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Per- and Polyfluoroalkyl Substances (PFAS) Background in Vermont Shallow Soils

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Motivations and objectives

- PFAS as emerging contaminants
- Widely detected in the environment
- Soil as environmental medium for PFAS
- Soil as potential reservoir for PFAS
- Potential health threat to humans

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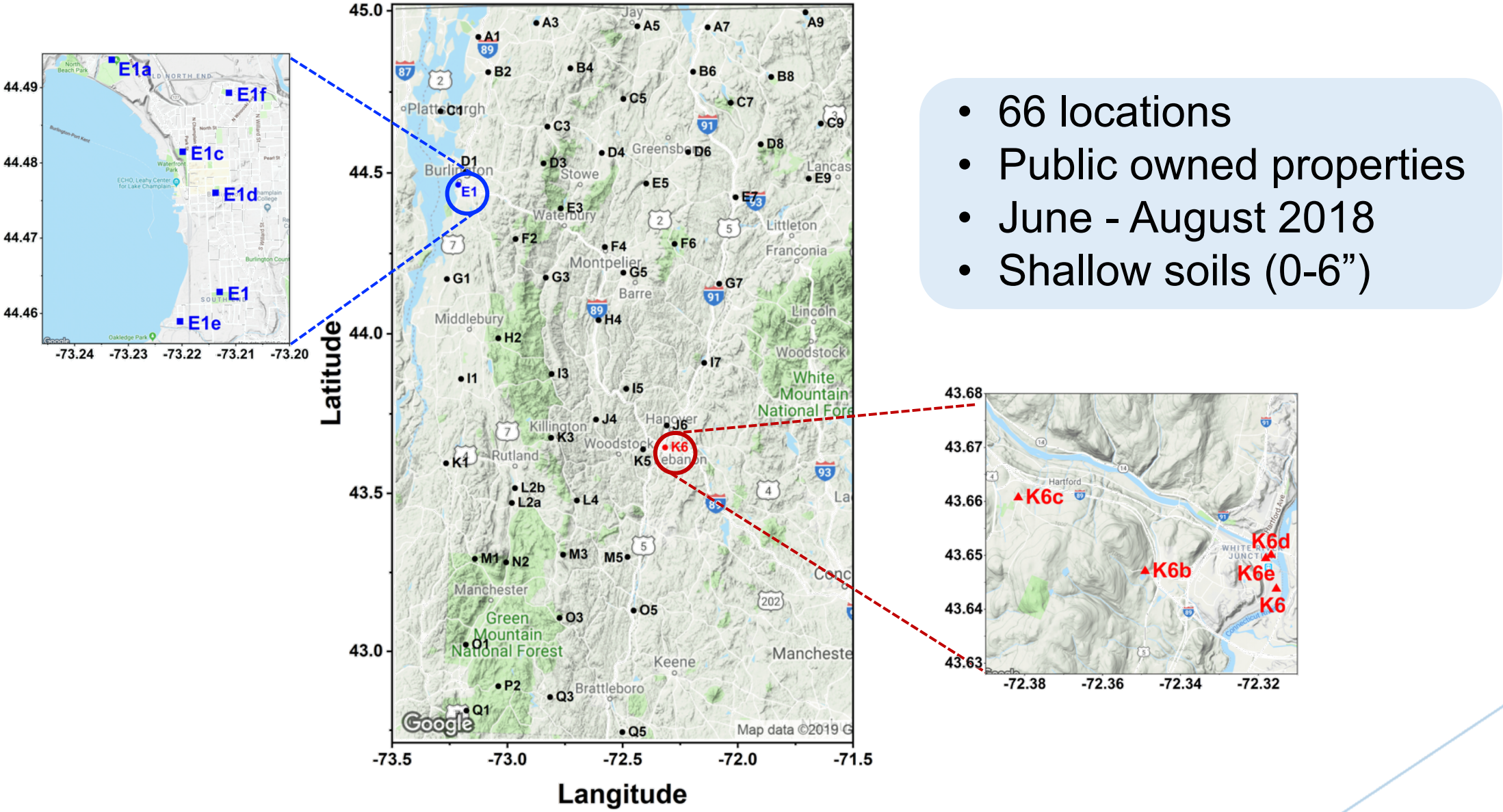
- PFAS background in Vermont shallow soils
- 95% Upper Tolerance Limit with 95% coverage (UTL95-95) of each PFAS compound
- Further investigations

Field Sampling



- 66 locations
- Public owned properties
- June - August 2018
- Shallow soils (0-6”)

Field Sampling








Targeted PFAS

Acronym	Name	MW	Formula	CAS#
PFBA	Perfluoro-n-butanoic acid	214.03	C_3F_7COOH	375-22-4
PFPeA	Perfluoro-n-pentanoic acid	264.05	C_4F_9COOH	2706-90-3
PFHxA	Perfluoro-n-hexanoic acid	314.05	$C_5F_{11}COOH$	307-24-4
PFHpA	Perfluoro-n-heptanoic acid	364.06	$C_6F_{13}COOH$	375-85-9
PFOA	Perfluoro-n-octanoic acid	414.07	$C_7F_{15}COOH$	335-67-1
PFNA	Perfluoro-n-nonanoic acid	464.08	$C_8F_{17}COOH$	375-95-1
PFDA	Perfluoro-n-decanoic acid	514.09	$C_9F_{19}COOH$	335-76-2
PFUnDA	Perfluoro-n-undecanoic acid	564.09	$C_{10}F_{21}COOH$	2058-94-8
PFDoDA	Perfluoro-n-dodecanoic acid	614.10	$C_{11}F_{23}COOH$	307-55-1
PFTrDA	Perfluoro-n-tridecanoic acid	664.11	$C_{12}F_{25}COOH$	72629-94-8
PFTeDA	Perfluoro-n-tetradecanoic acid	714.12	$C_{13}F_{27}COOH$	376-06-7
PFHxDA	Perfluoro-n-hexadecanoic acid	814.13	$C_{15}F_{31}COOH$	67905-19-5
PFODA	Perfluoro-n-octadecanoic acid	914.15	$C_{17}F_{35}COOH$	16517-11-6
PFBS	Perfluoro-1-butanesulfonic acid	299.95	$C_4F_9SO_3H$	375-73-5
PFHxS	Perfluoro-1-hexanesulfonic acid	399.94	$C_6F_{13}SO_3H$	355-46-4
PFOS	Perfluoro-1-octanesulfonic acid	499.94	$C_8F_{17}SO_3H$	1763-23-1
PFDS	Perfluoro-1-decanesulfonic acid	599.93	$C_{10}F_{21}SO_3H$	335-77-3

Laboratory analysis

Extraction

- Washington's method*

Analysis & quantification

- HPLC-MS/MS
- ABI Sciex 4000QTrap Pro
- 13 PFCAs, 4 PFBSs
- Unit: ng/kg dw

QA/QC

- Field QA/QC
  - ✓ Trip blanks, field blanks, equipment blanks
  - ✓ Field duplicate samples
- Laboratory QA/QC
  - ✓ Method blanks, lab control samples and duplicate samples
  - ✓ MDL, RL

*Rankin, et al., Chemosphere. 2016.

