United States
Environmental Protection
Agency

12th CECIA-IAUPR Symposium
Puerto Rico
February 17, 2017

PFOA and PFOS: Treatment and Analytics

Thomas F. Speth, Ph.D., P.E.
Craig L. Patterson, P.E.
Rajiv Khera, P.E.
Jody A. Shoemaker
Paul E. Grimmett
Brenda K. Boutin

Advisory Limits

- PFOA and PFOS are not regulated by the USEPA. However, in 2016, USEPA established a Lifetime Drinking Water Health Advisory limit of 0.07 µg/L for PFOA + PFOS

EPA United States Environmental Protection Agency Office of Water Mail Code 4304T EPA 822-R-16-005 May 2016

Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA)

EPA United States Environmental Protection Agency Office of Water Mail Code 4304T EPA 822-R-16-004 May 2016

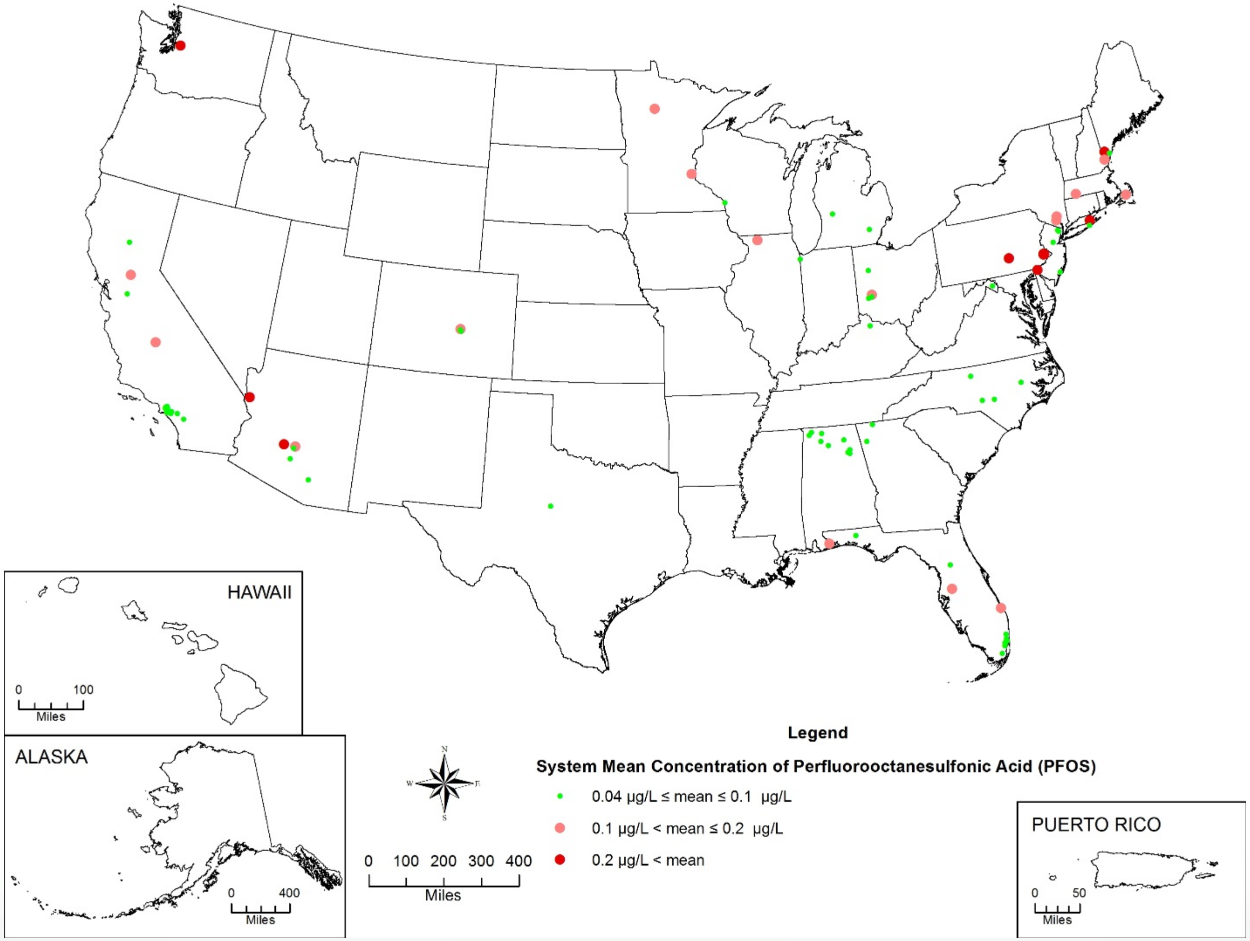
Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS)

https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

- PFOA and PFOS are on the draft CCL4

UCMR3 PFOA Results

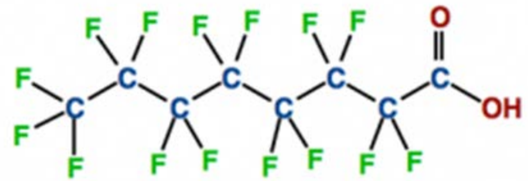
Mean Concentrations



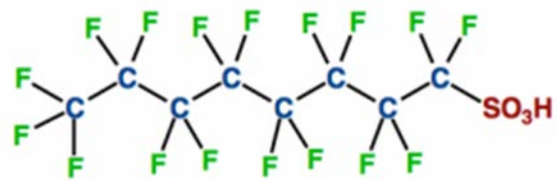
General Properties

Of note…

- Strong bonds - stable
- Negatively charged
- Low volatility
- High molecular weight
- Moderate solubility



PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

Publically Available Resource

- Interactive database that contains over 65 regulated and unregulated contaminants and covers 34 treatment processes commonly employed or known to be effective
- Referenced information gathered from thousands of literature sources assembled on one site
- Carbon tetrachloride, nitrate, **PFOA**, **PFOS**, strontium, 1,2,3-TCP, and cis 1,2-DCE added recently

http://iaspub.epa.gov/tdb/pages/general/home.do

Search: EPA TDB

Drinking Water Treatability Database

http://oaspub.epa.gov/tdb/pages/general/home.do

Water Treatability Database...

File Edit View Favorites Tools Help

U.S. ENVIRONMENTAL PROTECTION AGENCY

Drinking Water Treatability Database

Share

Contact Us

Search EPA: Go

You are here: EPA Home » Drinking Water Treatability Database » Welcome to the Drinking Water Treatability Database

- Home
- About the TDB
- Find a Contaminant
- Find a Treatment Process
- Help

Welcome to the Drinking Water Treatability Database

The Drinking Water Treatability Database (TDB) presents referenced information on the control of contaminants in drinking water. It allows drinking water utilities, first responders to spills or emergencies, treatment process designers, research organizations, academicians, regulators and others to access referenced information gathered from thousands of literature sources and assembled on one site. Over time, the TDB will expand to include over 200 regulated and unregulated contaminants and their contaminant properties. It includes more than 25 treatment processes used by drinking water utilities. The literature includes bench-, pilot-, and full-scale studies of surface waters, ground waters and laboratory waters. The literature includes peer-reviewed journals and conferences, other conferences and symposia, research reports, theses, and dissertations. By adding new contaminants and by upgrading references on existing contaminants, the TDB will always be a current source of information on drinking water contaminant control. Visit the About the TDB page for more information.

The TDB offers many features leading to the Data tab which is the heart of the TDB. After selecting a contaminant (Find a Contaminant), you will find a Treatment Processes tab that will present the list of treatment processes for which literature on the control of the contaminant was located. Selecting a treatment process, you will find a Data tab, like that shown below, that presents reference information, log or percent removal, water quality conditions and treatment process operational parameters. The Help page will aid you in navigating the TDB.

Getting Started
Find a Contaminant - Click here to find a contaminant within the TDB.
Find a Treatment Process - Click here to find a treatment process within the TDB.

