

Identification of smoke-impacted IMPROVE samples with FTIR

A. Yazdani¹, S. Takahama¹, S. Raffuse², A. M. Dillner², A. P. Sullivan³

¹ ENAC/IIE Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland

² Air Quality Research Center, University of California Davis, Davis, CA, USA

³ Department of Atmospheric Science, Colorado State University, Fort Collins, CO, USA

EPFL

UC DAVIS
UNIVERSITY OF CALIFORNIA

Overview and introduction

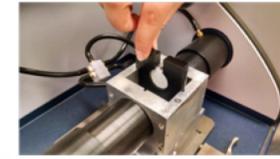
Smoke identification method using FTIR:

- Distinct spectral profiles
(Russell et al., *Proc. Nat. Acad. Sci.*, 2011; Bürki et al., *Atmos. Meas. Tech.*, 2020)
- Biomass burning tracer peaks (levoglucosan and lignin)
(Yazdani et al., *Atmos. Meas. Tech. Discuss.*, 2020; *this work*)

PTFE filters

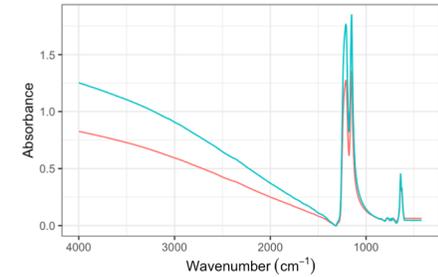


FTIR scan



< 5 minutes

Mid-infrared spectra



Comparisons:

- High resolution aerosol mass spectrometer (ToF-AMS)
in environmental chamber samples
- Satellite and ground-based observations
in IMPROVE network samples (5 sites, 2013)
- Ion chromatography (IC) measurements
in IMPROVE network samples (34 sites, 2008 and 2011)

Satellite



IC

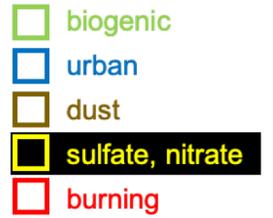
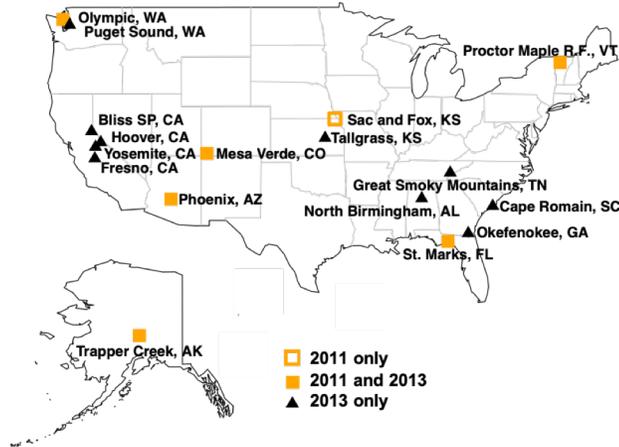


AMS

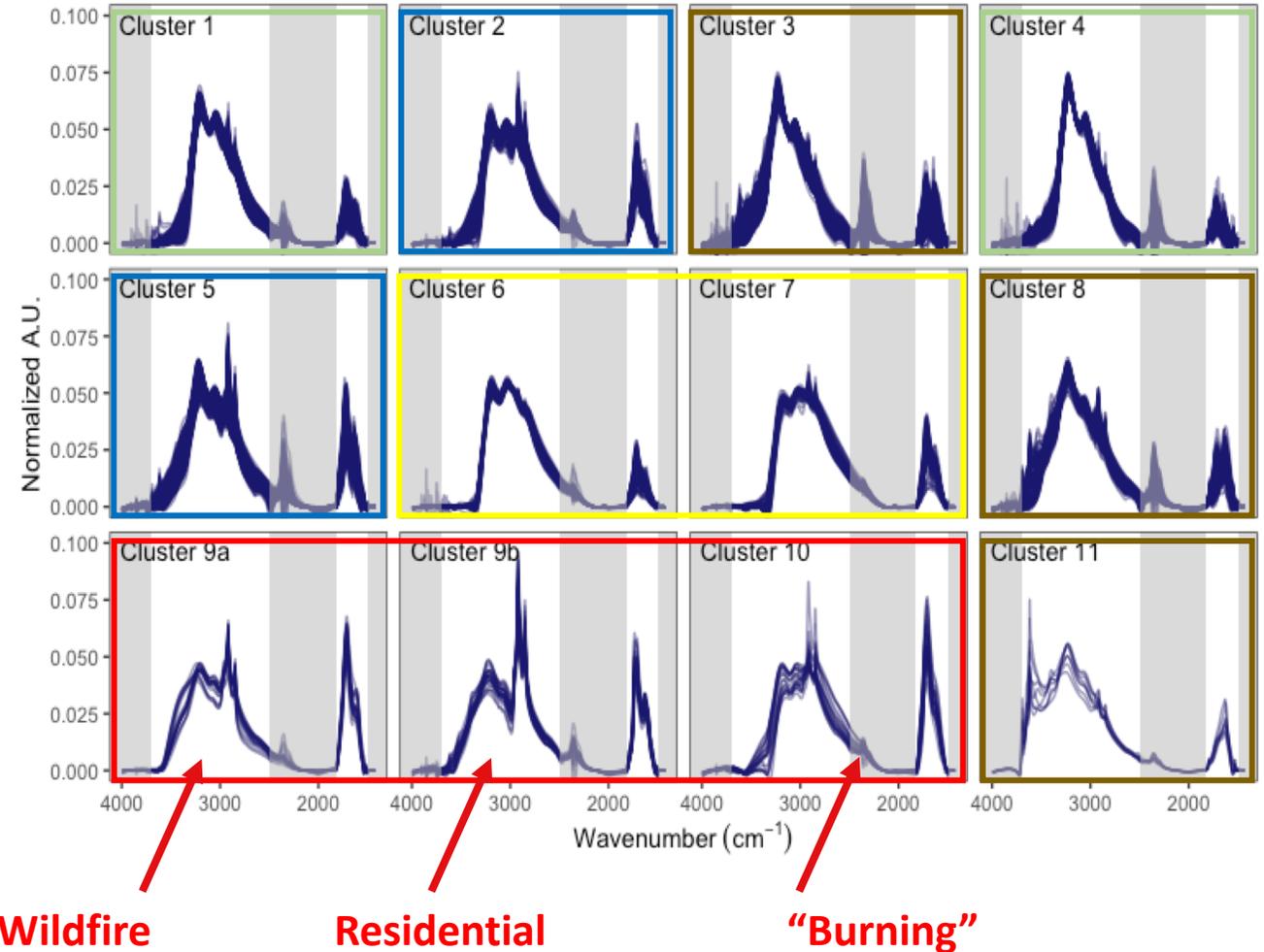


Smoke identification method with FTIR

FTIR smoke identification method – spectral profile



- Demonstrated in past field campaigns (Takahama et al., Atmos. Chem. Phys., 2011; Russell et al., Proc. Nat. Acad. Sci., 2011).
- **7 Sites in 2011 and 17 sites in 2013** (6 sites in common) in IMPROVE network
- **Biomass burning samples** have distinct spectral profiles



