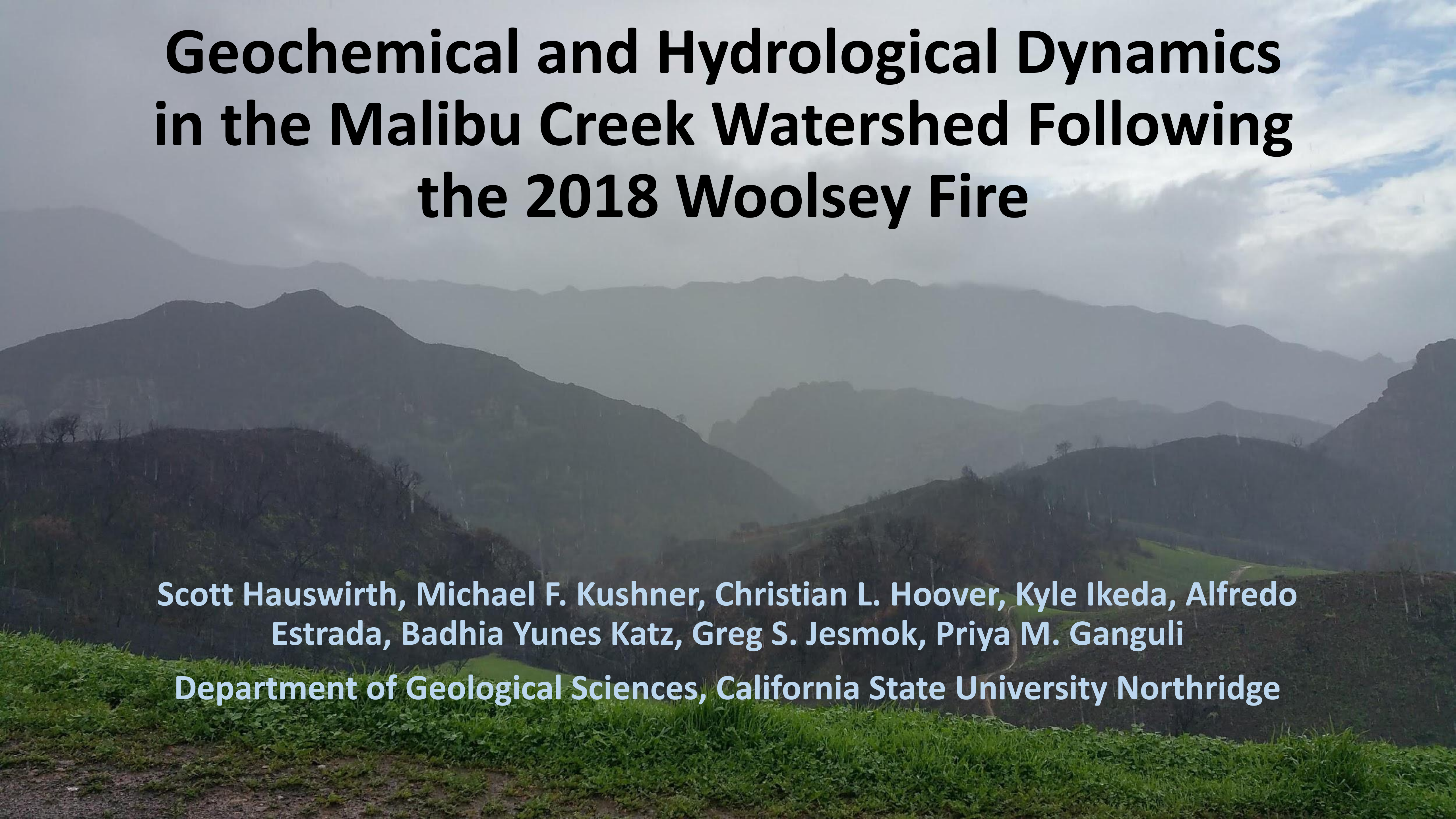

Geochemical and Hydrological Dynamics in the Malibu Creek Watershed Following the 2018 Woolsey Fire

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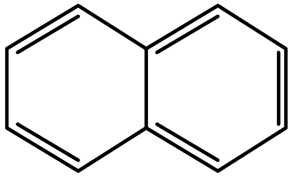
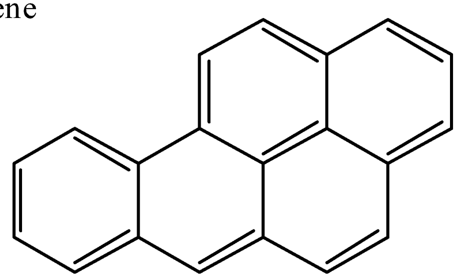
Wildfires are getting worse and potentially impacting water quality

- As more area burns, greater potential for impacts to water quality:
  - Increased erosion □ increased sediment load
  - Geochemical changes
  - Generation of polycyclic aromatic hydrocarbons (PAHs)



naphthalene

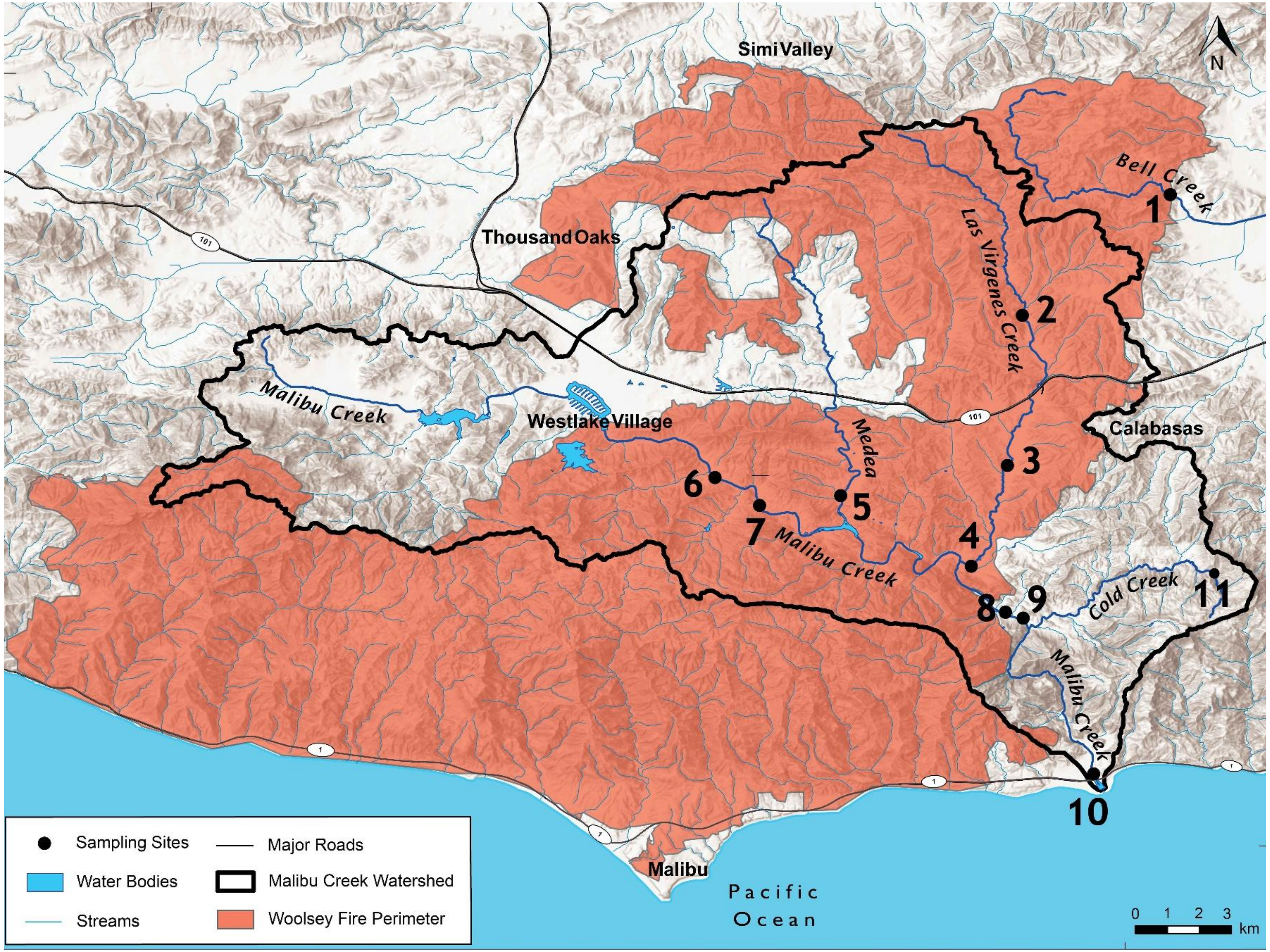


benzo(a)pyrene

- Mutagenic, **carcinogenic**, reproductive defects
- **Toxic to aquatic organisms**
- Potentially persistent in the environment

