Chemistry and Analytical Methodology Review of Perchlorate, 1,4-Dioxane and PFAS

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November 8, 2018

1 Essential Day: Regulatory Updates; Emerging Contaminants & Investigative Technologies

LONG ISLAND ASSOCIATION OF PROFESSIONAL GEOLOGISTS

Charles E.
SCHUMER
UNITED STATES SENATOR FOR NEW YORK

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Newsroom / Press Releases

03.06.17

GILLIBRAND, SCHUMER UNVEIL NEW PLAN TO ENSURE SAFER DRINKING WATER ACROSS NY; HARMFUL CONTAMINANTS FOUND IN NEW YORK DRINKING WATER—FROM HOOSICK FALLS TO NEWBURGH TO LONG ISLAND—REQUIRE FED ACTION; SENATORS INTRO LEGISLATION TO PROTECT NEW YORKERS FROM DANGEROUS TOXINS FROM NY WATER

?

New Bill Would Force EPA To Develop a Maximum Contaminant Level for Perfluorinated Compounds like PFOS & PFOA, and 1,4 Dioxane, Perchlorate

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Newsroom / Press Releases

01.27.17

SCHUMER, GILLIBRAND: POSSIBLE CANCER-CAUSING CHEMICAL FOUND IN LI WATER SUPPLY REQUIRES IMMEDIATE EPA SCRUTINY TO ENSURE PUBLIC HEALTH; SENATORS CALL ON EPA TO SPEED UP HEALTH RISK ASSESSMENT OF 1,4-DIOXANE & DELIVER ANSWERS TO ANXIOUS PUBLIC; NO TIME TO WASTE

Emerging Contaminants

- Perchlorate (UCMR 1 2001 – 2003)
- 1,4-Dioxane (UCMR 3 2013 – 2015)
- Per- and polyfluoroalkyl substances (PFAS) (UCMR 3 2013 – 2015)

UCMR- Collect data for contaminants suspected to be present in drinking water, but that do not have health-based standards set under the Safe Drinking Water Act (SDWA). Every five years.

– *"what we find in the environment often depends on what we look for and how hard we look"*

USGS website

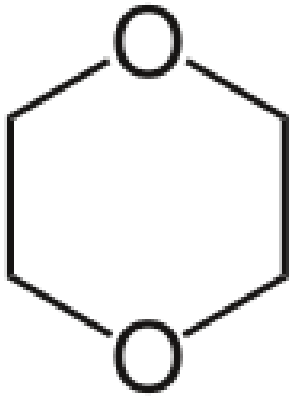
UCMR 3 (Unregulated Contaminant Monitoring Rule)

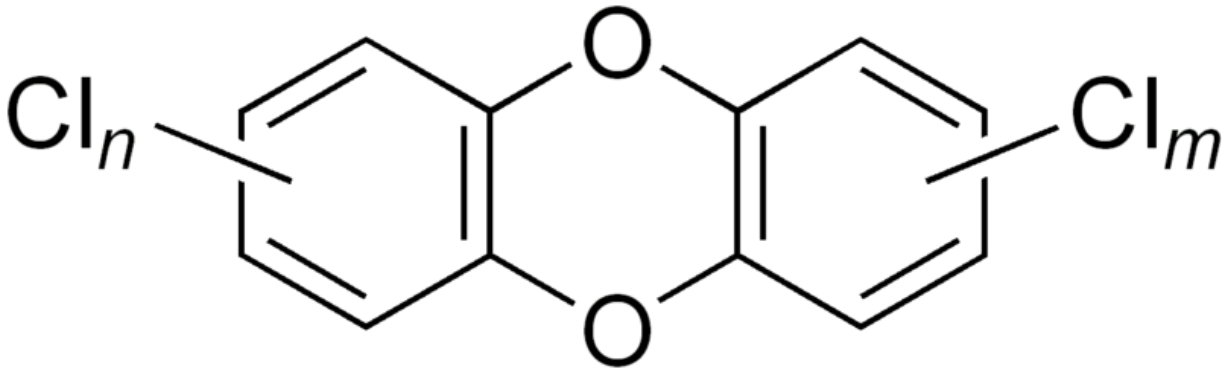
6 PFAS cmpds included

PFOS	EPA HAL	perfluorooctanesulfonic acid
PFOA	EPA HAL	perfluorooctanoic acid
PFNA	NJ GWQC	perfluorononanoic acid
PFHxS		perfluorohexanesulfonic acid
PFHpA		perfluoroheptanoic acid
PFBS		perfluorobutanesulfonic acid