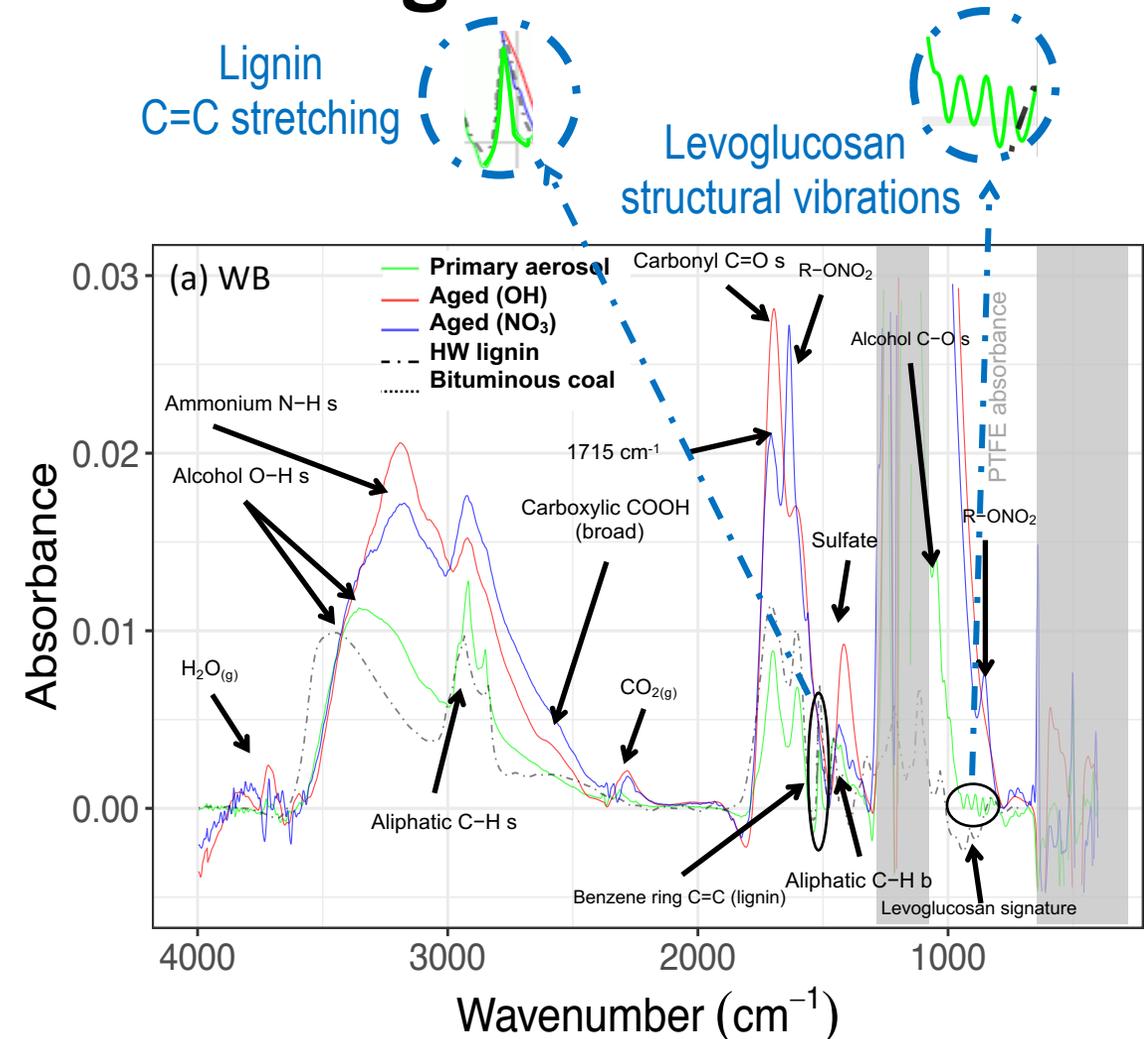
FTIR smoke identification method – tracer signatures

Levoglucosan:

- Important primary product of cellulose pyrolysis (Sullivan et al., *J. Geophys. Res. Atmos.*, 2008)
- C–O bond peaks observed by FTIR

Lignin:

- Third most abundant constituent of wood.
- C=C bond peaks observed by FTIR (Duarte et al., *Atmos. Environ.*, 2007)



Yazdani et al., *Atmos. Chem. Phys. Discuss.* (2020, in review)

Wood and coal
stove



Paul Scherrer Institute
environmental chamber



UV

Oxidants



ToF-AMS



Filter sample → FTIR

Environmental chamber experiments: FTIR tracer comparison with ToF-AMS

(20 samples over 10 experiments
wood burning and coal combustion)

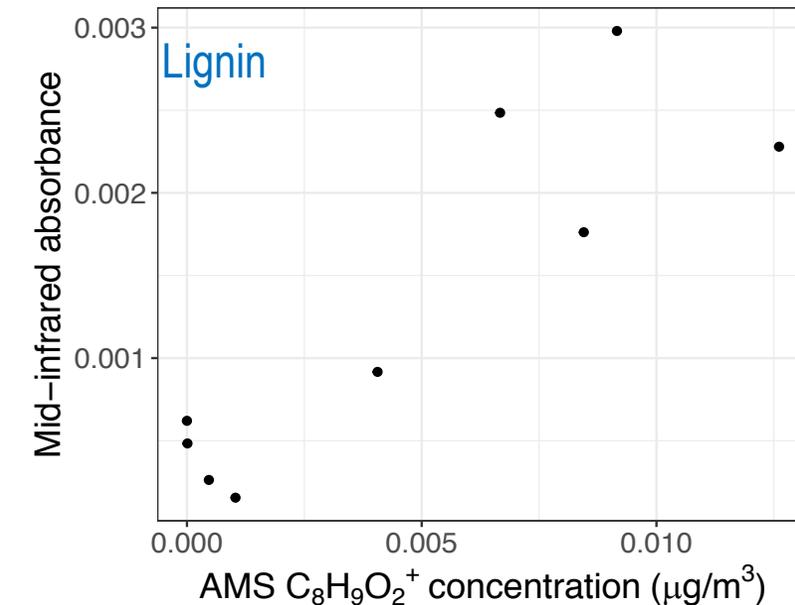
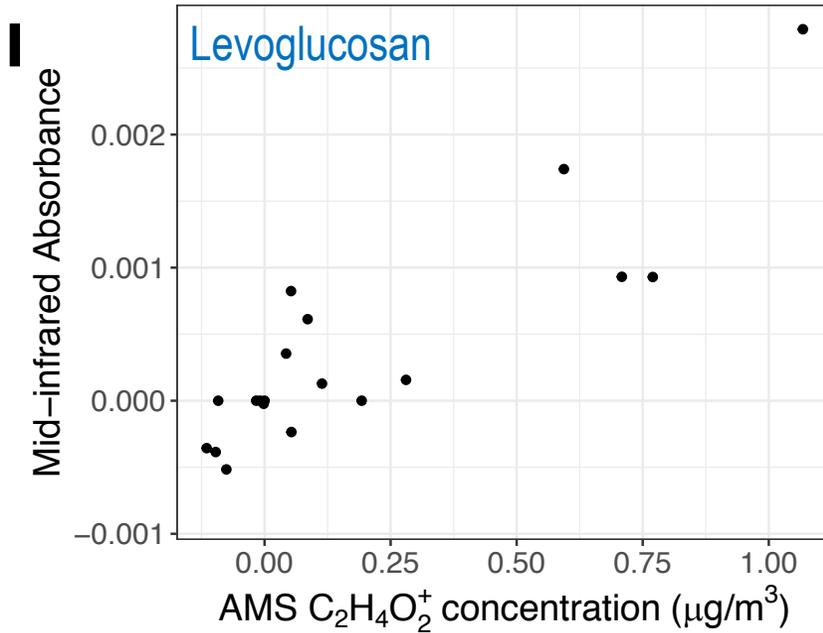
Good agreement for levoglucosan and lignin

