Wildfire-derived Polycyclic Aromatic Hydrocarbons in a Southern California Coastal Watershed

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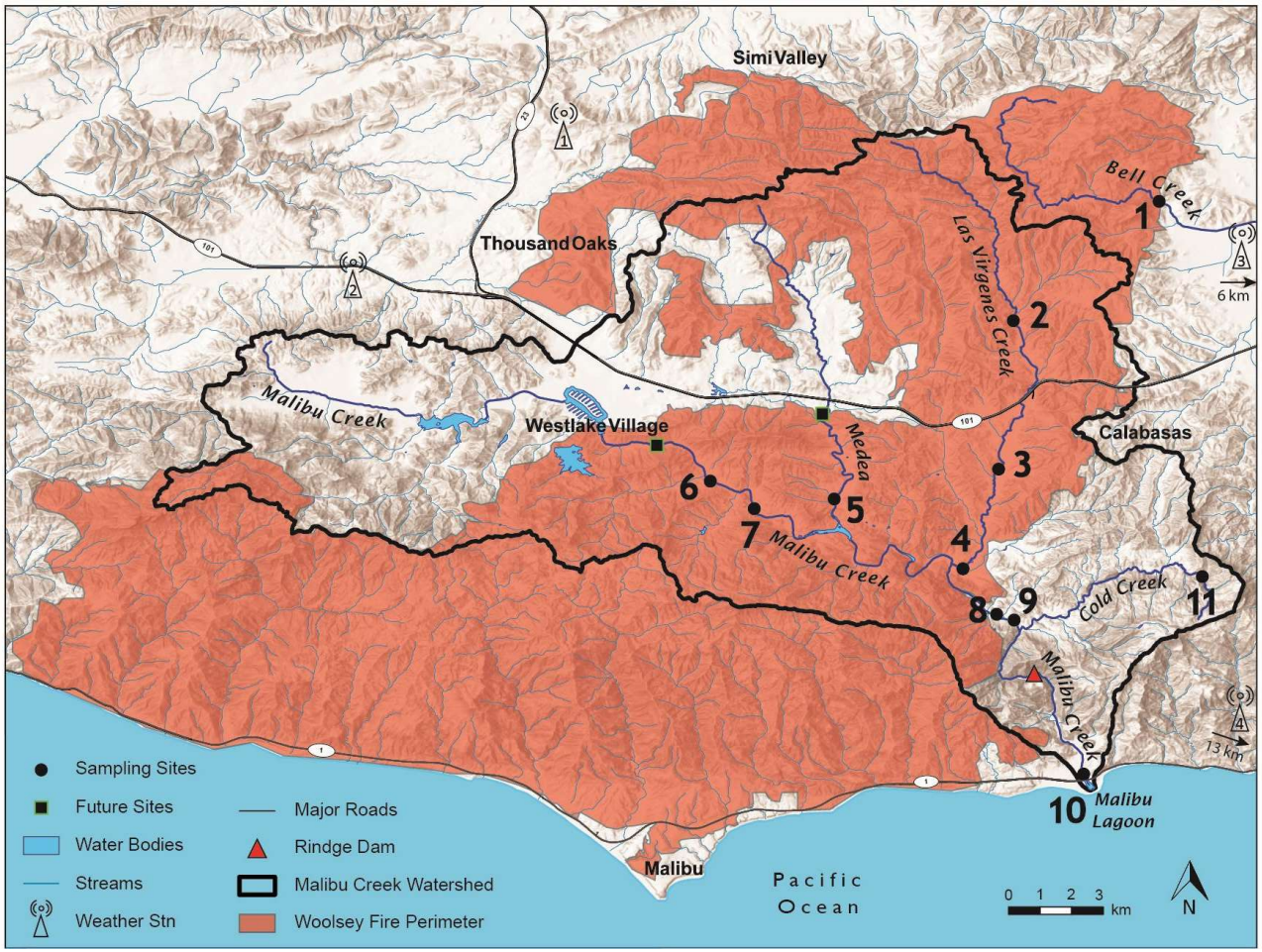
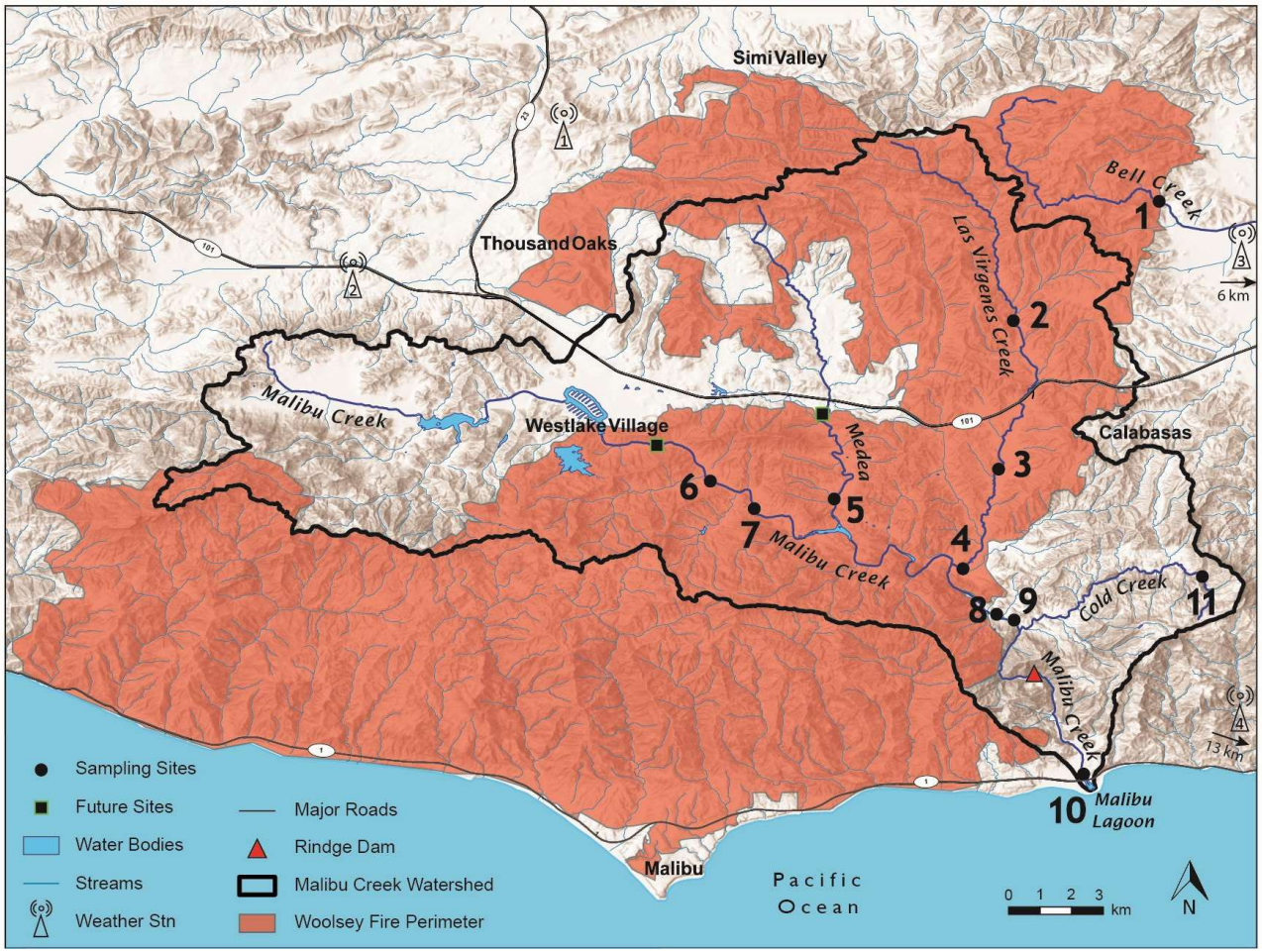
Study Site: Malibu Creek Watershed

- 2018 Woolsey Fire burned ~2/3 of Malibu Creek Watershed
- Ecologically sensitive: ~50 endangered and threatened species
- Varying land use, terrain, vegetation, burn intensity



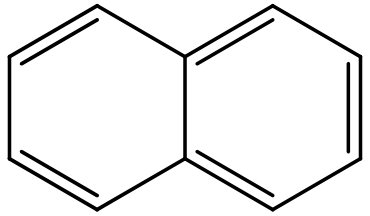
Study Site: Malibu Creek Watershed

- Question: How did Woolsey Fire impact water quality in watershed?
  - Larger study includes metals, mercury, nutrients
  - This talk focuses on organic polycyclic aromatic hydrocarbons (PAHs)

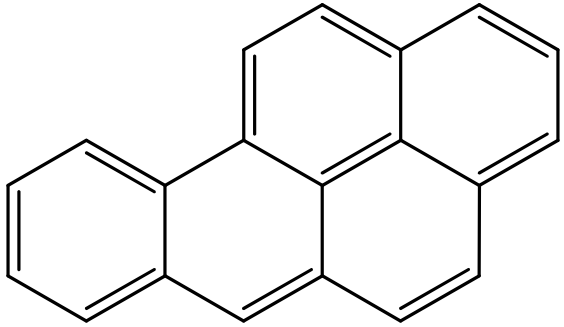


PAHs – Polycyclic Aromatic Hydrocarbons

- Made of multiple fused benzene rings
- Formed during incomplete combustion of organic matter and present in petroleum
- Mutagenic, **carcinogenic**, reproductive defects
- **Toxic to aquatic organisms**
- Bioaccumulate in lower organisms