Detection summary

Preliminary findings

Analyte	MDL	RL	Quant D	Quant F (%)	Min	Max
PFBA	100	520	0	0	N/A	N/A
PFPeA	70	350	5	7.6	140	1,300
PFHxA	7.6	39	33	50	50	4,400
PFHpA	4.4	22	59	89	44	900
PFOA	7.0	35	60	91	52	4,900
PFNA	9.7	48	61	92	51	5,000
PFDA	8.0	40	57	86	43	7,600
PFUnDA	7.0	35	48	73	38	2,600
PFDoDA	11	54	3	4.6	100	690
PFTrDA	13	65	1	1.5	N/A	130
PFTeDA	21	110	0	0	N/A	N/A
PFHxDA	23	110	0	0	N/A	N/A
PFODA	24	120	0	0	N/A	N/A
PFBS	6.0	30	42	63	33	1,600
PFHxS	14	72	29	44	76	880
PFOS	5.0	25	66	100	110	9,700
PFDS	5.3	26	23	35	32	920

Quant D:

- Quantitatively detected (>RL)

Quant F:

- Frequency of Quant D

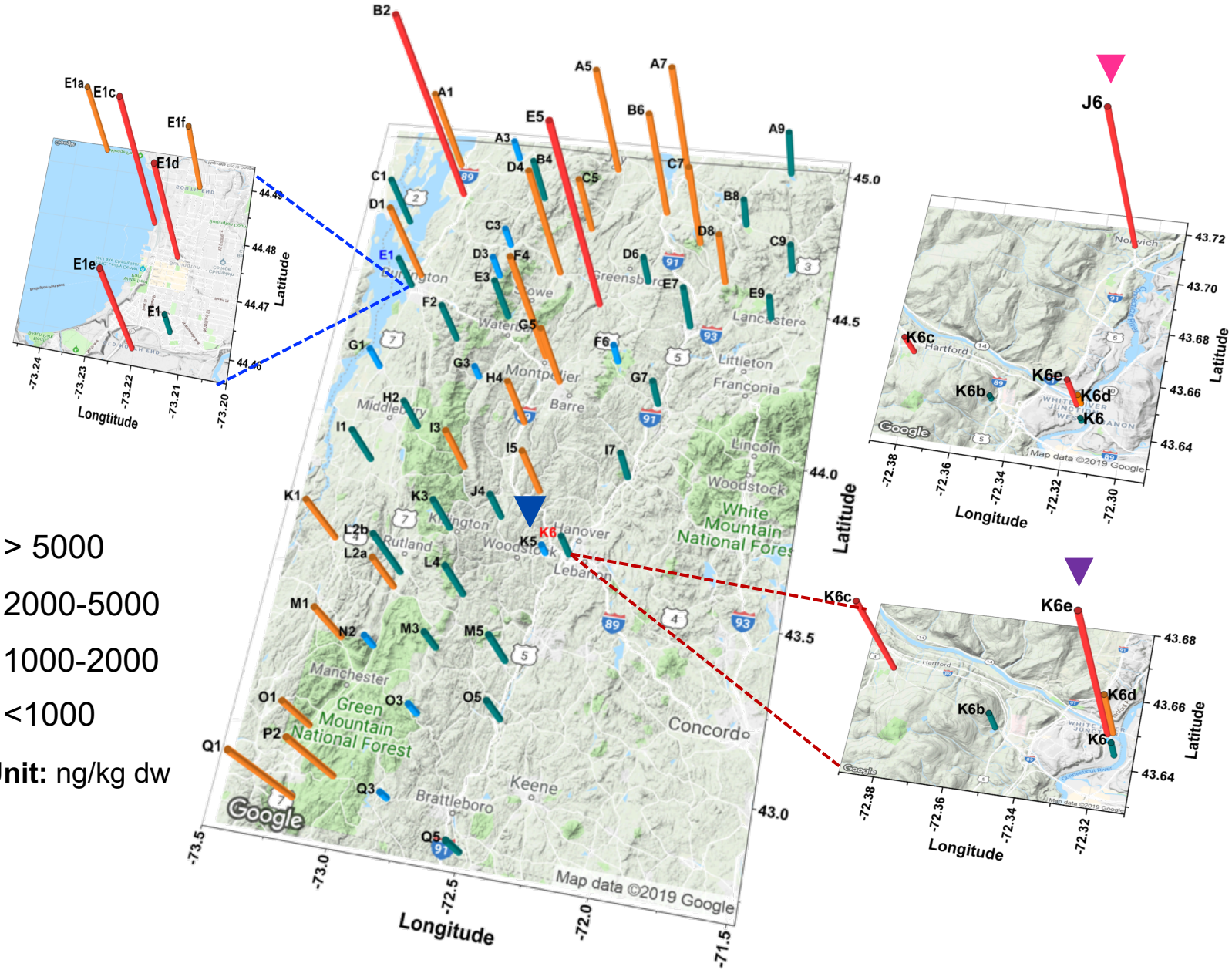
Quant F>30%

PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnDA
PFBS
PFHxS
PFOS
PFDS

- **Unit:** ng/kg dw
- Data have been rounded to two significant digits

PFAS in VT shallow soils

****Preliminary findings****



Highest ΣPFAS:

- **J6** (Norwich Green)
- 35,000 ng/kg dw

- **K6e** (9,400 ng/kg dw)
- **E5** (7,700 ng/kg dw)