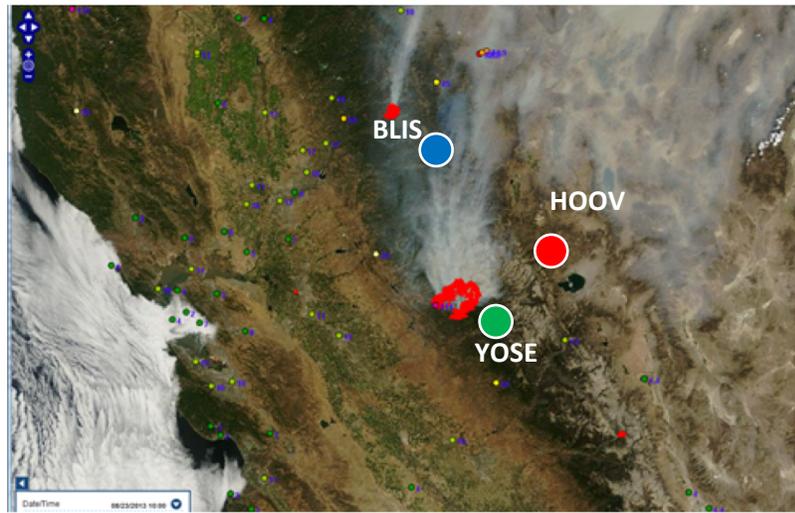
FTIR levoglucosan:

- High correlation with AMS fragment ($r \approx 0.90$)
- Levoglucosan mass fraction (~15-20%) of OM consistent with TAG-AMS and IC

FTIR lignin:

- High correlation with AMS ($r \approx 0.83$)
(AMS lignin estimate is approximate)





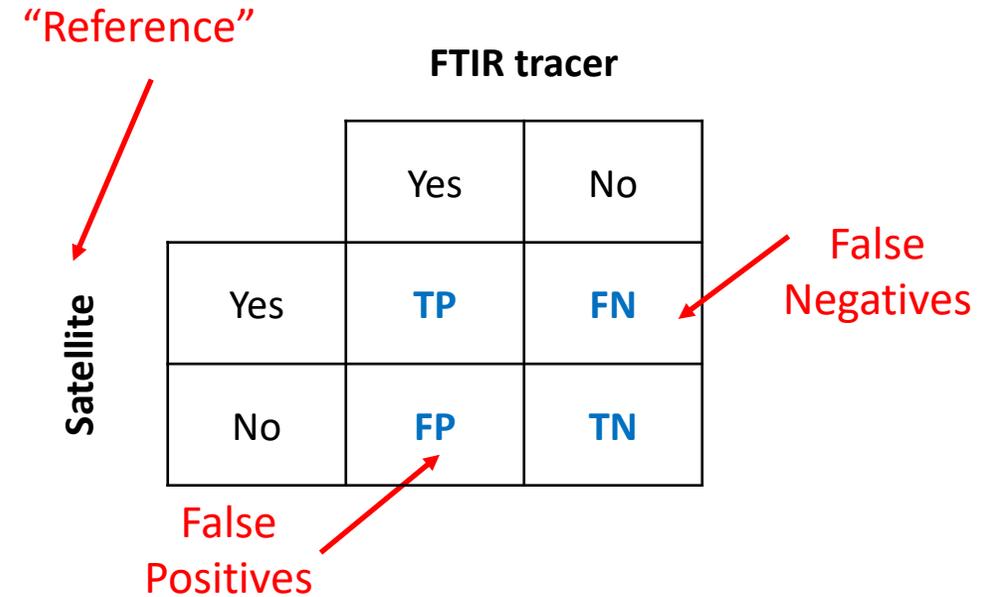
IMPROVE network samples: FTIR tracer comparison with satellite smoke classification

Forest fire (Rim Fire) in Yosemite in 2013 (138 samples)
YOSE, HOOV (northeast of Yosemite NP), BLIS (Lake Tahoe)

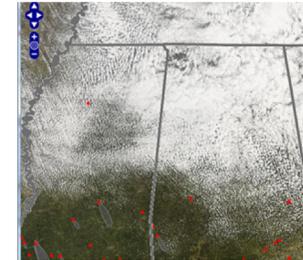
Prescribed burns in Southeast US in 2013 (90 samples)
ROMA (South Carolina), SAMA (Florida) OKEF (Georgia)

Satellite smoke classification method

- Daily detection of “hot spots” from a suite of satellite-based instruments
- Daily smoke polygons as interpreted by the NOAA Hazard Mapping System (HMS)
- Qualitative interpretation (e.g., visible imagery)
- Sample days categorized as **Probable**, **Maybe**, and **Carryover**.
- Some false positive/negatives expected (cloudy days, plume height, spatial resolution of 1 km²).



