA)	463	419	16	12	- 44	- 16	- 9
Perfluorodecanoic acid (PFDA)	513	469	17	14	-54	- 15	- 9
Perfluoroundecanoic acid (PFUA)	563	519	17	14	- 49	- 16	- 9
Perfluorododecanoic acid (PFDoA)	613	569	17	14	- 50	- 18	- 11
7H-Dodecafluoroheptanoic acid (7H-PFHpA)	345	281	14	12			
C13-Perfluorooctanoic acid ($^{13}C_2$-PFOA)	415	370			- 44	-14	- 8
C13-Perfluorodecanoic acid ($^{13}C_2$-PFDA)	515	470			- 55	-16	- 13

ANALYTICAL RESULTS

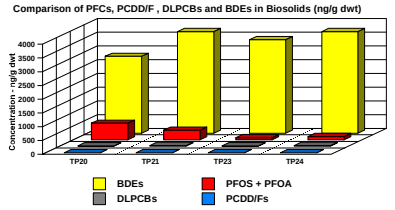
- PFCs detected in all Effluents tested
  Total PFCs – 40 to 240 ng/L
- Effluents PFCs profiles dominated by PFOS and PFOA
  PFOS - 9 to 210 ng/L PFOA - 7 to 55 ng/L
- Equivalent PFCs levels in GRK STP Influent and Effluent

- PFCs detected in all Biosolids tested
  Total PFCs - 83 to 615 ng/g dwt
- Biosolids PFCs profiles dominated by PFOS
  PFOS - 72 to 600 ng/g dwt PFOA - 0.7 to 0.9 ng/g dwt
- No correlation between PFCs and other POPs in Biosolids

STP Effluents and Biosolids Results Summary

	PFHxS	PFOS	PFOSA	PFHpA	PFOA	PFNA	PFDA	PFUA	PFDoA
Effluents - ng/L									
GRK STP – Influent	11	20	ND	ND	7	4	ND	ND	ND
GRK STP – Effluent	6	10	3	4	9	4	4	ND	ND
TM STP – Effluent	ND	43	ND	7	25	4	ND	ND	ND
HU STP – Effluent	5	10	ND	7	35	5	6	ND	ND
HC STP – Effluent	9	210	ND	3	15	5	ND	ND	ND
PK STP – Effluent	5	67	ND	ND	55	3	ND	ND	ND
K WPCP – Effluent	6	9	ND	4	27	4	ND	ND	ND
Limit of Detection (LOD)	4	1	1	2	1	2	4	2	2
Biosolids - ng/g dry weight									
GRK STP (TP20)	4.0	600		3.6	0.7	1.1	5.2		
TM STP (TP21)	1.3	350		ND	0.7	2.4	5.1		
NF STP (TP23)	2.5	72		3.2	0.9	1.9	2.5		
HW STP (TP24)	ND	120		ND	ND	0.4	3.1		
Limit of Detection (LOD)	0.2	0.1		0.2	0.1	0.2	0.2		

Comparison of PFCs, PCDD/F , DLPCBs and BDEs in Biosolids (ng/g dwt)



CONCLUSIONS

- PFCs detected in STP Influents and Final Effluents
- PFOS and PFOA dominated STP Final Effluents PFCs profiles
- PFCs survive or are created during STP treatment processes

- PFCs detected in all STP Biosolids
- PFOS dominated STP Biosolids PFCs profiles
- PFCs levels and profiles varied with Biosolids type
- No correlation observed between PCDD/Fs, DLPCBs, BDEs and PFCs levels in STP Biosolids

- Confirmation of PFCs levels and PFCs composition in Ontario STP Influents, Effluents and Biosolids should be conducted

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