Source Differentiation of Per- and Polyfluoroalkyl Substances in Environmental Source Inputs

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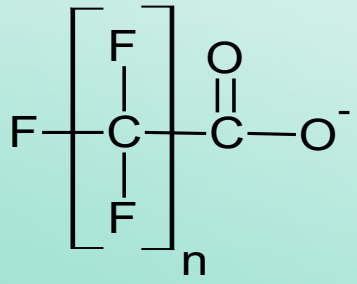
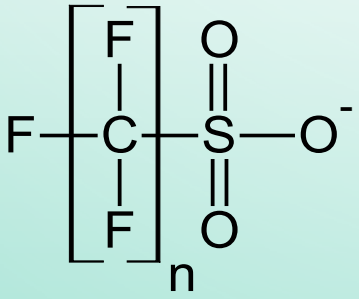
Background

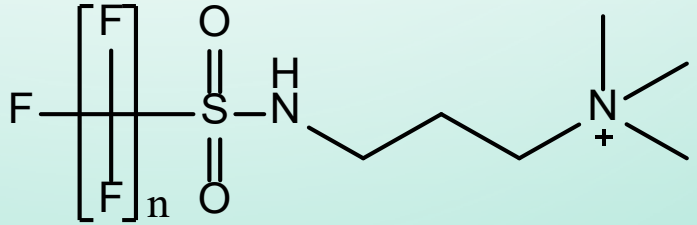
- Per- and Polyfluoroalkyl Substances (PFASs) chemistry
  - Carbon-fluorine chain attached to a polar head group
- Anthropogenic origins
- Applied in numerous sectors including consumer products, manufacturing processes, and in aqueous film forming foams (AFFFs) for suppression of hydrocarbon fuel fires
- Potentially 1000's of potential PFASs as a result of proprietary mixtures & impure chemistries



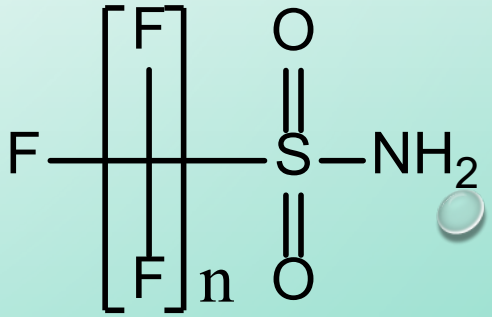
Ex. PFOA



Ex. PFOS



Ex. N-TAmP-FHxSA



Ex. FOSA

Regulation in the U.S.

- Health Advisory Limits set by the US EPA as 70ng/L for PFOS and PFOA or a combination of PFOS and PFOA (May 2016)
  - Drinking water only
- Not enforceable
- Set based on non-cancer endpoints
  - Reduced birthweight (PFOS), developmental effects in bones, accelerated puberty (PFOA)