Study Site: Malibu Creek Watershed

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

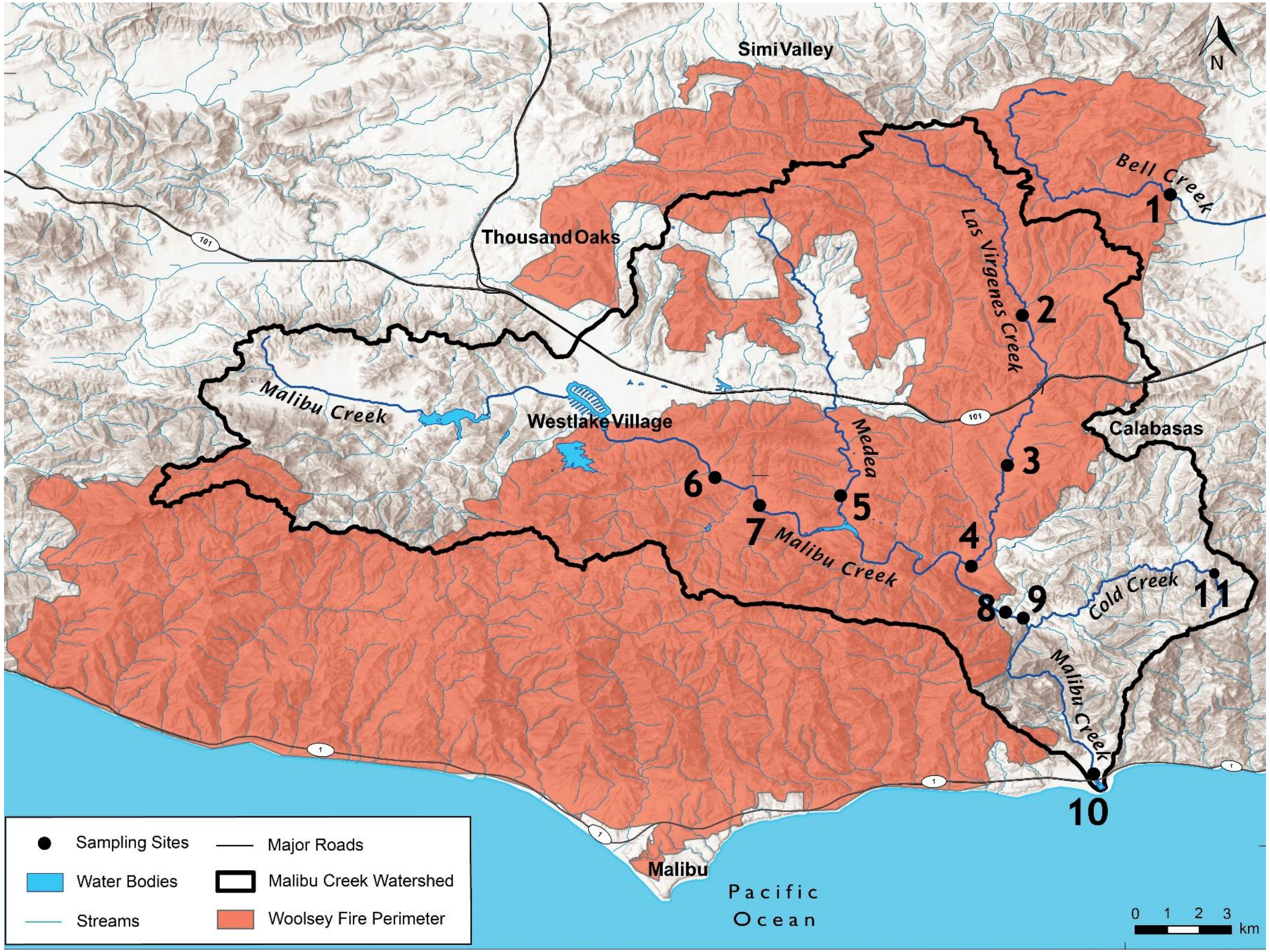


Study Site: Malibu Creek Watershed

- Question: **How did Woolsey Fire impact water quality in watershed?**

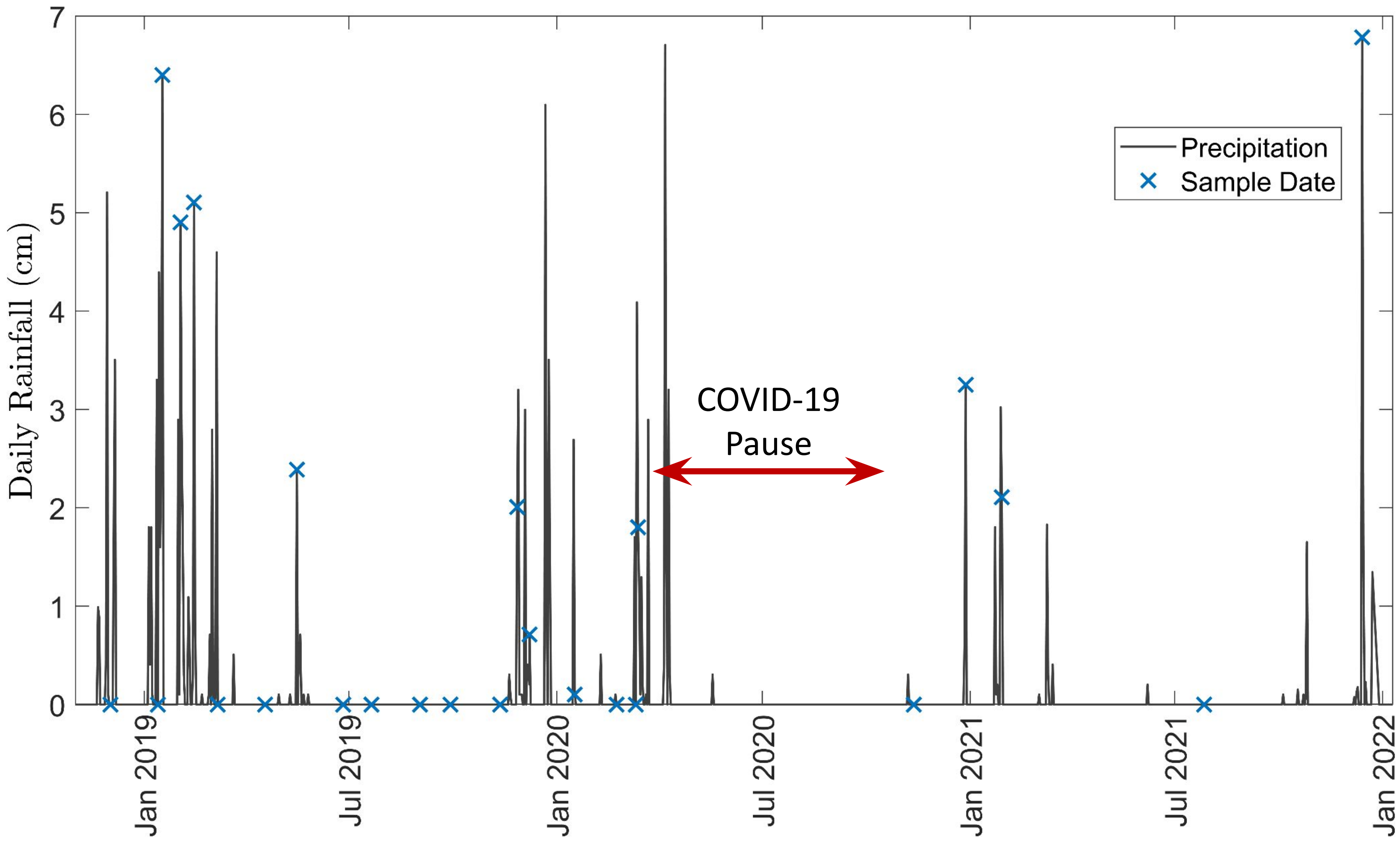
Study Site: Malibu Creek Watershed

- Soil samples collected throughout watershed shortly after fire
- Periodically thereafter at two sampling locations (Sites 2+3)
- 11 water sampling locations established



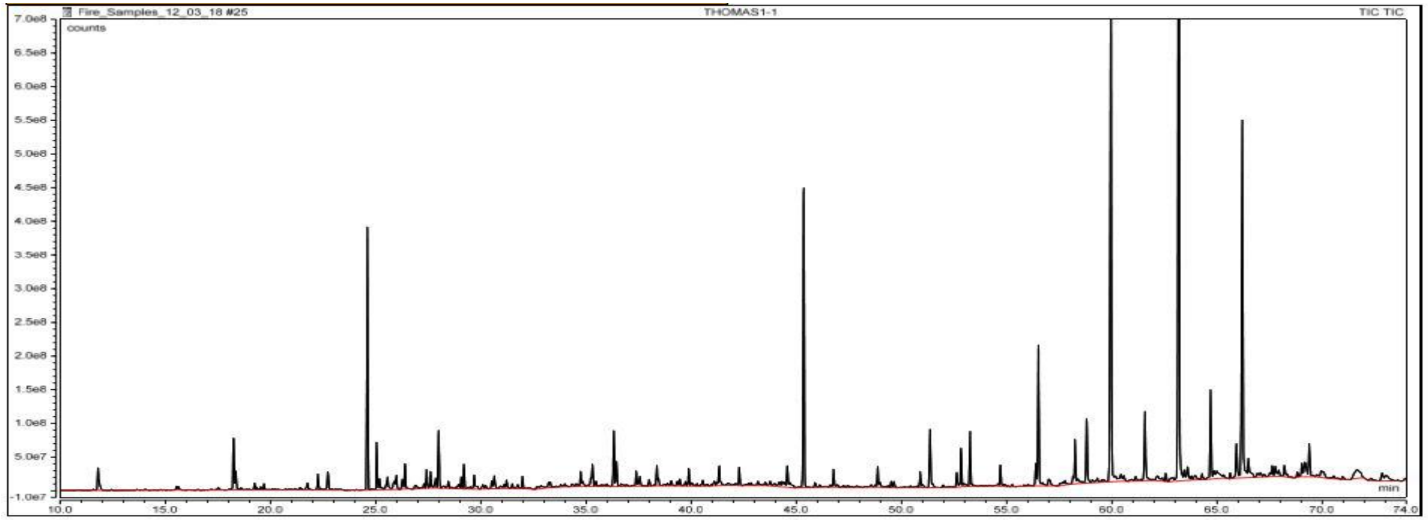
Surface Water Sampling Plan

- Samples collected during/after significant rain events Dec. 2018-Dec. 2021
- Approx. monthly during dry season
- Sampling paused March – November 2020 due to COVID-19

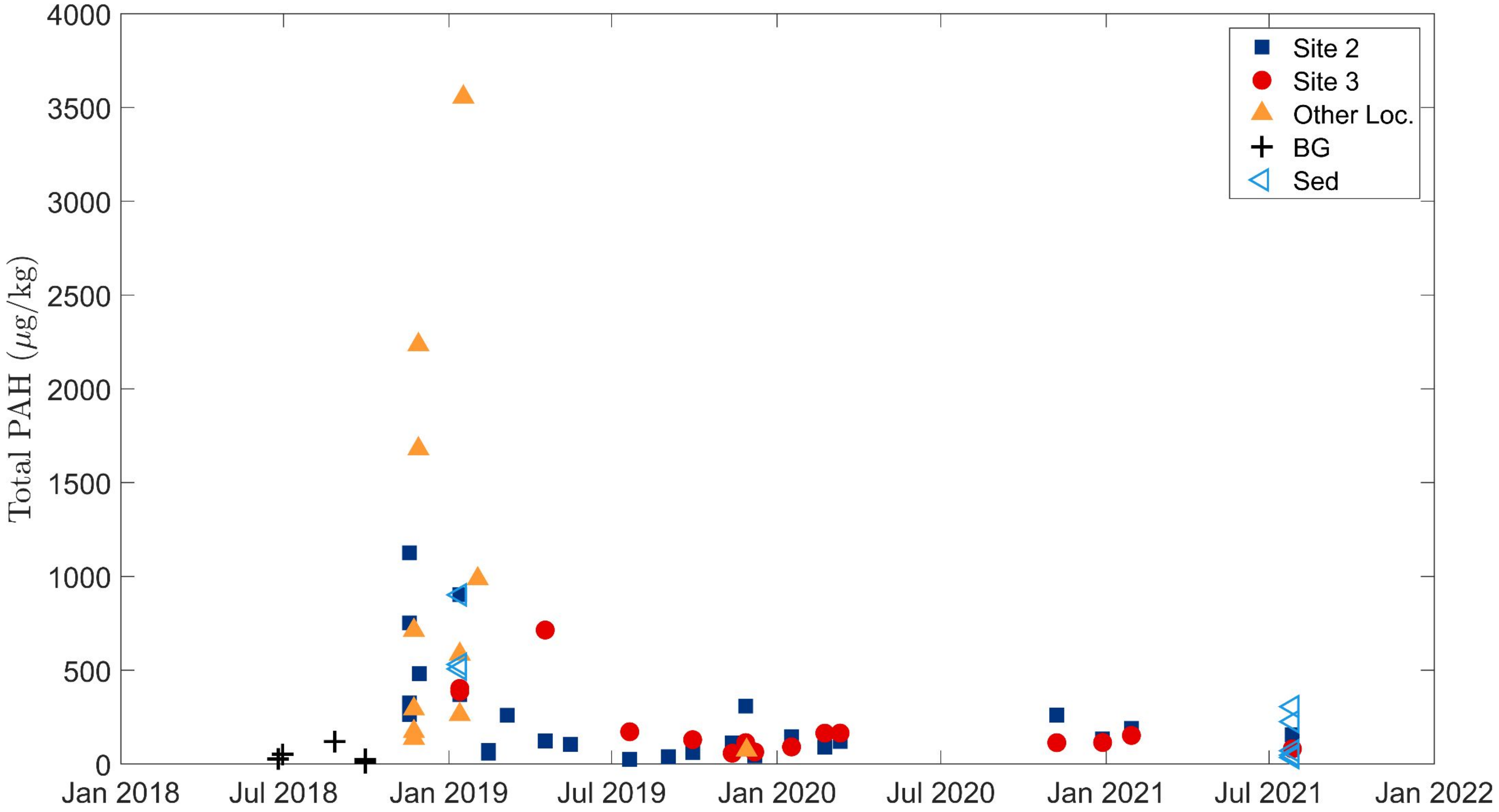


Methods

- Soil/sediment and water samples extracted (via Soxhlet + LLE)
- GC-MS analysis for:
  - 16 EPA + alkylated + other PAHs
  - C_{12} - C_{38} *n*-alkanes
  - 200+ compounds total
- SPM filtration/gravimetric
- Anions by ion chromatography
- Streamflow and precipitation data obtained from Los Angeles Dept. of Public Works
- Metal/Hg, DOC analyses pending