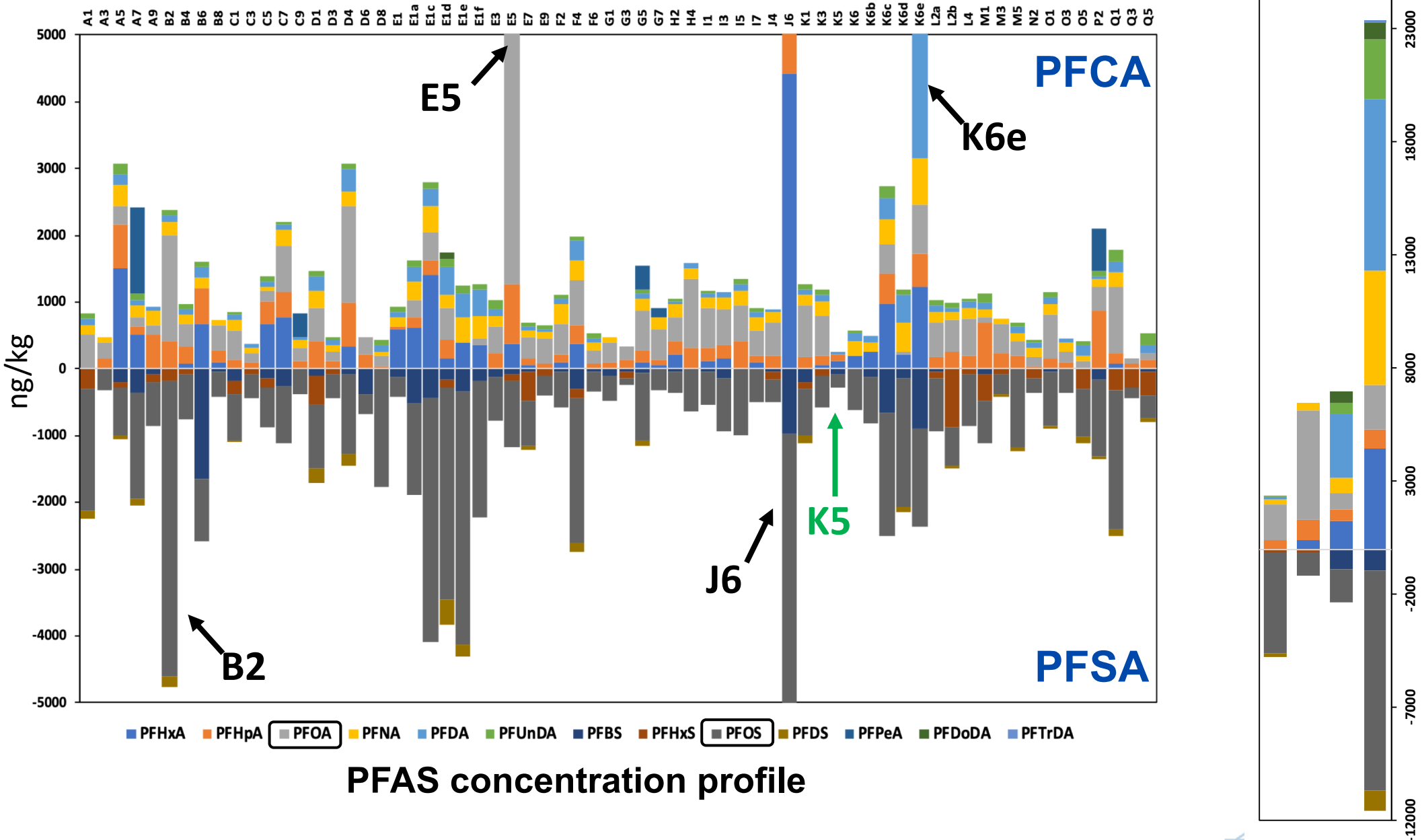
Lowest ΣPFAS:

- **K5** (Quechee State Park)
- 540 ng/kg dw

- **Area A-E**
- **Hartford Area**

Preliminary findings

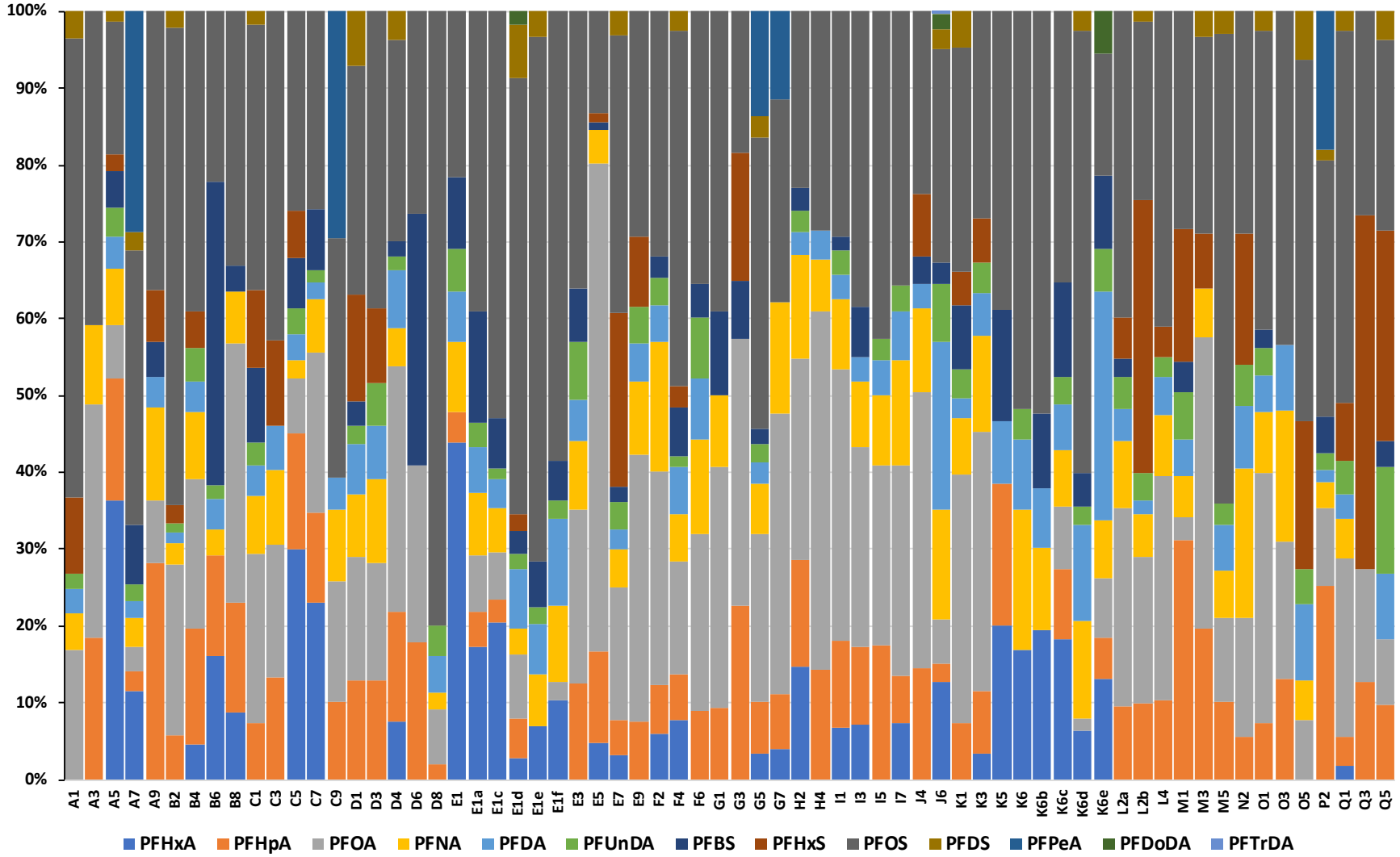
PFAS in VT shallow soils



PFAS concentration profile

PFAS in VT shallow soils

****Preliminary findings****



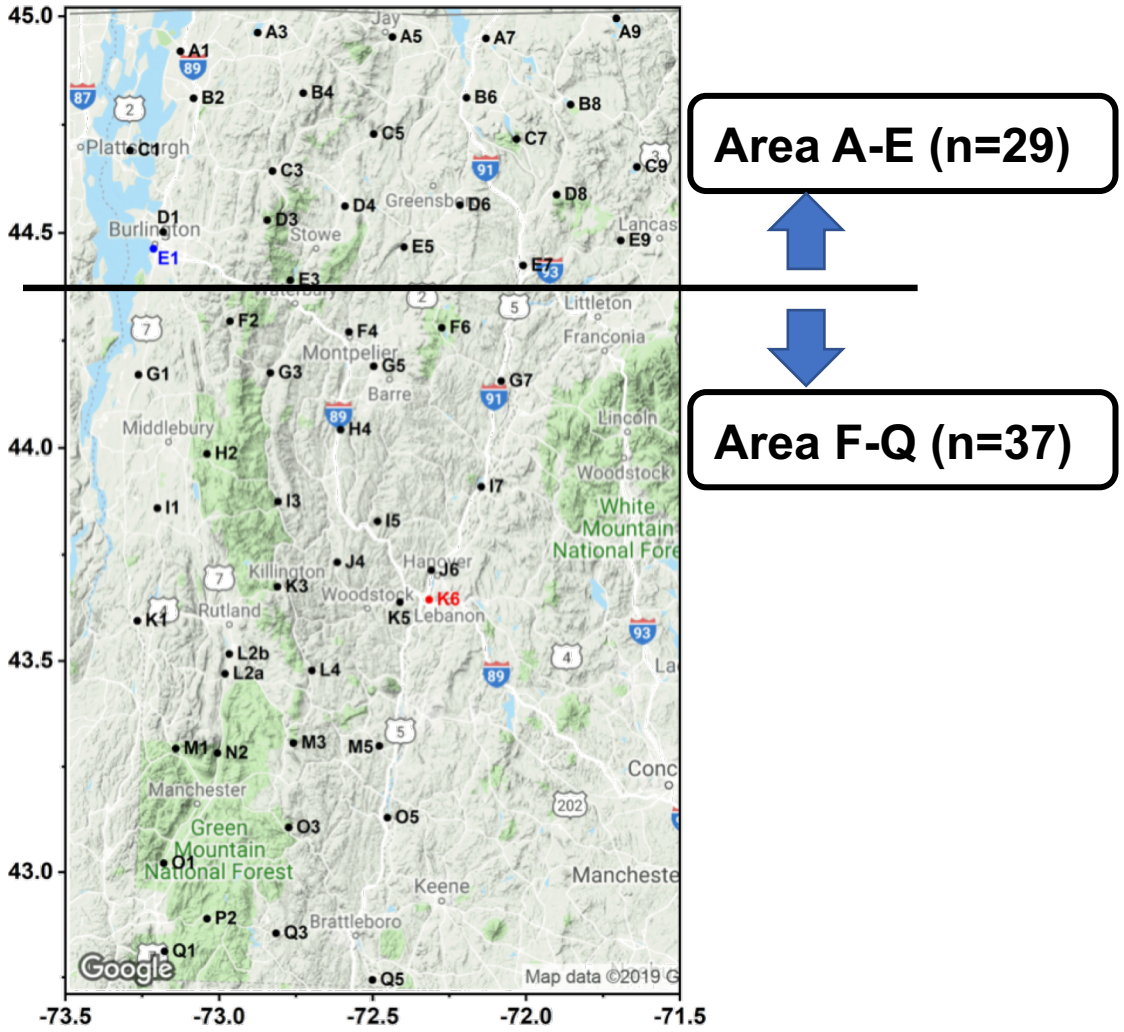
Composition profile of PFAS (%)

PFOS
- 110 - 9,700 ng/kg dw
- 13-80% of ΣPFAS

PFOA
- 52 - 4,900 ng/kg dw

PFAS in VT shallow soils

Preliminary findings



ΣPFAS	Area A-E	Area F-Q	Total
>5000	5	3	8
2000-5000	11	12	23
1000-2000	10	15	25
<1000	3	7	10

ΣPFCA	Area A-E	Area F-Q	Total
>5000	1	2	3
2000-5000	6	2	8
1000-2000	8	16	24
<1000	14	17	31

ΣPFSA	Area A-E	Area F-Q	Total
>5000	0	1	1
2000-5000	8	5	13
1000-2000	9	7	16
<1000	12	24	36