PFASs or products are **made**

Source Inputs Into the Environment are created

Landfills

WWTPs

FTAs

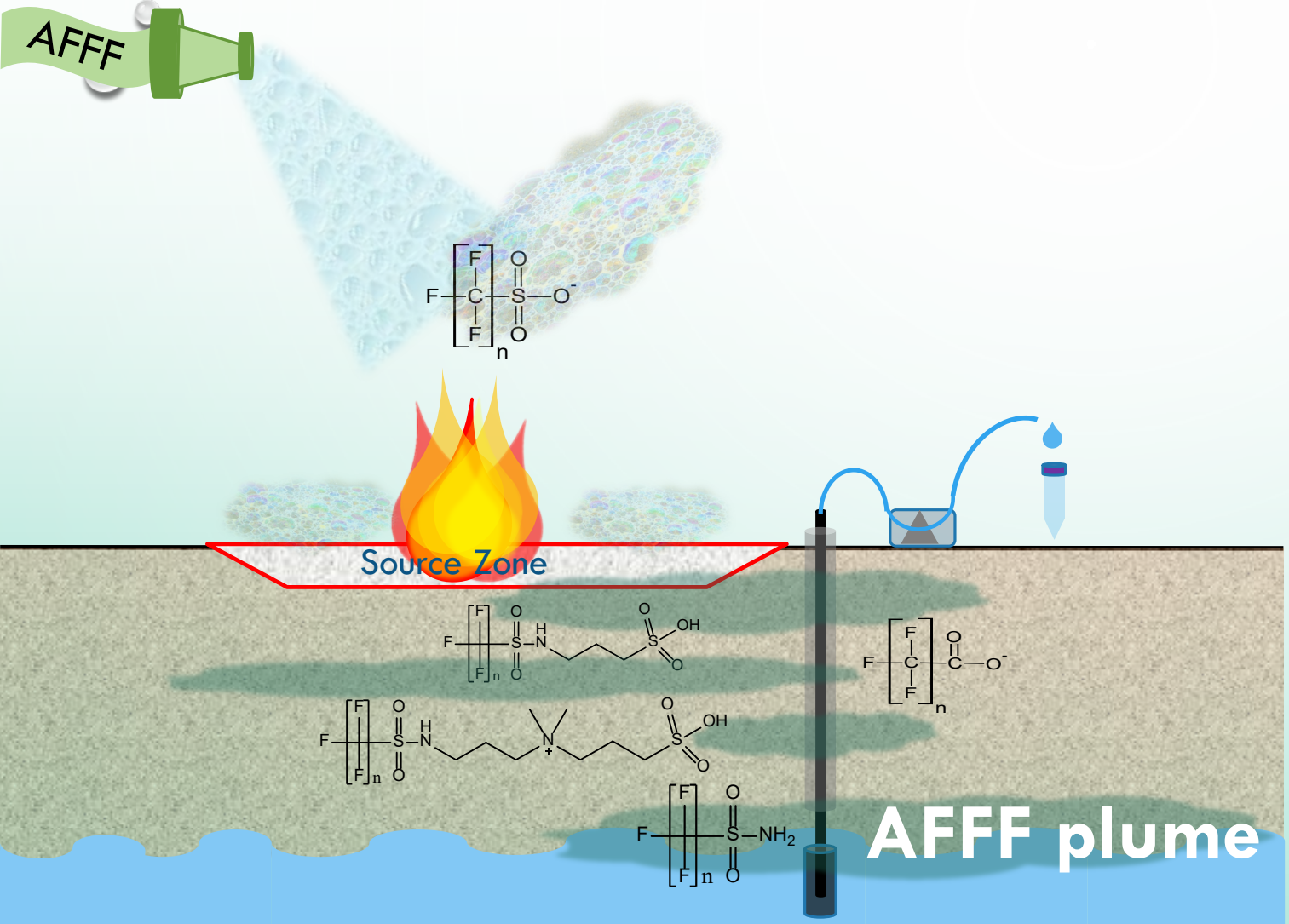
Contamination of Water Matrices

AFFF Impacted Groundwaters at Fire-Training Areas

- Aqueous Film-Forming Foams (AFFFs) are proprietary mixtures, commissioned by the US Military
- Fire-Training Areas
  - Used for fire-fighter training at military bases
  - Bi-monthly or monthly when active
- Why not AFFFs themselves?
  - Individual sources—the whole picture?

Photo Credit: Bill Gee

Application of AFFF at a military site



Contamination!

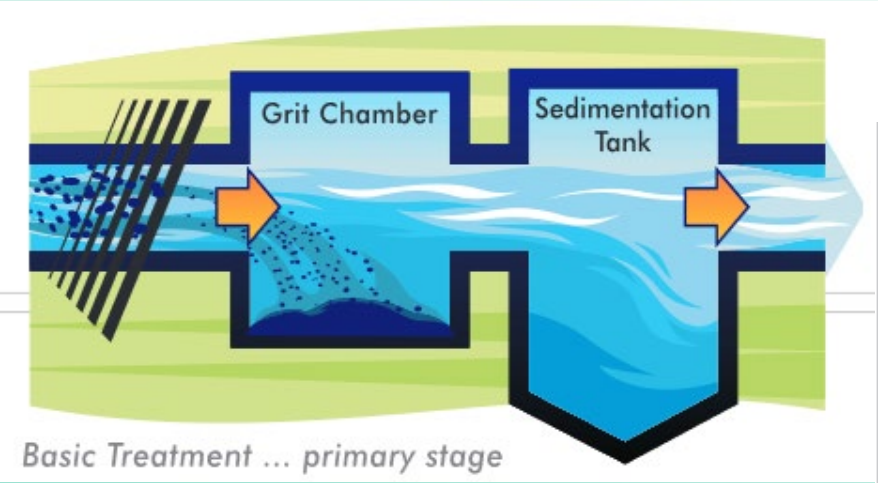
- Local water bodies
  - e.g. wetlands, ponds
- Aquifer
  - Confined
  - Unconfined
- Drinking water sources
- Soil/Sediment

