



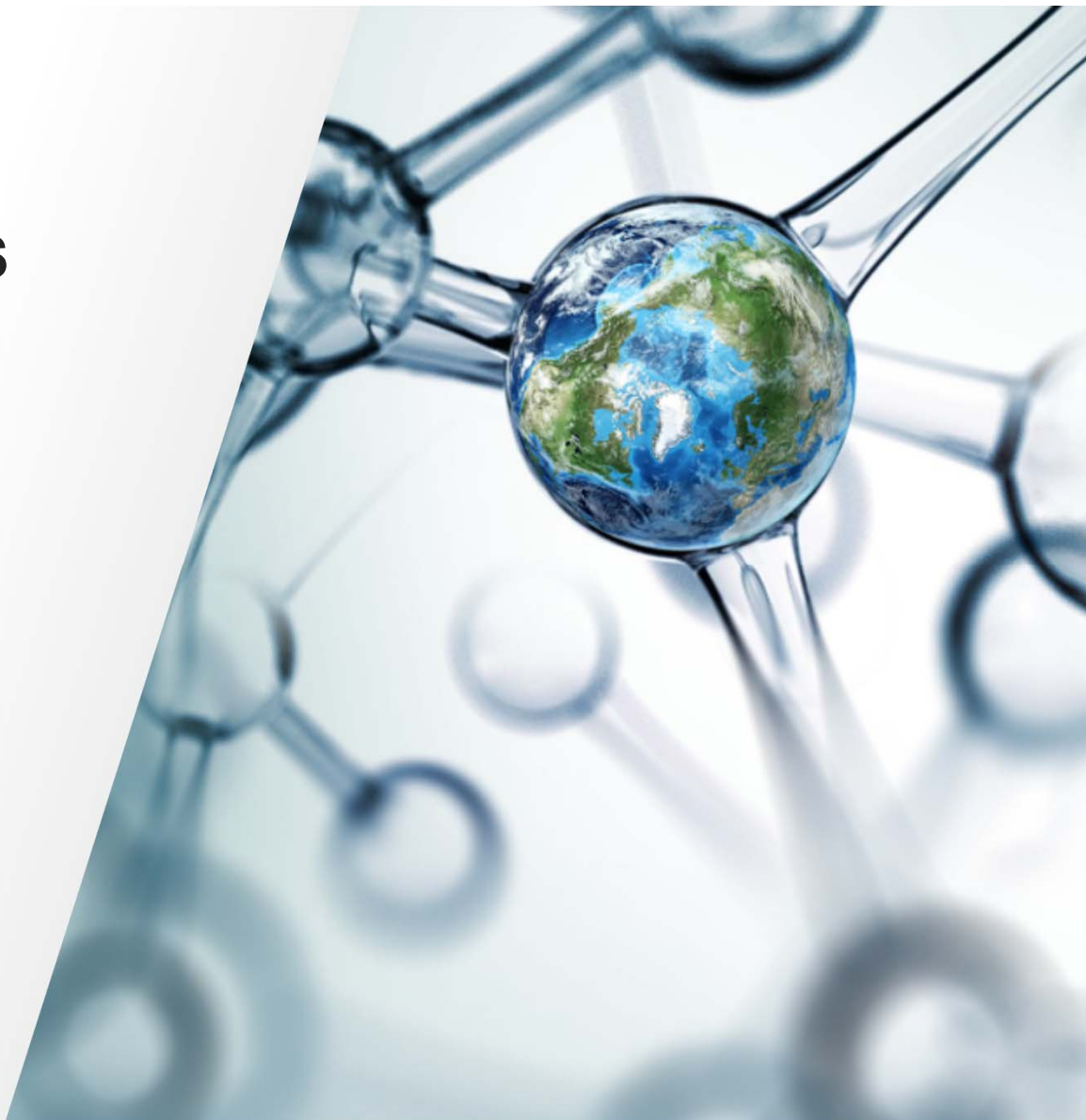
Extraction of Long-Chain PFAS from Soil using Accelerated Solvent Extraction (ASE)