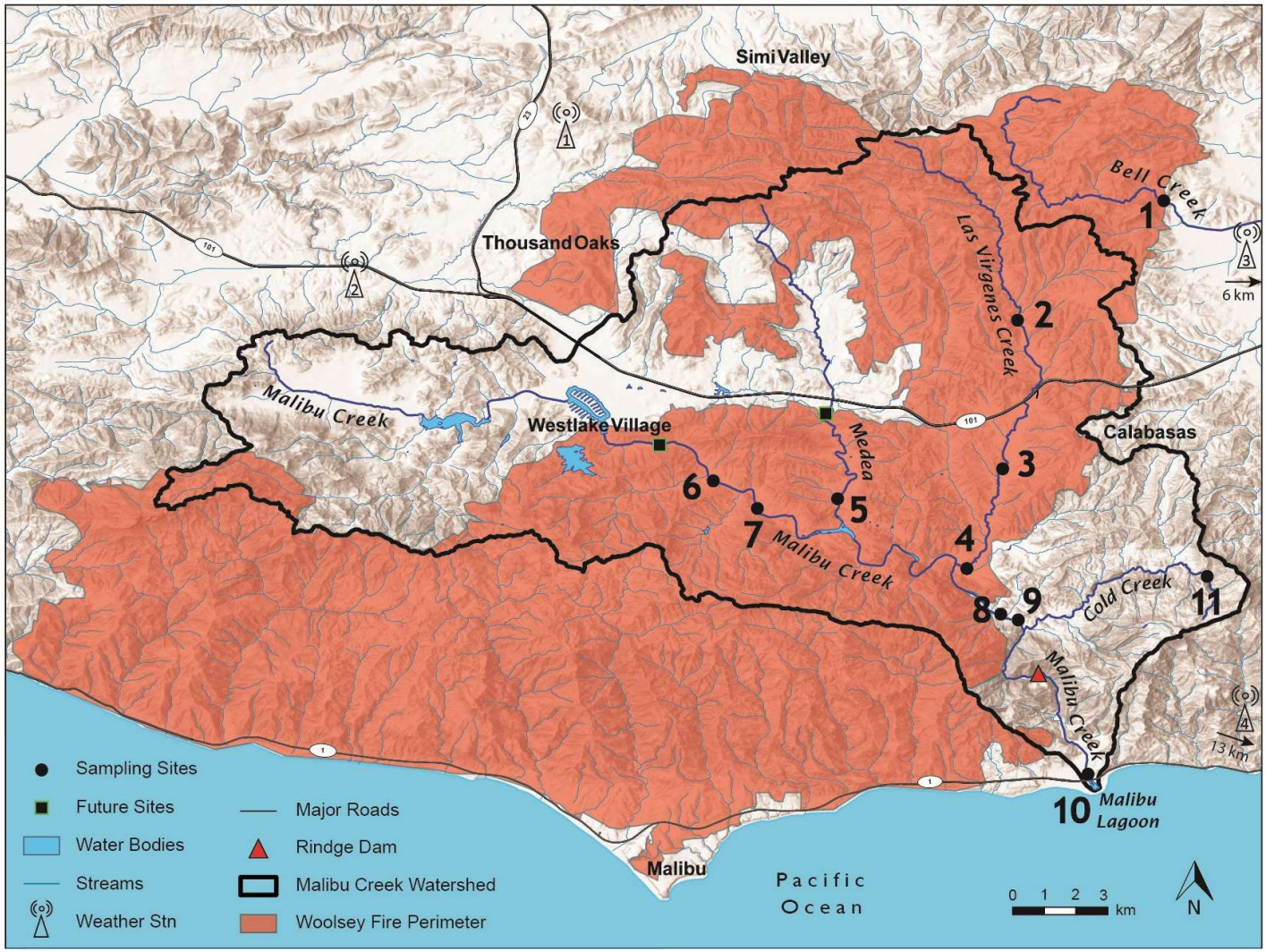
naphthalene



benzo(a)pyrene

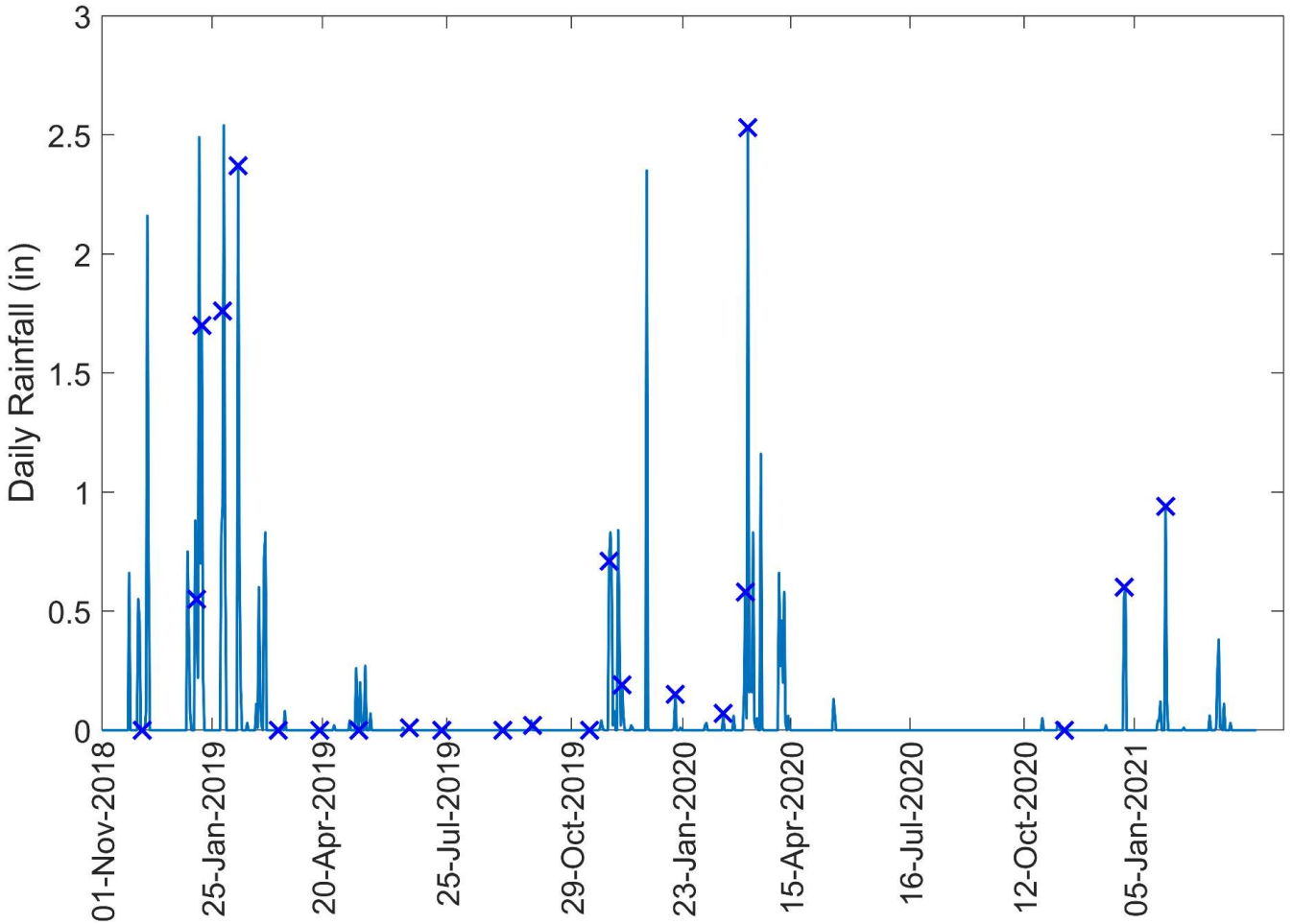
Sampling Plan

- Water sampling in Woolsey burn area
  - Malibu Creek and all major tributaries
  - Unburned Cold Ck.
  - Bell Ck (LA River watershed)