Preliminary findings

Proposed ULT95-95 for selected PFAS

Analyst	Method	UTL 95-95
PFHxA	95% Approx. Gamma UTL with 95% Coverage (WH)-KM	870
PFHpA	95% BCA UTL95% Coverage (Lognormal)	840
PFOA	95% BCA UTL95% Coverage (Lognormal)	1,600
PFNA	95% Approx. Gamma UTL with 95% Coverage (WH)-KM	440
PFDA	95% percentile	390
PFUnDA	95% percentile	180
PFBS	95% KM UTL (Lognormal) 95% Coverage	590
PFHxS	95% percentile	380
PFOS	95% UTL 95% Coverage (Lognormal)	3,400
PFDS	95% Approx. Gamma UTL with 95% Coverage (WH)-KM	150

- **Unit:** ng/kg dw
- Data have been rounded to two significant digits
- J6 was removed as an outlier

Statistics and GIS

Preliminary findings

Goals

- Search possible factors
- Search possible sources
- **Site J6, K6e and E5 as outliers**

Methods

Correlations among individual PFAS

- Spearman correlation

Correlations among sampling locations

- Across VT, Area A-E, Area F-Q
- Principal component analysis (PCA)

GIS analysis

- Land use data
- Spearman correlation

Correlations among PFAS

Preliminary findings

Spearman correlation (α=0.05)

Positive correlations

PFNA
PFDA
PFUnDA
PFHxA

PFNA
PFDA
PFUnDA
PFOS

PFOS
PFDS

PFOA
PFHpA

Negative correlation

PFHxA
PFHxS

Takeaways

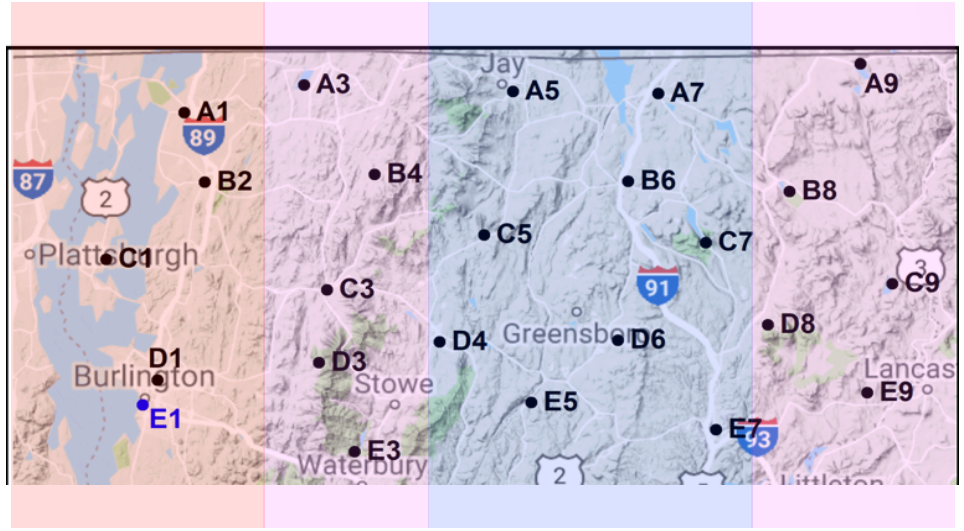
- PFAS positively correlated from similar sources
- PFNA, PFDA, PFUnDA were closely correlated
- Further study needed: PFHxA , PFHxS

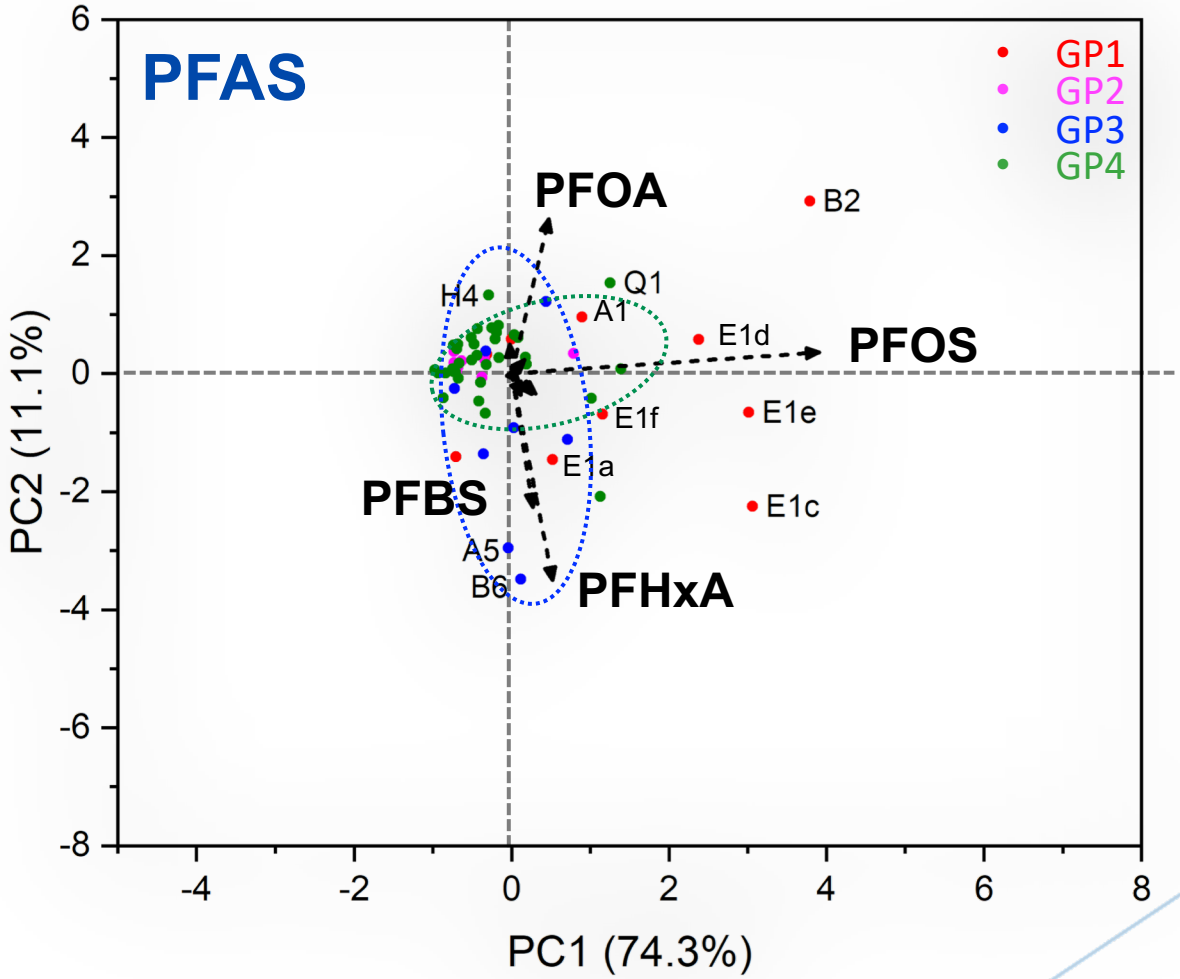
Preliminary findings

Correlations among sampling locations-PCA

PCA analysis

- Similarities and differences
- Area A-E: GP1, GP2, GP3
- Area F-Q: GP4
- Highest loading factors: PFOA, PFOS
- Similar PFAS patterns in GP2, GP4
- PFHxA and PFBS contributed to GP3