Data Tab Example: Arsenic/Ion Exchange (Click on the image to view this Data tab)

Quick Links

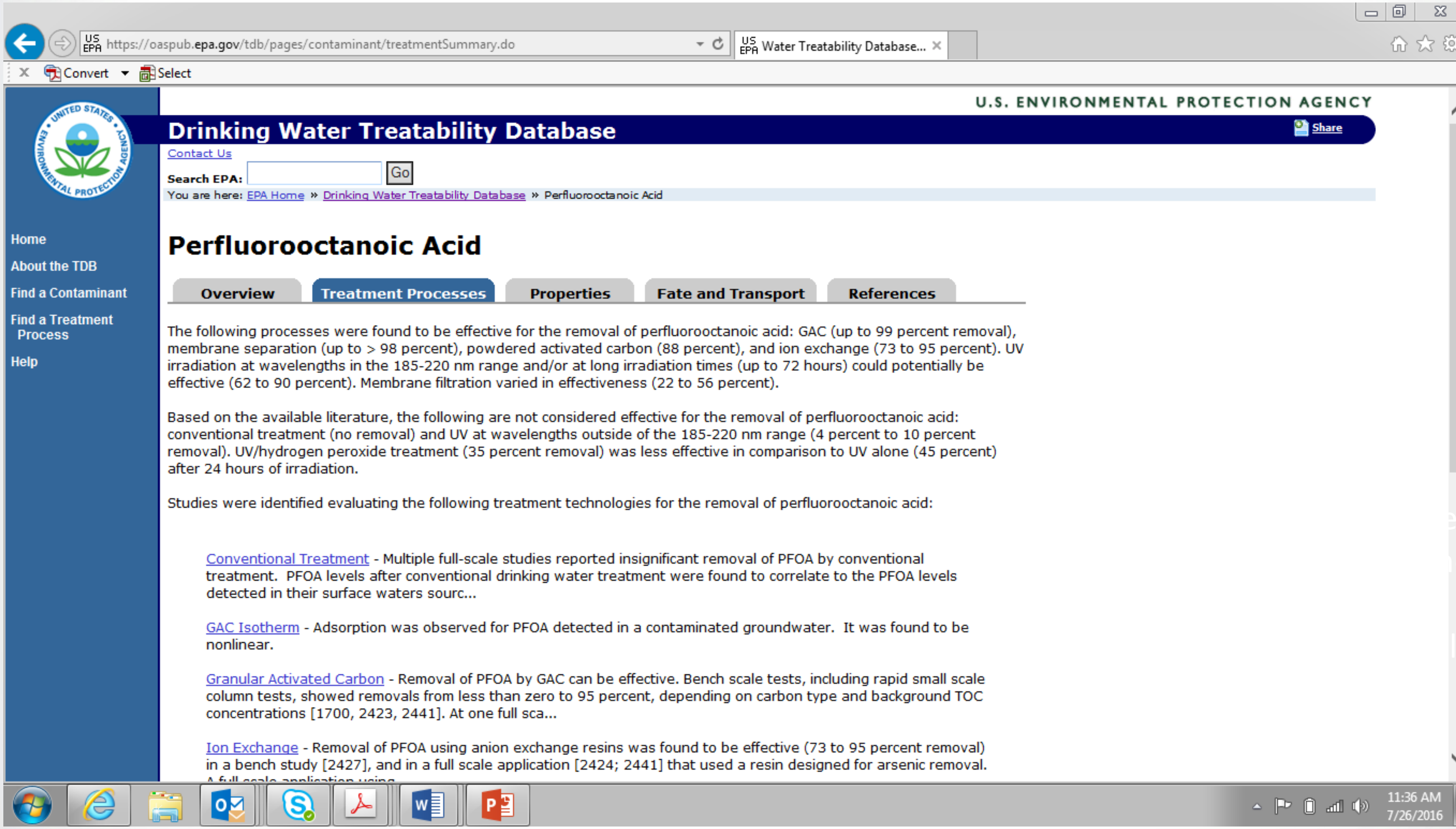
- EPA Drinking Water Standards
- EPA Water Contaminant Information Tool (WCIT)
- EPA Contaminant Candidate List
- EPA Analytical Methods
- EPA Integrated Risk Information System (IRIS) (Risk Documents)

Future Upgrades to the Drinking Water Treatability Database

Each year, as resources allow, the number of contaminants in the TDB will increase to include other regulated and unregulated drinking water contaminants. It will also upgrade information on contaminants already in the TDB to keep it current. The bottom of each page indicates when additions and upgrades were last incorporated into the TDB. Each contaminant Overview page indicates the most recent literature search date for the contaminant. View a List of Future Contaminants anticipated for the next upgrade and the anticipated upgrade date.

2:33 PM
11/20/2015

Drinking Water Treatability Database



https://oaspub.epa.gov/tdb/pages/contaminant/treatmentSummary.do

Water Treatability Database...

U.S. ENVIRONMENTAL PROTECTION AGENCY

Drinking Water Treatability Database

Share

Contact Us

Search EPA: Go

You are here: EPA Home » Drinking Water Treatability Database » Perfluorooctanoic Acid

Home

About the TDB

Find a Contaminant

Find a Treatment Process

Help

Perfluorooctanoic Acid

Overview | Treatment Processes | Properties | Fate and Transport | References

The following processes were found to be effective for the removal of perfluorooctanoic acid: GAC (up to 99 percent removal), membrane separation (up to > 98 percent), powdered activated carbon (88 percent), and ion exchange (73 to 95 percent). UV irradiation at wavelengths in the 185-220 nm range and/or at long irradiation times (up to 72 hours) could potentially be effective (62 to 90 percent). Membrane filtration varied in effectiveness (22 to 56 percent).

Based on the available literature, the following are not considered effective for the removal of perfluorooctanoic acid: conventional treatment (no removal) and UV at wavelengths outside of the 185-220 nm range (4 percent to 10 percent removal). UV/hydrogen peroxide treatment (35 percent removal) was less effective in comparison to UV alone (45 percent) after 24 hours of irradiation.

Studies were identified evaluating the following treatment technologies for the removal of perfluorooctanoic acid:

Conventional Treatment - Multiple full-scale studies reported insignificant removal of PFOA by conventional treatment. PFOA levels after conventional drinking water treatment were found to correlate to the PFOA levels detected in their surface waters sourc...

GAC Isotherm - Adsorption was observed for PFOA detected in a contaminated groundwater. It was found to be nonlinear.

Granular Activated Carbon - Removal of PFOA by GAC can be effective. Bench scale tests, including rapid small scale column tests, showed removals from less than zero to 95 percent, depending on carbon type and background TOC concentrations [1700, 2423, 2441]. At one full sca...

Ion Exchange - Removal of PFOA using anion exchange resins was found to be effective (73 to 95 percent removal) in a bench study [2427], and in a full scale application [2424; 2441] that used a resin designed for arsenic removal.