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Collaboration with Matthew MacLennan
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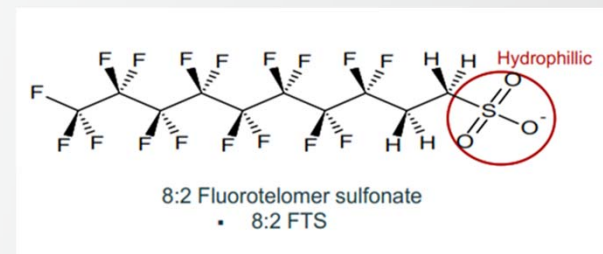
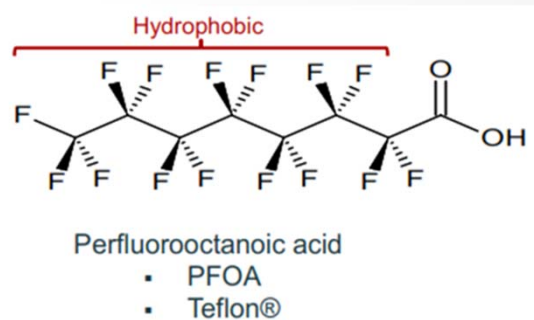
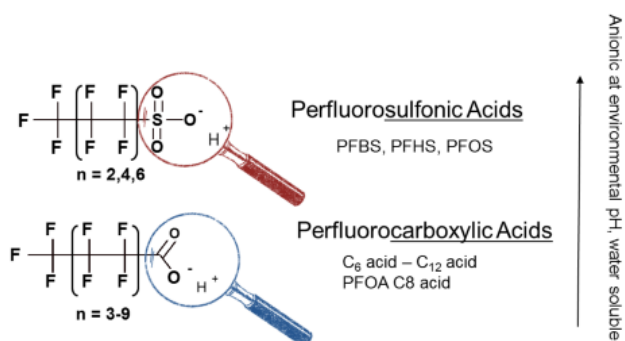
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Background

- PFAS = **P**er- and **P**oly- **F**luorinated **A**lky **S**ubstances
 - Class of structurally similar compounds
 - Hydrophobic C-F chain of various lengths with hydrophilic functional group on the end
 - Shorter carbon chains → More water soluble
 - Longer carbon chain → Less water soluble

>6000 varieties compared to
209 PCB congeners



Individual PFAS molecule is determined by chain length and functional group

PFAS are carried by water through soil systems

Short chain PFAS are more water soluble

Where are the Long-chain PFAS?

- “Incorporated into the soil matter”
- “stuck in the pores”
- “Run-off”



Spiking Studies

Spike samples only

- Spike soil with PFAS
- Sonicate or vortex in MeOH
- ~100% recovery!
- Spiked PFAS are “on” the soil particles (Lightly Bound)

Spike and sit samples

- Spike soil with PFAS
- Let the soil sit and dry over a weekend
- PFAS has time to migrate into the soil

Two Sample Prep Methods

Sonication and Vortex

- Sonicate soil sample (2-10 g) in 100% Methanol
- Filter particulates
- SPE if needed for clean-up

“Previously, we reported unsatisfactory (0–50%) recovery of long-chain PFAS from soil using vortex/sonication”

Matthew MacLennan at Pacific Rim Laboratories

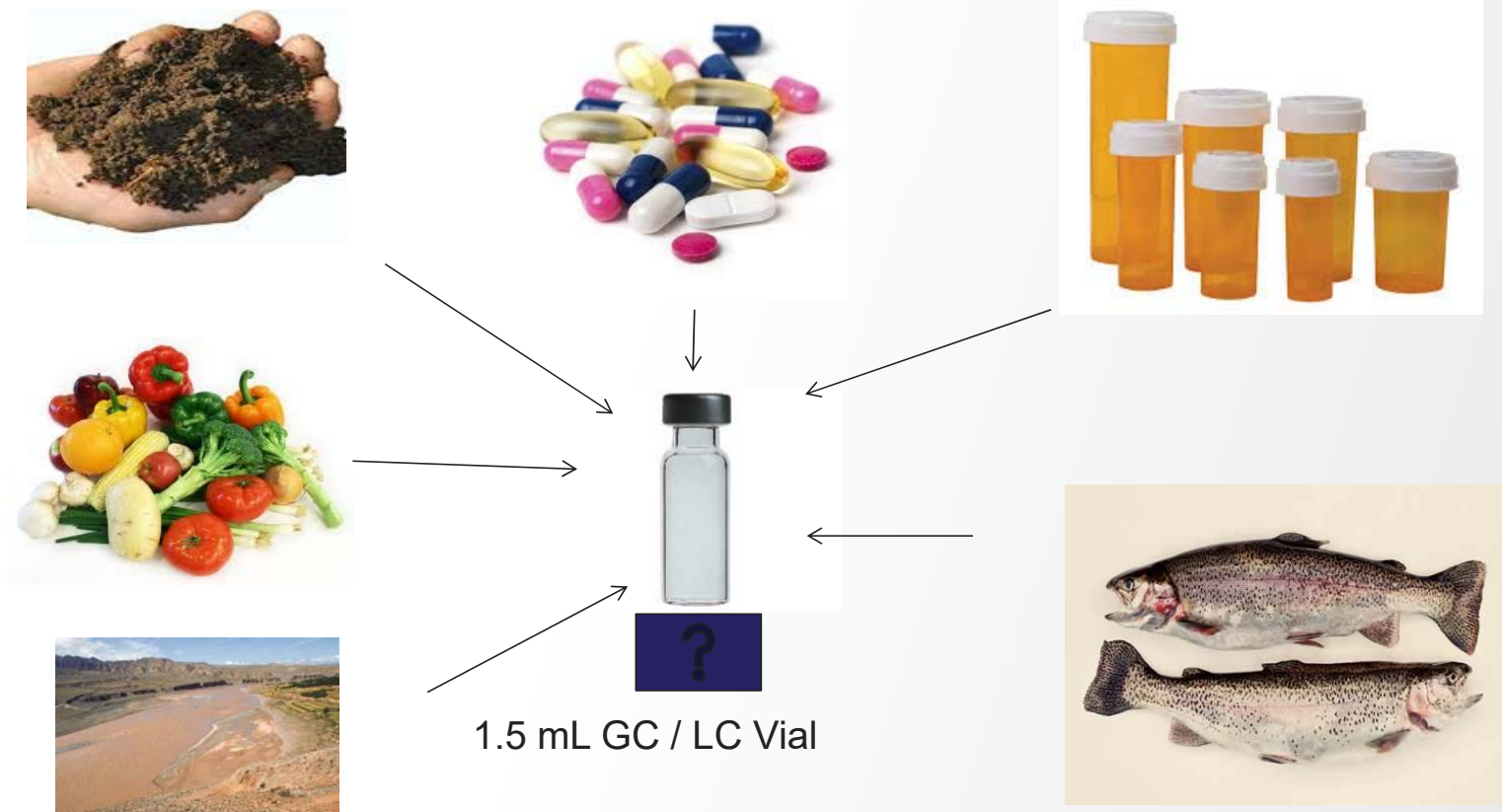
- Automated sample prep with Accelerated Solvent Extraction