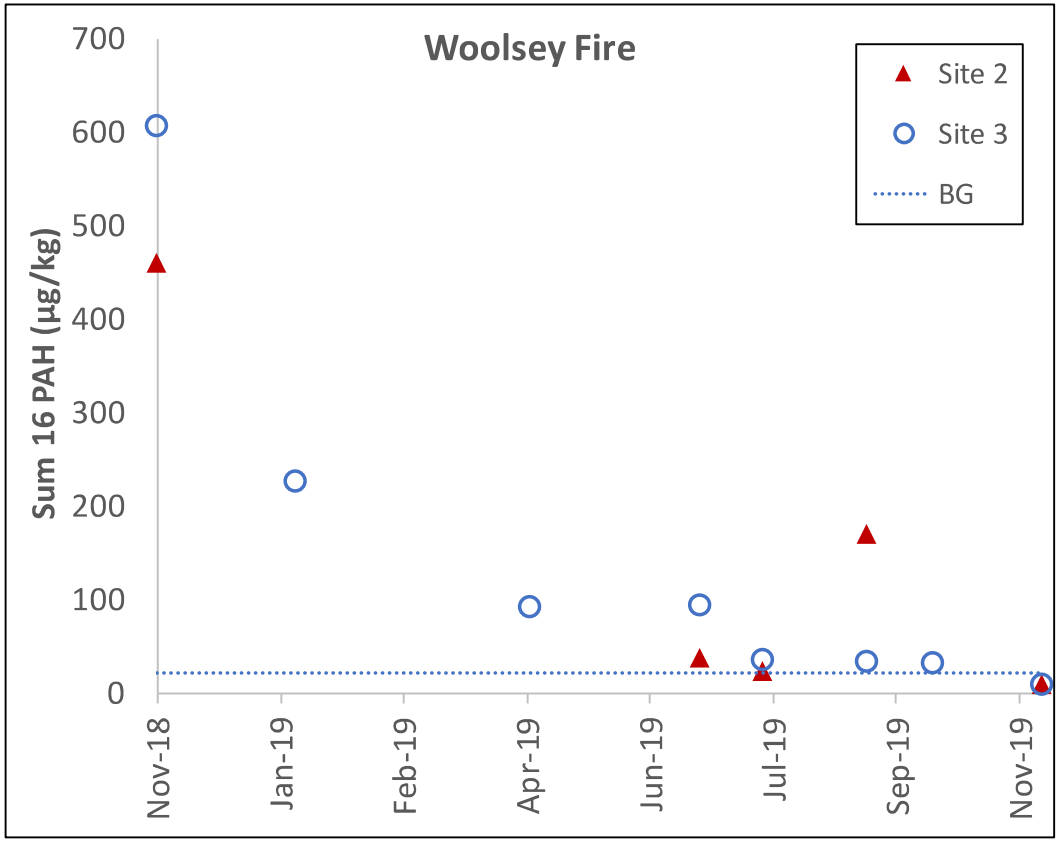
Methods

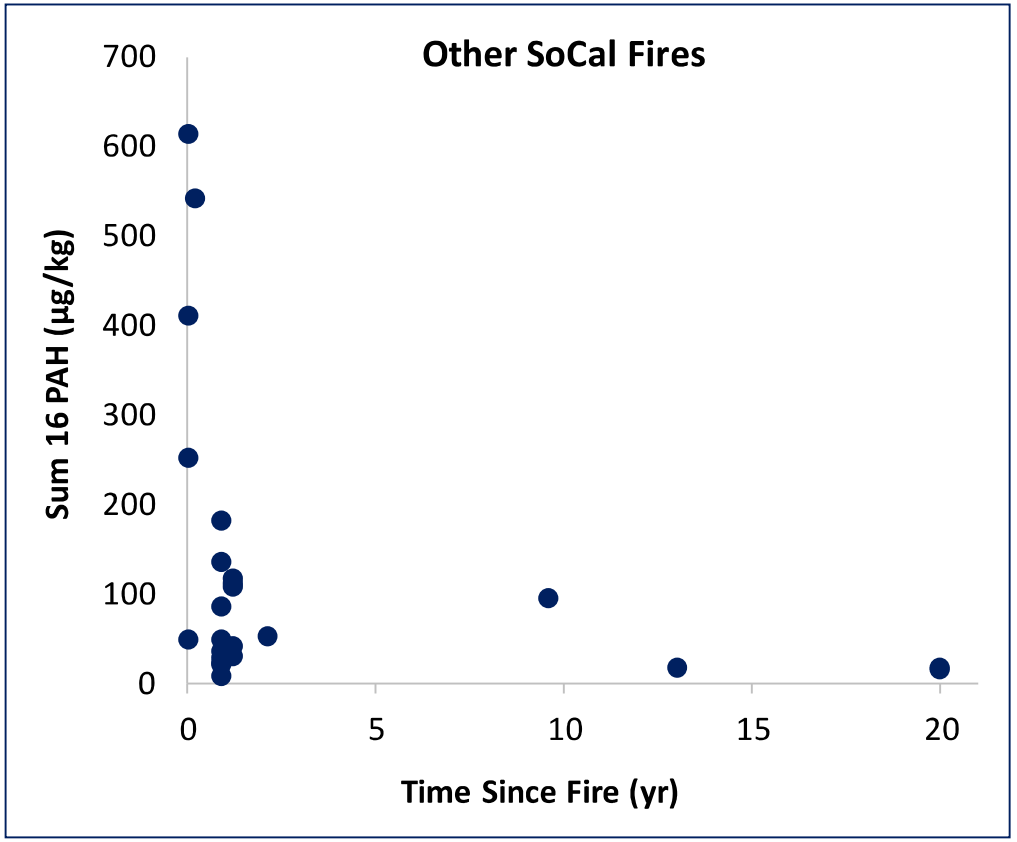
- Samples collected during 13 significant rain events Dec. 2018-Jan. 2021
- ~Monthly during dry season
- Soil samples collected shortly after fire and periodically after @ 2 sampling locations
- Sampling paused March – November 2020 due to COVID