Landfill Leachates

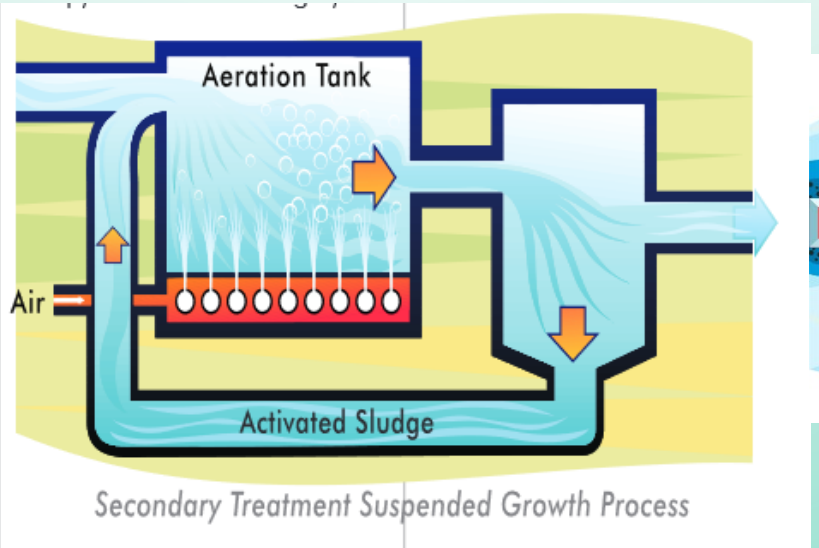
- Application of PFAS polymers to consumer products are typically as surface coatings (e.g. textiles, carpets) or are mixed in during production (e.g. papers)
  - biosolids from WWTPs (Figure 1), industrial or manufacturing waste, and construction & demolition
  - Become extremely anoxic over time and eventually become methanogenic
    - Intermediates as a result of biodegradation