An Emerging Contaminant

- Dioxane ……not Dioxin





- EPA removed 1,4-dioxane from VOC TCL
  - switched to SVOC TCL

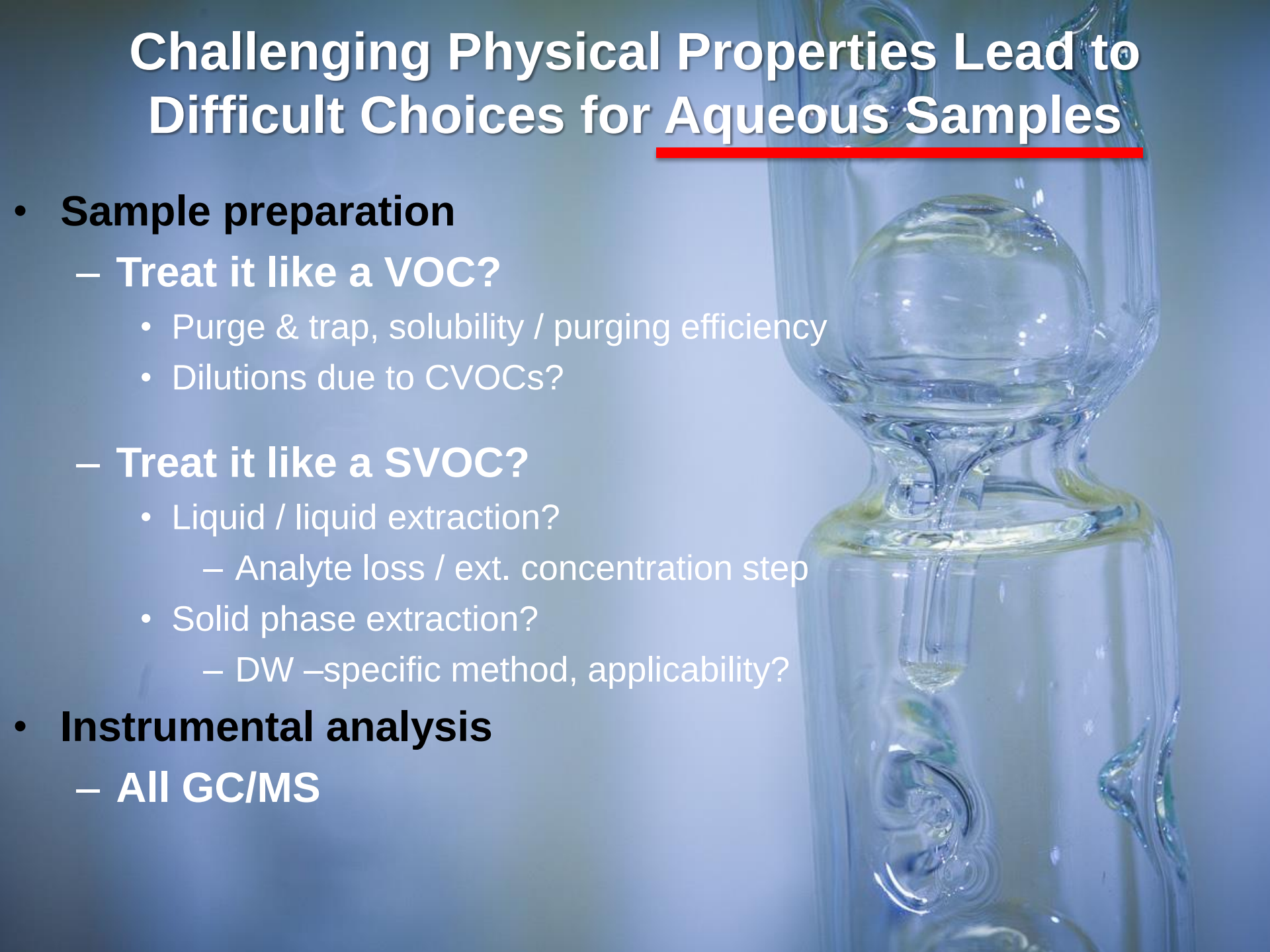
Emerging from Where?