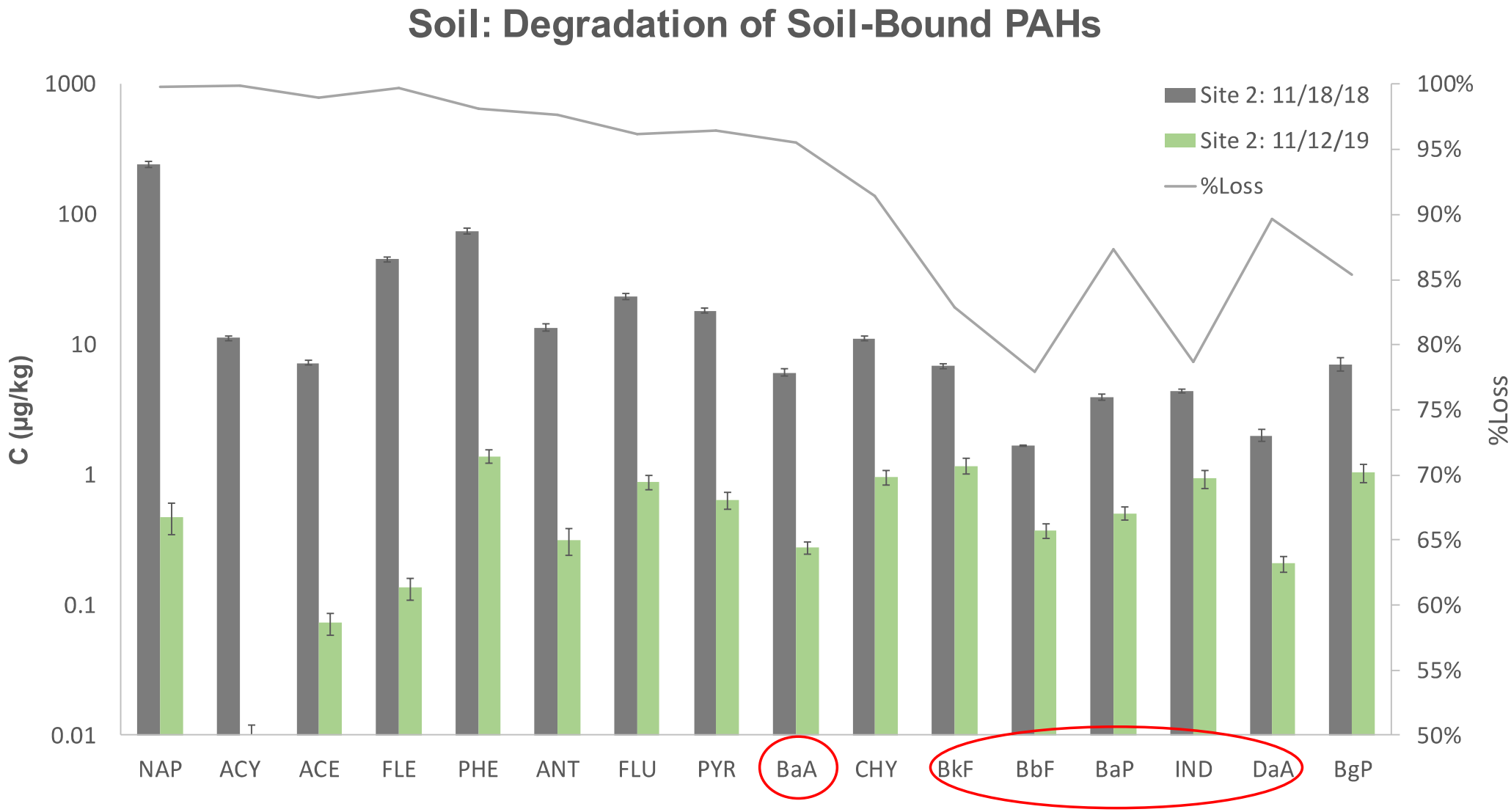


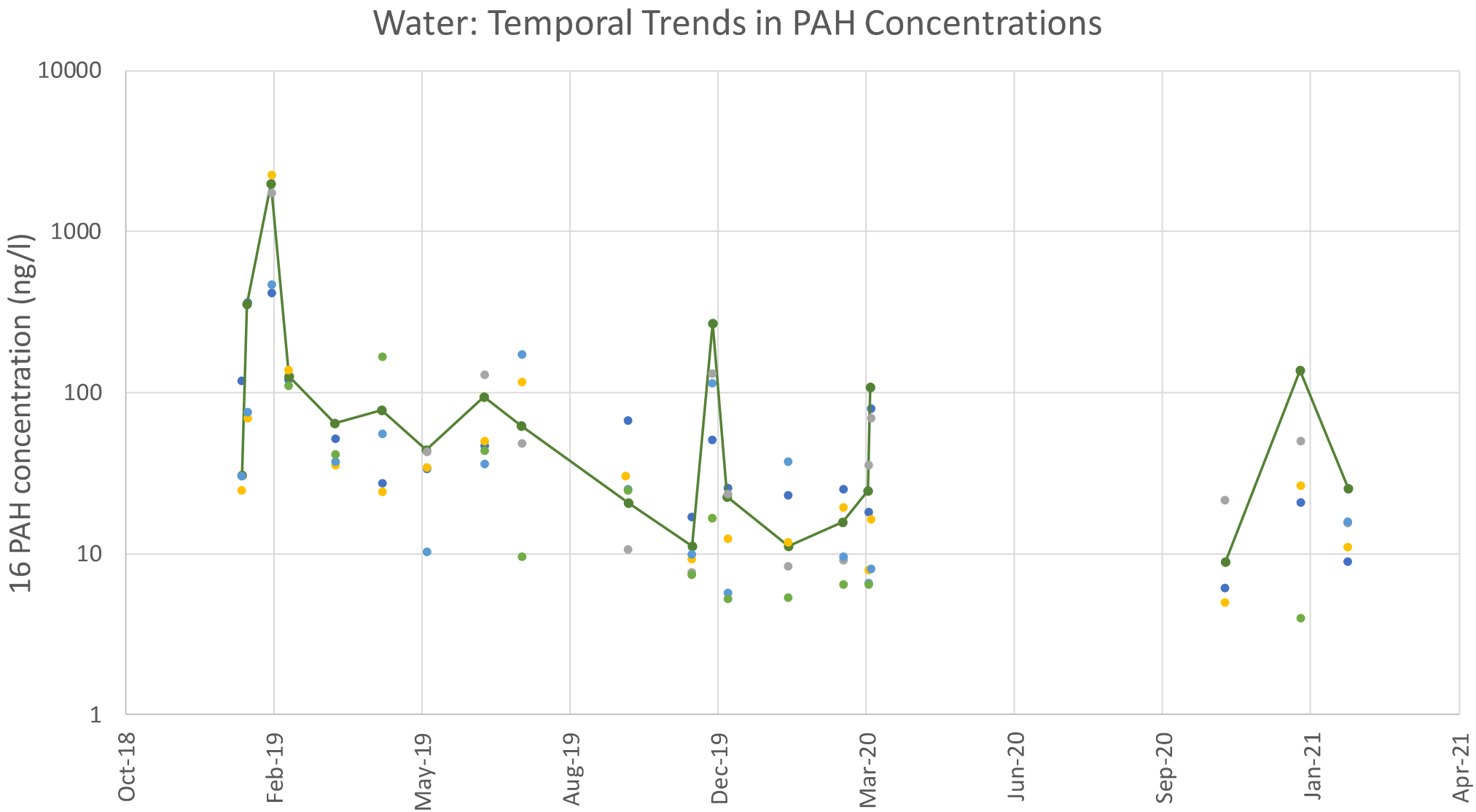
Results Highlights

- Soil PAH concentrations decline relatively rapidly after fire



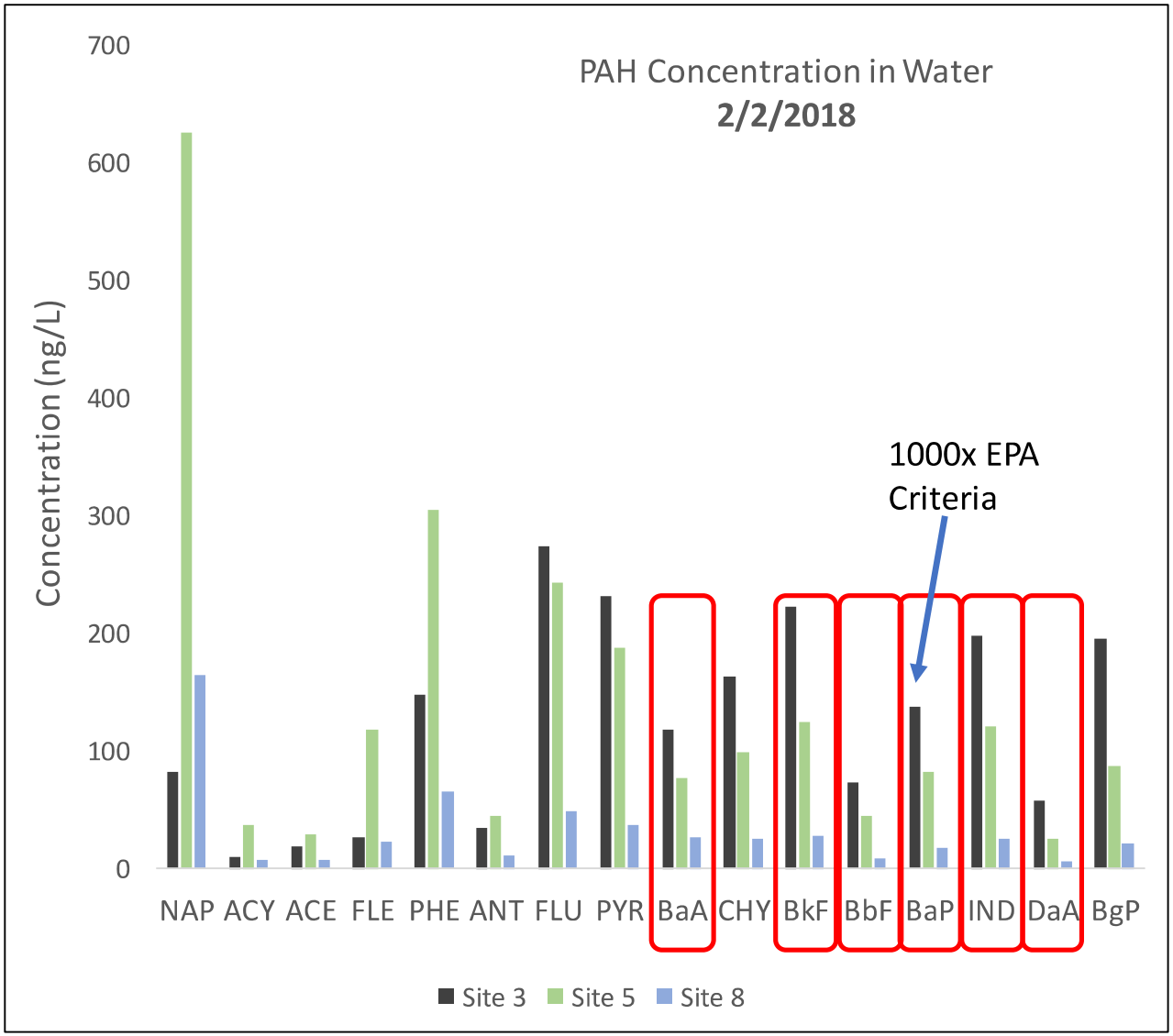


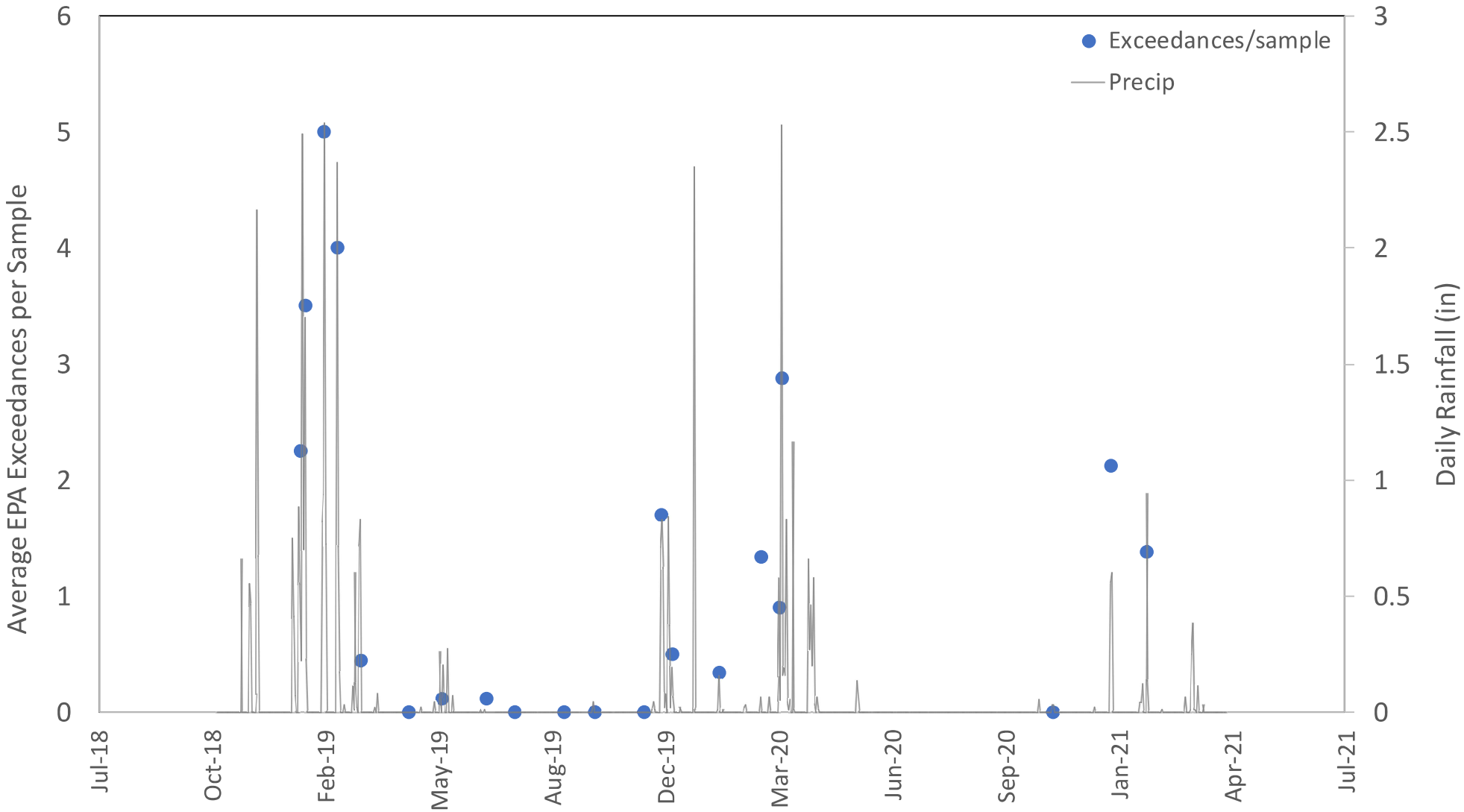

Soil: Degradation of Soil-Bound PAHs
Site 2: 11/18/18
Site 2: 11/12/19
%Loss
C (µg/kg)
%Loss
1000
100
10
1
0.1
0.01
100%
95%
90%
85%
80%
75%
70%
65%
60%
55%
50%
NAP
ACY
ACE
FLE
PHE
ANT
FLU
PYR
BaA
CHY
BkF
BbF
BaP
IND
DaA
BgP

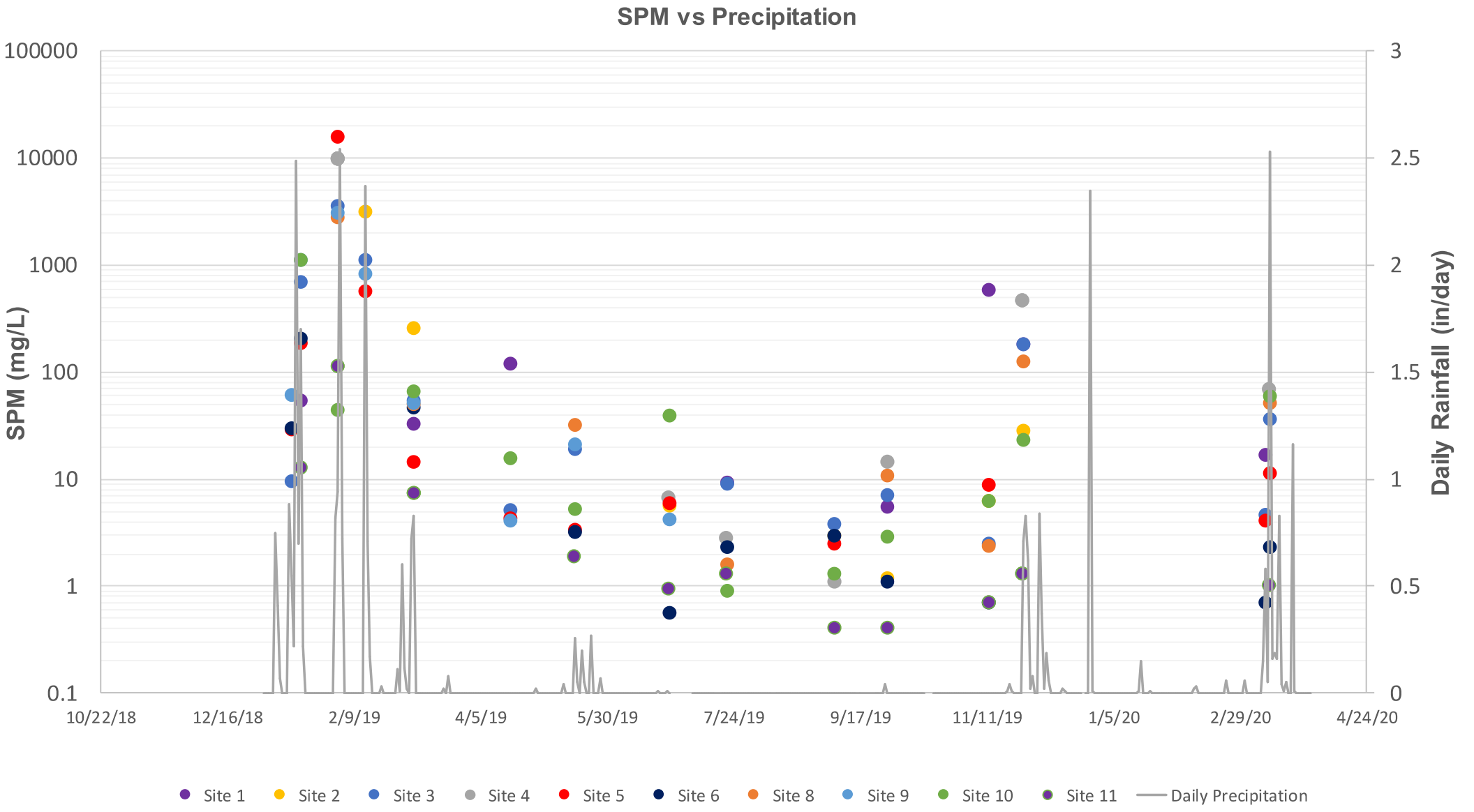

Water: Temporal Trends in PAH Concentrations
16 PAH concentration (ng/l)
10000
1000
100
10
1
Oct-18
Feb-19
May-19
Aug-19
Dec-19
Mar-20
Jun-20
Sep-20
Jan-21
Apr-21