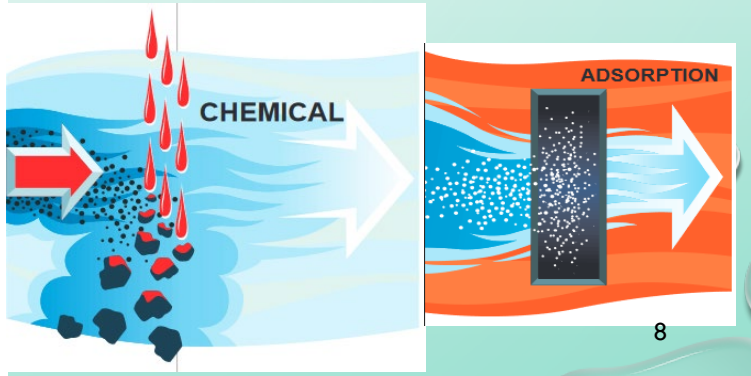
Wastewater Treatment Plants

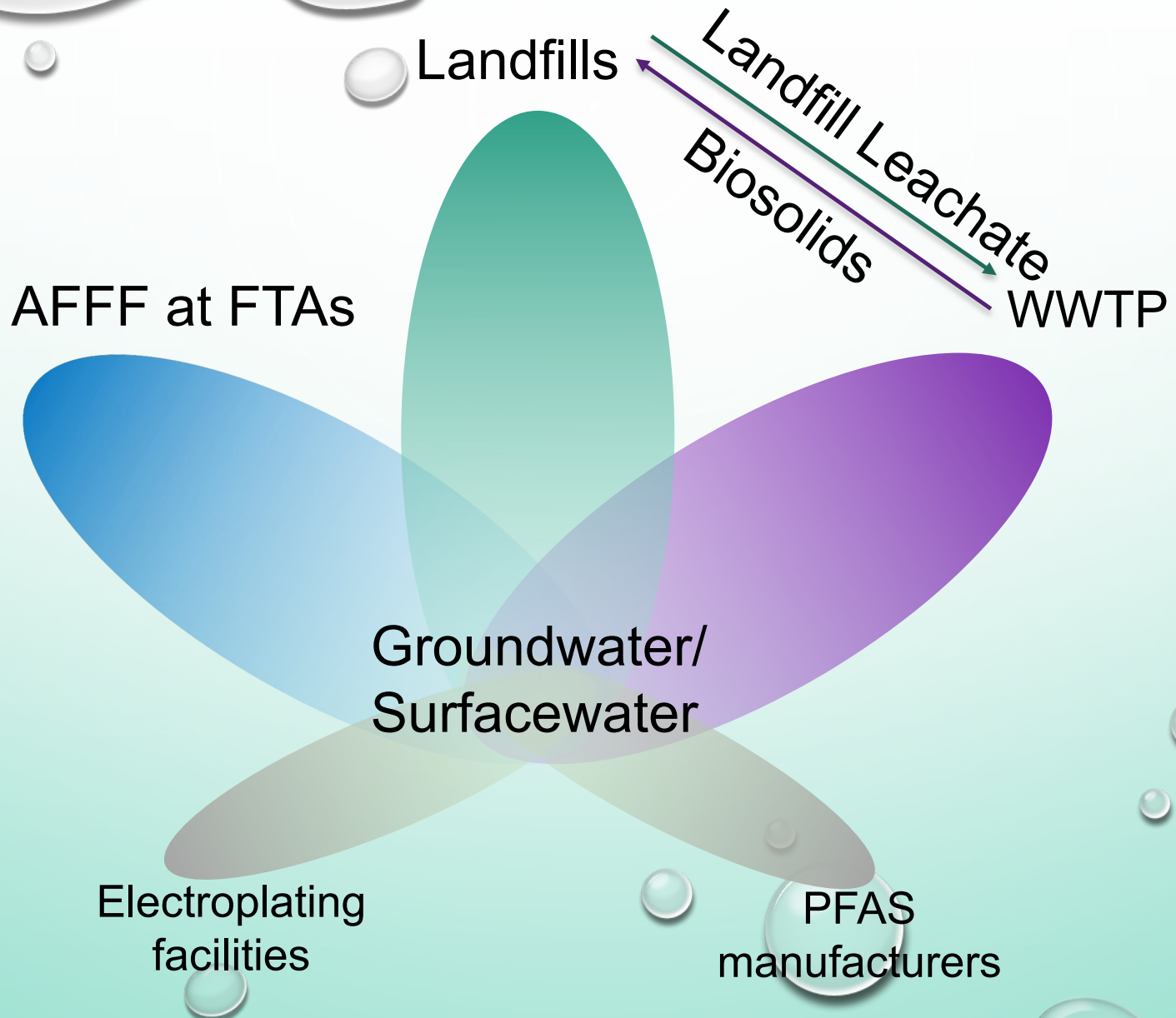
- Inputs from local weather events, domestic residences or businesses, industry and manufacturing, and from landfills in the form of landfill leachates
- Although many PFASs are sorbed during primary and secondary treatment to sludge PFASs have been observed in effluent\



https://www.epa.gov/sites/production/files/2015-09/documents/primer.pdf






Landfills
Landfill Leachate
Biosolids
WWTP
AFFF at FTAs
Groundwater/
Surfacewater
Electroplating
facilities
PFAS
manufacturers

What are the data gaps on PFASs?