- As a primary contaminant
  - Release of 1,4-dioxane itself
- As a secondary contaminant
  - Chlorinated solvent sites
    - Stabilizer for 111-TCA & other solvents
    - Small % of the released product
  - CVOCs can cause dilutions & high RLs
    - This is where much of the historical interest was

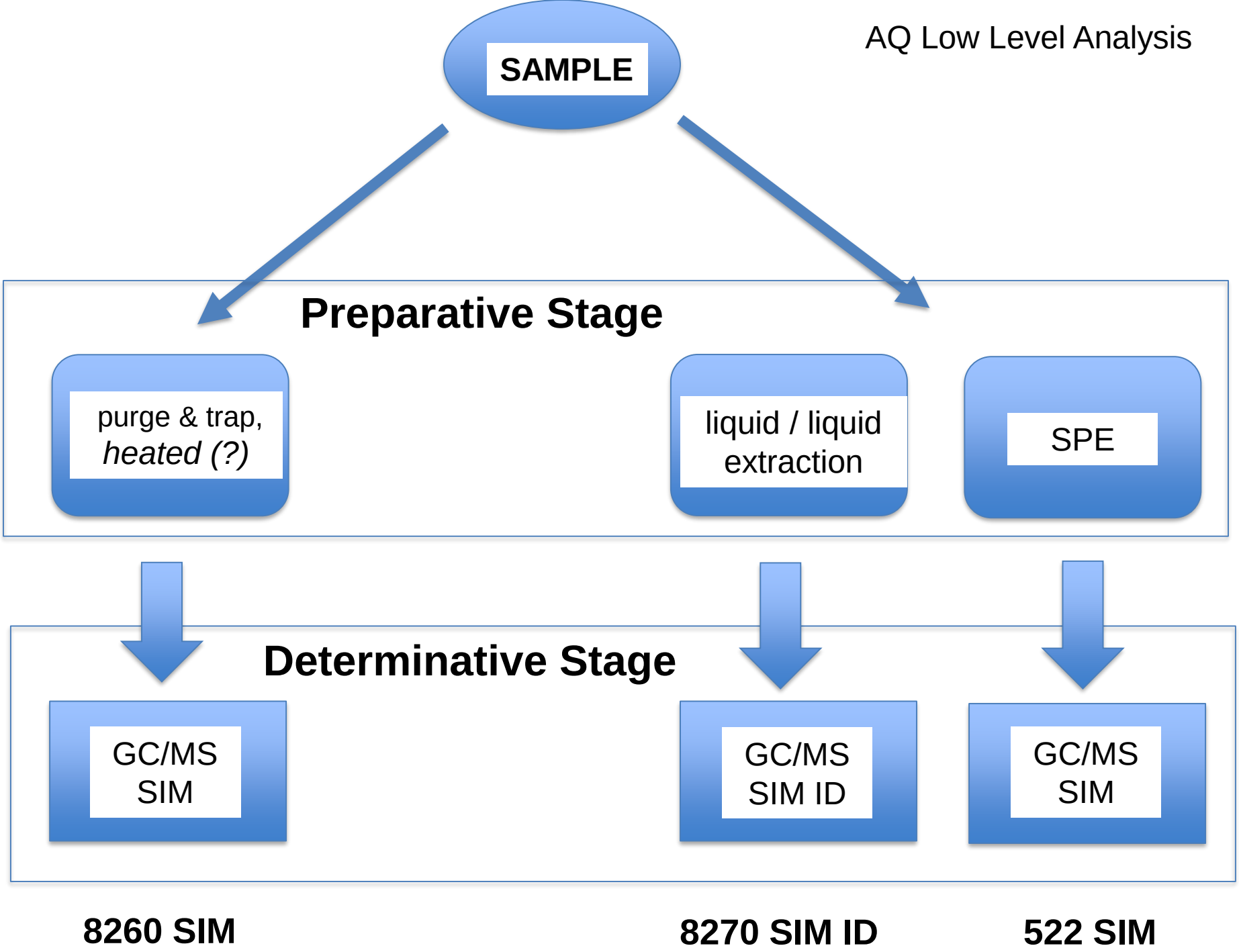
As a Secondary Contaminant

- Consumer / commercial products
  - As an ingredient
    - Home care / commercial products
      - paint, dyes, varnish removers, paint strippers, antifreeze, airplane deicing solutions, inks, adhesives, etc.
  - As an impurity / byproduct
    - Personal care / home products
      - Detergents, cosmetics, deodorants, shampoos, & food packaging
        - » Can be produced during sulfation of ethoxylated alcohols to make AES (Alcohol Ethoxysulphates), PEG 40, PEG 60, 1%
        - » WWTPs, septic systems…landfills