Soil PAH concentrations decline rapidly after fire



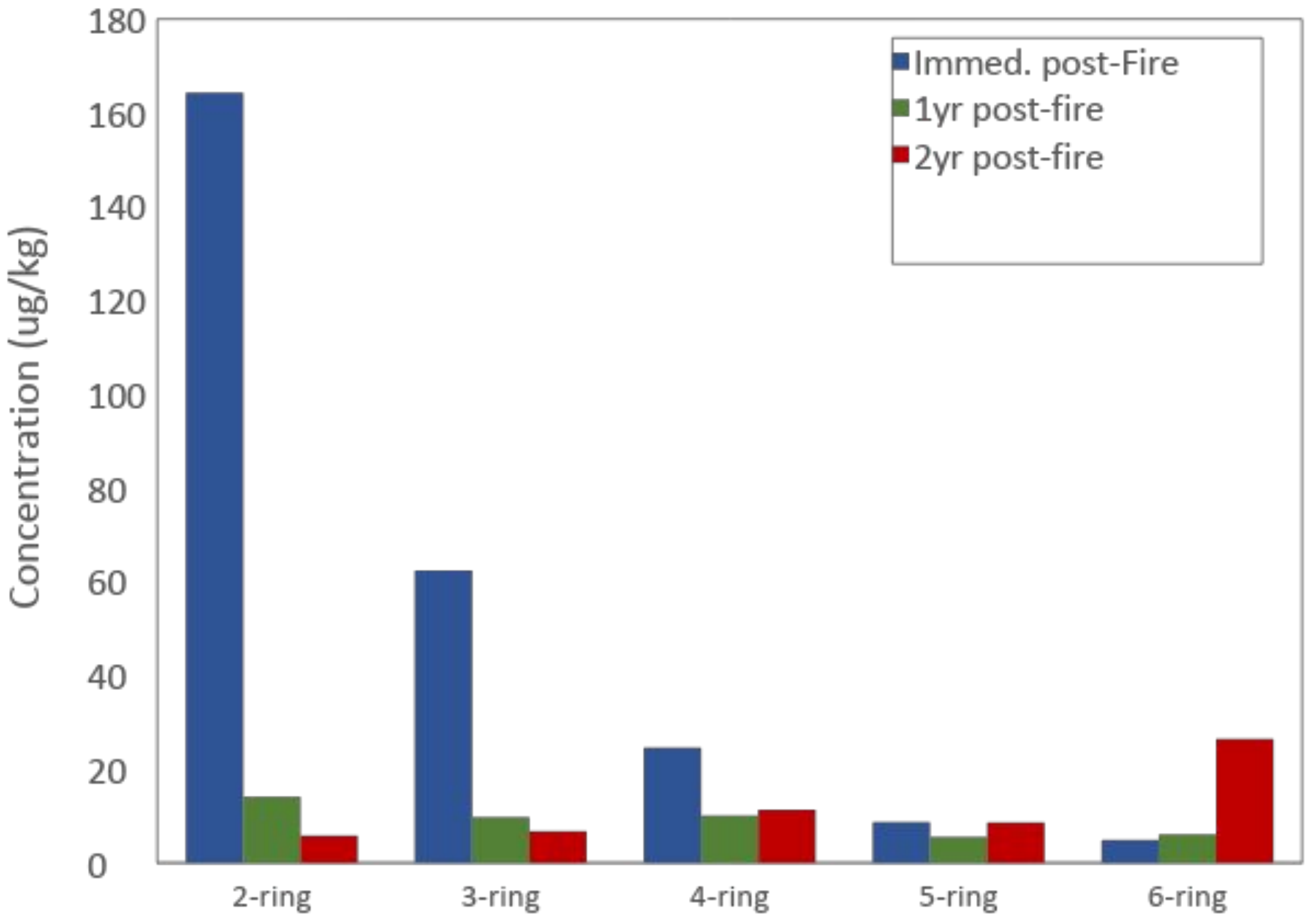
Total PAH = 16 EPA + C1-C4-NAP + C1-FLE + C1-C2 FLU/PYR + C1-C4 PHE/ANT + C1-C3 CHY/BaA + PAHs w/ MW276-302

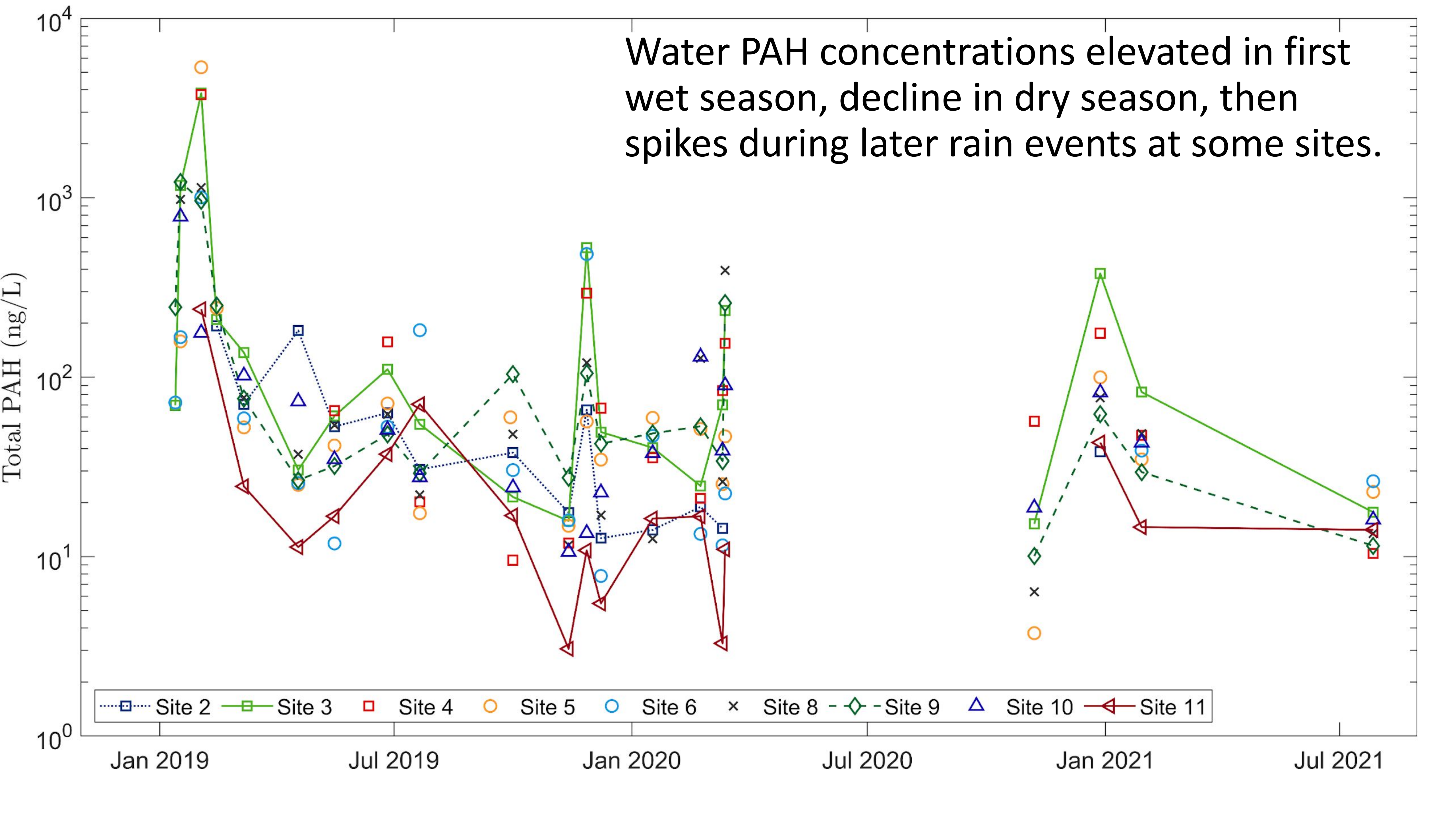
…but larger PAHs persist longer

Smaller PAHs (2-3 ring) largely lost within first year

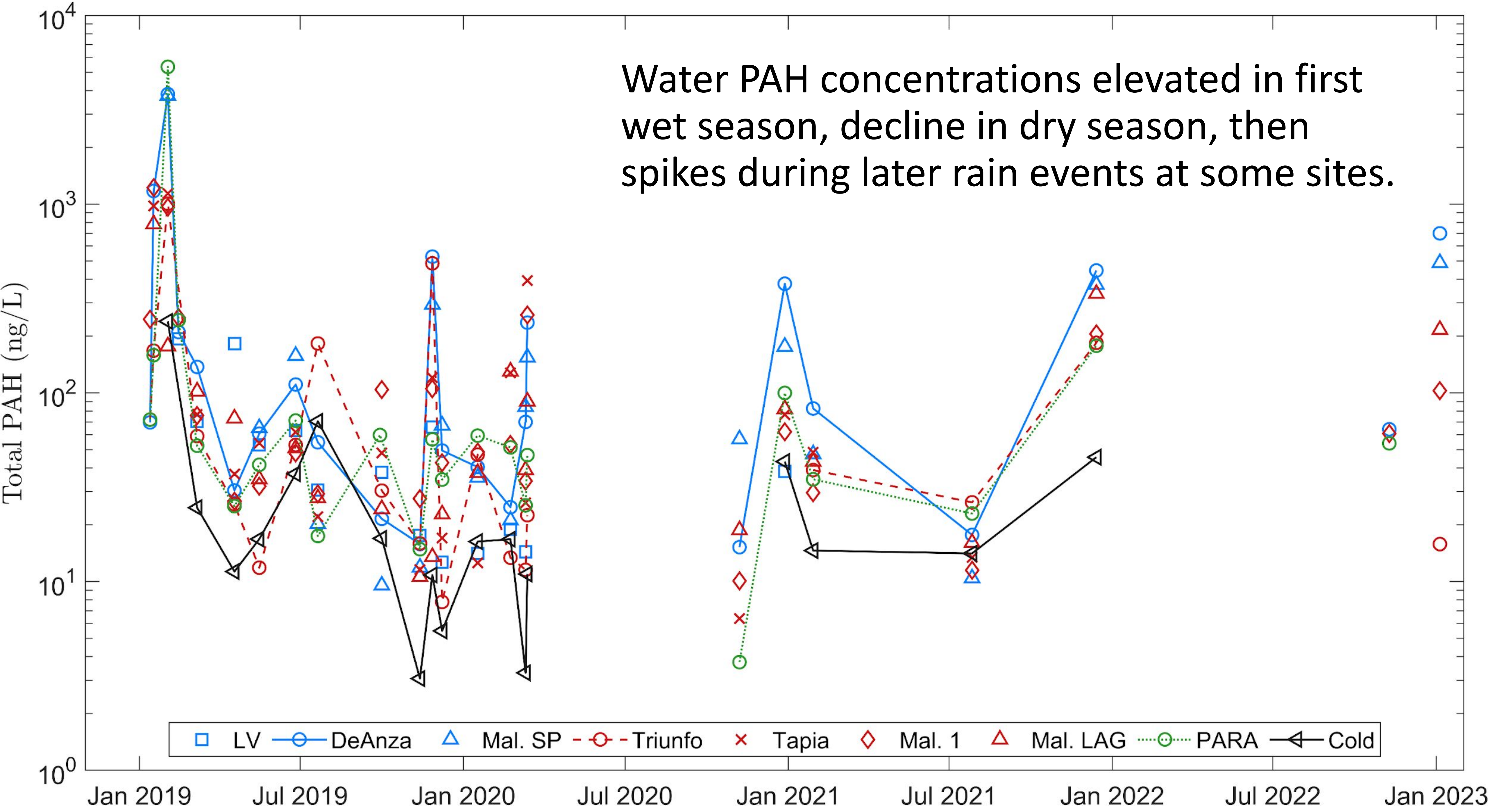
Larger PAHs (5-6 ring) show limited loses or even increasing concentrations

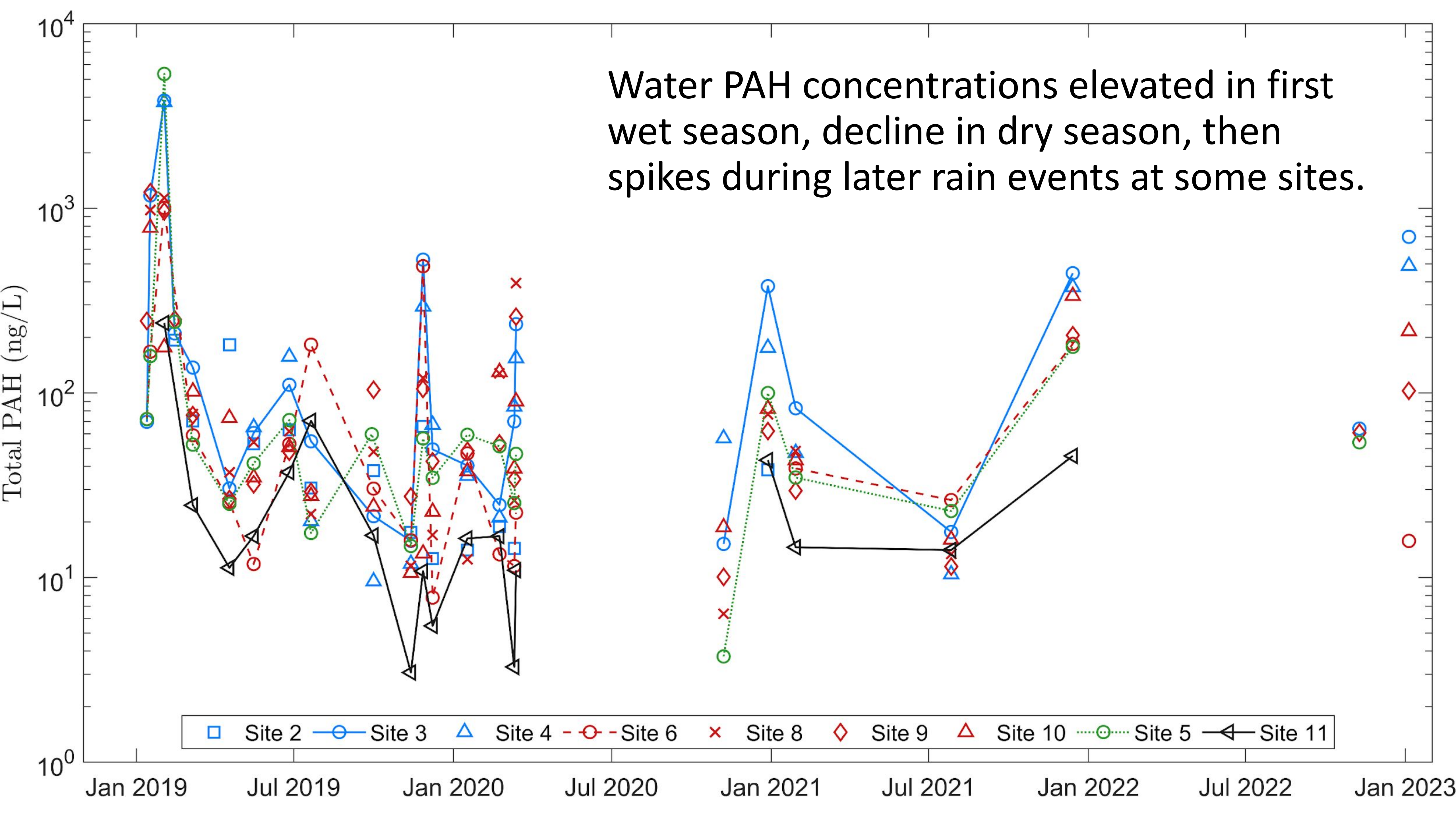
5-6 ring PAHs are the toxic/carcinogenic compounds!