11:36 AM 7/26/2016

PFOA Treatment: Ineffective

Treatment	Percent Removal
Conventional Treatment	0
Low Pressure Membranes	2 to 56 ^
UV Disinfection	0 to 90 * #
Advanced Oxidation	
UV – Peroxide	11 to 35 *
UV – Iron	< 5 *
UV – Persulfate	5 to 87 *
UV – Periodate	9 to 87 *

^ One data point for high removal results (little information about plant)
** All bench-scale data*
 # Up to 72 hours of exposure

PFOS Treatment: Ineffective

Treatment	Percent Removal
Conventional Treatment	0
Low Pressure Membranes	0 to 23
Biological Treatment (inc. slow sand)	0 to 15
Disinfection - Chloramines	0
Oxidation	
Permanganate	1 to 53 * #
Hydrogen Peroxide	0 to 2 *
Ozone	0 to 7
Advanced oxidation	
UV – TiO_2	15
UV – Ozone	0 *
Ozone – Peroxide	9

** All bench-scale data*

 # Up to 18 days of exposure

PFOA Treatment: Effective

Treatment	Percent Removal
Anion Exchange Resin *	73 to 95 [@]
High Pressure Membranes	> 98
Powdered Activated Carbon (PAC)	20 to 88 ^
Granular Activated Carbon (GAC) *	
Extended Run Time [#]	0
Frequent GAC Replacement	90 to > 99

* Non-steady state process
[@] No bed volume fed data for cost analysis
^ Dose, water, and carbon dependent
# Extended run time with no regeneration

PAC Dose to Achieve

50% Removal	28 mg/l
90% Removal	>50 mg/L

Dudley et al., 2015

PFOS Treatment: Effective

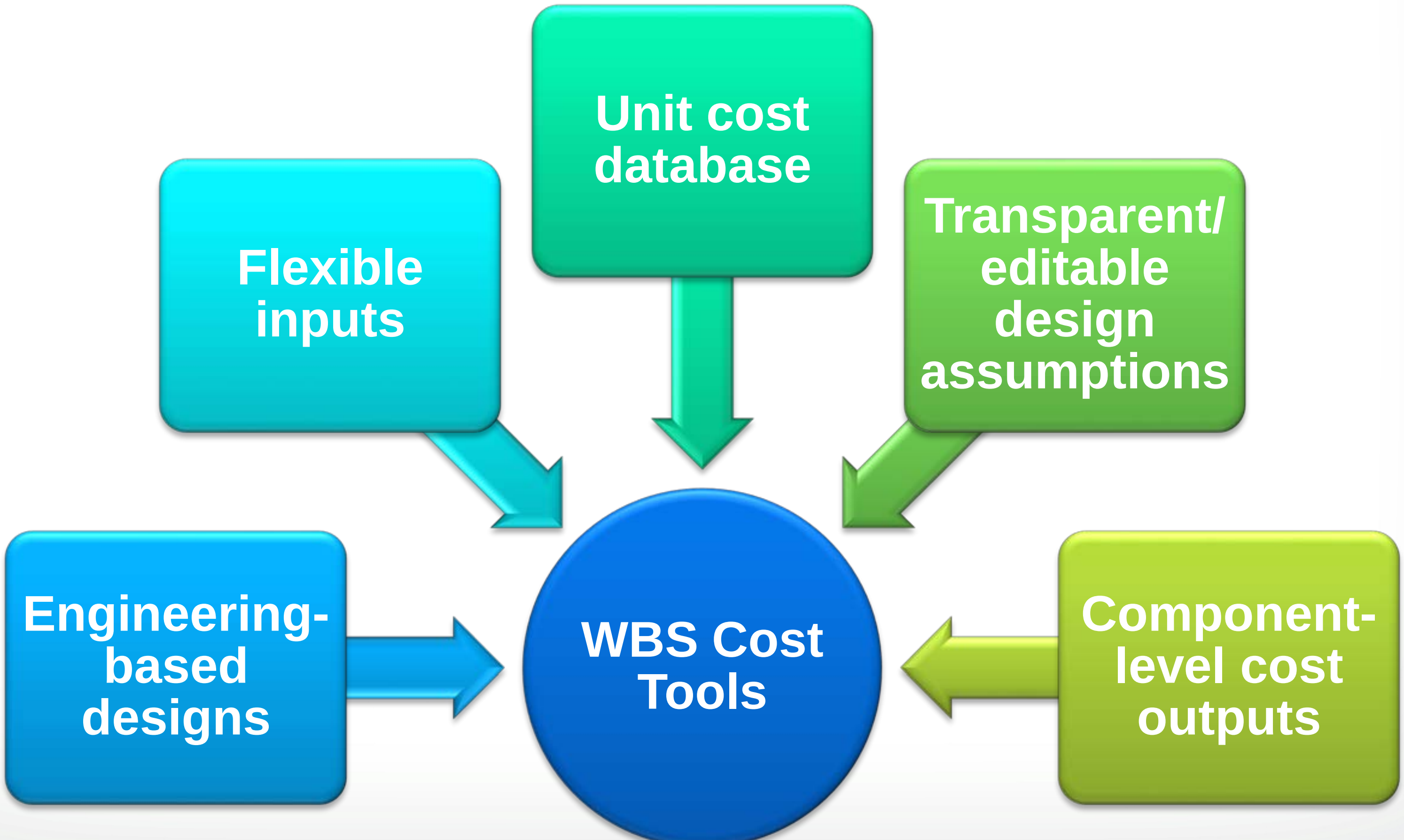
Treatment	Percent Removal
Anion Exchange Resin *	90 to 99 @
High Pressure Membranes	93 to 99
Powdered Activated Carbon (PAC)	10 to 97 ^
Granular Activated Carbon (GAC) *	
Extended Run Time #	0 to 26
Frequent GAC Replacement	> 89 to > 98

* Non-steady state process
@ No bed volume fed data for cost analysis
^ Dose, water, and carbon dependent
\# Extended run time with no regeneration

PAC Dose to Achieve	
50% Removal	16 mg/l
90% Removal	>50 mg/L

Dudley et al., 2015

WBS cost tools meet multiple criteria



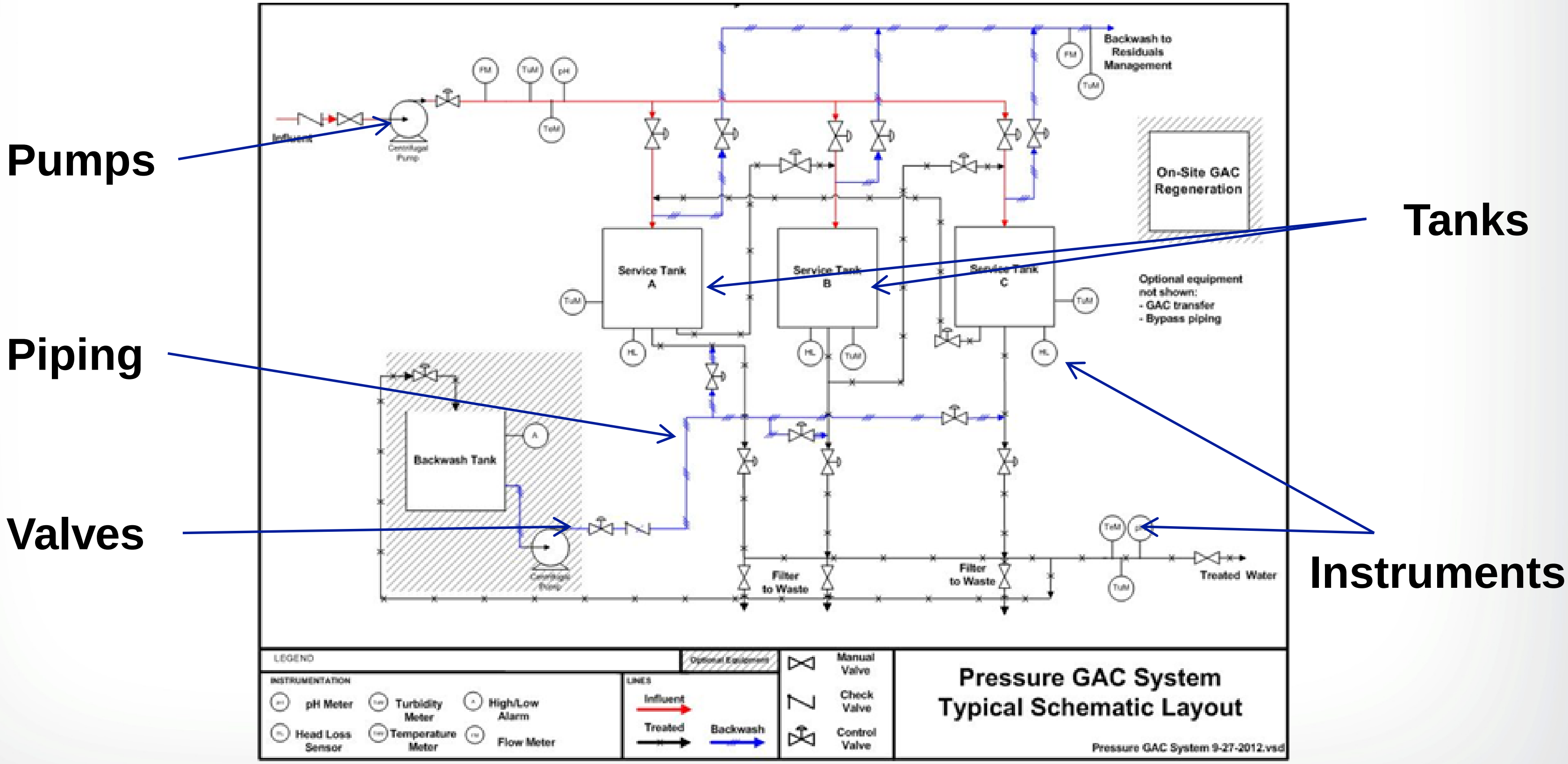
Design treatment process using inputs and assumptions and estimate costs