Challenging Physical Properties Lead to Difficult Choices for Aqueous Samples



- **Sample preparation**
  - **Treat it like a VOC?**
    - Purge & trap, solubility / purging efficiency
    - Dilutions due to CVOCs?
  - **Treat it like a SVOC?**
    - Liquid / liquid extraction?
      - Analyte loss / ext. concentration step
    - Solid phase extraction?
      - DW –specific method, applicability?
- **Instrumental analysis**
  - **All GC/MS**


SAMPLE
Preparative Stage
purge & trap,
heated (?)
liquid / liquid
extraction
SPE
Determinative Stage
GC/MS
SIM
GC/MS
SIM ID
GC/MS
SIM
8260 SIM
8270 SIM ID
522 SIM

Mass Spectrometric Techniques

- Selected Ion Monitoring (SIM)
  - scanning mode in which only a limited mass-to-charge ratio range is transmitted/detected by the instrument
  - Focus on specific COCs Vs. full TCL
    - INCREASED SENSITIVITY
  - No library searches / TICs

- Isotopic Dilution (ID)
  - addition of known amount of isotopically-enriched, compound-specific internal standard
    - PRIOR TO SAMPLE PREPARATION
  - Analysis-specific, analyte-specific concentration normalization

As a VOC…

- Method 8260 full scan
  - NA for low level work
- Method 8260 SIM
  - Lower RLs
    - With heated purge & trap?
      - Heated purge to try to mitigate poor purging efficiency
        - » w/ HCl preservative will compromise some additional analytes
- VOCs present > ~250 PPB will raise dioxane RL due to dilutions
- Sub 1 PPB dioxane analysis pushes instrumentation to the absolute limit, with increased variability expected

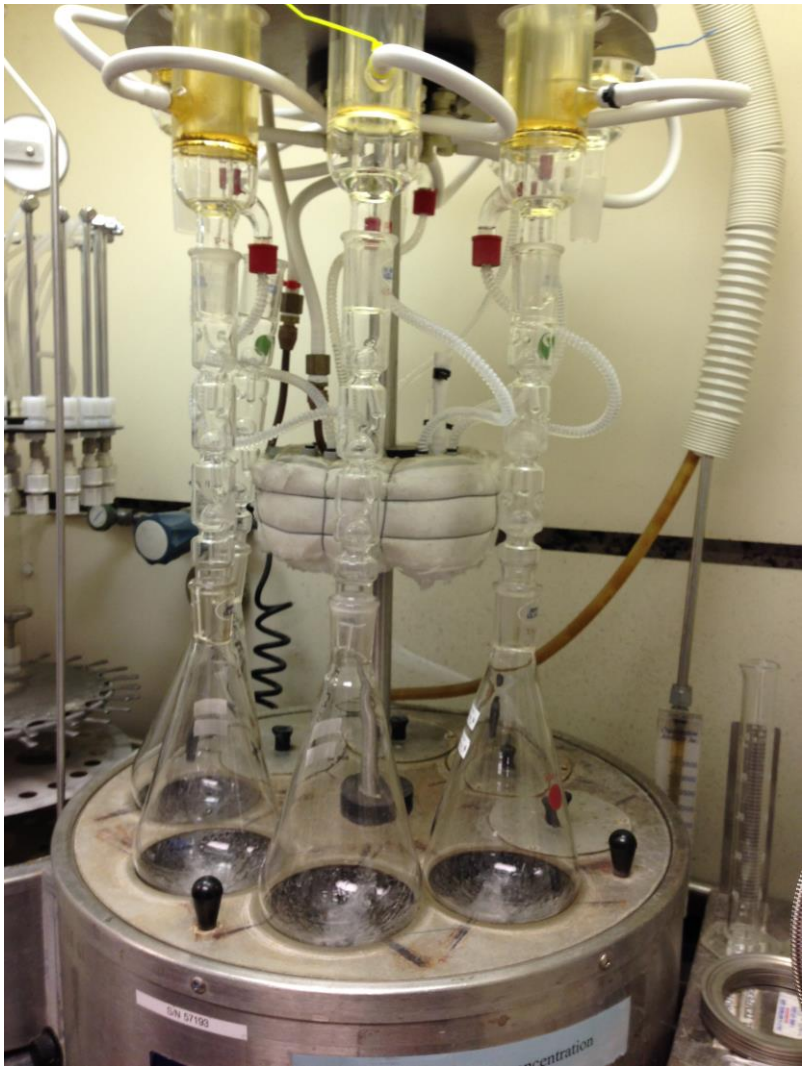
As a SVOC… Method 8270 SIM Isotope Dilution