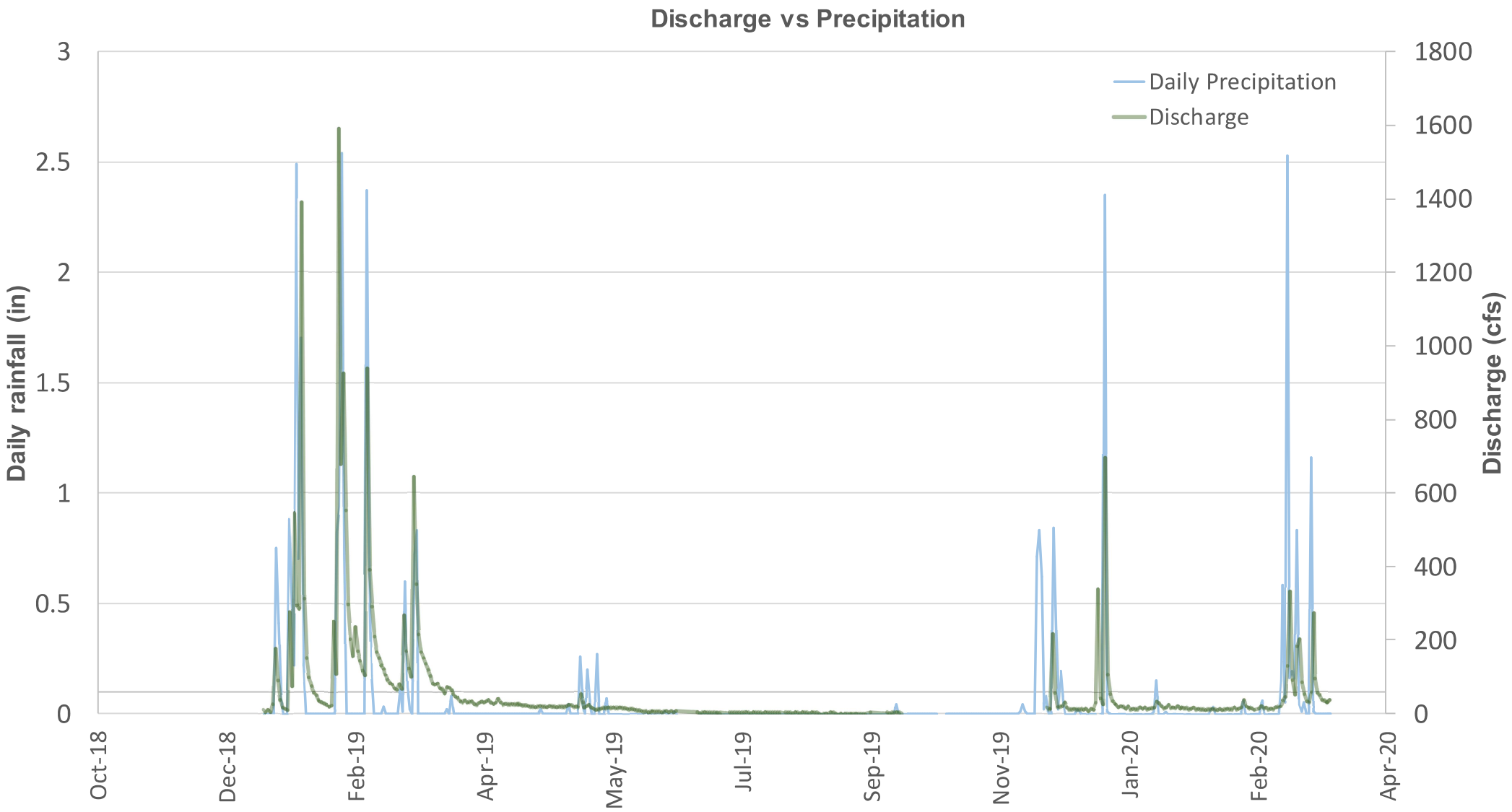
Results Highlights

- **Water concentrations consistently below drinking water MCLs**
- Numerous exceedances of US EPA “Human Health Criteria for Ambient Waters”
- Up to 1000x criteria!



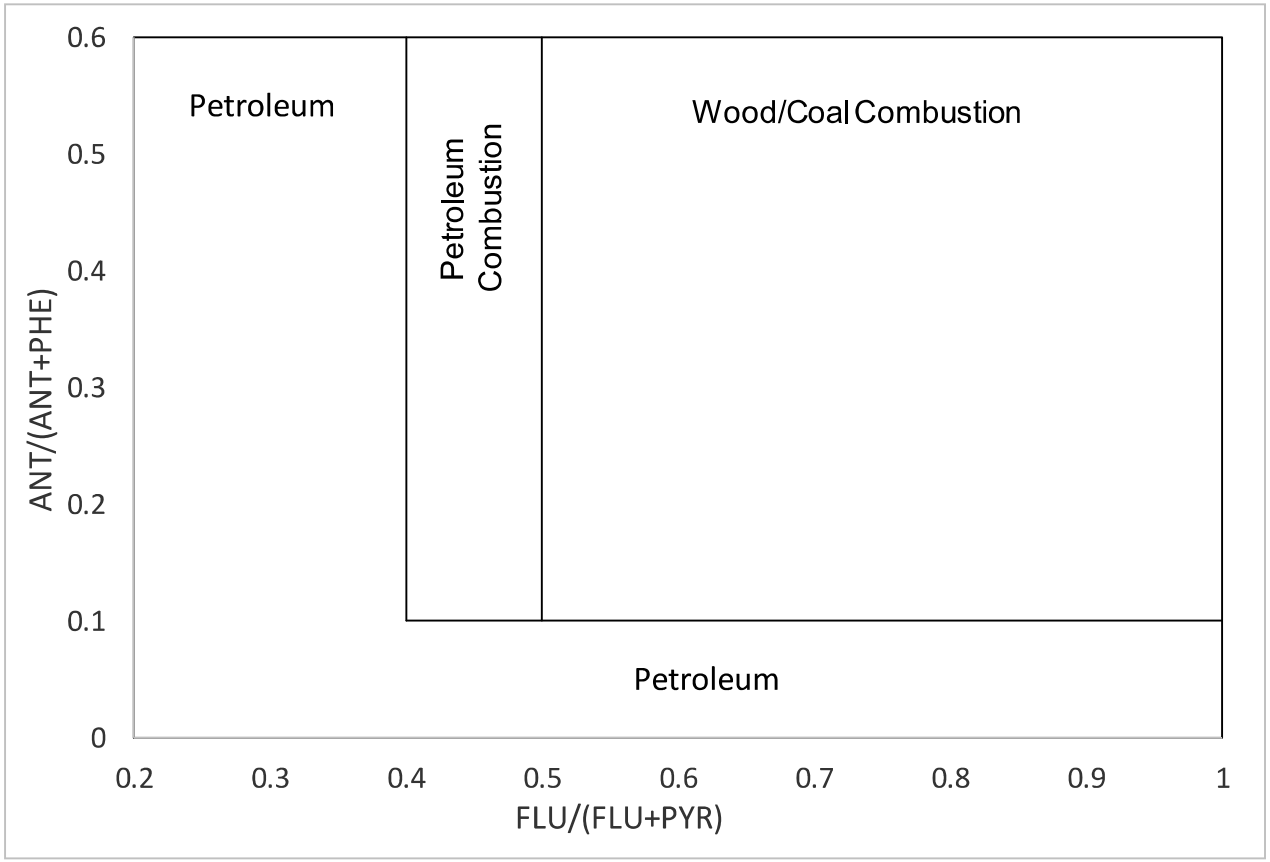

Exceedances/sample
Precip
Average EPA Exceedances per Sample
Daily Rainfall (in)
0
1
2
3
4
5
6
0
0.5
1
1.5
2
2.5
3
Jul-18
Oct-18
Feb-19
May-19
Aug-19
Dec-19
Mar-20
Jun-20
Sep-20
Jan-21
Apr-21
Jul-21


SPM vs Precipitation
SPM (mg/L)
Daily Rainfall (in/day)
100000
10000
1000
100
10
1
0.1
3
2.5
2
1.5
1
0.5
0
10/22/18
12/16/18
2/9/19
4/5/19
5/30/19
7/24/19
9/17/19
11/11/19
1/5/20
2/29/20
4/24/20
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6
Site 8
Site 9
Site 10
Site 11
Daily Precipitation

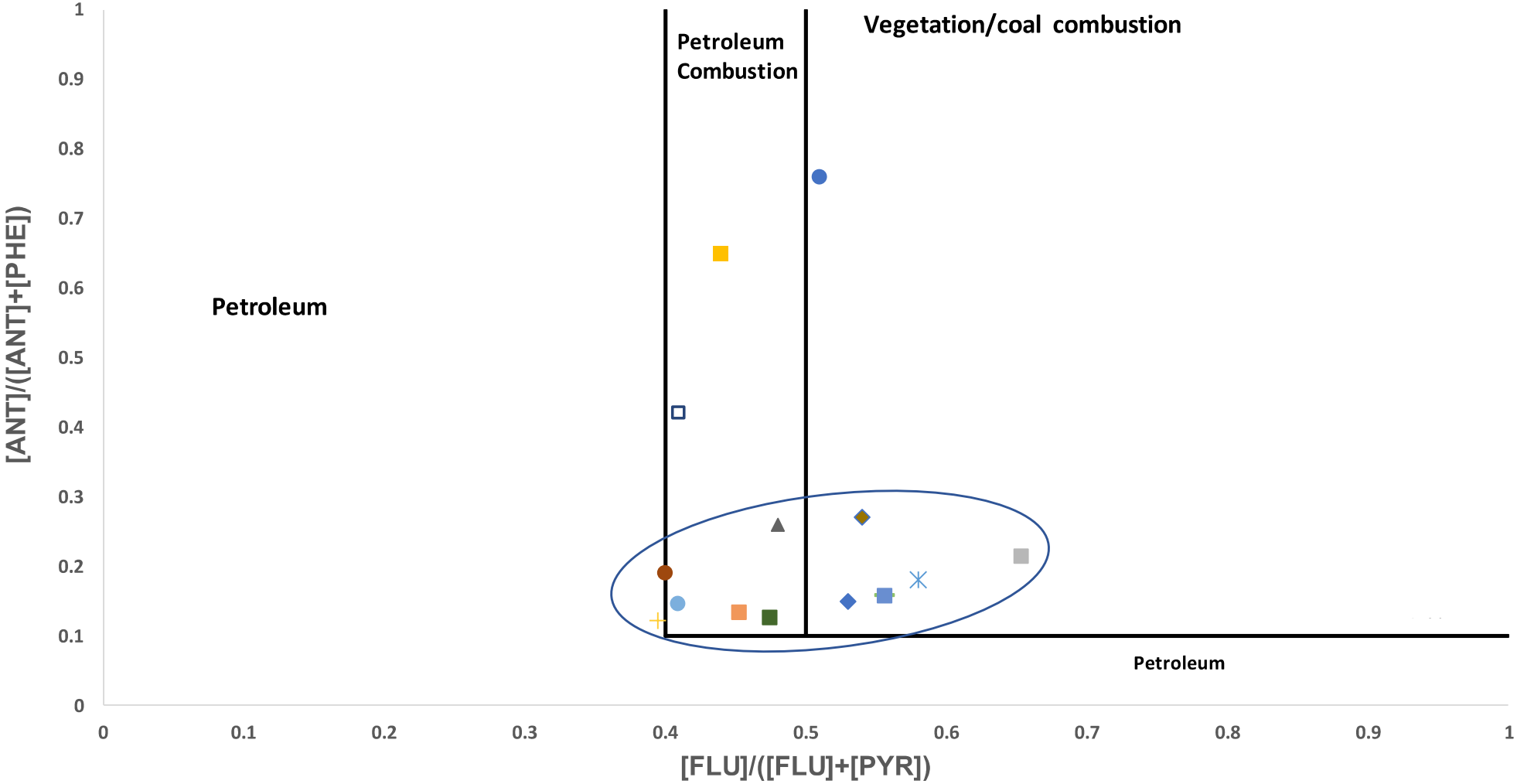

Discharge vs Precipitation
Daily Precipitation
Discharge
Daily rainfall (in)
Discharge (cfs)
3
2.5
2
1.5
1
0.5
0
1800
1600
1400
1200
1000
800
600
400
200
0
Oct-18
Dec-18
Feb-19
Apr-19
May-19
Jul-19
Sep-19
Nov-19
Jan-20
Feb-20
Apr-20