- Capital costs (e.g., equipment size / quantity)
- Operating costs

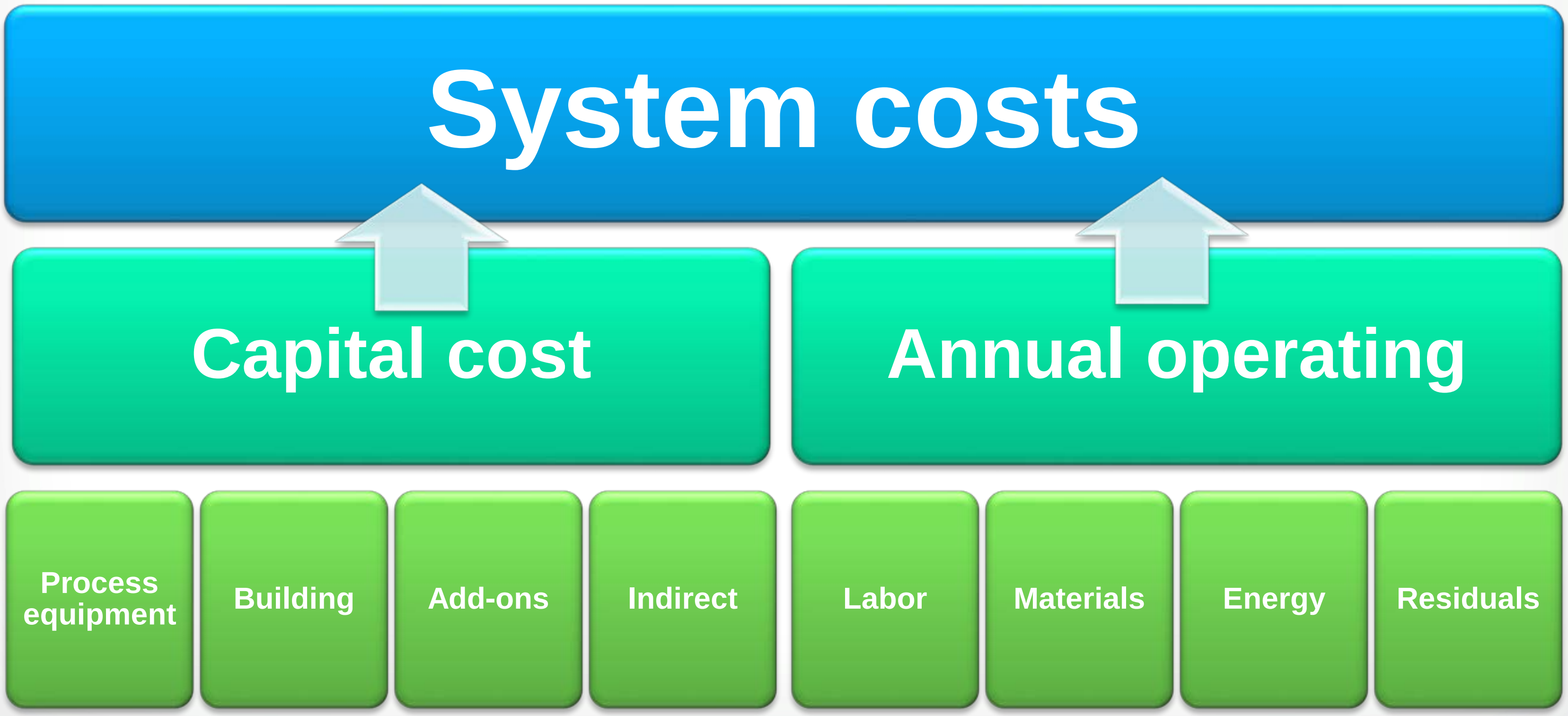
Flexible inputs and assumptions allow designs to adapt

- Different contaminants
- Different baseline / compliance conditions

What is a Work Breakdown?



System costs include capital and operating costs



Example: Granular Activated Carbon

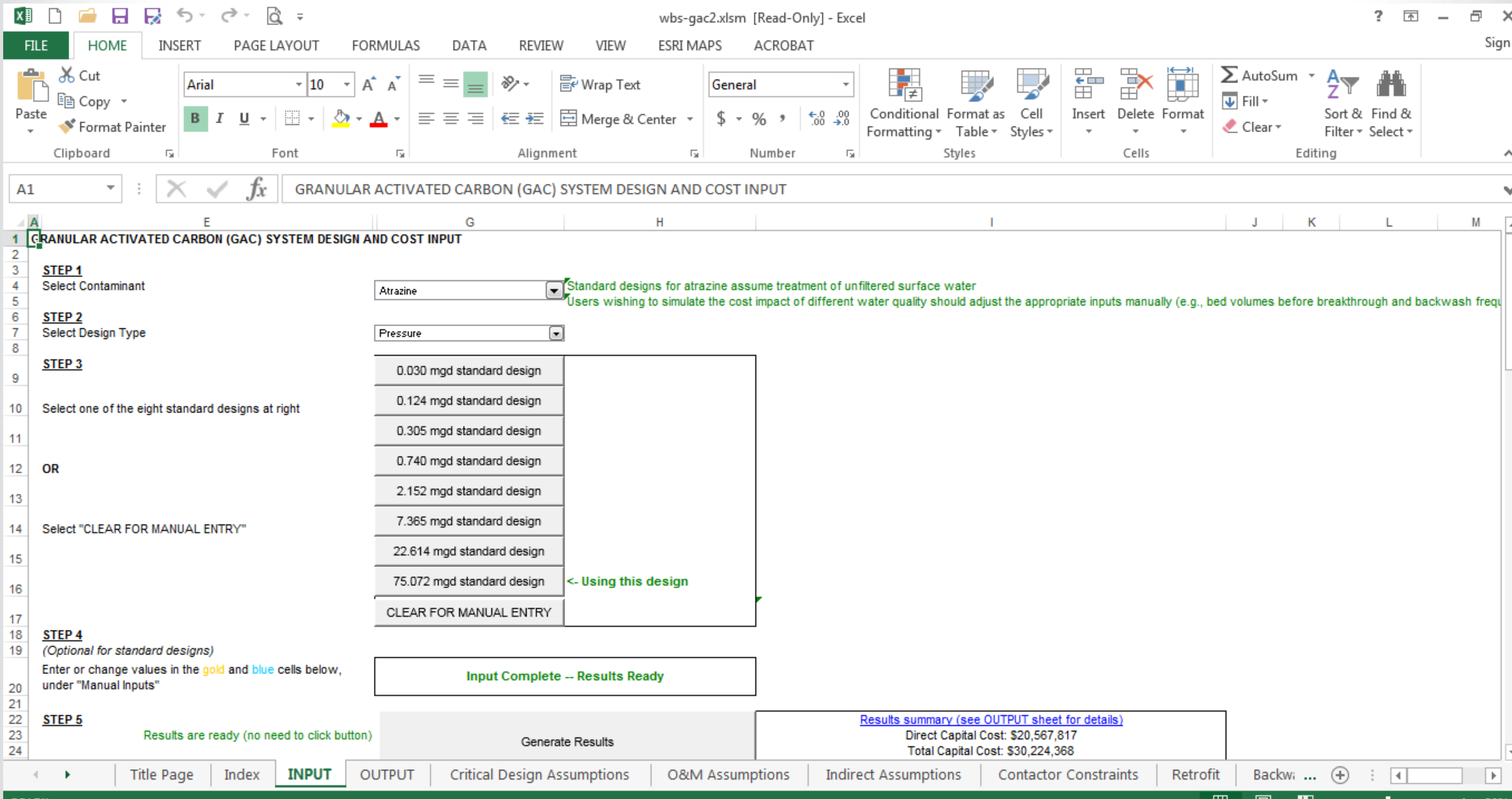
Design options

- User inputs (e.g., 40,000 bed volumes and 10 min empty bed contact time)