The Principles of Accelerated Solvent Extraction

How does accelerated solvent extraction help sample preparation?

The Challenge for Analysis



How do we get analytes out of these samples?

The Important Parameters for Sample Prep

- Solvent Use
 - Amount of solvent consumed for the extraction
 - Solvents are expensive; reducing use reduces costs
- Extraction Time
 - Amount of time required for each extraction to occur
 - Reducing extraction time increases lab throughput
- % Recovery
 - Amount of analyte recovered following the extraction
 - Low % recovery yields poor analytical results
- % Relative Standard Deviation (RSD)
 - Measure of reproducibility between extractions
 - Extraction results have greater reproducibility with lower %RSDs

These Parameters Evaluate SP Techniques

Important Parameters for Liquid-Solid Extraction

Parameter	Effect on the Extraction Process
Temperature	Elevated temperature increases analyte diffusion from the matrix and improves analyte solubility in the extraction solvent.
Pressure	Increased pressure enables liquid solvents to be used at high temperature.
Analyte Solubility	Increases as temperature increase to improve extraction efficiency (e.g. solubility of anthracene increases 13-fold in DCM (50°C to 150°C)).
Solvent Viscosity	Decreases as temperature increases. Improves solvent migration through the matrix to increase extraction efficiency.
Solvent Surface Tension	Decreases as temperature increases. Allows solvent to better coat the matrix and helps improve analyte diffusion.

In the Beginning There Was Soxhlet...



Franz von Soxhlet
(1848 – 1926)