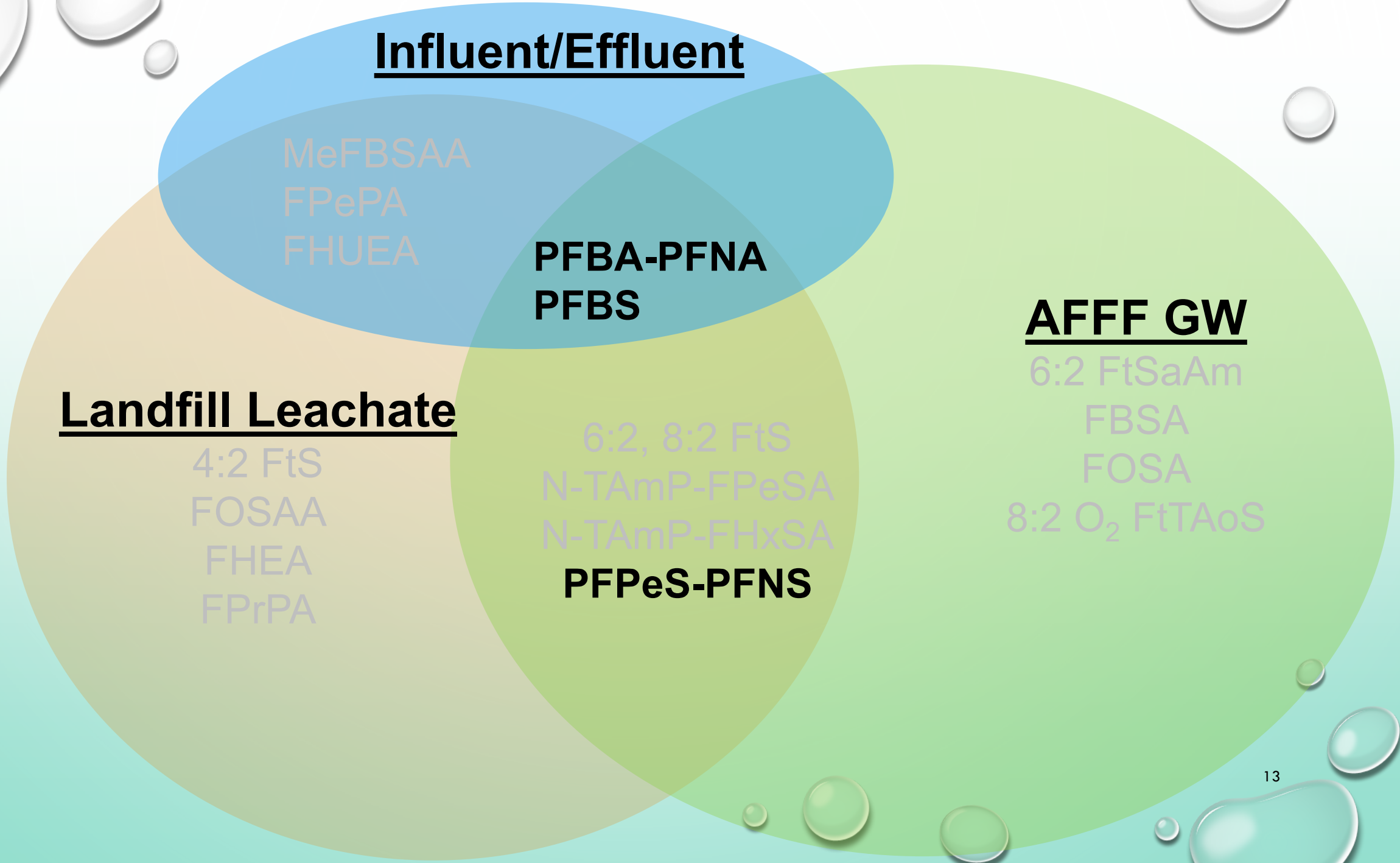
- Exposure to PFASs is primarily through drinking water*
- How does drinking water get contaminated?
  - Source inputs!
- Which source inputs contribute?
  - How could you tell?
  - What matrix would you measure?
- Has anyone tried source differentiation?
  - Anderson et al., 2015 (groundwater/surfacewater), Hu et al., 2016 (drinking water), Zhang et al., 2013 (surfacewater), Xiao et al., 2012 (wastewater)

Quantification

- Agilent 1100 LC attached to a Waters TQD
- Analysis for 56 PFASs based off of source zone AFFF impacted groundwater collected by suspect screening LC-QToF based on Barzen Hanson et al., 2017.
- Challenges: Lack of analytical standards
  - Calibration of available standards will be applied to those analytes which are novel or do not have available standards as in Backe et al, 2013 and Allred et al.,2014.

Results

- In first pass, preliminary proof-of-concept study:
  - 1 AFFF impacted groundwater
  - 1 Landfill leachate
  - 1 Wastewater treatment samples (influent and effluent)
    - 0.6% flow input of landfill leachate during 24 flow-proportional composite collection


Influent/Effluent
MeFBSAA
FPePA
FHUEA
PFBA-PFNA
PFBS
Landfill Leachate
4:2 FtS
FOSAA
FHEA
FPrPA
6:2, 8:2 FtS
N-TAmP-FPeSA
N-TAmP-FHxSA
PFPeS-PFNS
AFFF GW
6:2 FtSaAm
FBSA
FOSA
8:2 O_2 FtTAoS