Cost curve outputs

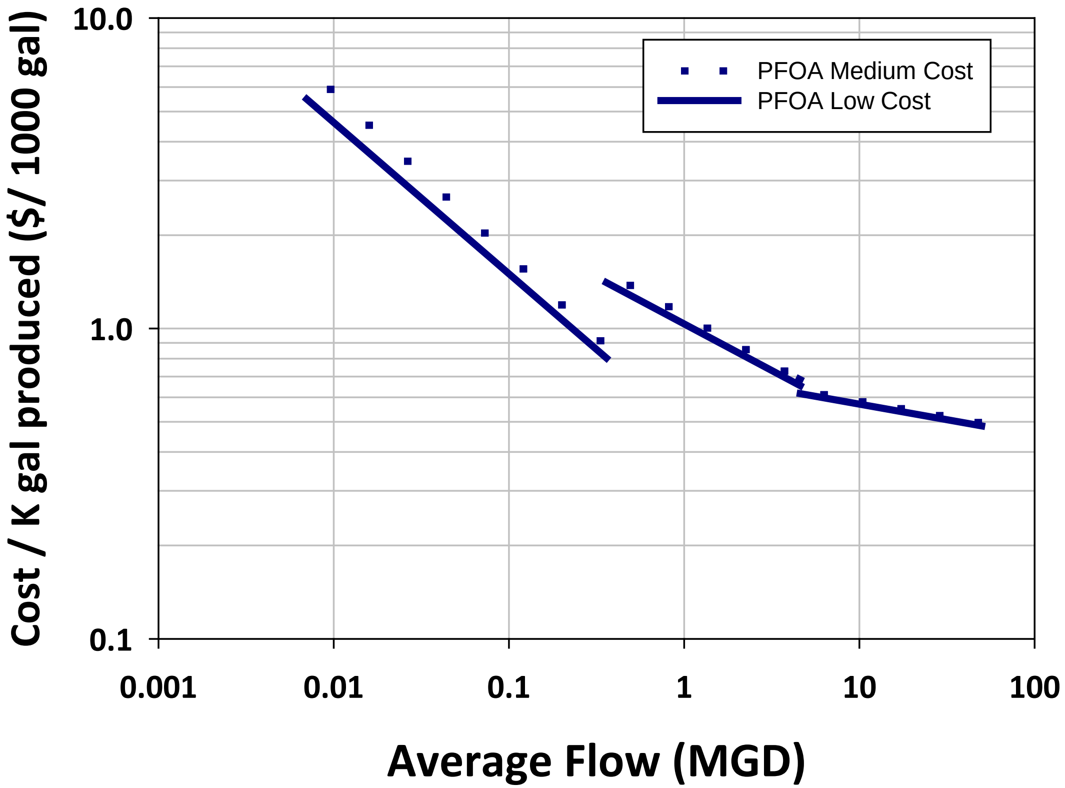
- Capital costs
- O&M costs

Drinking Water Treatment Cost Models



Cost /1000 gal: PFOA

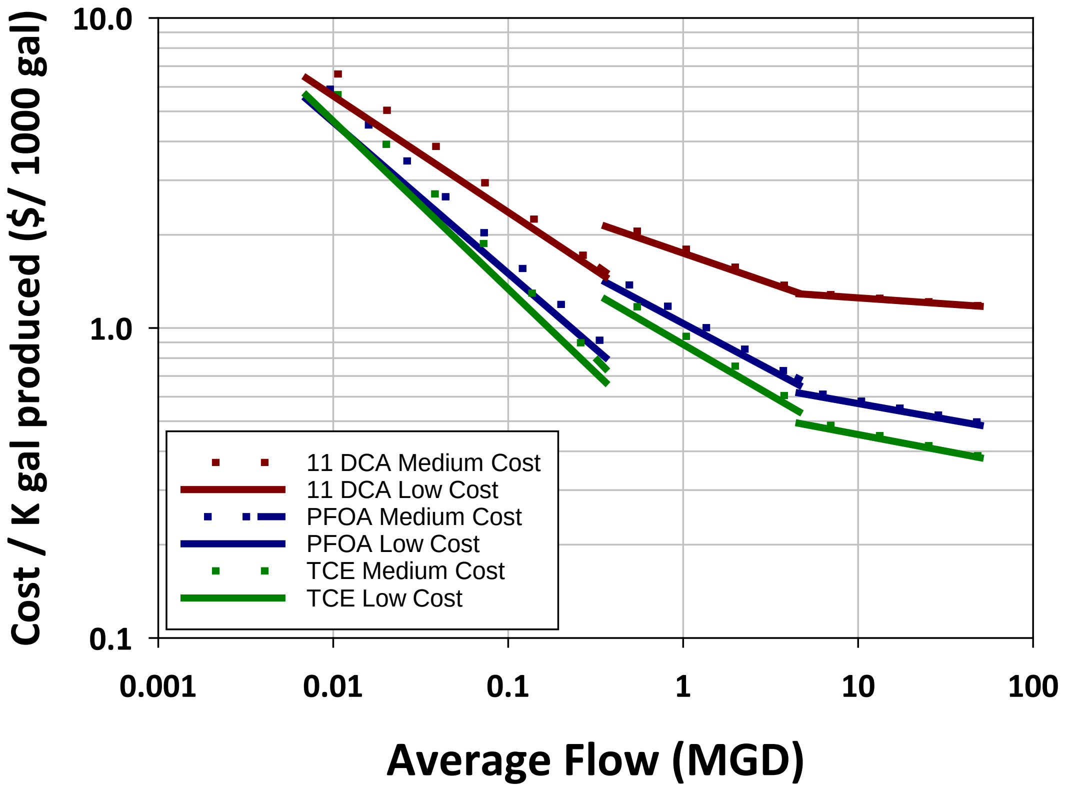
PFOA will break through before PFOS



- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 70K bed volumes to breakthrough for PFOA