GIS-Land use

ArcGIS Pro

- Land use data (%)

Human Activities

- Pasture/Hay
- Row Crops

- Low Intensity Residential (R)
- High Intensity Residential (R)
- Developed, Medium Intensity (D)
- Developed, Medium Intensity (D)

Nature

- Shrub/Scrub
- Grasslands/Herbaceous
- Woody wetlands
- Emergent Herbaceous wetlands
- Water

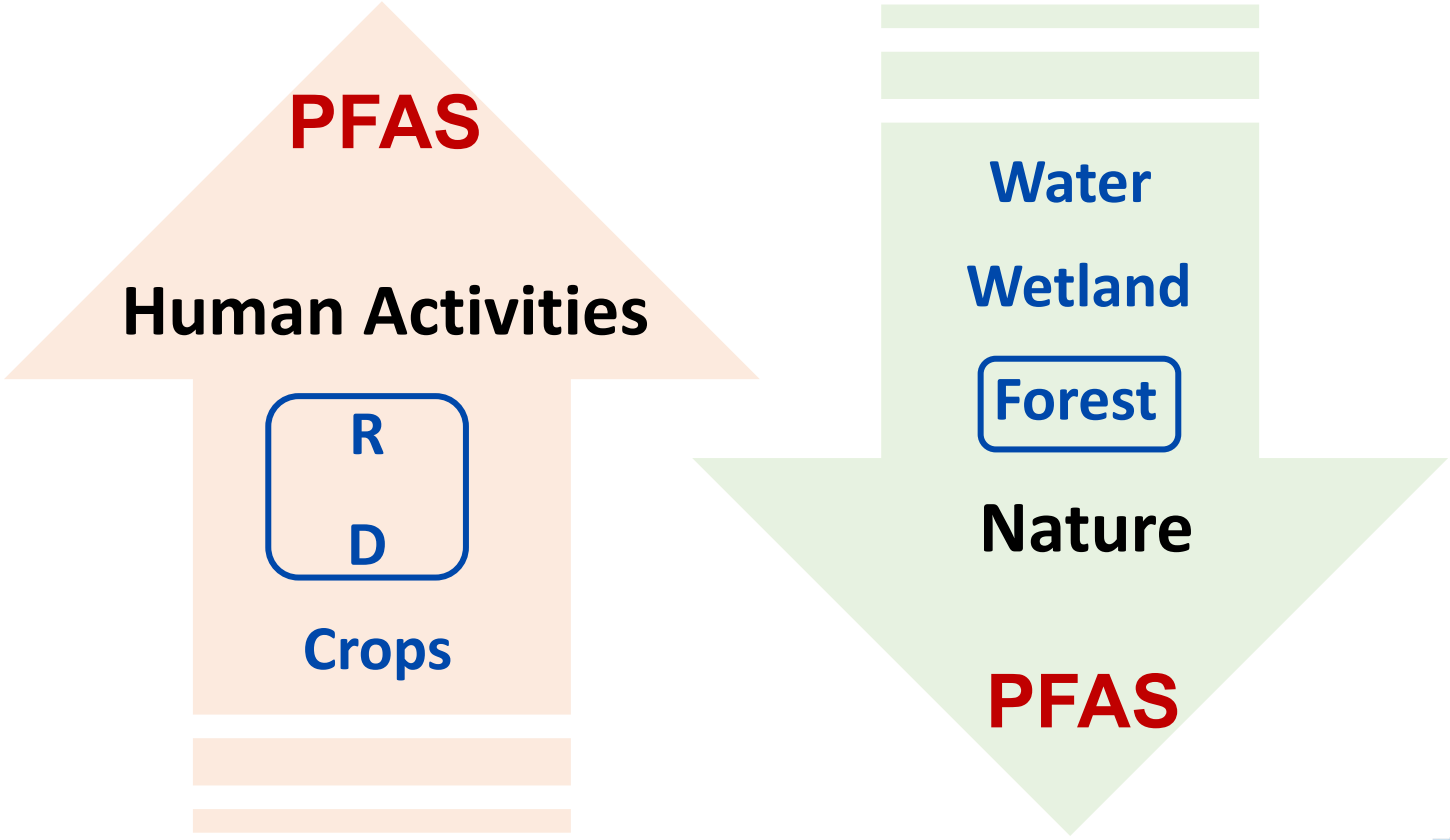
- Deciduous forest
- Evergreen forest

Impacts of land use

Preliminary findings

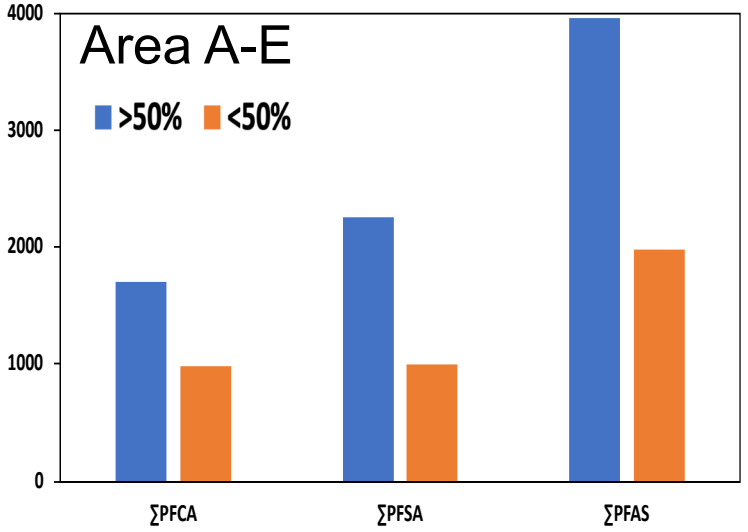