Cloudy days:
No satellite
detection



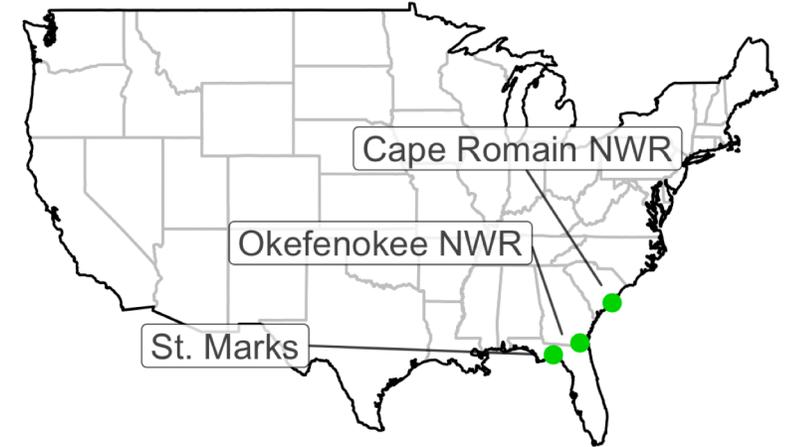
High plumes:
Ground sites not
impacted



FTIR - Satellite product comparison (prescribed fires)

Prescribed fires in Southeastern US in 2013

ROMA (South Carolina), SAMA (Florida), OKEF (Georgia).



X = Levoglucosan
O = Lignin

Methods Agreement

Date	Okefenokee			St. Marks			Cape Romain	
	Satellite	FTIR Tracer		Satellite	FTIR Tracer		Satellite	FTIR Tracer
2013-01-13	Carryover	XO				Carryover		
2013-01-16	Probably					Maybe		
2013-01-19	Maybe	X			X			
2013-01-22	Maybe	XO			XO	Maybe	XO	
2013-01-25	Maybe	X		Maybe	X	Maybe	XO	
2013-01-31				Maybe	XO			
2013-02-03		XO					O	
2013-02-06						Probably	X	
2013-02-18				Maybe	XO			
2013-03-05						Maybe	O	
2013-03-08	Probably	XO		Probably	XO	Probably	XO	
2013-03-14				Probably	XO	Maybe	XO	
2013-03-17								
2013-03-29	Probably	XO		Probably	XO	Probably	XO	
2013-04-10				Maybe		Maybe		

FTIR tracer

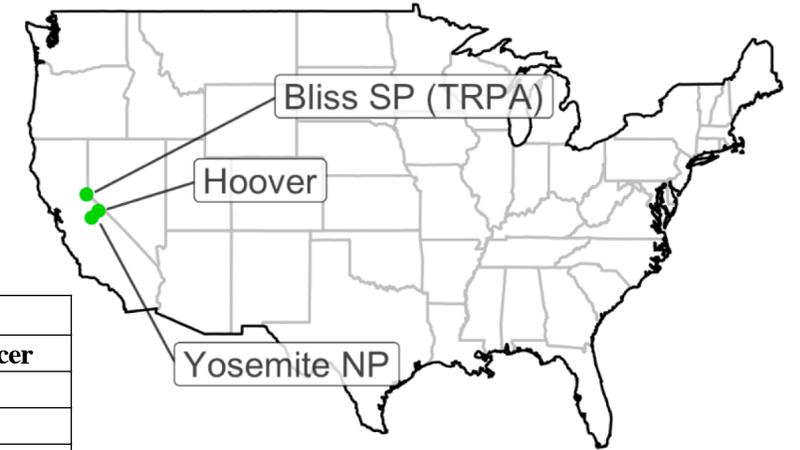
		FTIR tracer	
		Yes	No
Satellite	Yes	19	7
	No	6	58

Many have both tracer and profiles indicative of burning

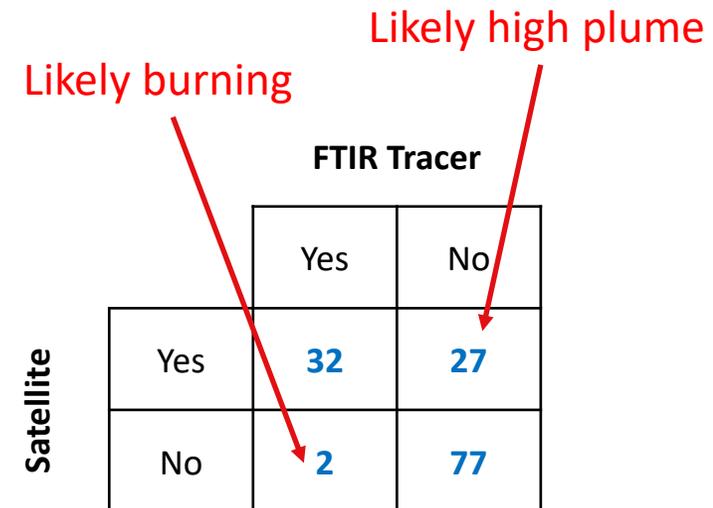
FTIR - Satellite product comparison (wildfires)

Forest fire (Rim Fire) in Yosemite in 2013.

YOSE, HOOV (northeast of Yosemite NP), BLIS (Lake Tahoe).