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Landfill Leachate

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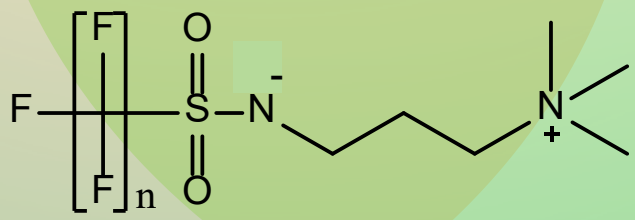
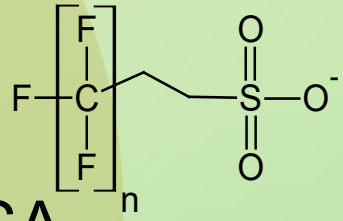
PFPeS-PFNS





AFFF GW

6:2 FtSaAm
FBSA
FOSA
8:2 O_2 FtTAoS

Influent/Effluent

MeFBSAA
FPePA
FHUEA

PFBA-PFNA
PFBS

Landfill Leachate

4:2 FtS
FOSAA
FHEA
FPrPA

6:2, 8:2 FtS
N-TAmP-FPeSA
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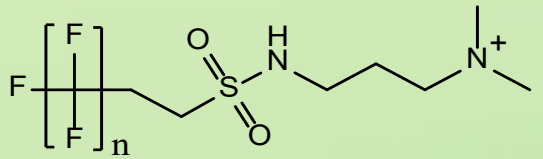
PFPeS-PFNS



AFFF GW

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FOSA
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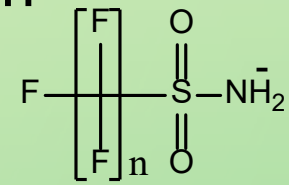
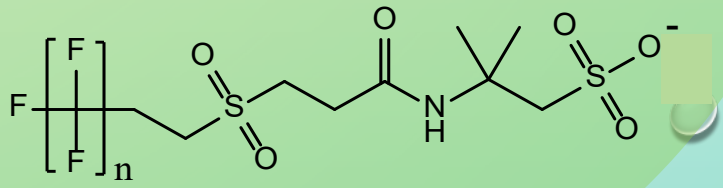
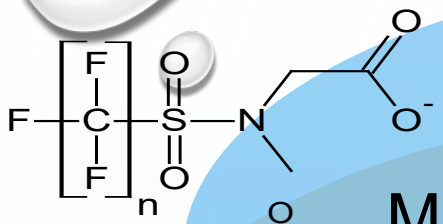
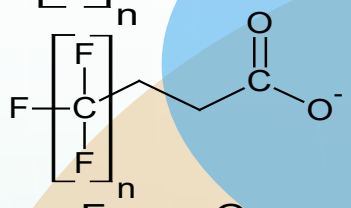
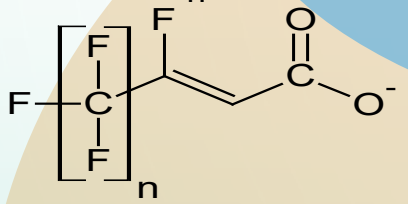