Cost / 1000 gal: PFOA, TCE, & 11 DCA

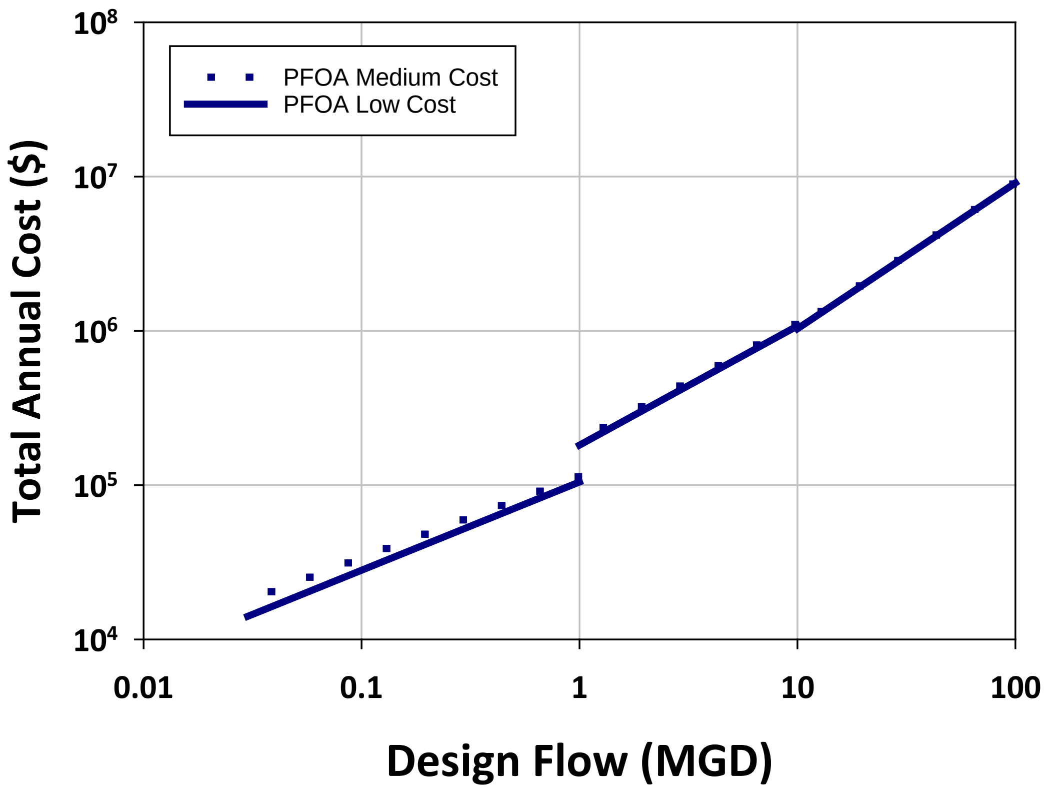
PFOA will break through before PFOS



- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 135K, 70K, and 11K bed volumes to breakthrough for TCE, PFOA, and 11DCA, respectively.

GAC Total Cost: PFOA

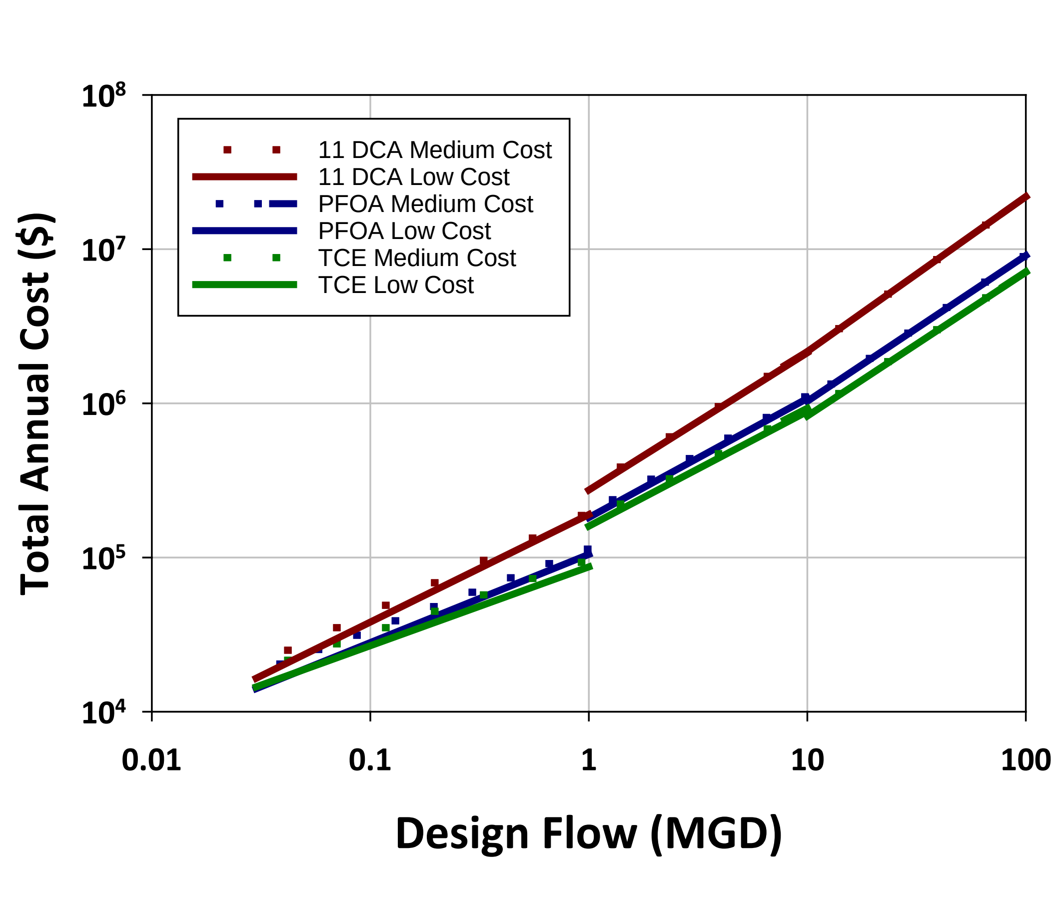
PFOA will break through before PFOS



- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 70K bed volumes to breakthrough for PFOA

GAC Total Cost: PFOA, TCE, and 11 DCA

PFOA will break through before PFOS



- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 135K, 70K, and 11K bed volumes to breakthrough for TCE, PFOA, and 11DCA, respectively.

Low Flow Considerations

Specific Design Modifications for Smaller Systems within the Cost Model

(Considers flows under 1 MGD)

- Construction issues (building)
- Residual handling flexibility
- Reduced spacing between vessels
- Smaller and no redundant vessels
- Reduced instrumentation
- No booster pumps
- No backwash pumps
- Reduced concrete pad thickness
- Reduced indirect costs

Finished

- Adsorptive media
- **Anion exchange**
- **Biological treatment**
- Cation exchange
- **GAC**
- Greensand filtration
- Microfiltration / ultrafiltration
- **Multi-stage bubble aeration**

- **Non-treatment**
- **Packed tower aeration**
- POU/POE
- Reverse Osmosis / Nanofiltration
- UV disinfection
- UV Advanced Oxidation

http://www2.epa.gov/dwregdev/drinking-water-treatment-technology-unit-cost-models-and-overview-technologies **Search: EPA WBS**

Finished

- Adsorptive media
- Anion exchange
- Biological treatment
- Cation exchange
- GAC
- Greensand filtration
- Microfiltration / ultrafiltration
- Multi-stage bubble aeration

- Non-treatment
- Packed tower aeration
- **POU/POE**
- Reverse Osmosis / Nanofiltration
- UV disinfection
- UV Advanced Oxidation

http://water.epa.gov/type/drink/pws/smallsystems/compliancehelp.cfm

Search: EPA small system compliance help

TDB + Cost Model

Concept

To have a system where the treatment performance information feeds directly into the cost models.

Benefits

- A transparent system for costing of future regulations
- Reduces the effort needed to access treatment performance data and design criteria.
- Provides an opportunity to focus on contaminants of interest to small systems
- Enhances university stakeholder interactions through supplementing and using treatability data.

Treatability: PFOA/PFOS

What is missing?