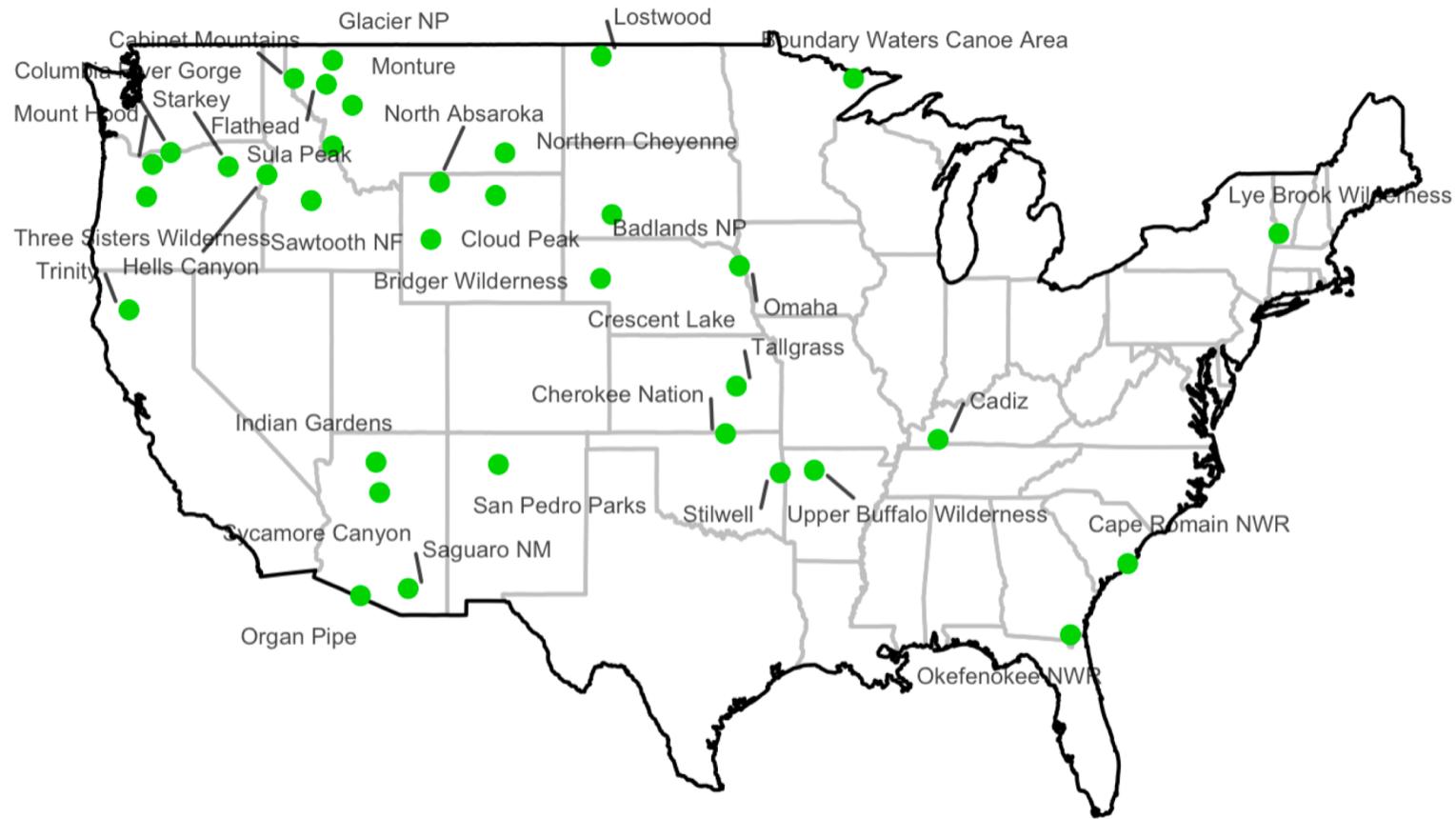


Date	Yosemite			Bliss S. P.			Hoover	
	Satellite	FTIR Tracer		Satellite	FTIR Tracer		Satellite	FTIR Tracer
2013-06-18	M	XO						
2013-06-30	M			M			M	
2013-07-03	M	X		M	X		M	
2013-07-09				M	O			
2013-07-18	P			P			P	
2013-07-24	M						M	
2013-07-27	M					M	XO	
2013-07-30	P	XO		P			XO	
2013-08-02	M	XO				P	XO	
2013-08-05	M	XO		M		P	XO	
2013-08-08	M			M			M	
2013-08-11	M	XO				M		
2013-08-17		XO		M	XO			
2013-08-20				M	XO		XO	
2013-08-23	M	XO				P	XO	
2013-08-26	M			P	XO	P	XO	
2013-08-29	P			P	XO	P		
2013-09-01	P	XO		M	XO	P	XO	
2013-09-04	M			M	XO		M	
2013-09-07	P			P	XO	M	O	
2013-09-10	P	O		M	XO	M	O	
2013-09-13	P	O				M		
2013-09-16	M			M				
2013-09-19	M	XO		M	XO			



X = Levoglucosan
O = Lignin

Methods Agreement



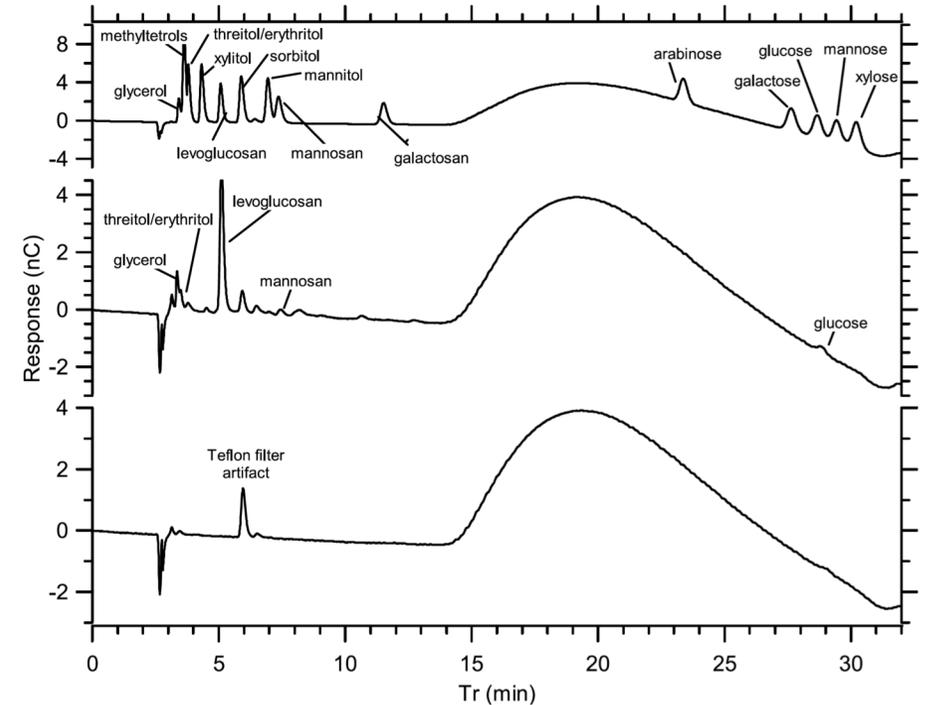
IMPROVE network samples: FTIR comparison with ion chromatography (IC) levoglucosan measurements

304 PTFE samples from 34 sites in 2008 and 2011 (Spring, Summer, Fall)

IC carbohydrate measurements

High-performance anion-exchange chromatography–pulsed amperometric detection (HPAEC-PAD):

- PTFE filters extracted in deionized water (destructive)
- Water-soluble organic carbon (WSOC) from total organic carbon (TOC) analyzer
- Levoglucosan (also mannosan and galactosan) from IC
- “Smoke-impacted” defined as
 $Levoglucosan\ C / WSOC > 1\%$



Sullivan et al., J. Geophys. Res. Atmos. (2011)