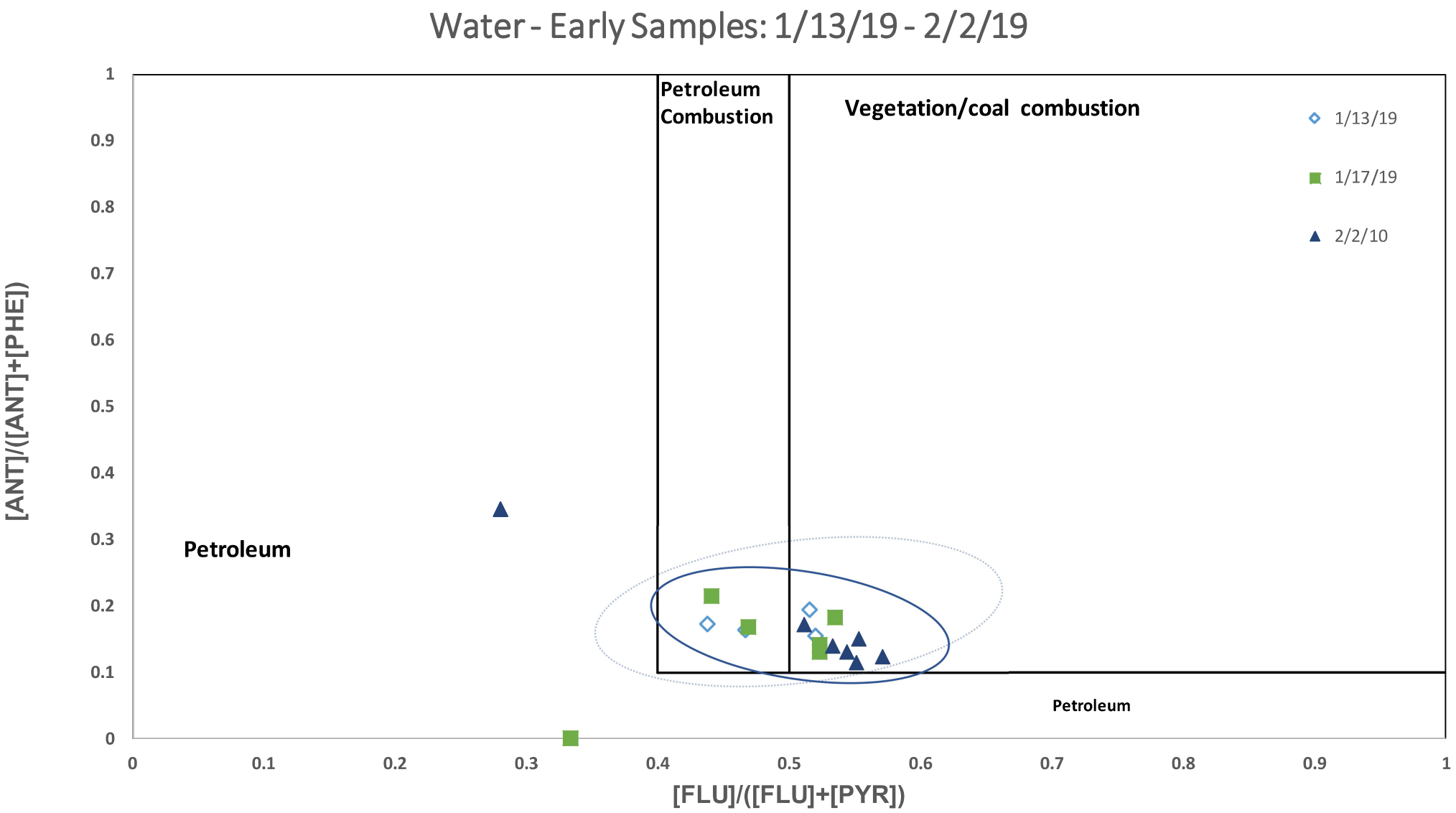
Are PAHs from the fire?

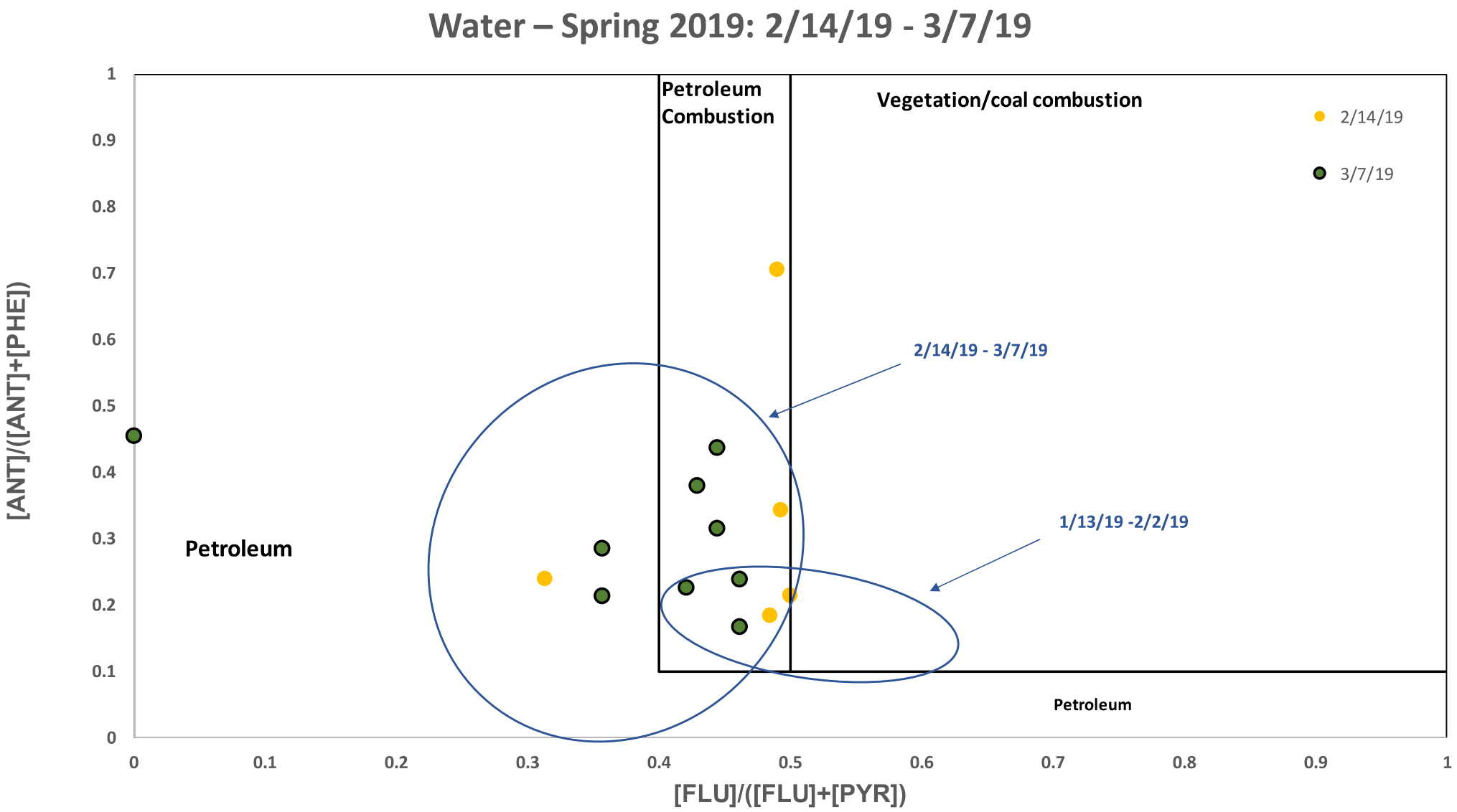
- PAHs may come from fire vs road runoff (oil) vs fossil fuel combustion
- Simple molecular ratio approach → imperfect, but gives some indication
- Other molecular ratio approaches and potentially isotopic methods in progress