Water PAH concentrations elevated in first wet season, decline in dry season, then spikes during later rain events at some sites.
Total PAH (ng/L)
10^4
10^3
10^2
10^1
10^0
Jan 2019
Jul 2019
Jan 2020
Jul 2020
Jan 2021
Jul 2021
Site 2
Site 3
Site 4
Site 5
Site 6
Site 8
Site 9
Site 10
Site 11


Water PAH concentrations elevated in first wet season, decline in dry season, then spikes during later rain events at some sites.
Total PAH (ng/L)
10^0
10^1
10^2
10^3
10^4
Jan 2019
Jul 2019
Jan 2020
Jul 2020
Jan 2021
Jul 2021
Jan 2022
Jul 2022
Jan 2023
LV
DeAnza
Mal. SP
Triunfo
Tapia
Mal. 1
Mal. LAG
PARA
Cold


Water PAH concentrations elevated in first wet season, decline in dry season, then spikes during later rain events at some sites.
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10^4
10^3
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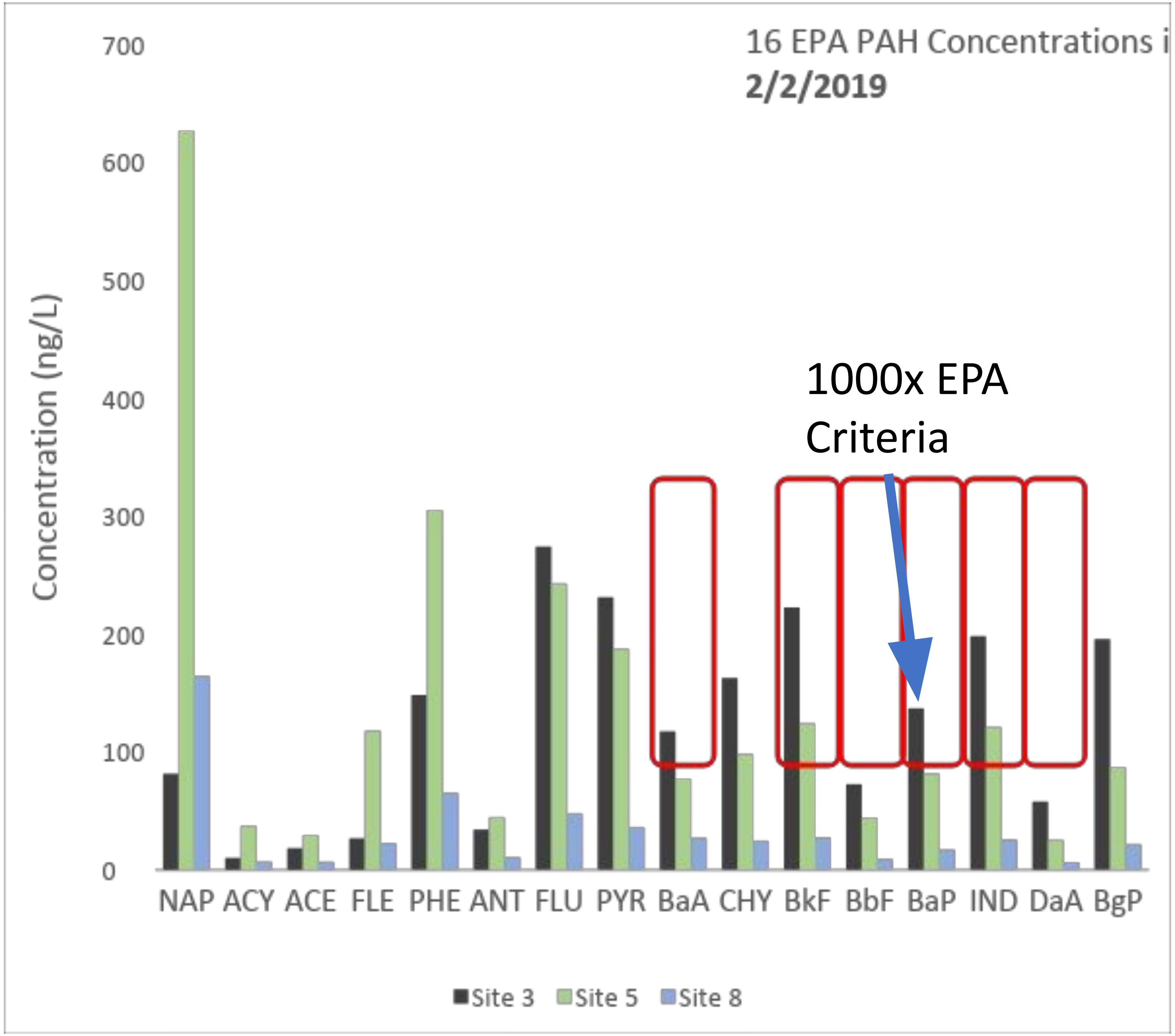
Jul 2020
Jan 2021
Jul 2021
Jan 2022
Jul 2022
Jan 2023
Site 2
Site 3
Site 4
Site 6
Site 8
Site 9
Site 10
Site 5
Site 11

PAH concentrations in water below U.S. drinking water maximum contaminant levels (MCLs)

…but numerous exceedances of US EPA *"Human Health Criteria for Ambient Waters"*

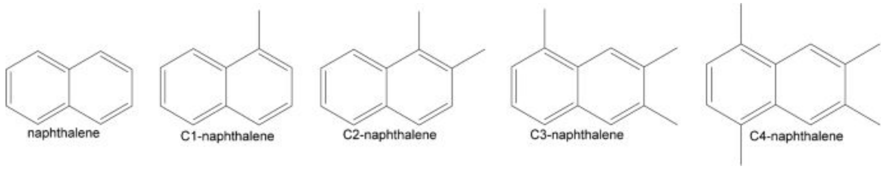
Up to 1000x criteria!

Also, some exceedances of CA PHG for BaP and many exceedances of Canadian "Water Quality Guidelines for the Protection of Aquatic Life" values