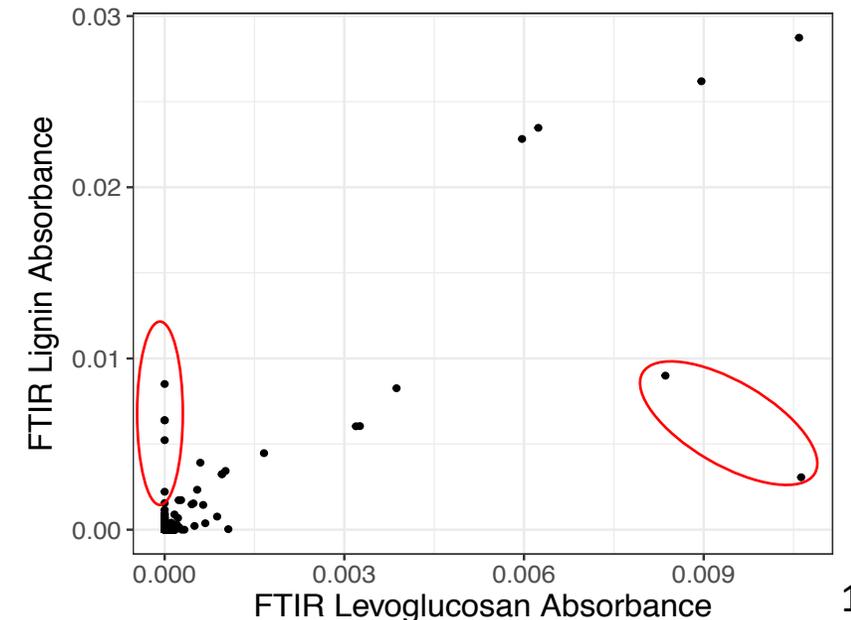
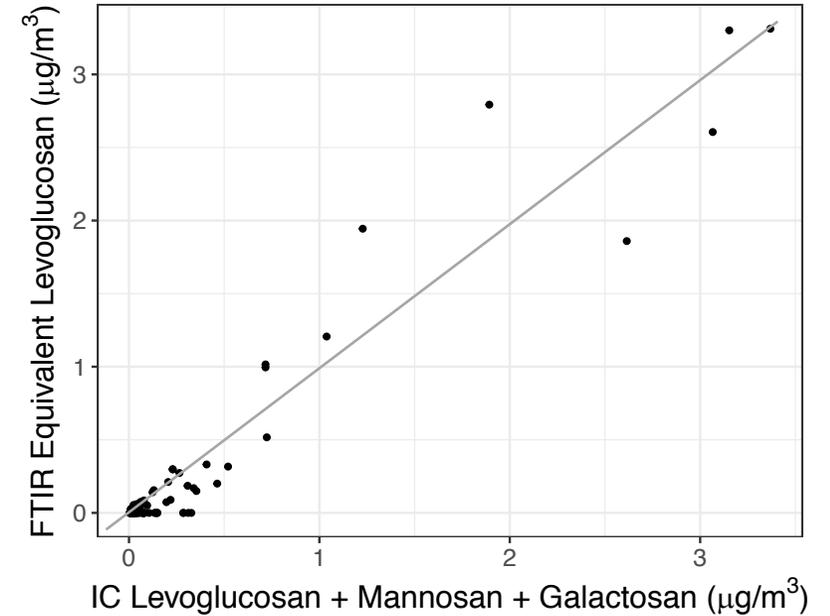
FTIR levoglucosan and lignin both informative

FTIR levoglucosan:

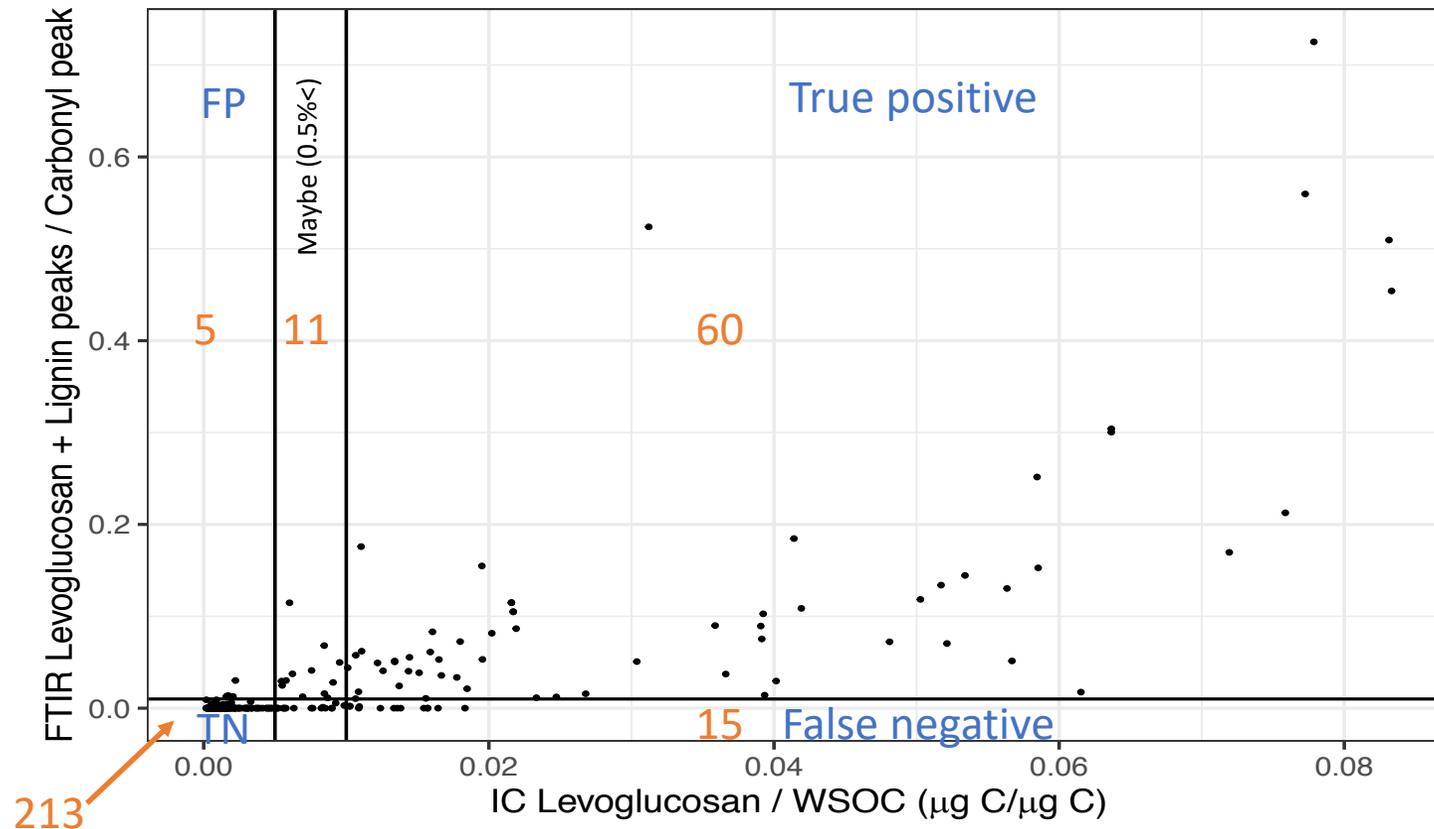
- High correlation with IC ($r=0.96$)
- Close estimated levoglucosan concentrations (slope=1.1)

FTIR lignin:

- Lignin absorbance is not always correlated with levoglucosan but is abundant in burning samples.
- Lignin can be used as another smoke identifier.