- L / L extraction, extract concentration
  - Generally poor % recovery observed without ID

- With Isotope Dilution:
  - 1,4-dioxane-d8, internal standard role
    - spiked into the sample **before / at the time of extraction**
      - extraction efficiency similar to the target 1,4-dioxane

  - 1,4-dichlorobenzene-d4, surrogate spike role
    - 1,4-DCB-d4, regular internal standard used as surrogate
      - **added after extraction / before analysis**
        - » % recovery calculated

- Acceptable performance for low level analysis
  - ID accounts for extraction efficiency, normalizes result
  - High VOC concentrations do not interfere



As a SVOC…Method 522

- Solid phase extraction (SPE) sample prep
- GC/MS SIM

- Acceptable performance for low level analysis
  - Most sensitive method
  - High VOC concentrations do not interfere

- Drinking water method
  - Other matrices, applicability to GW, turbidity, silty samples, etc.
  - Sample preservation requirements

Can I Run 1,4-Dioxane as TCL SVOC?

Answer: NO

Why:

TCL SVOC

- Higher Reporting limit than required
- Unable to use Isotope Dilution (Data Bias)
- Generally run as full scan (no SIM)

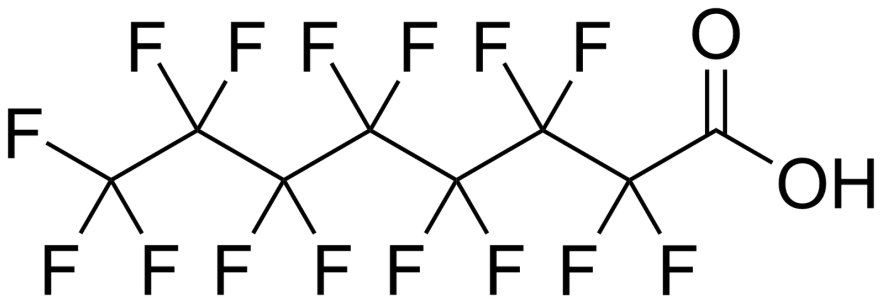
Summary of 1,4 Dioxane

- Methods for Water
  - Drinking Water Sources: EPA Method 522 SIM, SPE
  - Other Water Sources: 8270 SIM with Istope Dilution

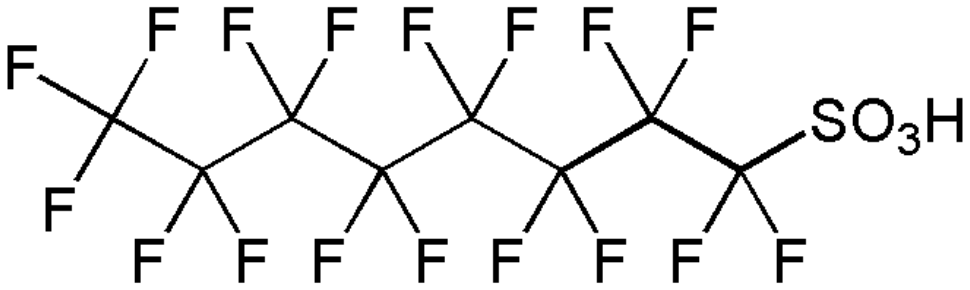
- Certification
  - New York does offer certification

- RL/MDL
  - NYS: No higher than 0.28 ug/L
  - RL 0.15 ug/L

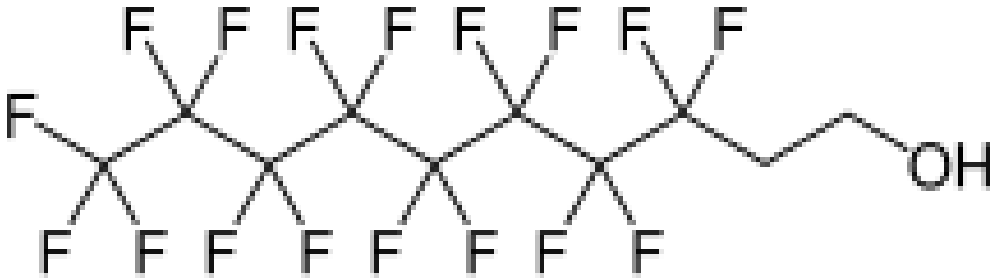
Perfluorochemicals (PFCs)