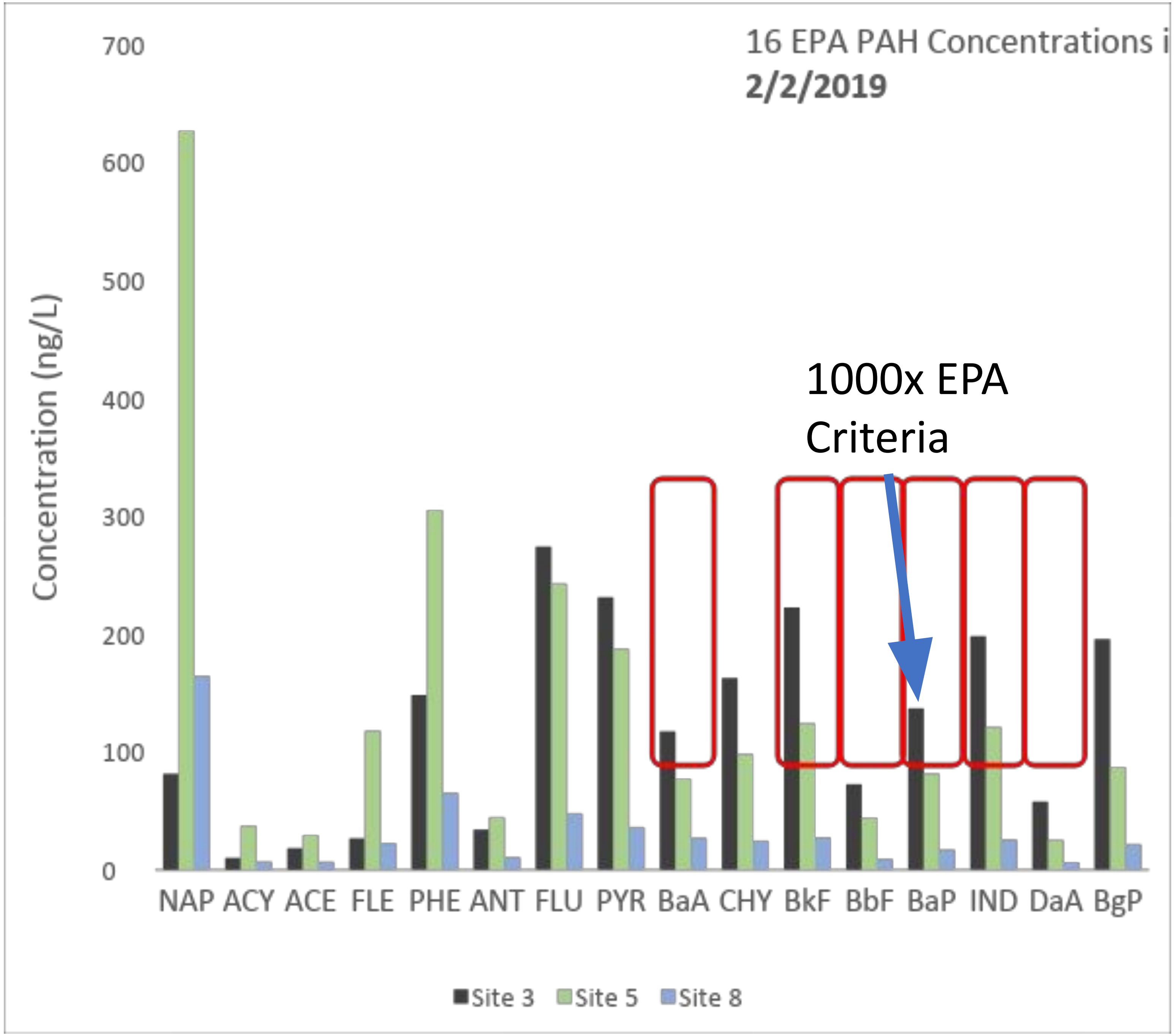


Other compounds likely contribute to toxicity in unknown ways

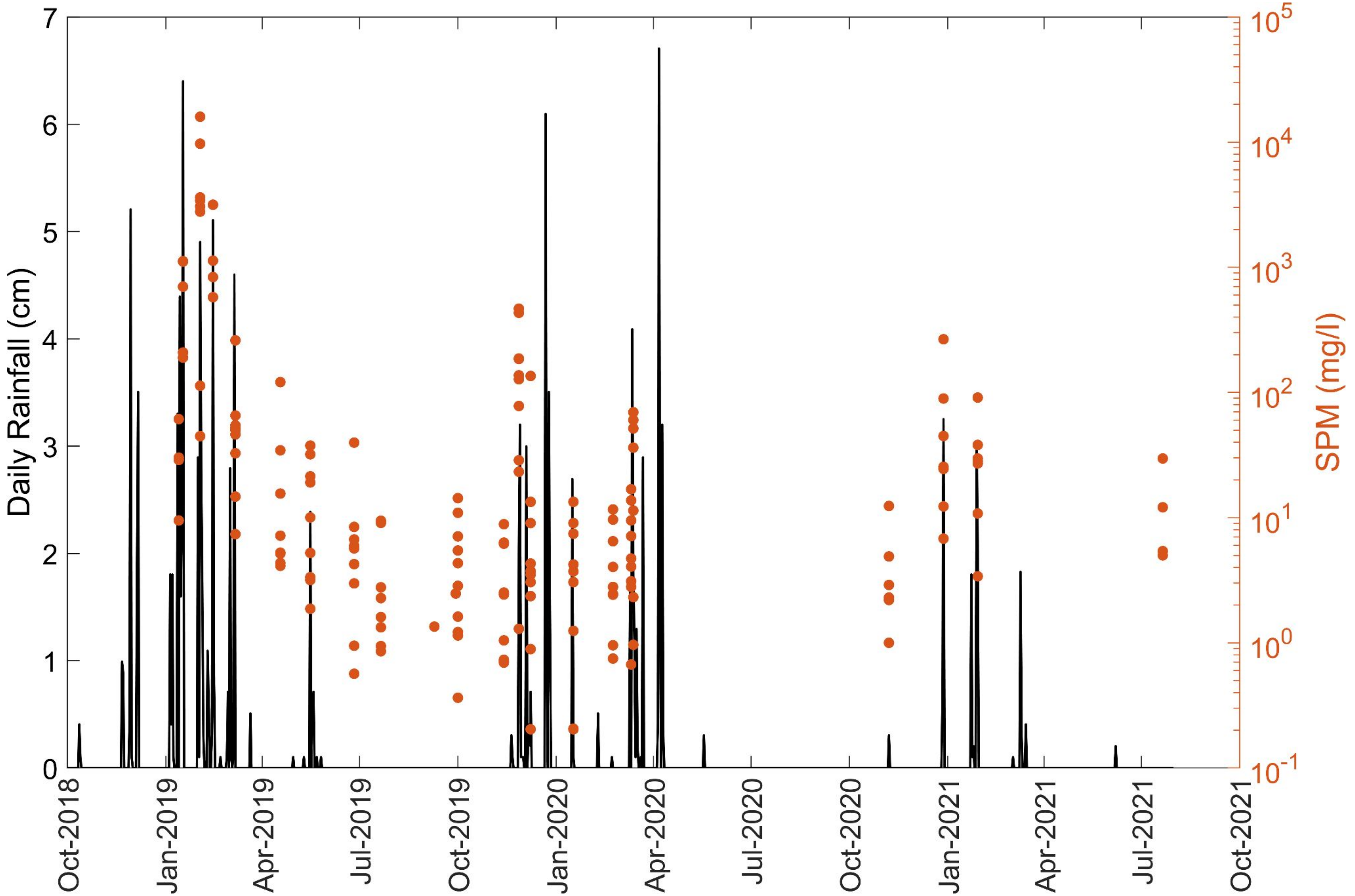
- **Alkylated PAHs understudied but may be drivers of toxicity**



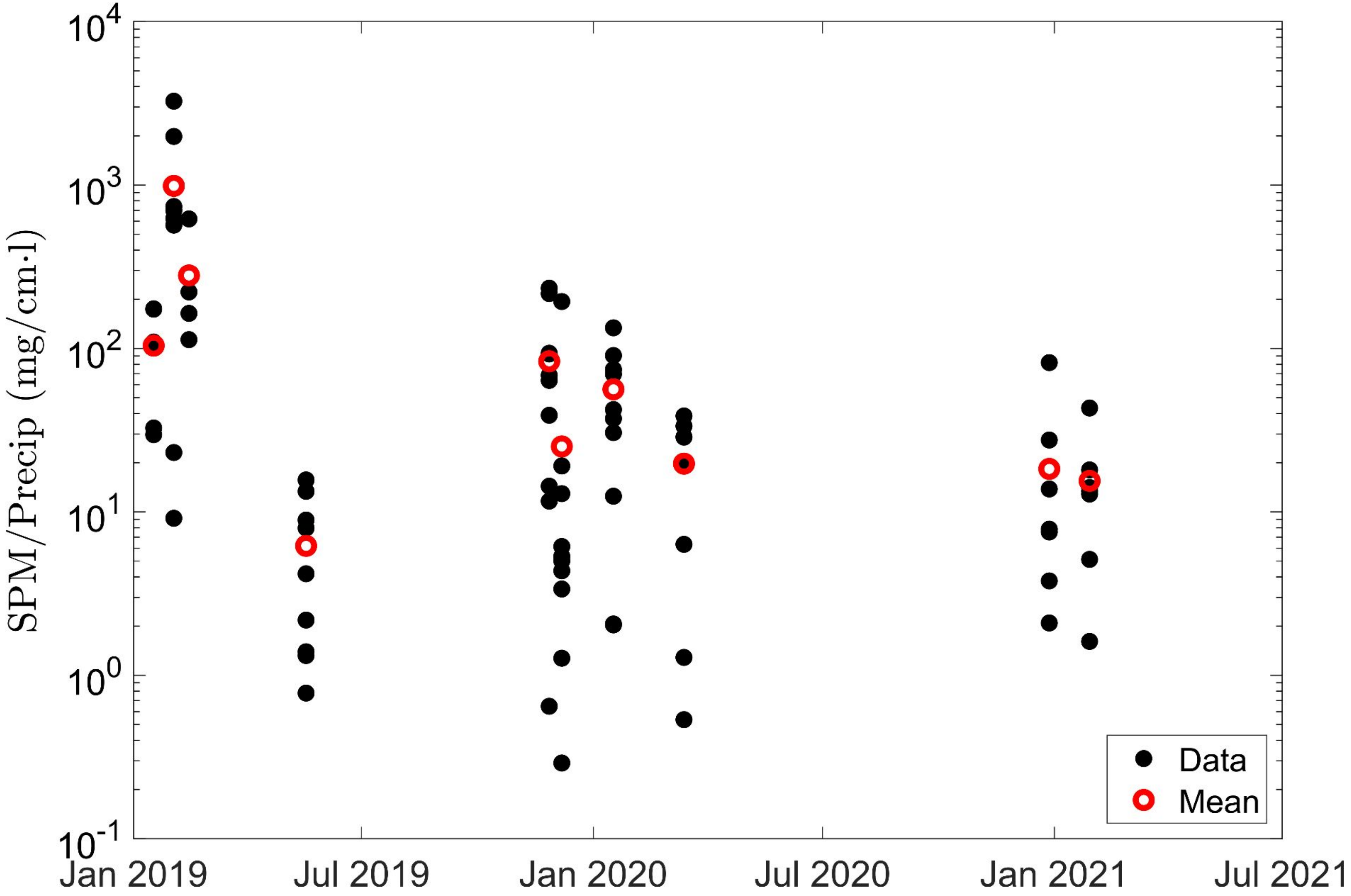
- **Photodegradation of PAHs greatly INCREASES toxicity: formation of quinones and other compounds**
- **Metals synergistic in terms of toxic effects**