de facto standard for solvent extraction

Slow, high solvent usage

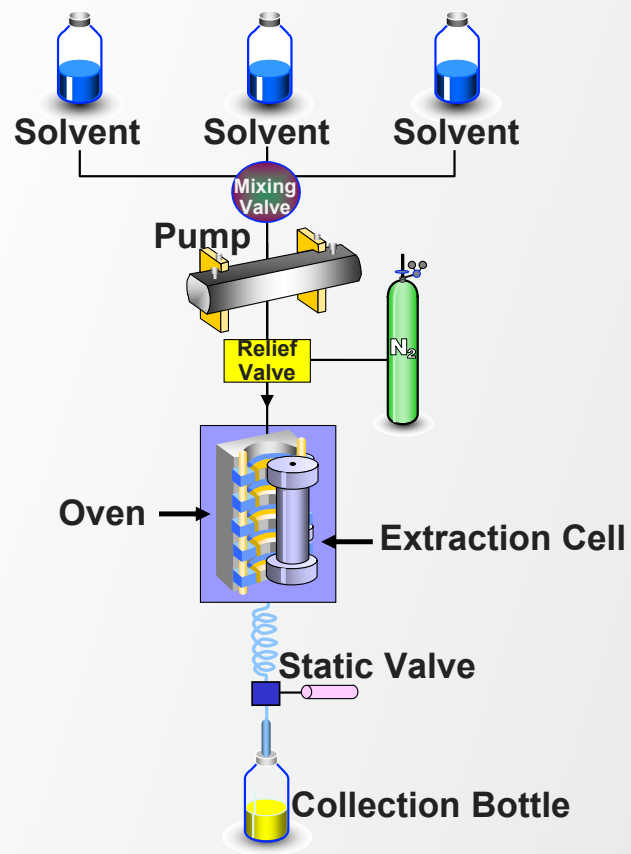
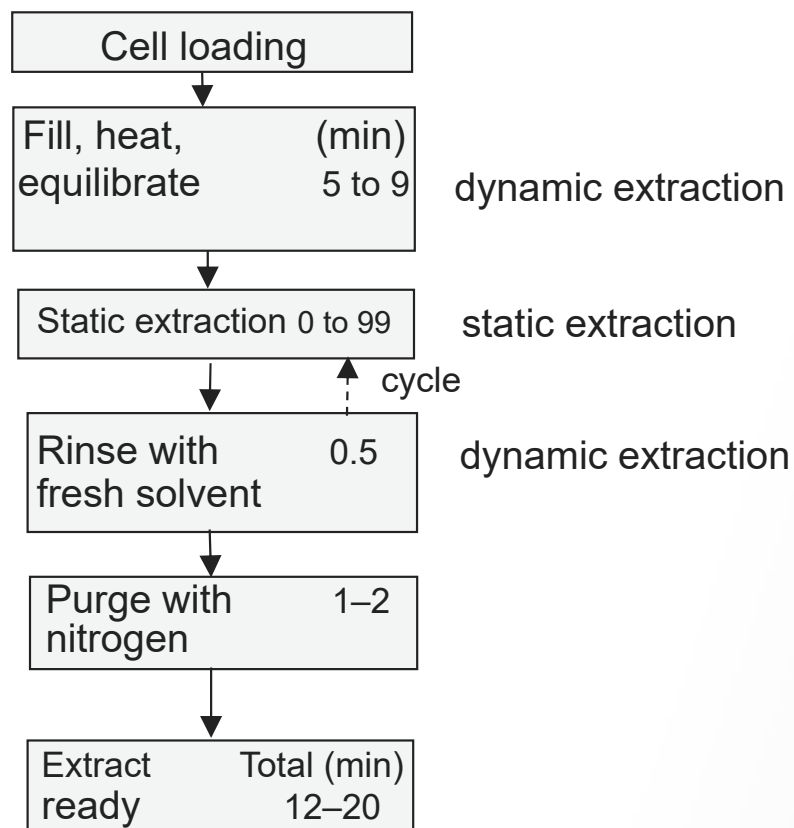
Now . . . Accelerated Solvent Extraction

- Automates sample preparation for solid and semisolid samples using solvents at elevated temperatures and pressure.
- Operates above the boiling point of extraction solvents by using sealed extraction cells.
- pH Hardened pathways allows use of strong acids and bases for sample pretreatment
- Well established and proven technique that is superior to Soxhlet and approved for U.S. EPA Method 3545A.



**Thermo Scientific™ Dionex™ ASE™ 350
Accelerated Solvent Extractor system**

How Does Accelerated Solvent Extraction Work?



Global Industries Using ASE

ThermoFisher
SCIENTIFIC



Water Treatment Plants



BRIDGESTONE

Rubber & Polymers



Natural Products



Environmental

Contract Laboratories



Government Agencies



the nature network®

PhytoLab

Dietary Supplements



Biotech/Pharmaceutical



Nestlé

Food and Beverage

International Agency Acceptance of ASE 350



United States

U.S. EPA Method 3545A (OCP, OPP, BNA, TPH, PCDD, herbicides and semi-volatiles)

U.S. EPA Method 8267 (Toxaphene)

U.S. EPA Method 6860 (Perchlorate)

NOAA Method NWFS-NWFSC-59 (Hydrocarbons)

ASTM D-7210 (Polymer Additives)



China

Method GB/T 19649-2006 for 475 pesticides in grains and grain products

Method GB/T 23376-2009, pesticides in tea leaves

Method GB/T 22996-2008, ginsenosides in ginseng



Mexico

National Standard NMX-AA-146-SCFI-2008 for PAHs in soils and sediments



Germany

Method L00.00-34 for pesticides in foodstuffs

Accelerated Solvent Extraction (ASE)

Thermo Fisher Scientific™ Dionex™ ASE 350™ Accelerated Solvent Extractor



- **Extraction Conditions**
- Extraction Solvent: Methanol
- Temperature: 100 °C
- Pressure: 1600 psi
- Heat Time: 5 min
- Static Time: 5 min
- Flush Volume: 70%
- Purge Time: 120 s
- Static Cycles: 3
- Total Extraction Time: 25 min per sample