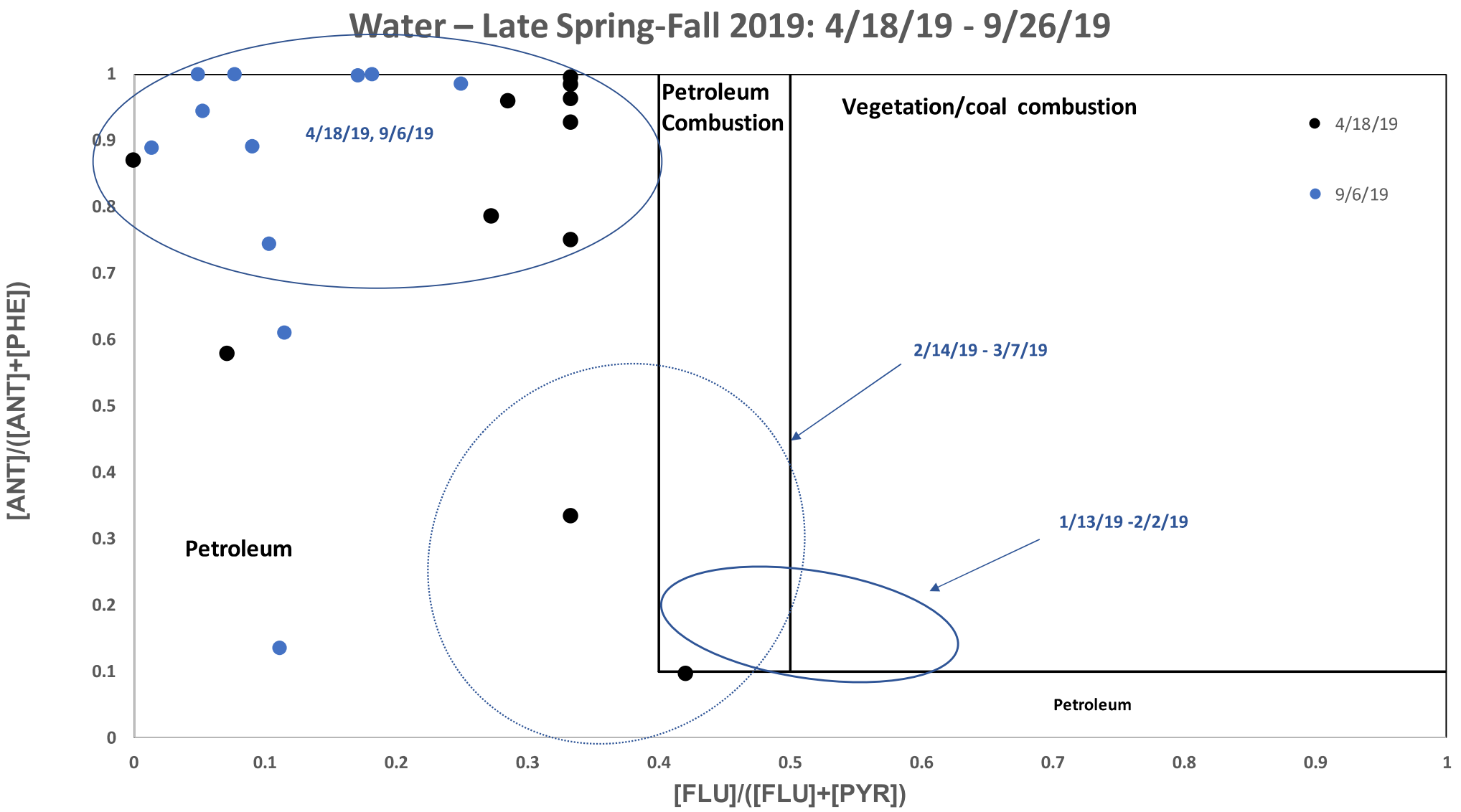


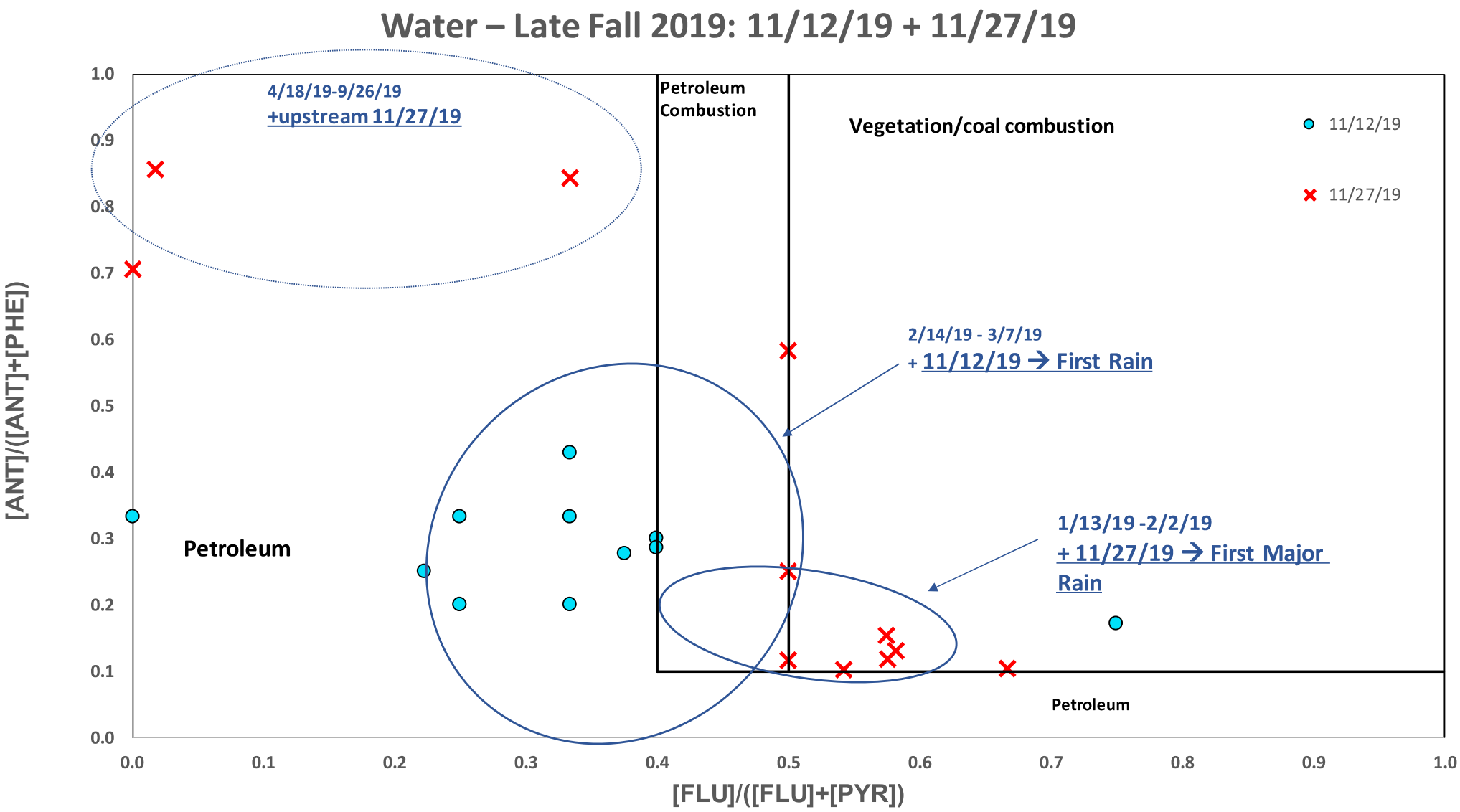
Soil

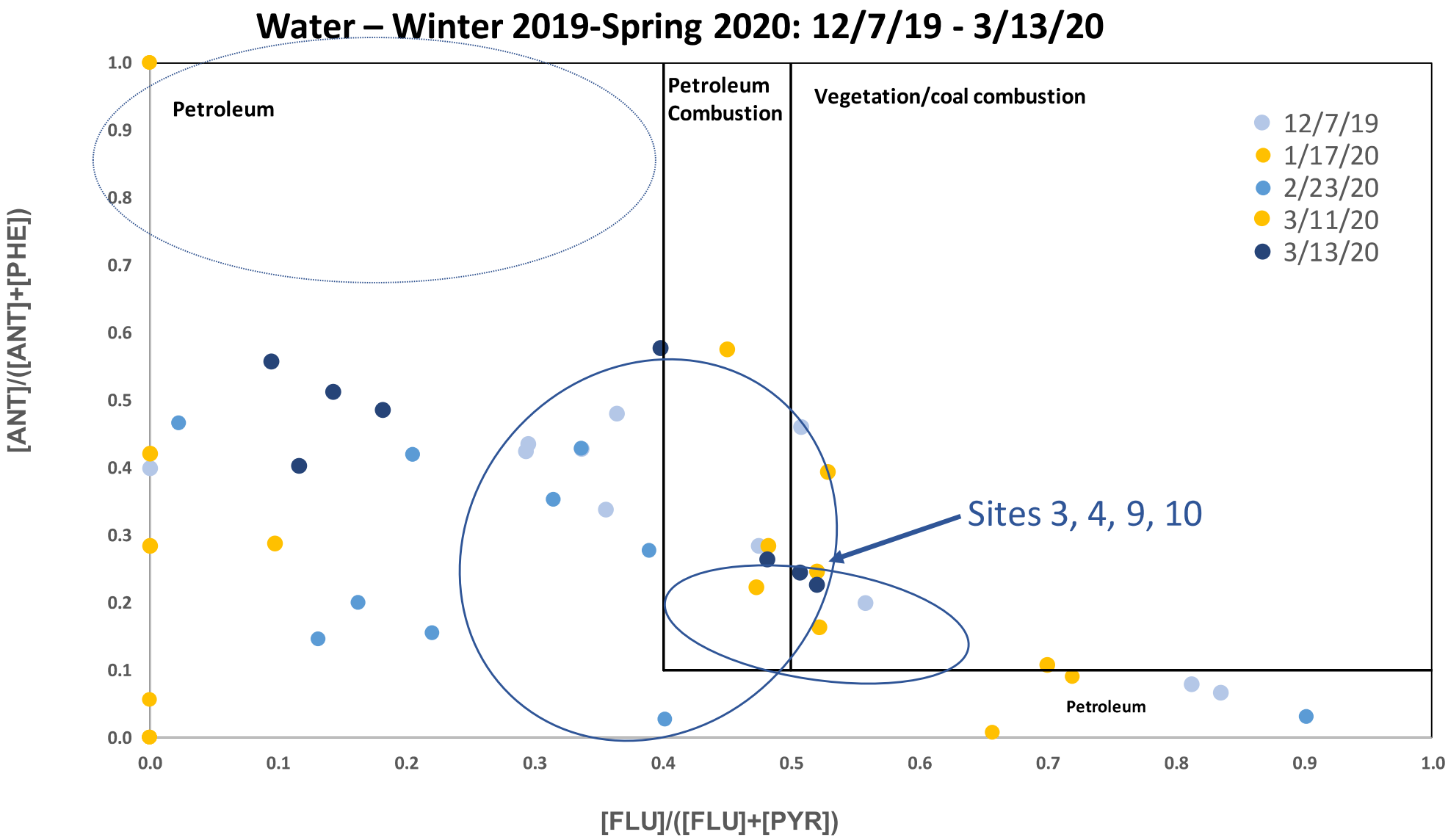

Petroleum
Combustion
Vegetation/coal combustion
Petroleum
Petroleum
[ANT]/([ANT]+[PHE])
[FLU]/([FLU]+[PYR])
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