Spikes in PAH concentrations correlate with rain events when SPM also spikes



During first rainy season, higher SPM per unit precipitation than later years

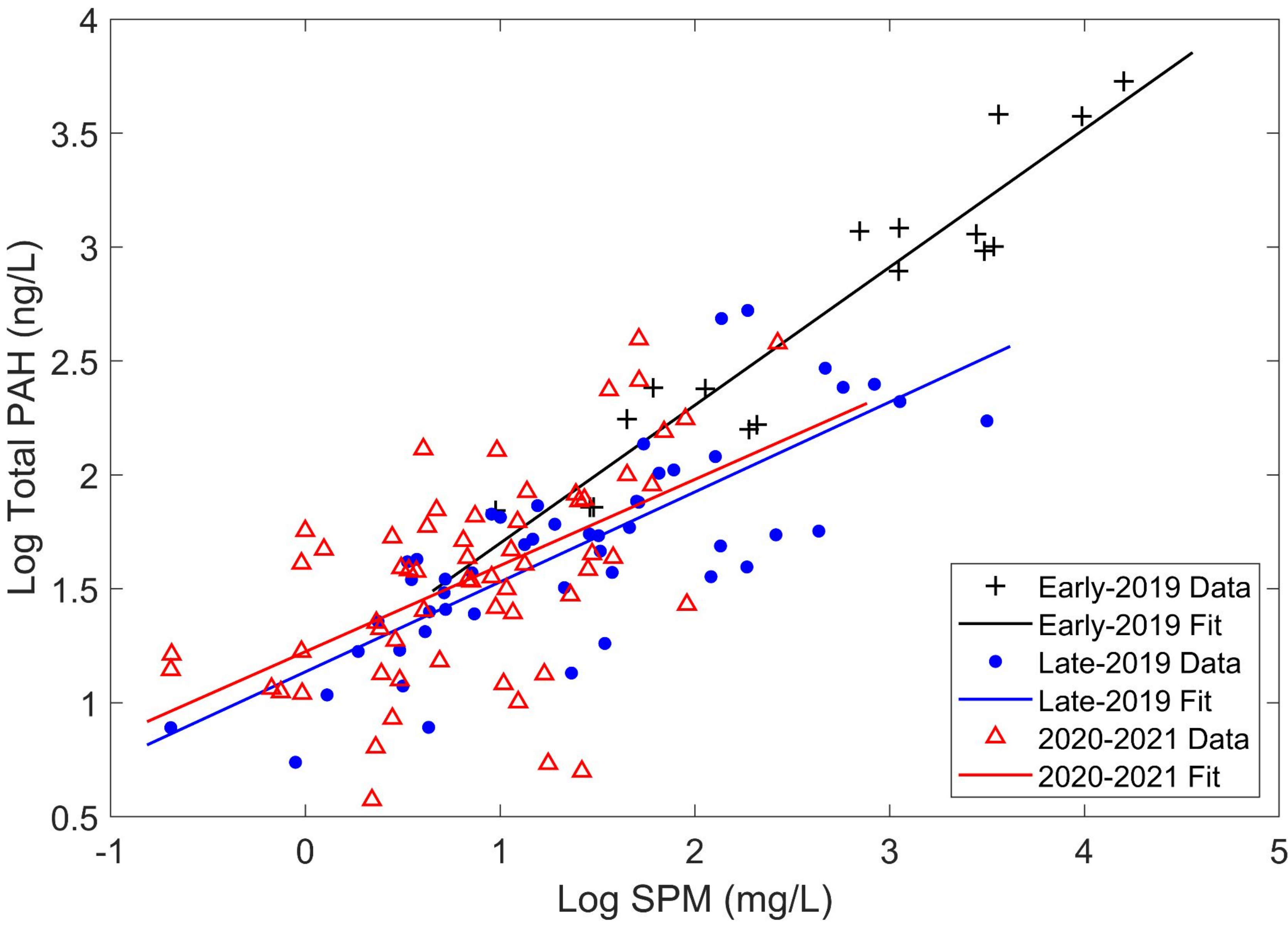


PAH-SPM relationship reasonably well fit by Power law

Slope decreases from first rainy season to second, then relatively constant

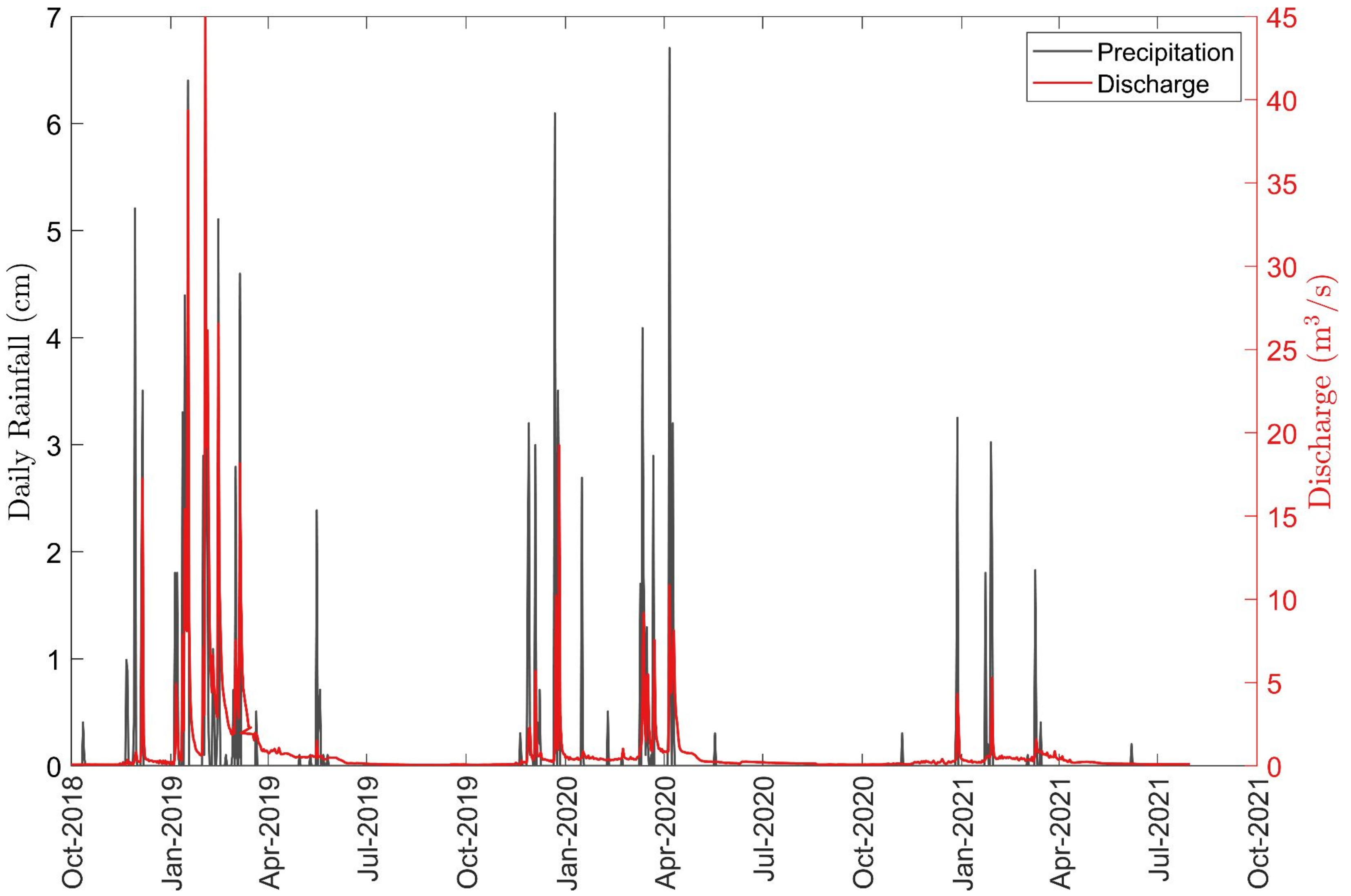
Consistent with:

1. Lower soil PAH concentrations
2. Less erosion of burned soil into streams



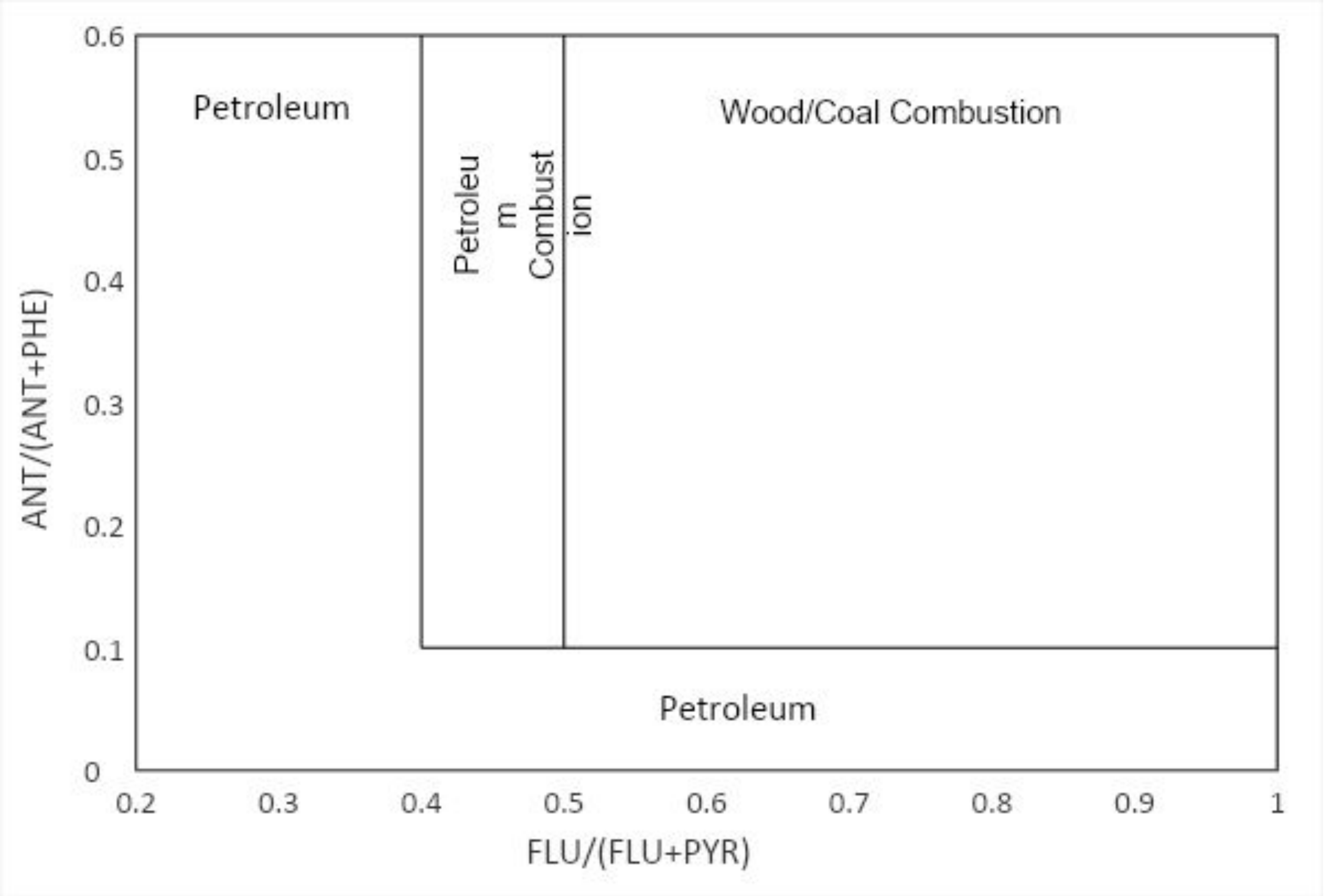
Streamflow appears much higher in first post-fire wet season for a given amount of precipitation

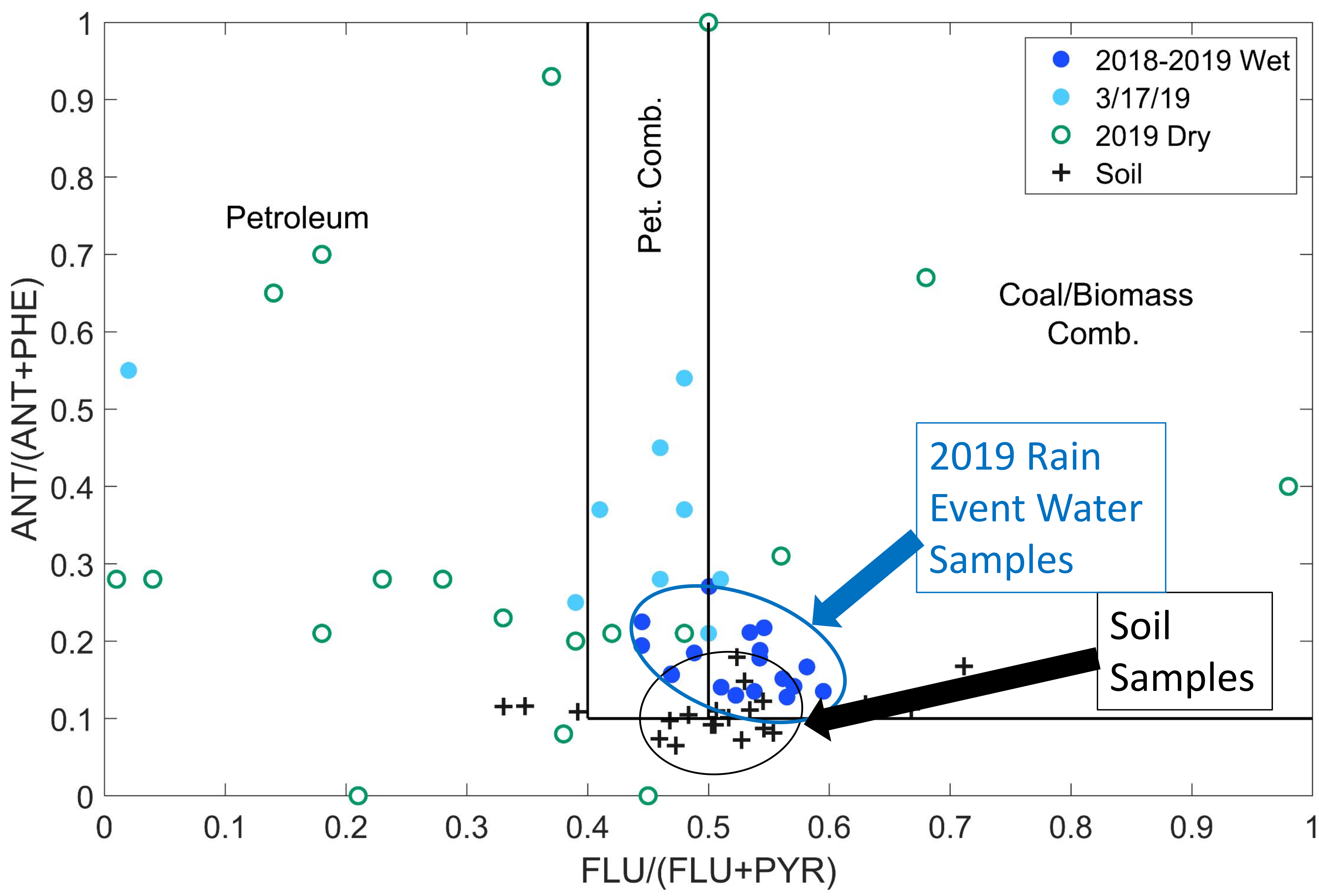
(But confounding factors)

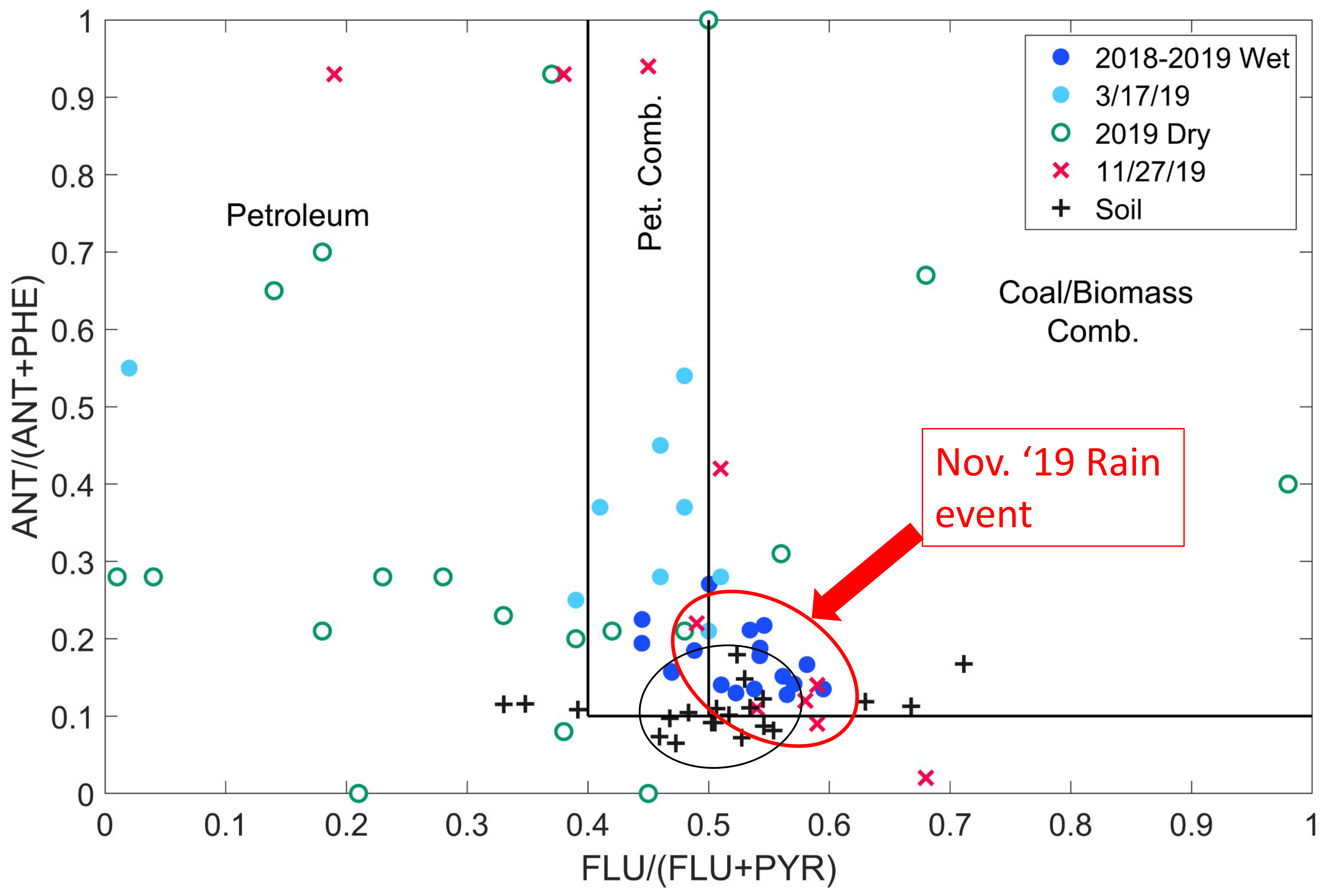


Are PAHs from the fire? Can we use them as a tool?