Instrumentation

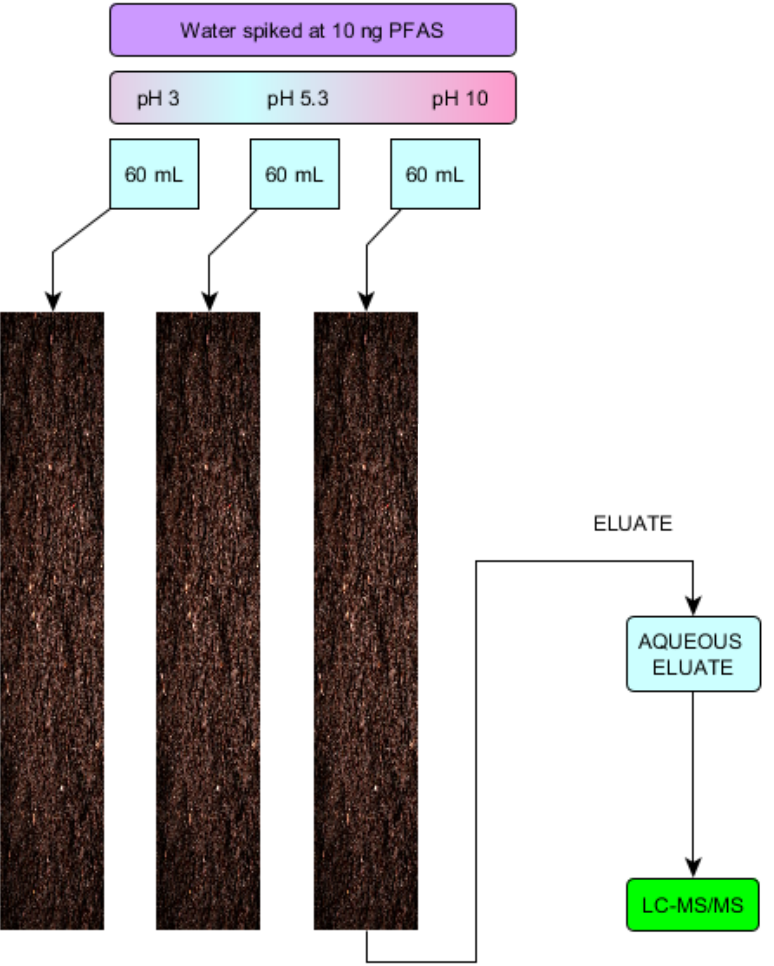
ThermoFisher
SCIENTIFIC

Thermo Fisher Scientific™ Vanquish™ HPLC System with
PFC Free Kit

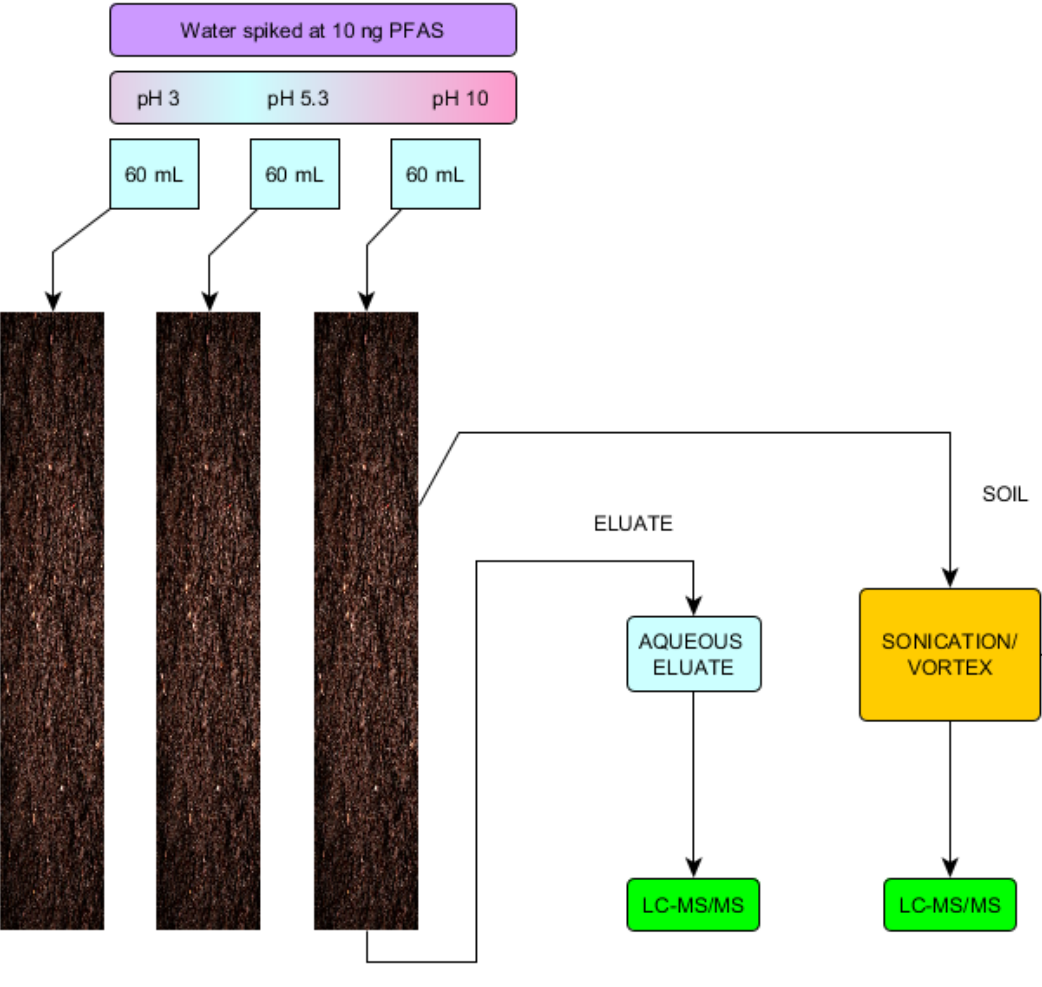


Thermo Fisher Scientific™ TSQ Quantis™ Mass Spectrometer

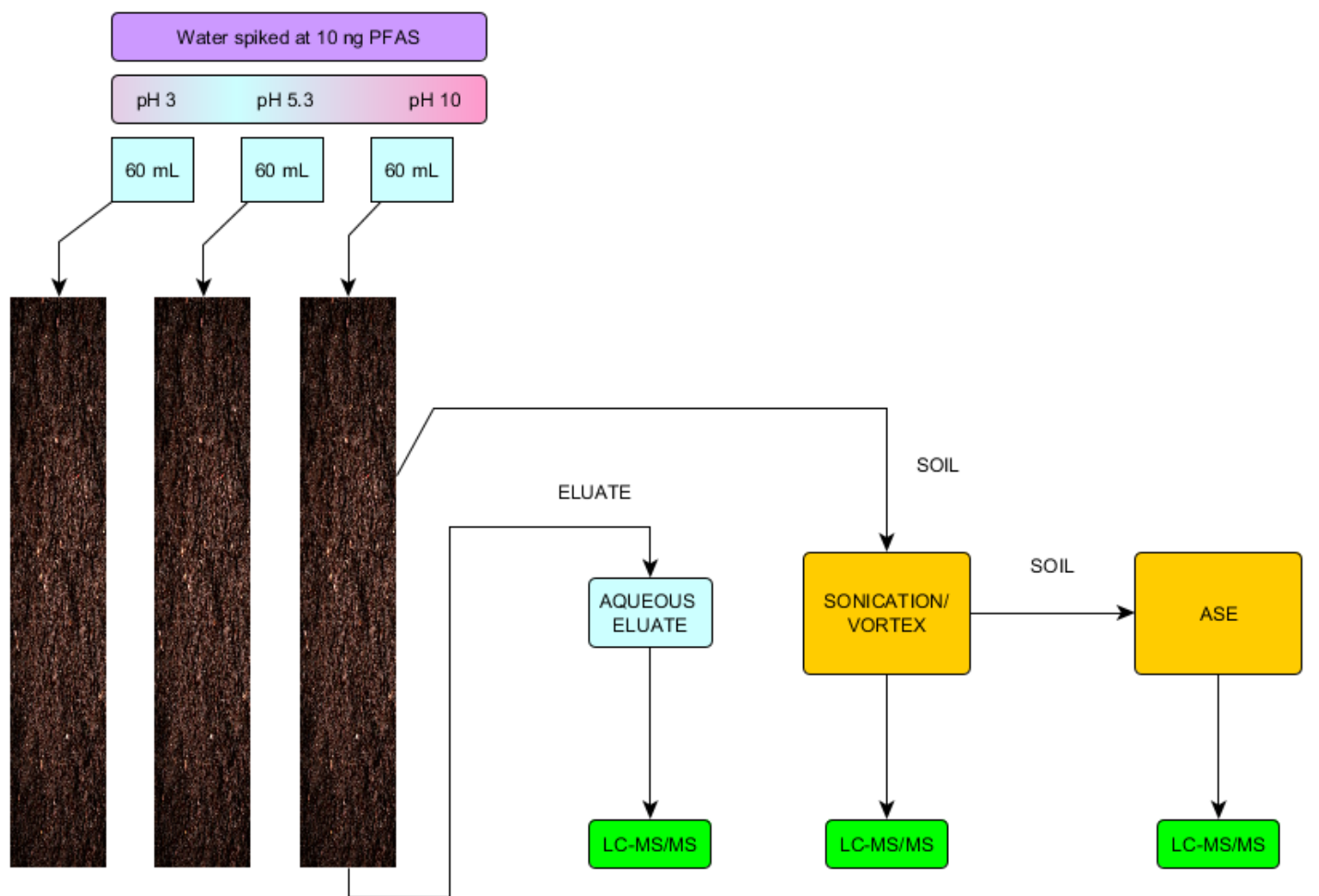
Extraction Efficiency Experiment



Extraction Efficiency Experiment



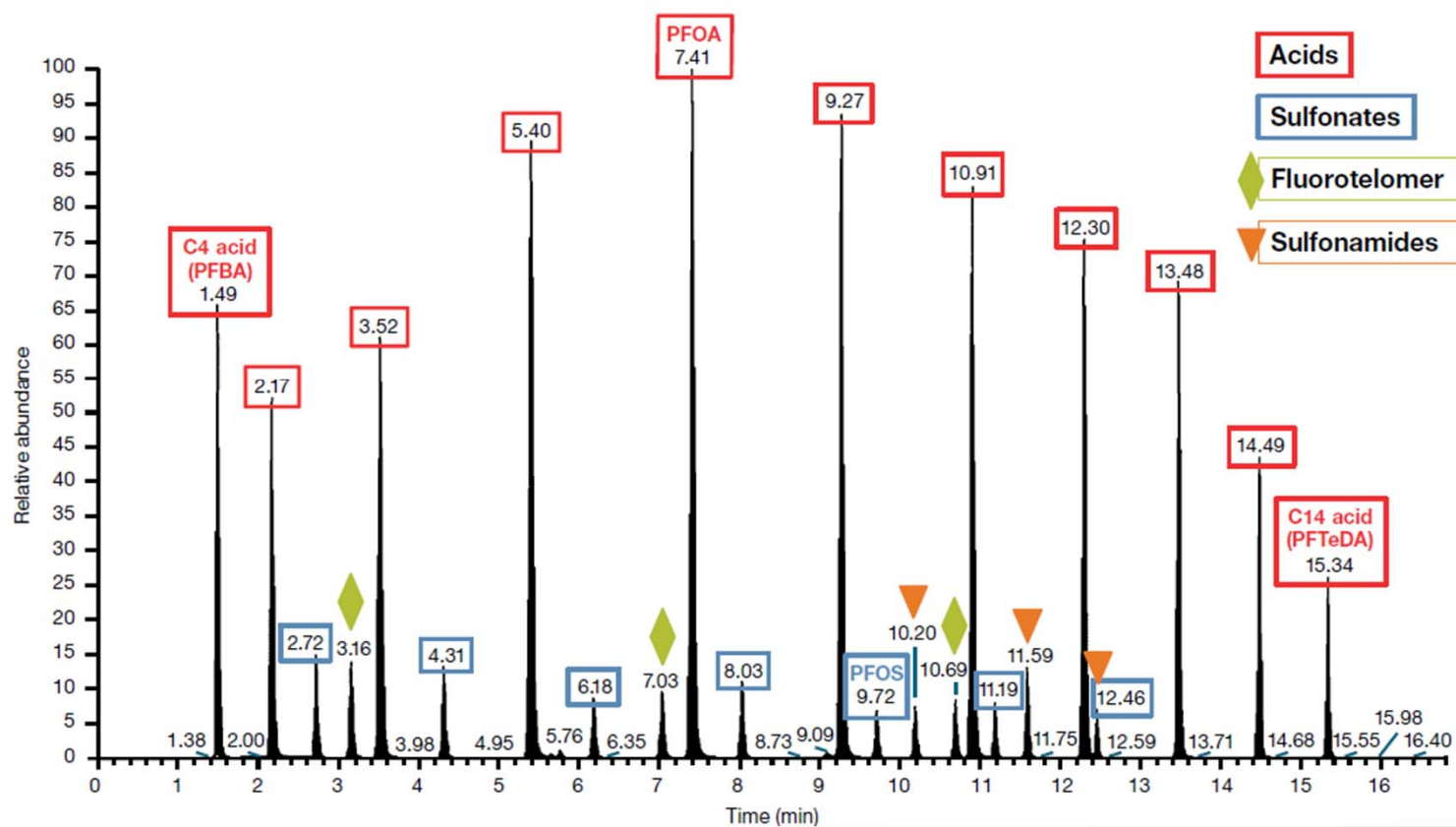