PFOA



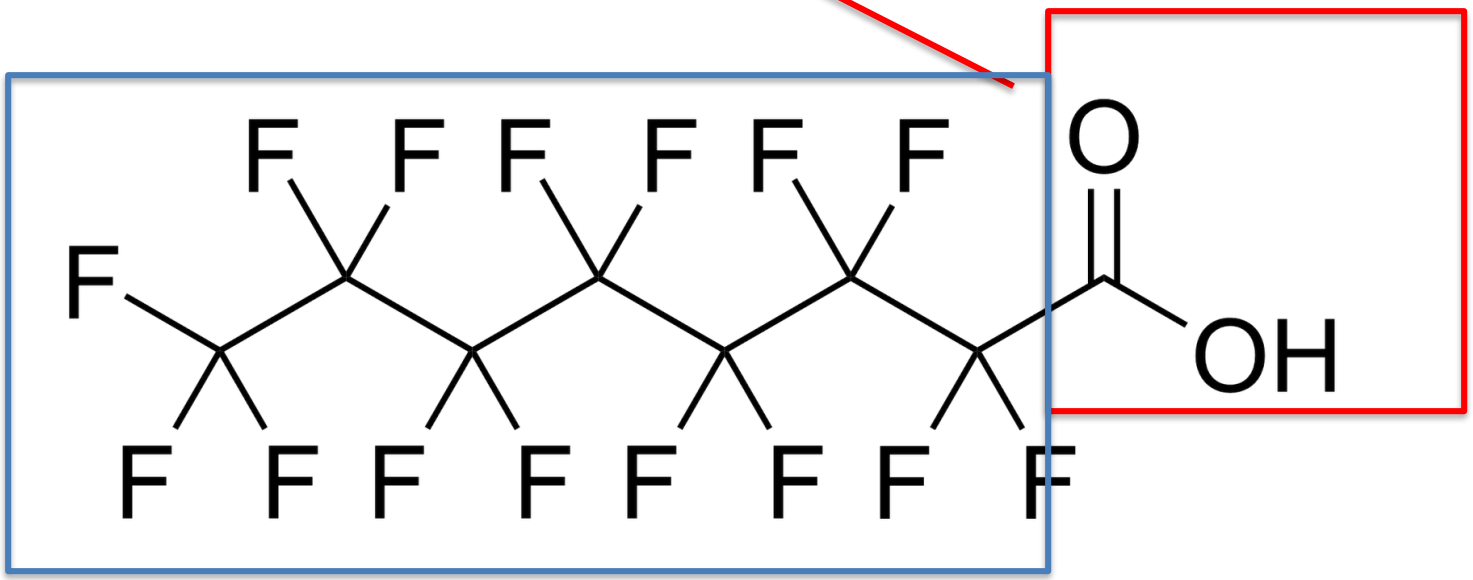
PFOS



8:2 Fluorotelomer Alcohol

Per- and polyfluoroalkyl Substances (PFAS)

hydrophilic “head”



hydrophobic “tail”

PFAS - Sources of Contamination

- Industrial uses / commercial products
  - PFOA (perfluorooctanoic acid) “C8”
    - non-stick pan coatings, waterproof clothing, stain repellents, etc. Used in production of PTFE (polytetrafluoroethylene i.e.“teflon”)
      - Dupont…, 1990’s West Virginia
    - PTFE used as raw material in manufacturing of many products
      - St Gobain Performance Plastics Hoosick Falls NY, NH & VT
  - PFOS (perfluorooctanesulfonate)
    - Fabric protectors, stain repellents
    - Primary manufacturer 3M, i.e. “Scotchguard”
- *Paints, adhesives, upholstery, fabric softeners, packaging, clothing, aluminum foil, cosmetics, pesticides, sunscreen, pizza boxes, microwave popcorn bags, etc. etc. etc.*
  - C8 manufacturing phased out…replacements?

AFFF (Aqueous Film Forming Foam)

- Fire training, military bases, airports, etc.

All contain fluorinated surfactants

Older stocks contain PFOS, other C8s can still be used

AFFF currently being manufactured with C6 cmpds

Replacements????.....