FTIR - IC comparison

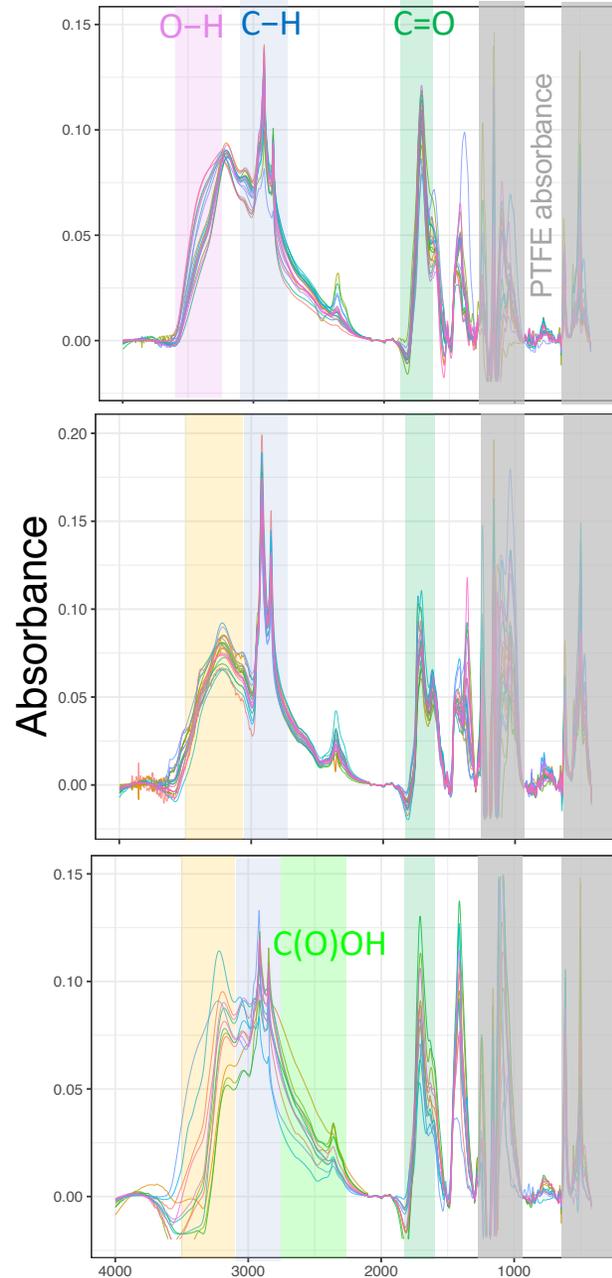


		FTIR	
		Smoke-impacted	
IC	Smoke-impacted	Yes	No
	Yes	60	15
No	No	5 (+11)	213

Annotations:
 - Red arrow pointing to 15: spectral profile resembles burning
 - Red arrow pointing to 5 (+11): lignin still visible

- FTIR smoke identification by combined levoglucosan and lignin
- FTIR carbonyl can be used as a proxy to WSOC
- False negatives appear up to 2% Levoglucosan/WSOC

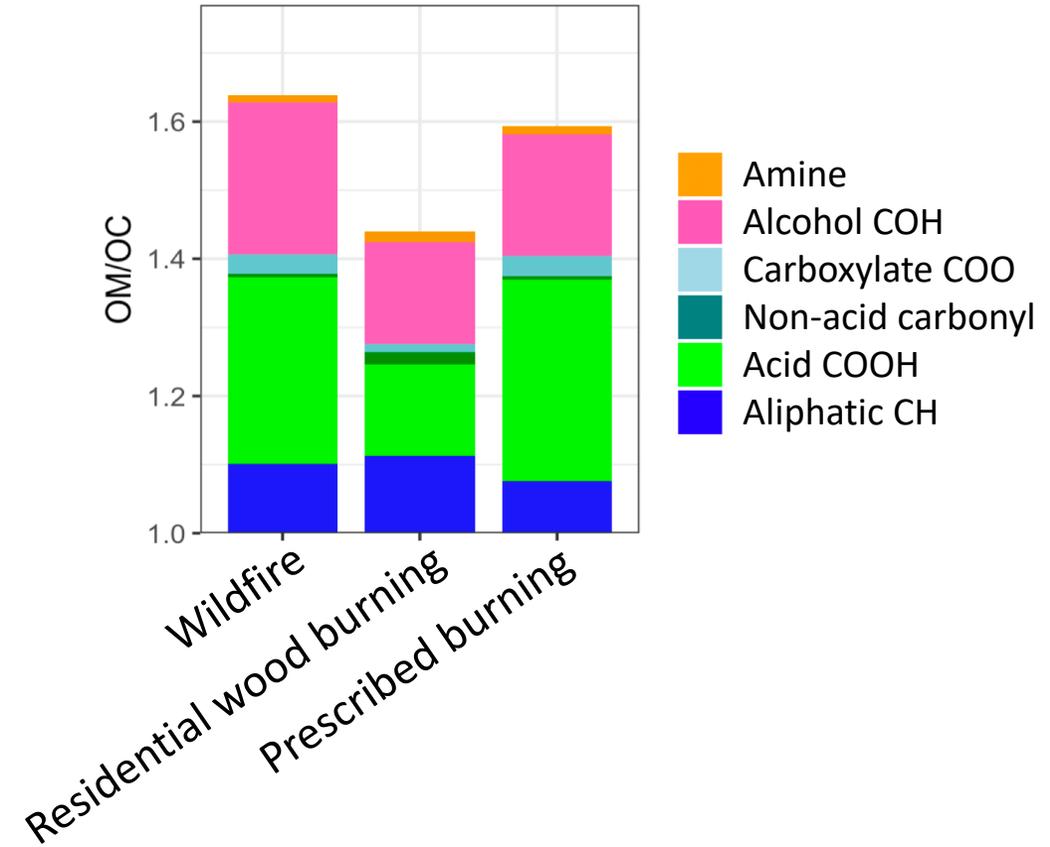
More chemical information for smoke-impacted samples



Wildfire

Residential wood burning

Prescribed burning



Summary

- FTIR on PTFE filters used to quantify levoglucosan and lignin **rapidly** and **non-destructively** in the IMPROVE network.



- **FTIR** measurements generally agree with **AMS** and **IC** and are supported by **satellite** and ground-based observations.

	FTIR	ToF-AMS	Satellite	IC + TOC
Pros	<ul style="list-style-type: none"> • Multiple methods of identification: levoglucosan, lignin, spectral profile • Rapid and non-destructive to PTFE filter 	<ul style="list-style-type: none"> • Online measurement 	<ul style="list-style-type: none"> • Remote sensing, good coverage 	<ul style="list-style-type: none"> • Very sensitive to levoglucosan
Cons	<ul style="list-style-type: none"> • Interferences esp. for low OM 	<ul style="list-style-type: none"> • Expensive equipment and labor costs • Mass fragments are not fully specific • Not scalable to network 	<ul style="list-style-type: none"> • Misidentification due to size resolution, plume rise, cloudy day, reflection 	<ul style="list-style-type: none"> • Destroys PTFE filter