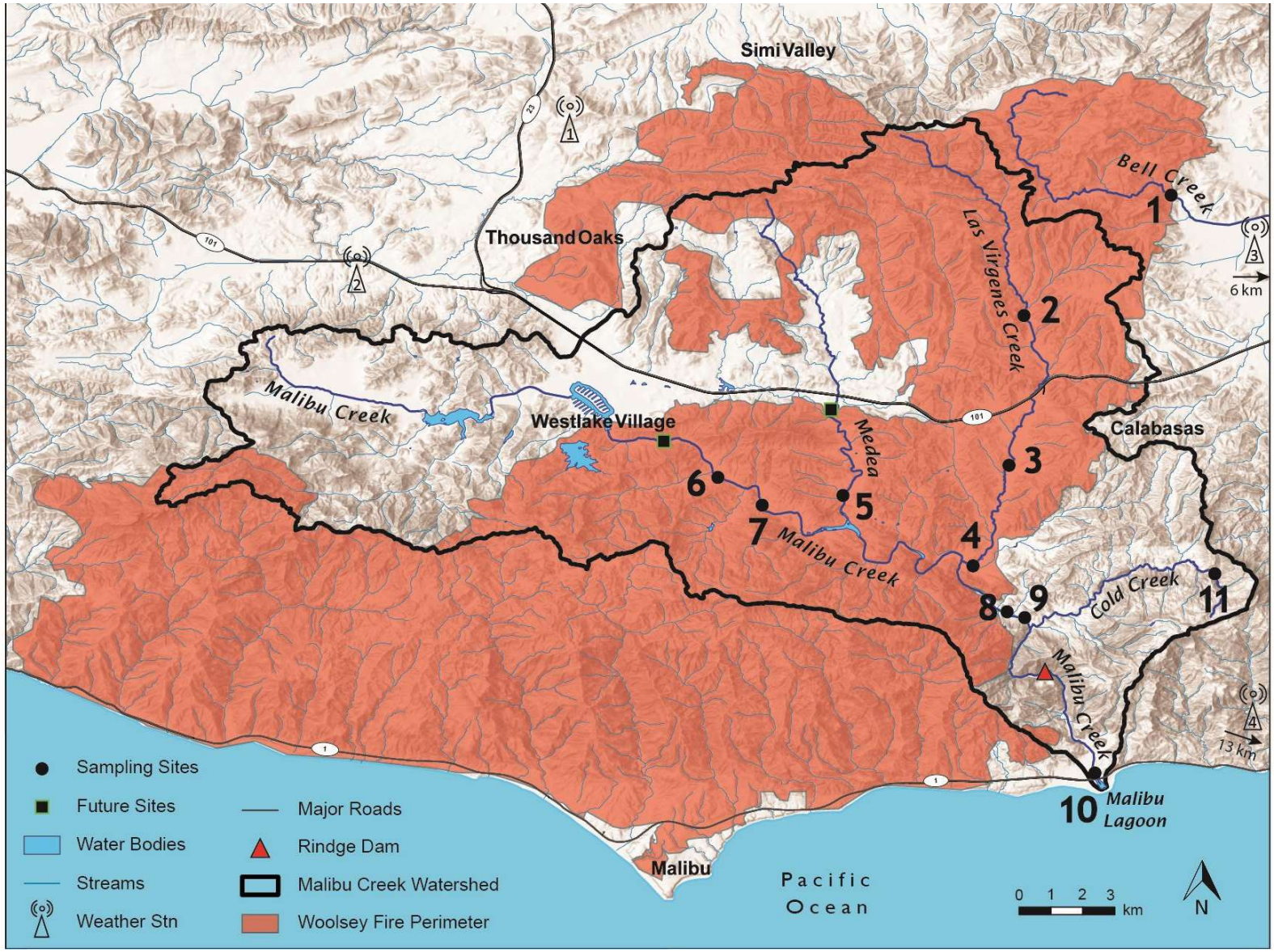

Water - Early Samples: 1/13/19 - 2/2/19
Petroleum Combustion
Vegetation/coal combustion
Petroleum
Petroleum
1/13/19
1/17/19
2/2/10
[ANT]/([ANT]+[PHE])
[FLU]/([FLU]+[PYR])
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

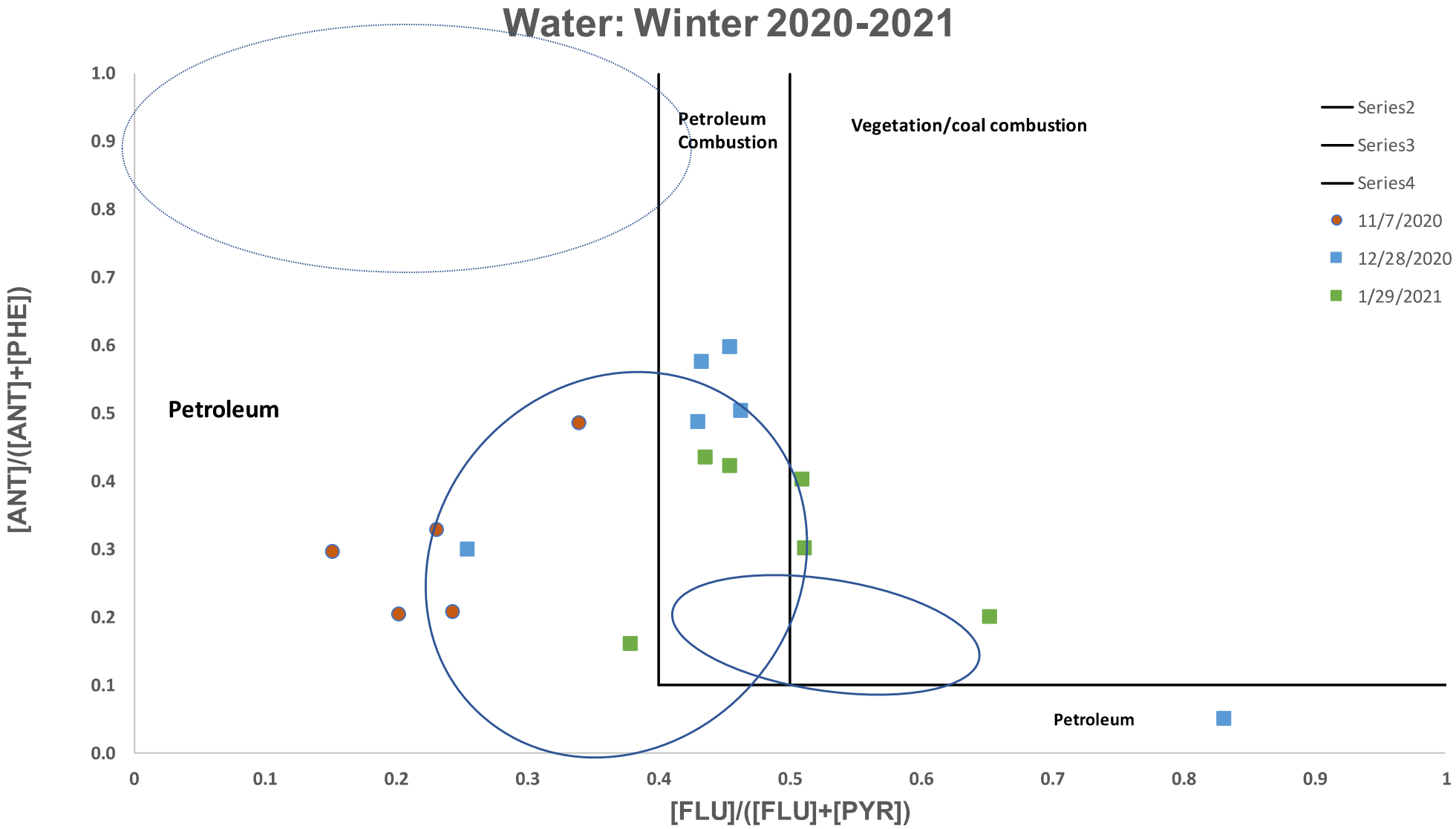

Water – Spring 2019: 2/14/19 - 3/7/19
Petroleum Combustion
Vegetation/coal combustion
2/14/19
3/7/19
2/14/19 - 3/7/19
1/13/19 -2/2/19
Petroleum
Petroleum
[ANT]/([ANT]+[PHE])
[FLU]/([FLU]+[PYR])
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1


Water – Late Spring-Fall 2019: 4/18/19 - 9/26/19
Petroleum Combustion
Vegetation/coal combustion
4/18/19
9/6/19
4/18/19, 9/6/19
2/14/19 - 3/7/19
1/13/19 -2/2/19
Petroleum
Petroleum
[ANT]/([ANT]+[PHE])
[FLU]/([FLU]+[PYR])
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1


Water – Late Fall 2019: 11/12/19 + 11/27/19
4/18/19-9/26/19
+upstream 11/27/19
Petroleum Combustion
Vegetation/coal combustion
11/12/19
11/27/19
2/14/19 - 3/7/19
+ 11/12/19 → First Rain
1/13/19 -2/2/19
+ 11/27/19 → First Major Rain
Petroleum
Petroleum
[ANT]/([ANT]+[PHE])
[FLU]/([FLU]+[PYR])
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


Water – Winter 2019-Spring 2020: 12/7/19 - 3/13/20
Petroleum
Petroleum Combustion
Vegetation/coal combustion
12/7/19
1/17/20
2/23/20
3/11/20
3/13/20
Sites 3, 4, 9, 10
Petroleum
[ANT]/([ANT]+[PHE])
[FLU]/([FLU]+[PYR])
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


Simi Valley
Thousand Oaks
Westlake Village
Calabasas
Malibu
Malibu Creek
Las Virgenes Creek
Bell Creek
Medea
Cold Creek
Malibu Creek
Malibu Lagoon
Pacific Ocean
1
2
3
4
5
6
7
8
9
10
11
6 km
13 km
0 1 2 3 km
N
Sampling Sites
Future Sites
Water Bodies
Streams
Weather Stn
Major Roads
Rindge Dam
Malibu Creek Watershed
Woolsey Fire Perimeter


Water: Winter 2020-2021
Petroleum Combustion
Vegetation/coal combustion
Petroleum
Petroleum
Series2
Series3
Series4
11/7/2020
12/28/2020
1/29/2021
[ANT]/([ANT]+[PHE])
[FLU]/([FLU]+[PYR])
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Conclusions

- PAHs do not exceed drinking water MCLs, but do exceed EPA ambient water quality criteria during/after rain events
- Soil PAH concentrations decreasing (source degrading), but preferentially low MW (less toxic) compounds
- PAH concentrations in water linked to SPM → Discharge → Precipitation
  - Interrelationships appear to be changing over time
- Continued contributions into second rainy season after fire. Losing fire "signal" at some locations, then essentially lost by third year.

Ongoing and Future Work

- Other source differentiation approaches being applied (other PAH ratios, ADPI, alkanes-based approaches, isotopes)
- Continue analyzing samples for metals, Hg, DOC
- Continued sampling – at least during rain events → what is "baseline"?
- Further assessment of spatial variation + impact of fire intensity, land use, other factors

- Applying similar methods for investigating fire history in paleosols with Dr. Jen Cotton and Adit Ghosh

Thanks!

- Thanks to:
  - Dr. Priya Ganguli – CSUN collaborator on this project
  - All students involved: Michael Kushner, Christian Hoover, Kyle Ikeda, Peter Nahas, Greg Jesmok, Rachel Hohn, Alfredo Estrada, Emily Honn