Influent/Effluent



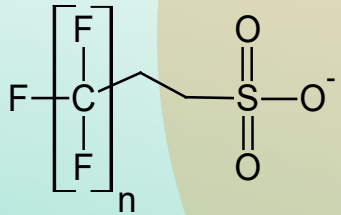


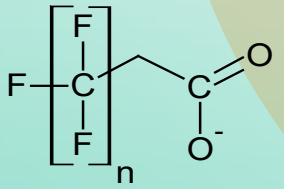


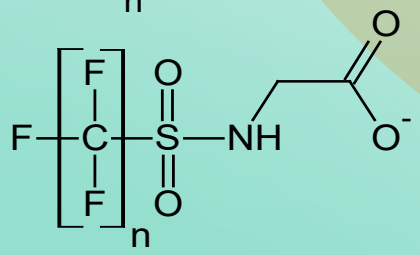
MeFBSAA
FPePA
FHUEA

PFBA-PFNA
PFBS

Landfill Leachate







4:2 FtS
FOSAA
FHEA
FPrPA

6:2, 8:2 FtS
N-TAmP-FPeSA
N-TAmP-FHxSA
PFPeS-PFNS

AFFF GW

6:2 FtSaAm
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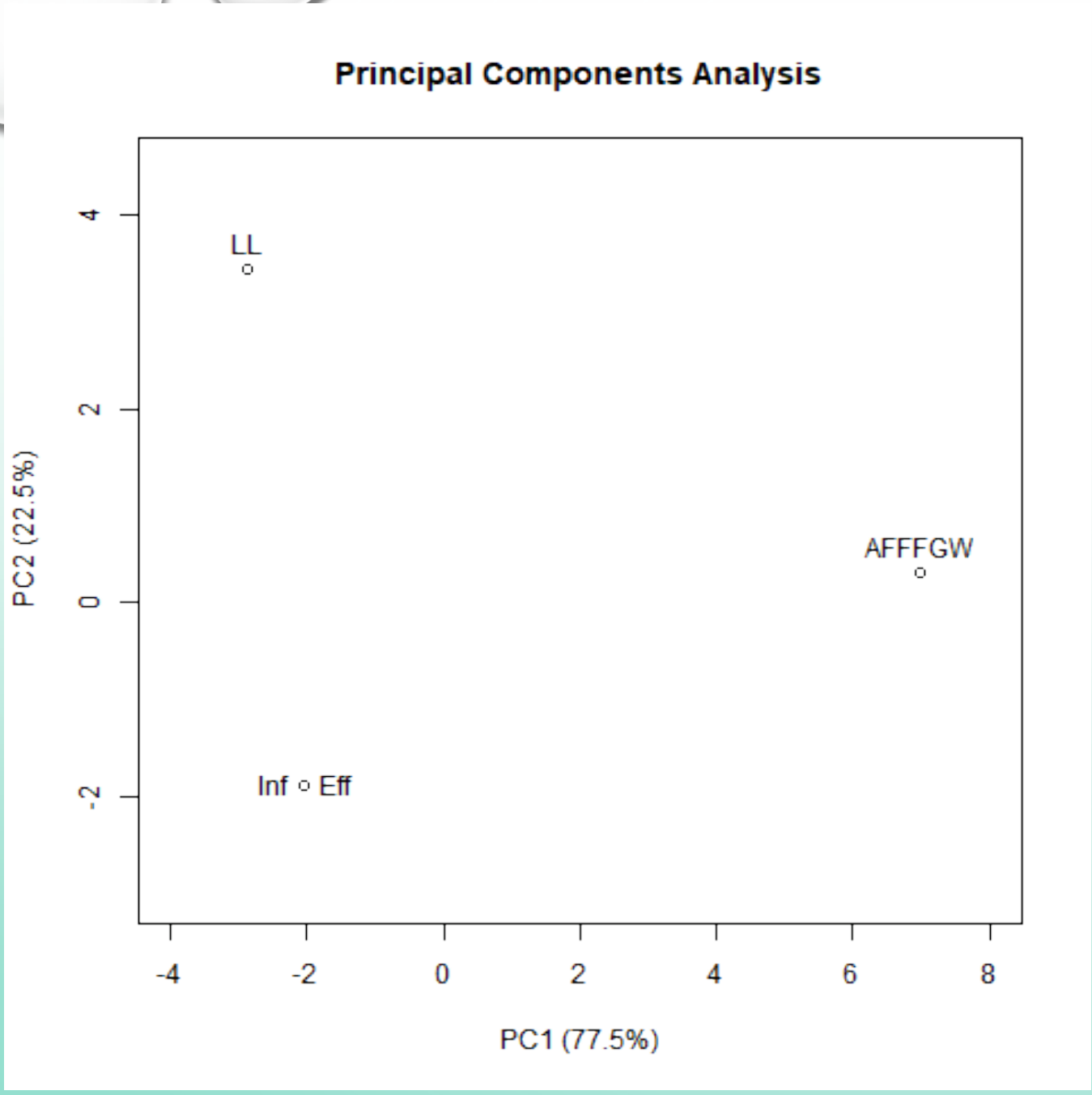
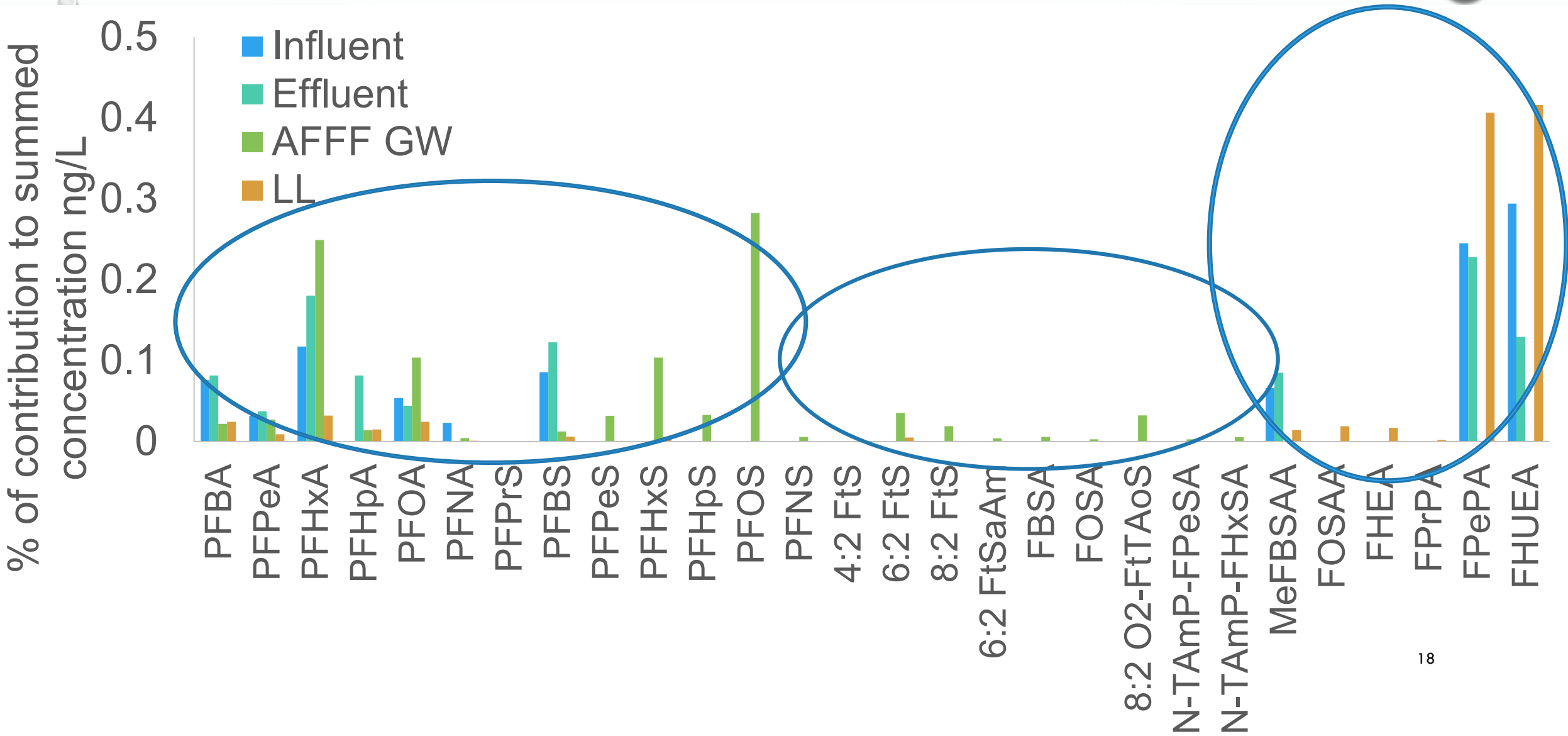