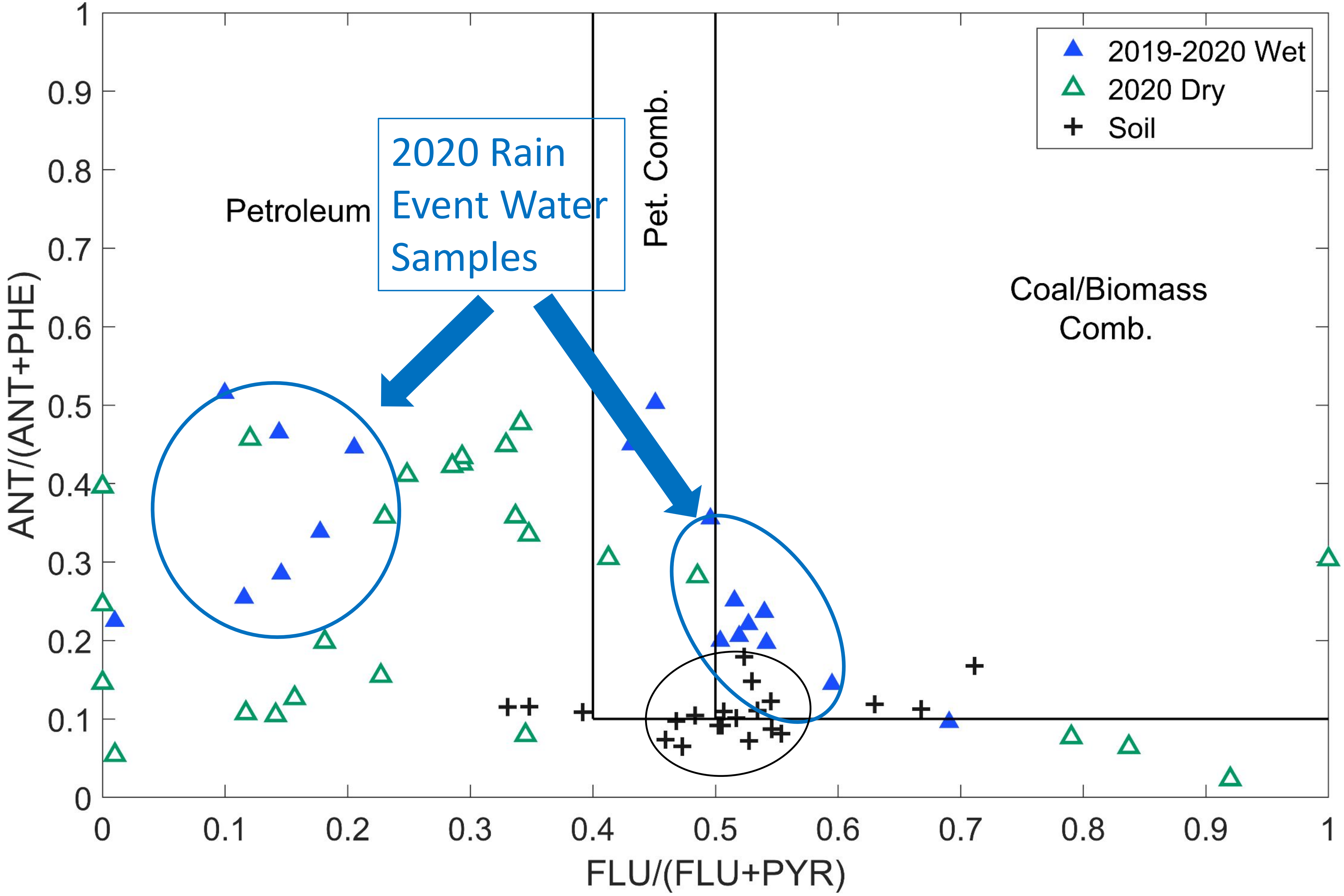
- PAHs may come from fire vs road runoff (oil) vs fossil fuel combustion
- Simple molecular ratio approach imperfect, but gives some indication
- Other molecular ratio approaches and potentially isotopic methods in progress



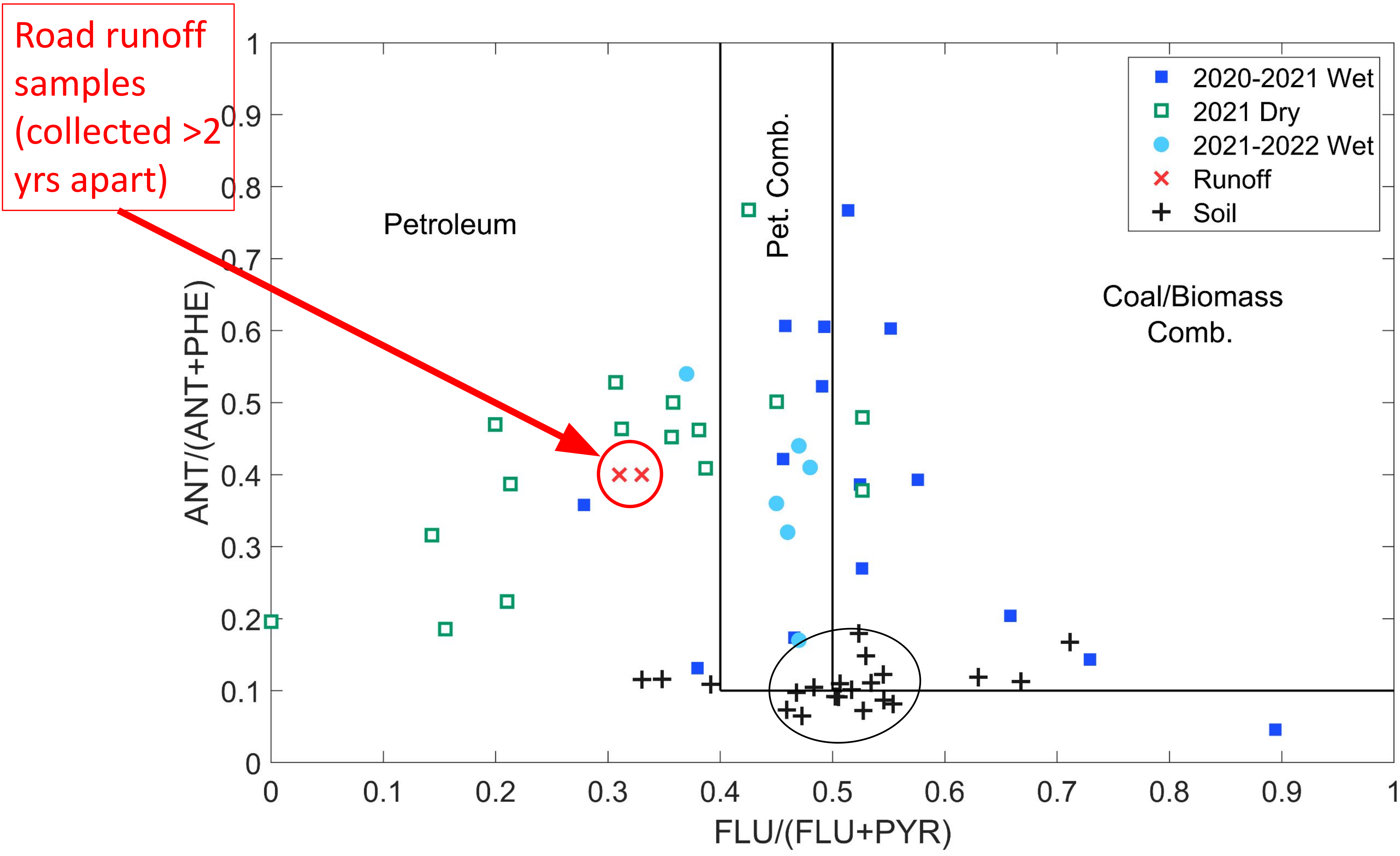

2018-2019 Wet
3/17/19
2019 Dry
Soil
Petroleum
Pet. Comb.
Coal/Biomass
Comb.
2019 Rain
Event Water
Samples
Soil
Samples
ANT/(ANT+PHE)
FLU/(FLU+PYR)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1



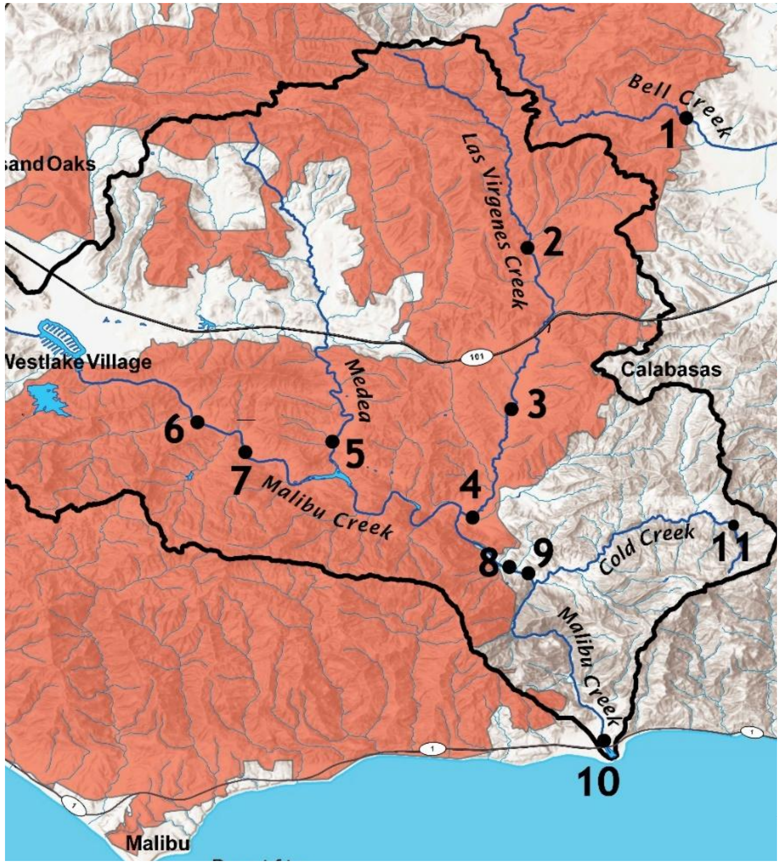
2018-2019 Wet
3/17/19
2019 Dry
11/27/19
Soil
Petroleum
Pet. Comb.
Coal/Biomass Comb.
Nov. '19 Rain event
ANT/(ANT+PHE)
FLU/(FLU+PYR)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