Spearman correlation

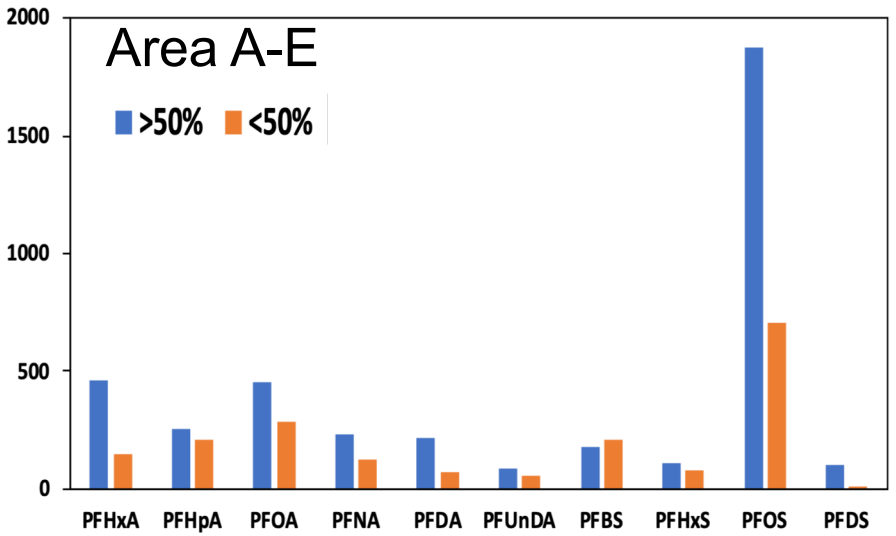
- PFAS positively related to Human Activities (R+D)
- PFAS negatively related to Nature (Forest)
- Area A-E, Area F-Q
- PFSA, PFCA, and individual PFAS



Example: Effects of R+D-100m

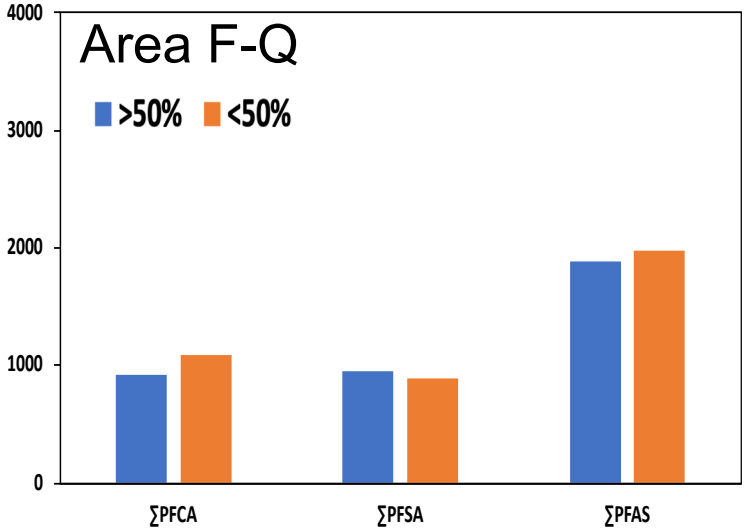
Preliminary findings

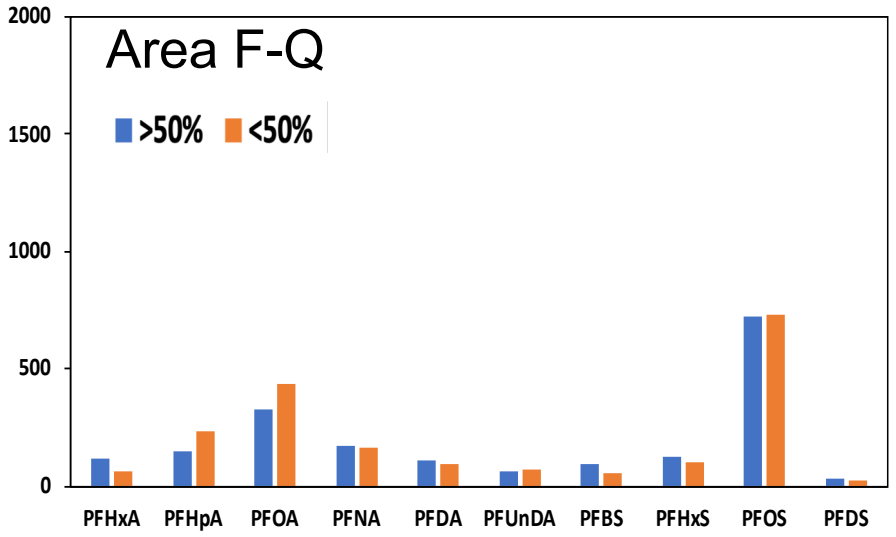




A-E

- More R+D,
  More ΣPFCA, ΣPFSA, ΣPFAS
- More R+D,
  More PFHxA, PFNA, PFDA, PFUnDA, PFOS