- <LOD/<LOQ are recorded as zeros (will be left censored)
- Mean centered, auto-scaled
- PC1-separation of AFFF GW, driven by AFFF specific compounds
- PC2- separation by concentration rather than identity of PFASs

Results


Influent
Effluent
AFFF GW
LL
% of contribution to summed concentration ng/L
0.5
0.4
0.3
0.2
0.1
0
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFPrS
PFBS
PFPeS
PFHxS
PFHpS
PFOS
PFNS
4:2 FtS
6:2 FtS
8:2 FtS
6:2 FtSaAm
FBSA
FOSA
8:2 O2-FtTAoS
N-TAmP-FPeSA
N-TAmP-FHxSA
MeFBSAA
FOSAA
FHEA
FPrPA
FPePA
FHUEA

Conclusions and future work

- Conclusions-
  - Using 4 samples (AFFF impacted groundwater, Landfill leachate, influent/effluent for wastewater treatment plant) differences unique to each source zone including PFASs present, C4/C8 ratios, PFASs present and ECF vs telomere composition indicate differentiation is possible.
- Future work-
  - Additional samples for AFFF impacted ground water, landfill leachate, influent/effluent for WWTP will be analyzed by LC-HRMS in suspect screening mode for approximately 1200 PFASs
  - Statistical analysis will be applied to additional data to further highlight fingerprinting of source zones (hierarchical clustering, PCA, canonical variation, etc)

Acknowledgements

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Thank you!

Questions?