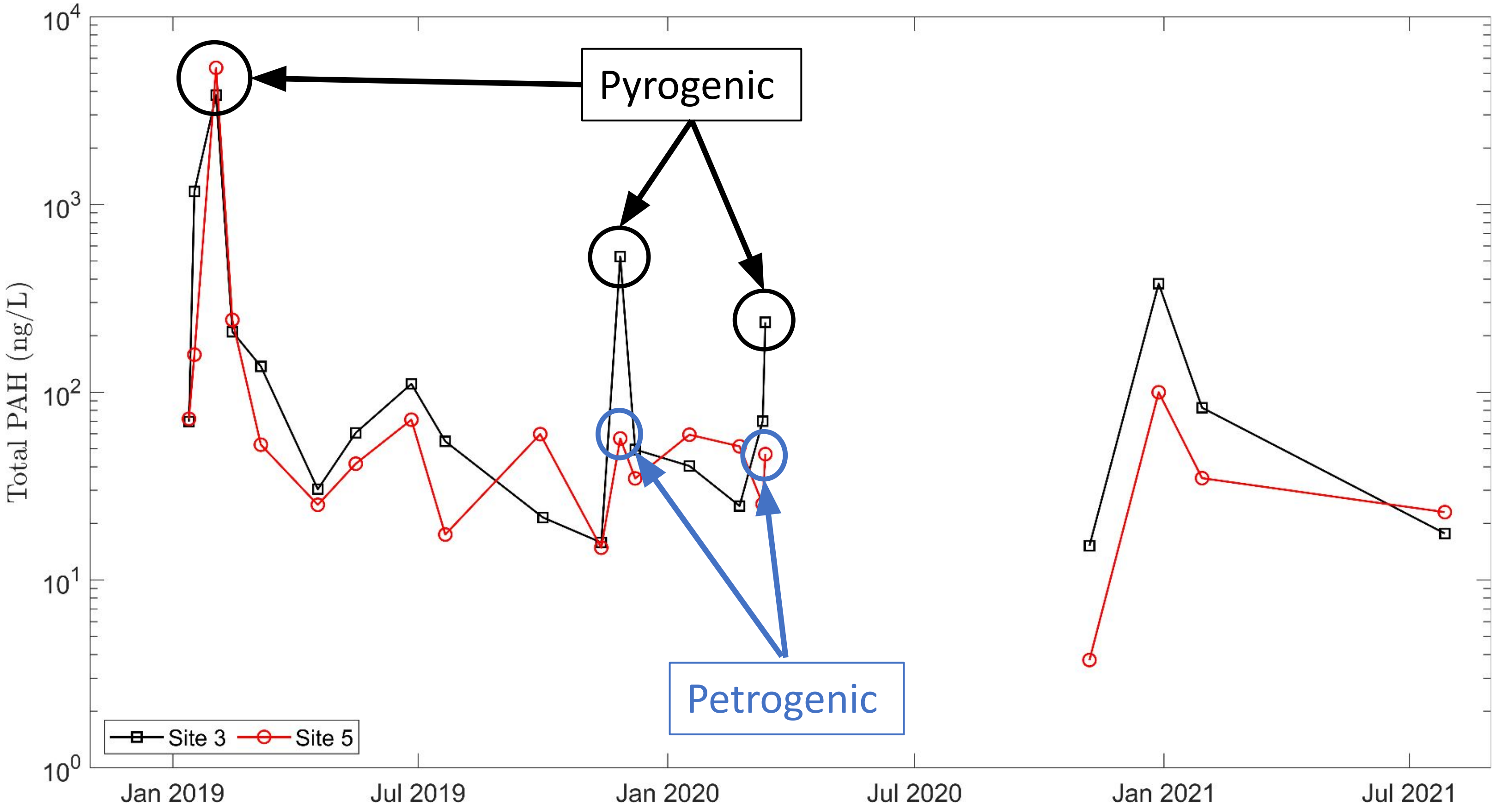


2019-2020 Wet
2020 Dry
Soil
2020 Rain Event Water Samples
Petroleum
Pet. Comb.
Coal/Biomass Comb.
ANT/(ANT+PHE)
FLU/(FLU+PYR)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

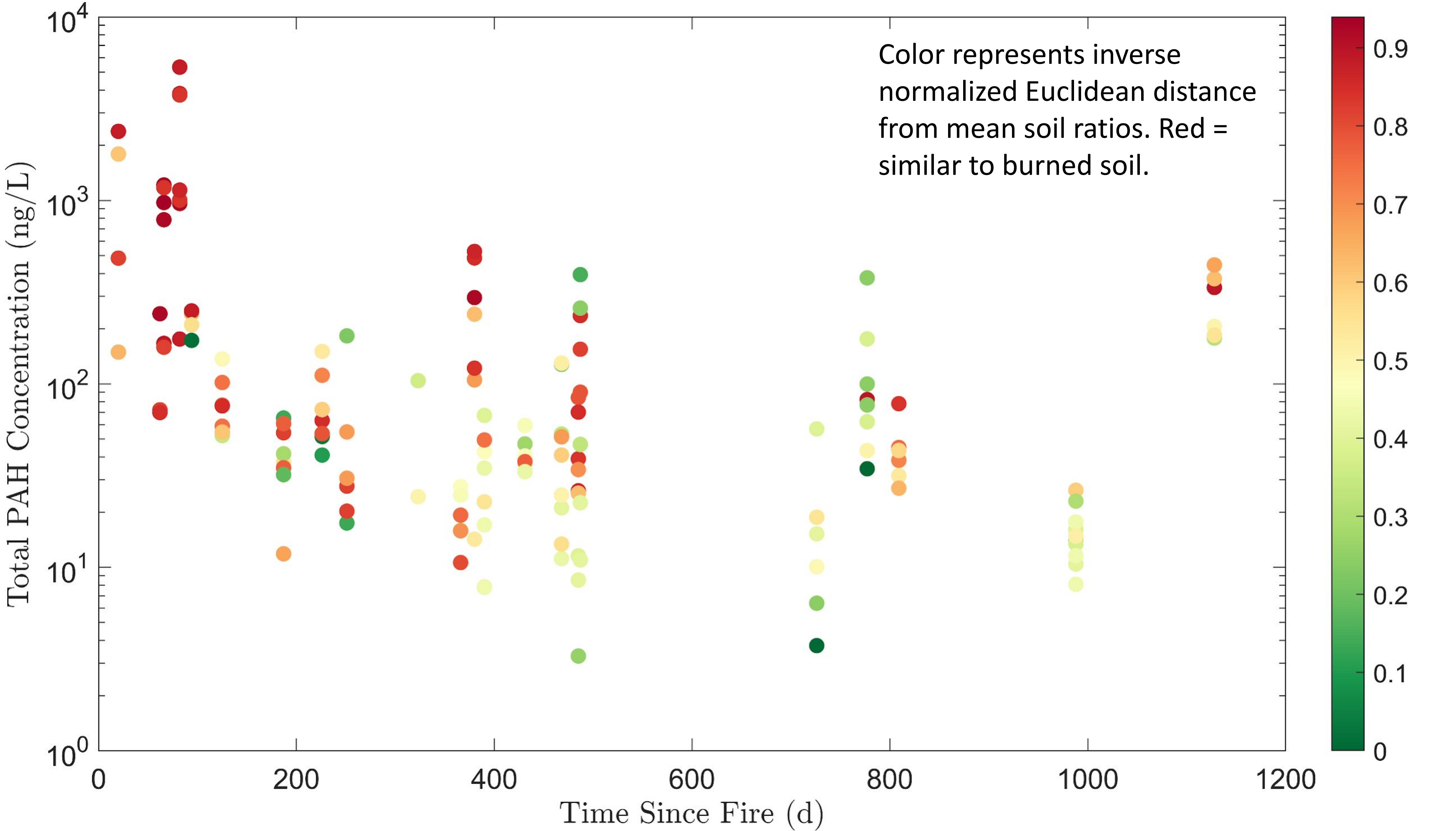

Road runoff samples (collected >2 yrs apart)
Petroleum
Pet. Comb.
Coal/Biomass Comb.
2020-2021 Wet
2021 Dry
2021-2022 Wet
Runoff
Soil
ANT/(ANT+PHE)
FLU/(FLU+PYR)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Why differences between sites?





What does this look like over time?



Conclusions

- Soil PAH concentrations decrease relatively quickly, but more toxic compounds show less decline
- PAHs exceed water quality criteria (but not drinking water MCLs) during/after rain events
- PAH concentrations in water decreasing due to combined affects of:
  - Soil PAH losses
  - Lower SPM generated during rain events
  - Lower stream flows
- PAH ratios allow tracking of fire inputs: declining, but continued contributions into 2nd rainy season (depending on location), fire "signal" mostly lost by third year

Continuing Work

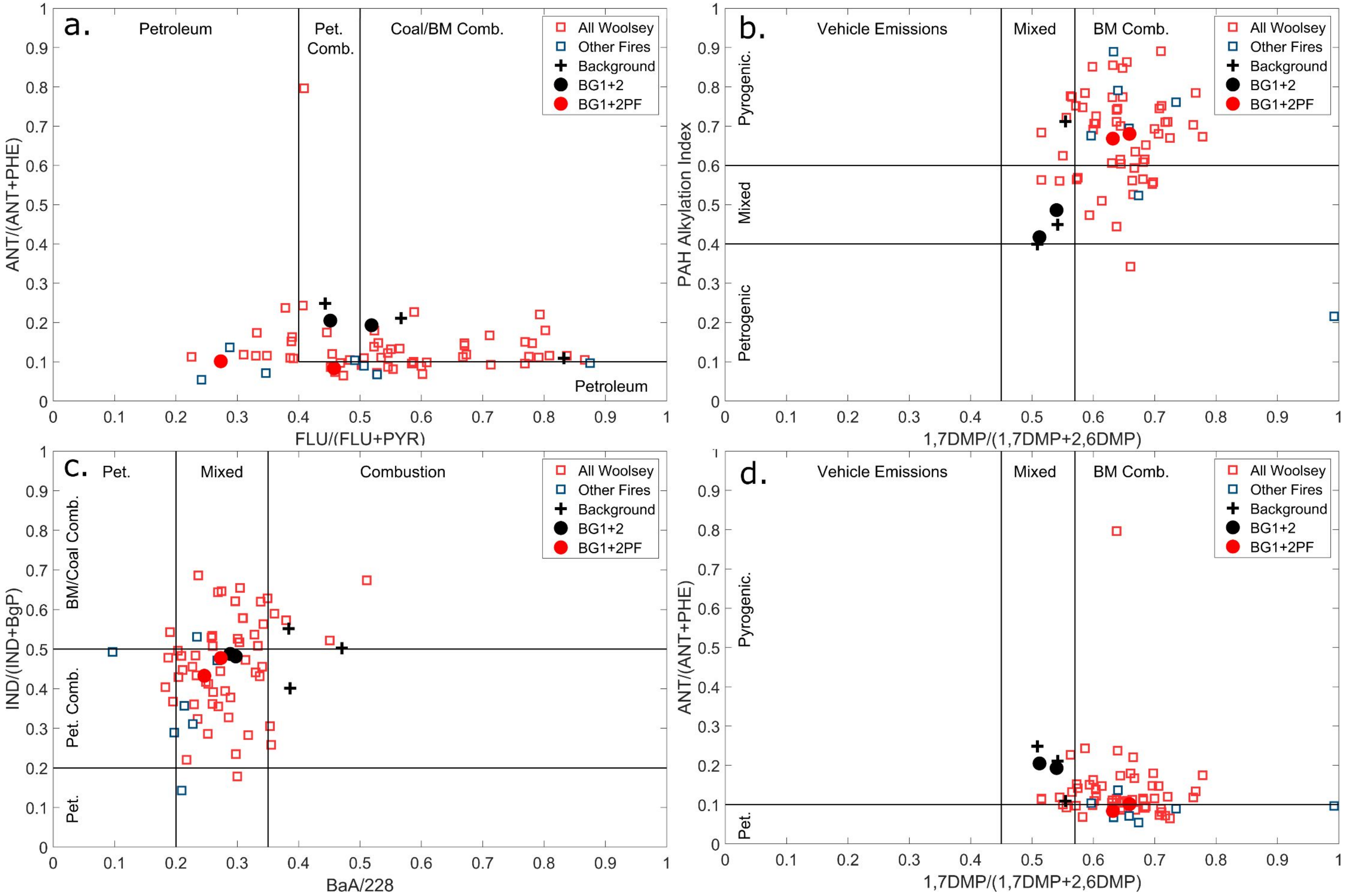
- Continue analyzing samples for metals, Hg, DOC
- Further assessment of spatial variation + impact of fire intensity, land use, other factors
- Other source differentiation+biomarker approaches being applied (other PAH ratios, ADPI, alkanes-based approaches, isotopes)
- Applying similar methods for investigating fire history in paleosols with Dr. Jen Cotton
- Lots more data available now (alkanes, detailed PAH data, nutrients) or coming soon (metals) – contact me for more information (**scott.hauswirth@csun.edu**)!

Thanks to all the students and others who have worked on this project!

Dr. Priya Ganguli, Michael Kushner, Christian Hoover, Kyle Ikeda, Georgina Campos, Danielle Bram, Peter Nahas, Greg Jesmok, Rachel Hohn, Alfredo Estrada, Emily Honn, Cindy de Jesus Bartolo, Oscar Martinez

PAH Ratios for Soils: Background vs Wildfire

Other ratios may better distinguish between wildfire and non-wildfire sources



Do n-alkanes tell us anything? Maybe…

- Carbon preference index (CPI) is measure of odd over even n-alkanes
  - Odds (n-C29, n-C31) indicative of higher plant waxes
  - Evens indicative of petroleum (or other things)
- CPI shows increasing trend, indicating increasing plant input