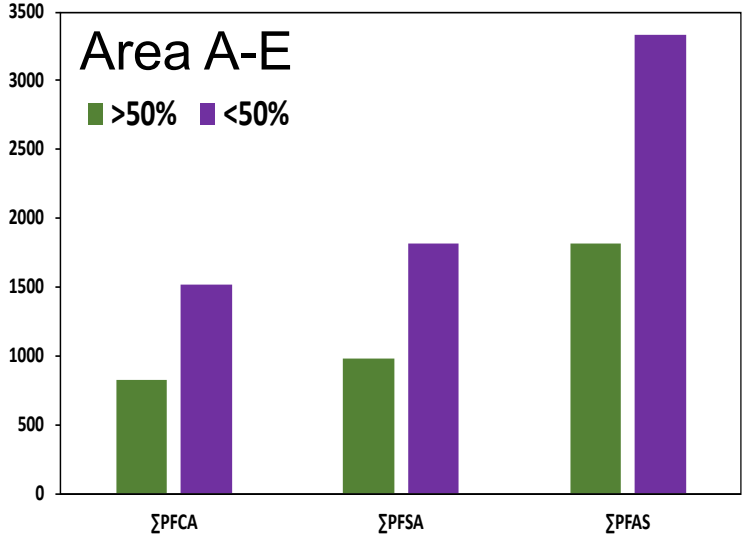


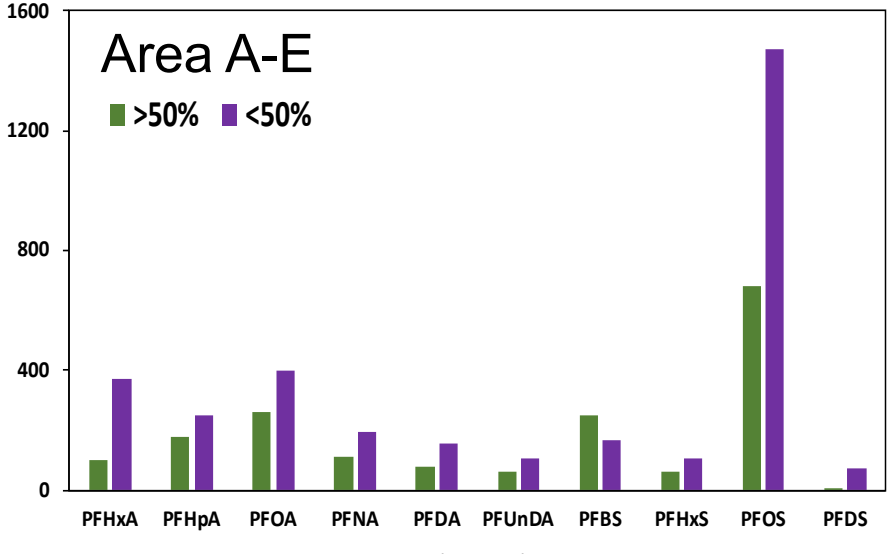
F-Q

- No significant difference

Example: Effects of Forest-100m

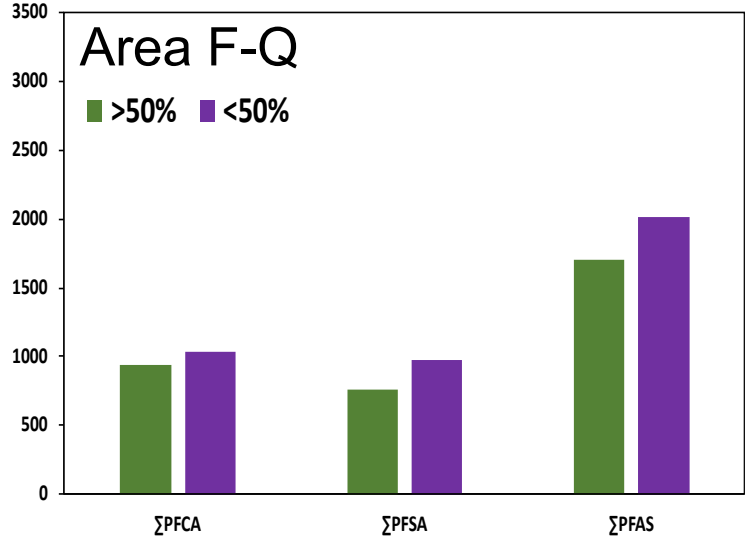
****Preliminary findings****

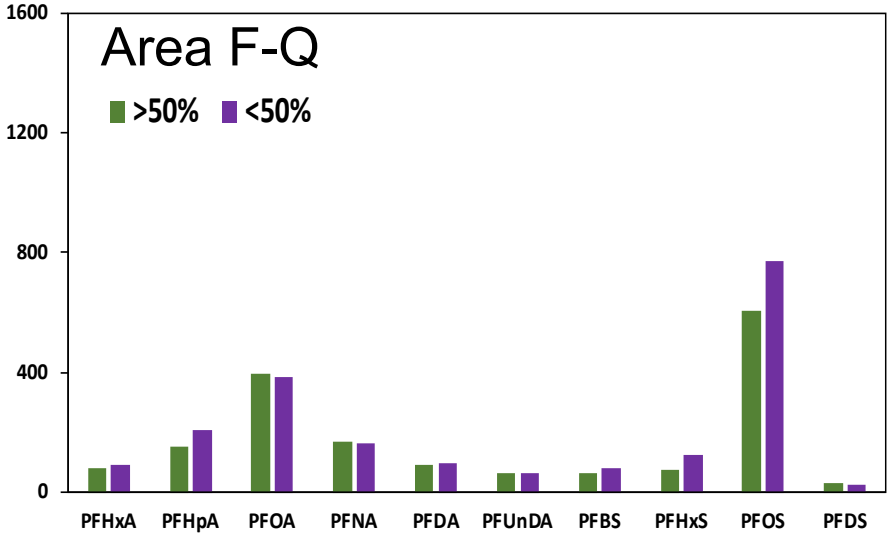




A-E

- More forest, Less ΣPFCA, ΣPFSA, ΣPFAS
- More forest, Less PFHxA, PFNA, PFDA, PFUnDA, PFOS





F-Q

- No significant difference

Impact of land use

Preliminary findings

Spearman correlation

- PFAS positively related to Human Activities (R+D)
- PFAS negatively related to Nature (Forest)
- Area A-E:
  - PFCA and PFSA were significantly correlated to R+D and Forest
  - PFHxA, PFNA, PFDA, PFUnDA and PFOS were closely affected by R+D and Forest
- Area F-Q:
  - No significant correlation to land use

Takeaways

- Occurrence of PFAS in A-E area may be more remarkably affected by local sources
- PFHxA, PFNA, PFDA, PFUnDA and PFOS may from similar sources

Possible source appointment

****Preliminary findings****

PFOA, PFHpA
- Correlated to each other
- No significant correlation to land use
- Manufacture, industrial and consumer uses (e.g. food package)

PFOS
- Positively affected by R, D (RD)-local sources
- Manufacture and industrial uses

PFHxA, PFNA, PFDA, PFUnDA
- Closely correlated to each other
- Positively affected by R, D (R+D)-local sources
- Manufacture and industrial uses

PFAS in VT shallow soils

Preliminary findings

- Various PFAS existed in VT soils
- Two dominant PFAS: PFOS, PFOA
- PFAS positively related to Human Activities (R+D)
- PFAS negatively related to Nature (Forest)
- Different PFAS patterns in Area A-E and Area F-Q
- Types of land use significantly affects PFAS in Area A-E
- PFHxA, PFNA, PFDA, PFUnDA, PFOS closely related
- Sites J6, K6e, E5 need further investigation

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Thank You!