- A great deal of the treatment data is at concentrations higher than the level of the 2016 Health Advisory
- Although the general trends regarding the efficacy of various treatment technologies are known, certain technologies need additional pilot- or full-scale testing
  - GAC: Data needed to address adsorption kinetics and competitive adsorption for various carbons
  - Ion Exchange: A number of studies are needed to address the impact of water quality parameters, different resins, and the impact of regeneration conditions

Technologies exist to treat for PFOA and PFOS although pilot-scale data under a wider range of water quality conditions would be valuable

Analytics: PFOA/PFOS

Background

- EPA Method 537 was developed for PFAAs in response to heightened concern by the public and the scientific community over these chemicals of emerging concern
- In 2009, PFOS and PFOA were placed on the Contaminant Candidate List 3 (CCL 3)
- Revision 1.1 of Method 537 was released September 2009

Analytics: PFOA/PFOS

Method 537: SPE-LC/MS/MS
14 Perfluorinated Alkyl Acids (PFAA)

Perfluorocarboxylic acids (9)	**Perfluorosulfonates (3)**
Perfluorosulfonamidoacetic acids (2)	

Method Analytes on CCL 3

PFOA – perfluorooctanoic acid
PFOS – perfluorooctane sulfonic acid

Method Analytes in UCMR 3

PFOA	**– perfluorooctanoic acid**	**PFOS**	**– perfluorooctane sulfonic acid**
PFHpA	**– perfluoroheptanoic acid**	**PFHxS**	**– perfluorohexanesulfonic acid**
PFNA	**– perfluorononanoic acid**	**PFBS**	**– perfluorobutanesulfonic acid**

Challenges: wide range of water solubilities (C_4-C_{14}), laboratory and field blank contamination, LC contamination