So What Do You Analyze For?

consumer products

Industry
- PFOA +
- Impurities
- New cmpds

PFOA / PFOS
UCMR 6
Method 537 14

Landfills

"a little of everything"

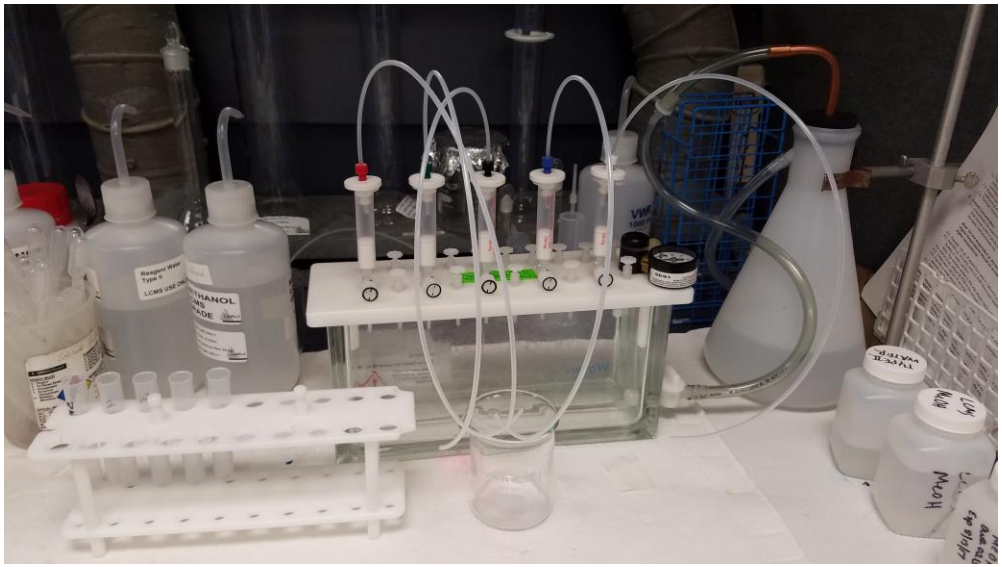
Mixed bag, not consistent

AFFF
- PFOS
- Technical grade mix
- New cmpds

Expanded List …but not consistent site to site

Analytical Methodologies

- Prep
  - Solid phase extraction (SPE), *aqueous samples*
- Instrument
  - LC/MS/MS
- Primary method (Aq) Drinking Water Sources
  - EPA 537 w/SPE
    - 14 compounds
    - EPA Technical Advisory 815-B-16-021
- Method 537 not amenable to expanded list of compounds
  - Isotope dilution approach
  - Modified?



ALPHA ANALYTICAL
World Class Chemistry

EPA Method 537 - List of 14 Compounds

Perfluorooctanoic acid (PFOA)
Perfluorooctane Sulfonate (PFOS)
Perfluorobutanesulfonic acid (PFBS)
Perfluoroheptanoic acid (PFHpA)
Perfluorohexane Sulfonate (PFHxS)
Perfluorononanoic acid (PFNA)
Perfluorohexanoic acid (PFHxA)
Perfluorodecanoic acid (PFDA)
Perfluoroundecanoic acid (PFUdA)
N-methyl perfluorooctanesulfonamidoacetic acid (MeFOSAA)
Perfluorododecanoic acid (PFDoA)
N-ethyl perfluorooctanesulfonamidoacetic acid (EtFOSAA)
Perfluorotridecanoic acid (PRTrDA)
Perfluorotetradecanoic acid (PFTeDA)

Expanded List By Isotope Dilution

ANALYTE NAME	Acronym	CAS
PERFLUOROALKYLCARBOXILIC ACIDS (PFCAS)		
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1
Perfluoro-n-undecanoic acid	PFUdA	2058-94-8
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-butanoic acid	PFBA	375-22-4
PERFLUOROALKYLSULFONATES (PFASs)		
Perfluoro-1-decanesulfonate	PFDS	335-77-3
Perfluoro-1-nonanesulfonate	PFNS	68259-12-1
Perfluorooctanesulfonate	PFOS	1763-23-1
Perfluoro-1-heptanesulfonate	PFHpS	375-92-8
Perfluorohexanesulfonate	PFHxS	355-46-4
Perfluoro-1-pentanesulfonate	PFPeS	2706-91-4
Perfluoro-1-butanesulfonate	PFBS	375-73-5
PERFLUOROOCTANESULFONAMIDES (FOSAs)		
Perfluoro-1-octanesulfonamide	FOSA	754-91-6
TELOMER SULFONATES		
1H,1H,2H,2H-perfluorodecane sulfonate (8:2)	8:2FTS	39108-34-4
1H,1H,2H,2H-perfluorooctane sulfonate (6:2)	6:2FTS	27619-97-2
1H,1H,2H,2H-perfluorohexane sulfonate (4:2)	4:2FTS	n/a
PERFLUOROOCTANESULFONAMIDOACETIC ACIDS		
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6
N-methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9