Extraction Efficiency Experiment



Sequential Extractions of PFAS from Soil

		% RECOVERY			
		AQUEOUS	AFTER		
		ELUATE	SONIC/ VORTEX	AFTER ASE	
	ng spiked				
C6	pfhxa	10.00	98%	3%	10%
C7	pfhpa	10.00	225%	0%	5%
C8	pfoa	10.00	188%	14%	9%
C9	pfna	10.00	92%	98%	24%
C10	pfda	10.00	9%	192%	43%
C11	pfuda	10.00	1%	106%	61%
C12	pfdoa	10.00	0%	44%	67%
C13	pftrda	10.00	0%	38%	80%
C14	pfteda	10.00	0%	0%	92%
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PFAS results using ASE 350



PFAS Recovery

Compound	Recovery (%)
$^{13}\text{C}_4$ -PFBA	71
$^{13}\text{C}_5$ -PFPeA	93
$^{13}\text{C}_5$ -PFHxA	97
$^{13}\text{C}_4$ -PFHpA	96
$^{13}\text{C}_8$ -PFOA	94
$^{13}\text{C}_9$ -PFNA	104
$^{13}\text{C}_6$ -PFDA	99
$^{13}\text{C}_7$ -PFUdA	95
$^{13}\text{C}_2$ -PFDaA	97
$^{13}\text{C}_2$ -PFTeDA	108