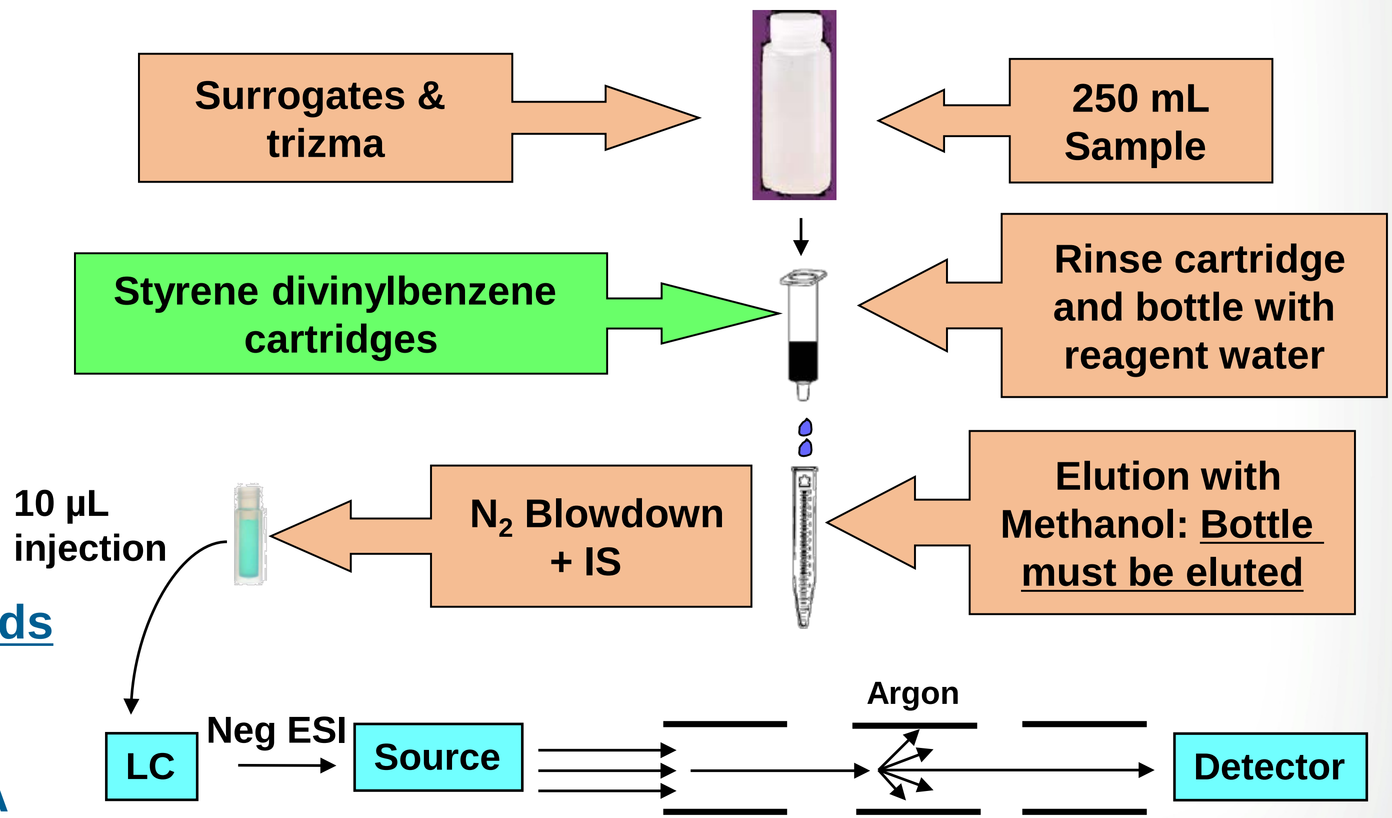
Analytics: PFOA/PFOS

Method 537 Approach

Preservative
trizma

Surrogates
^{13}C-PFHxA
^{13}C-PFDA
d_5-NEtFOSAA

Internal Standards
^{13}C-PFOA
^{13}C-PFOS
d_3-NMeFOSAA

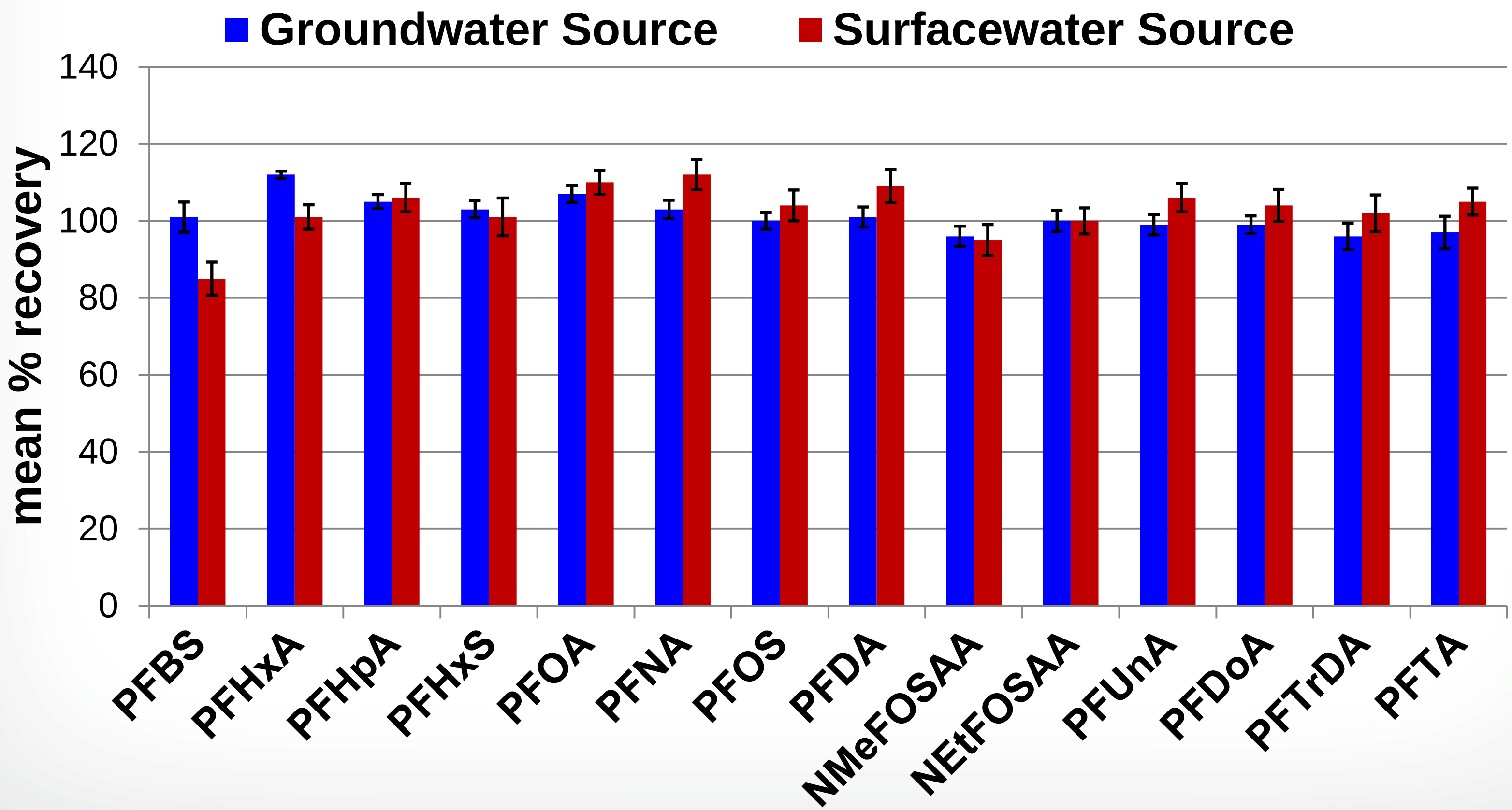


LC/MS/MS - Selected Reaction Monitoring

Analytics: PFOA/PFOS

Method 537 Performance Data

Fortified at 37-202 ng/L (n=7)



Analytics: PFOA/PFOS

Health Reference Level (HRL)
Lowest Concentration Minimum Reporting Level (LCMRL)
Minimum Reporting Limit (MRL)

Analyte	LCMRL (ng/L)
PFBS	3.7
PFHxA	2.9
PFHpA	3.8
PFHxS	8.0
PFOA	**5.1**
PFOS	**6.5**
PFNA	5.5
PFDA	3.8
NMeFOSAA	14
NEtFOSAA	14
PFUnA	6.9
PFDoA	3.5
PFTrDA	3.8
PFTA	4.7

2009 CCL 3 Health Reference Level (HRL)
PFOA - 1100 ng/L
PFOS – 200 ng/L

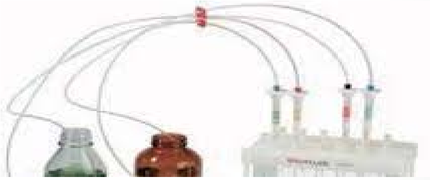
2016 EPA Drinking Water Health Advisory
When both PFOA and PFOS are found in drinking water, the combined concentrations of PFOA and PFOS should be compared with the 70 ng/L health advisory level.

Method 537 Implementation Suggestions

General:

- wide range of water solubilities (C_4-C_{14}) which can affect recoveries through adsorption or extraction losses

SPE:



- Method recommends use of a polypropylene transfer tube system, which transfers the sample directly from the sample container to the SPE cartridge.
- PFBS Recovery – may be adversely affected if SPE loading flow rate is too high
- Rinsing the sample bottle with the SPE elution solvent is required and is critical for recovery of the PFAAs with ≥8 carbon chains

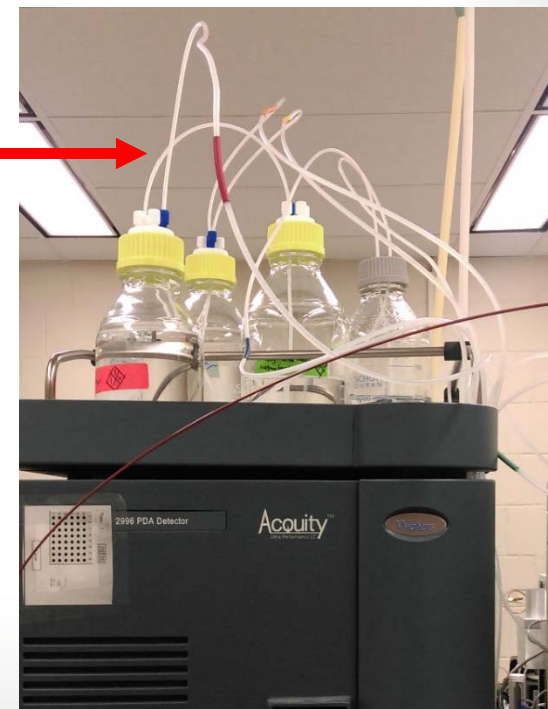
Laboratory and field blank contamination:

- Many lab supplies and equipment can contain PFAAs.
- Personnel must be aware of potential PFAA contamination consumer products and take measures to avoid these sources of PFAAs.
- Section 8.3.1 requires a field reagent blank (FRB), Sampler must open the shipped FRB in the field and pour the preserved reagent water into the empty shipped sample bottle and seal the FRB. Ensures PFAAs were not introduced into the sample during sample collection/handling or from preservatives and bottles.

Method 537 Implementation Suggestions

LC:

- Polypropylene (PP) vials/caps are necessary to prevent contamination of the sample from PTFE coated septa.
  - ✓ PP caps do not re-seal, so evaporation occurs after injection.
  - ✓ Multiple injections from the same vial are not possible.
  - ✓ Suggest splitting extract before injection
- PFAAs can build up in the PTFE solvent transfer lines on the LC during inactivity.
  - ✓ Recommend replacing PTFE lines with PEEK tubing
  - ✓ Recommend replacing PTFE solvent frits with stainless steel frits



LC: (cont.)

- Modifications to LC conditions should still produce conditions such that co-elution of method analytes is minimized to reduce the probability of suppression/enhancement effects.
- PFAAs, from LC system components and mobile constituents, will build up on the head of the LC column during mobile phase equilibration.
  - ✓ Keep post-equilibration time constant and as short as possible

5 min post-equilibration

LC Gradient		
Time (min)	% 20 mM ammonium acetate	% Methanol
Initial	60.0	40.0
1.0	60.0	40.0
25.0	10.0	90.0
32.0	10.0	90.0
32.1	**60.0**	**40.0**
37.0	**60.0**	**40.0**

Laboratory Analysis of Drinking Water Samples for PFOA Using EPA M537 Rev. 1.1

EPA has recently learned that laboratories have identified different approaches for implementation of EPA Method 537 Rev 1.1 for analysis of PFOA.

- Some laboratories have analyzed PFOA by quantitation of only the linear isomer while others have quantified both linear and branched-chain isomers to determine the concentration of PFOA.
- The linear isomer represents the predominant form of PFOA, but samples may also have some degree of branched-chain isomers.

https://www.epa.gov/sites/production/files/2016-09/documents/pfoa-technical-advisory.pdf

EPA Technical Advisory

How should laboratories quantitate PFOA using EPA Method 537?

To account for linear and branched isomers of PFOA, EPA recommends that integration and quantitation of real-world drinking water samples include peaks that represent both linear and branched isomers.

- There is currently no certified quantitative PFOA standard that contains both linear and branched isomers, thus EPA recommends labs calibrate instrumentation using a certified quantitative standard containing only the linear isomer.
- Identify the branched isomers by analyzing a “qualitative/semi-quantitative” PFOA mixed standard that includes both linear and branched isomers and compare retention times and MS/MS transitions.
- Quantitate PFOA by integrating the total response (linear + branched isomers) and relying on the initial calibration with the linear-isomer quantitative standard.

Analytics: PFOA/PFOS

Conclusions

- Sensitive and accurate method developed for 14 PFAAs
- EPA Method 537 used in UCMR 3 to gather nationwide occurrence data for 6 PFAAs
- Method 537 requires
  - Careful avoidance of lab sources of PFAA
  - Minimization of instrument sources of PFAA
  - Careful attention to SPE steps to avoid losses
  - Following all QC practices

Disclaimer

The views expressed in this presentation are those of the individual authors and do not necessarily reflect the views and policies of the US EPA. Mention of trade names or commercial products does not constitute endorsement or recommendation for use

Questions?

Rajiv.Khera@epa.gov
Patterson.Craig@epa.gov
Speth.Thomas@epa.gov
Shoemaker.Jody@epa.gov