NYSDEC UPDATE Oct 2017

For GW, SW, soils, & sediments lab should be directed to report all calibrated PFAS cmpds.

Reported cmpds will include at a minimum (current Oct 2017)

ELAP offers DW cert for PFOA / PFOS. No certification for other matrices but lab should hold PFAS DW cert. "modified" method 537 or ISO 25101

Expected PFOA / PFOS RL 2 ng/L AQ, 3 ug/Kg soil

Full PFAS Target Analyte List

Perfluoroalkyl sulfonates	**Perfluorobutanesulfonic acid**	**PFBS**	**375-73-5**
	Perfluorohexanesulfonic acid	**PFHxS**	**355-46-4**
	Perfluoroheptanesulfonic acid	PFHpS	375-92-8
	Perfluorooctanessulfonic acid	**PFOS**	**1763-23-1**
	Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluoroalkyl carboxylates	Perfluorobutanoic acid	PFBA	375-22-4
	Perfluoropentanoic acid	PFPeA	2706-90-3
	Perfluorohexanoic acid	PFHxA	307-24-4
	Perfluoroheptanoic acid	**PFHpA**	**375-85-9**
	Perfluorooctanoic acid	**PFOA**	**335-67-1**
	Perfluorononanoic acid	**PFNA**	**375-95-1**
	Perfluorodecanoic acid	PFDA	335-76-2
	Perfluoroundecanoic acid	PFUA/PFUdA	2058-94-8
	Perfluorododecanoic acid	PFDoA	307-55-1
	Perfluorotridecanoic acid	PFTriA/PFTrDA	72629-94-8
	Perfluorotetradecanoic acid	PFTA/PFTeDA	376-06-7
Fluorinated Telomer Sulfonates	6:2 Fluorotelomer sulfonate	6:2 FTS	27619-97-2
	8:2 Fluorotelomer sulfonate	8:2 FTS	39108-34-4
Perfluorooctane-sulfonamides	Perfluroroctanesulfonamide	FOSA	754-91-6
Perfluorooctane-sulfonamidoacetic acids	N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9
	N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6

Regulatory Criteria & Standards

- EPA Health Advisory Levels (HALs) adopted May 2016
  - PFOA 70 ppt / PFOS 70 ppt (total can not exceed 70 ppt)
- NHDES adopted 70 ppt for AGQS
- NJ MCL -14 ppt for PFOA/13 ppt for PFOS, 13 ppt for PFNA
- NY standard 70 ppt for PFOA/PFOS (Total)
- Reporting limits (RLs)
  - NYS
    - 2 ppt for PFOA and PFOS
  - NJ
    - 3 ppt
  - NHDES
    - 5 ppt

PFAS Sampling?

- Recommendation:
  - *Sample naked…and don't shower that day!*
  - *Not quite…but*

see EPA / state guidelines

"sharpies", field books, "post its", coated Tyvek, Teflon bailers/caps, etc. etc.

Sampling:
need to address possible sources of contamination

OK

- Field Equipment
  - HDPE bottles, silicon tubing, loose paper, aluminum/Masonite clipboards, Alconox / Liquinox@, nitrile gloves
- Clothing / PPE
  - “Well laundered”, preferably cotton
- Personal care products
  - None, see “allowable” sun screens & insect repellants

NOT OK

- Field Equipment
  - LDPE bottles, Teflon@ caps, Teflon@ tubing, waterproof field books, plastic clipboards/binders, Post It @ notes, chemical (blue ice)
- Clothing / PPE
  - No fabric softener, Gor-Tex@, “dri -fit”, Tyvek @
- Personal care products
  - No cosmetics, moisturizers, etc. as part of personal cleaning/showering routine on morning of sampling
  - Verify allowable sun screens / insect
  - Food packaging

Questions ????

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