Compound	Recovery (%)
$^{13}\text{C}_3$ -PFBS	98
$^{13}\text{C}_3$ -PFHxS	95
$^{13}\text{C}_8$ -PFOS	91
$^{13}\text{C}_3$ -HFPODA	56
$^2\text{H}_3$ -NMEFOSAA	93
$^2\text{H}_3$ -NETFOSAA	90
$^{13}\text{C}_8$ -FOSA	92
$^{13}\text{C}_2$ -4:2FTS	110
$^{13}\text{C}_2$ -6:2FTS	93
$^{13}\text{C}_2$ -8:2FTS	98

- Excellent Recoveries between 71% and 110%
- Only exception is HFPO-DA;

Analysis of Blanks

Spike level batch	1 ng/g spike		20 ng/g spike	400 ng/g spike
	ng/g	ng/g	ng/g	ng/g
PFBA	0.01	0.01	0.05	0.05
PFPeA	n.d.	n.d.	n.d.	n.d.
PFHxA	0.01	0.01	0.03	0.04
PFHpA	n.d.	n.d.	0.02	0.01
PFOA	0.01	0.01	0.04	0.04
PFNA	n.d.	n.d.	n.d.	n.d.
PFDA	n.d.	n.d.	n.d.	n.d.
PFUdA	n.d.	n.d.	n.d.	n.d.
PFDoA	n.d.	n.d.	n.d.	n.d.
PFTRDA	n.d.	n.d.	n.d.	n.d.
PFTEDA	n.d.	n.d.	n.d.	n.d.
NMEFOSAA	n.d.	n.d.	n.d.	n.d.

Spike level batch	1 ng/g spike		20 ng/g spike	400 ng/g spike
	ng/g	ng/g	ng/g	ng/g
NETFOSAA	n.d.	n.d.	n.d.	n.d.
FOSA	n.d.	n.d.	n.d.	n.d.
PFBS	n.d.	n.d.	0.01	n.d.
PFPeS	n.d.	n.d.	n.d.	n.d.
PFHxS	n.d.	n.d.	n.d.	n.d.
PFHpS	n.d.	n.d.	n.d.	n.d.
PFOS	n.d.	n.d.	n.d.	n.d.
PFNS	n.d.	n.d.	n.d.	n.d.
PFDS	n.d.	n.d.	n.d.	n.d.
4:2FTS	n.d.	n.d.	n.d.	n.d.
6:2FTS	n.d.	n.d.	n.d.	n.d.
8:2FTS	n.d.	n.d.	n.d.	n.d.

Blanks are very clean
 Very little background PFAS

Method Linearity

Spike level	1 ng/g	5 ng/g	20 ng/g	100 ng/g	400 ng/g	Slope	r ²
PFBA	0.979	5.05	21.7	101.0	408	1.020	1.000
PFPeA	1.035	5.22	22.0	101.4	423	1.058	1.000
PFHxA	1.024	5.15	22.1	102.4	429	1.073	1.000
PFHpA	0.985	5.28	22.4	99.2	423	1.056	1.000
PFOA	1.02	5.02	22.1	100.7	425	1.062	1.000
PFNA	1.032	5.21	21.8	102.6	426	1.064	1.000
PFDA	1.000	5.06	21.5	100.5	428	1.071	1.000
PFUdA	0.982	5.01	22.6	96.8	418	1.044	1.000
PFDoA	1.05	5.43	23.5	77.3	339	0.841	0.999
PFTRDA	0.567	3.65	15.5	45.4	200	0.496	0.998
PFTEDA	1.076	5.57	23.9	76.6	317	0.786	0.999
NMEFOSAA	1.13	4.86	22.8	97.2	368	0.915	1.000
NETFOSAA	1.097	5.18	19.5	117.0	424	1.061	0.999
FOSA	0.991	5.16	21.7	93.0	438	1.097	0.998
PFBS	0.966	5.14	22.4	104.6	453	1.133	1.000
PFPeS	0.915	4.93	21.1	99.6	433	1.084	1.000
PFHxS	0.945	4.98	21.6	110.6	451	1.129	1.000
PFHpS	0.976	4.55	22.8	111.4	467	1.169	1.000
PFOS	1.076	6.14	20.3	108.2	468	1.172	1.000
PFNS	0.893	5.51	21.4	107.1	462	1.156	1.000
PFDS	0.999	5.54	20.8	104.4	447	1.119	1.000
4:2FTS	1.129	5.89	22.2	57.8	272	0.672	0.997
6:2FTS	1.128	6.19	21.8	89.2	430	1.074	0.998
8:2FTS	1.149	5.43	21.0	79.8	384	0.958	0.998

Conclusions

- Accelerated solvent extraction with ASE 350 is an excellent preparation method for PFAS soil analysis
 - Sonication is inadequate for extraction of long-chain PFAS from soil
- Accelerated solvent extraction can extract a variety of PFAS
 - acids
 - sulfonates
 - fluorotelomer sulfonates
 - sulfonamide compounds
- Better recovery, wide linear range (1 to 400 ppb) and low carryover



**Collaborators: Matthew S. MacLennan, Daniel Ng,
and David Hope**

Thank you!

Thank you for your time and attention!

Questions?