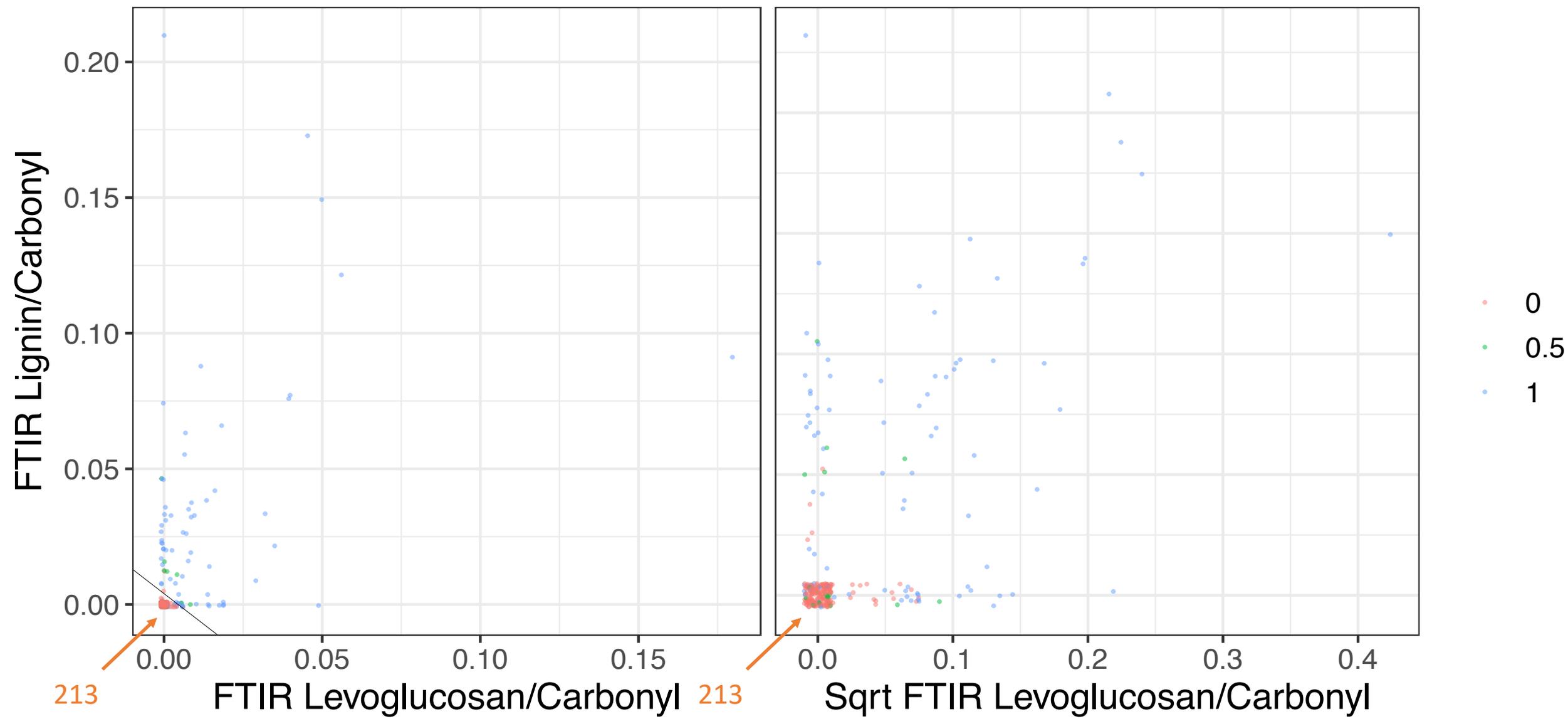
- There is physical basis for building a classifier that can be used operationally at the scale of the network (work in progress).

Thank you for your attention!

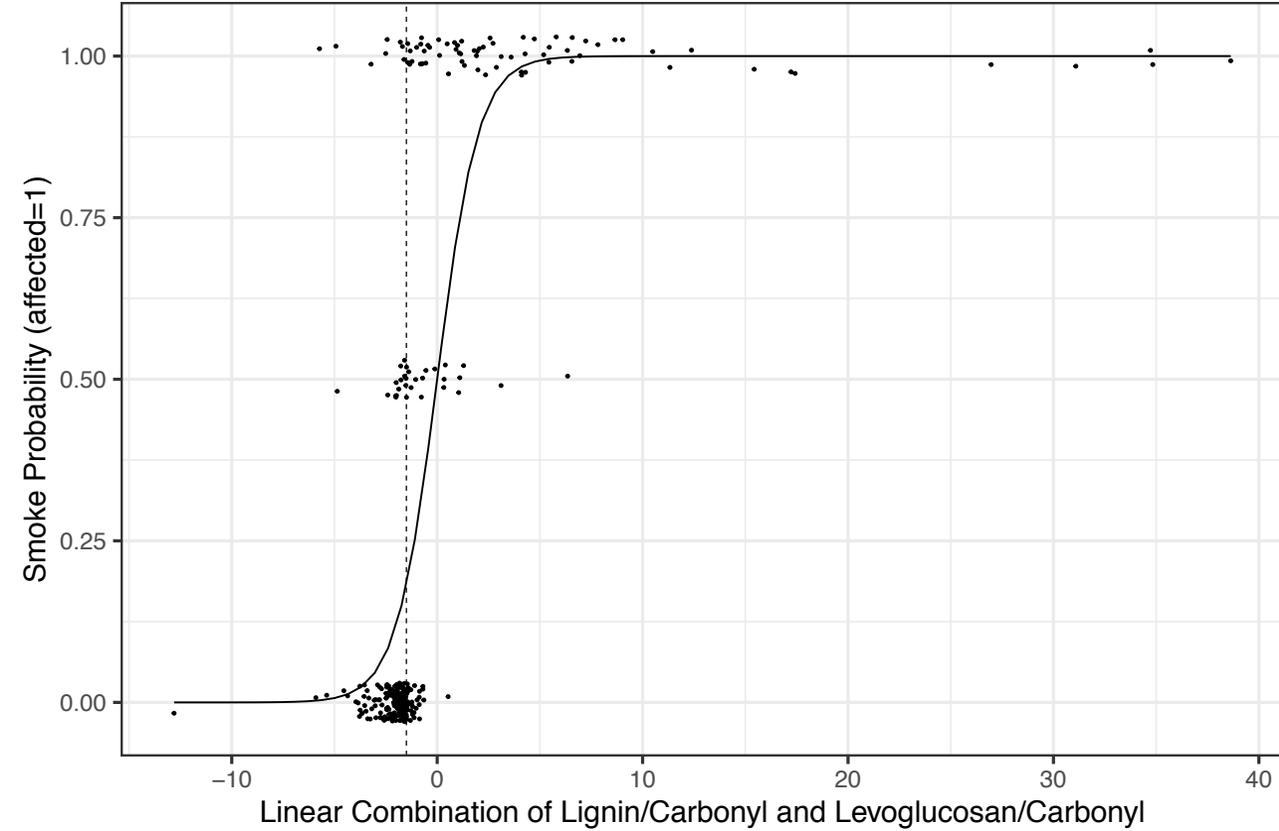
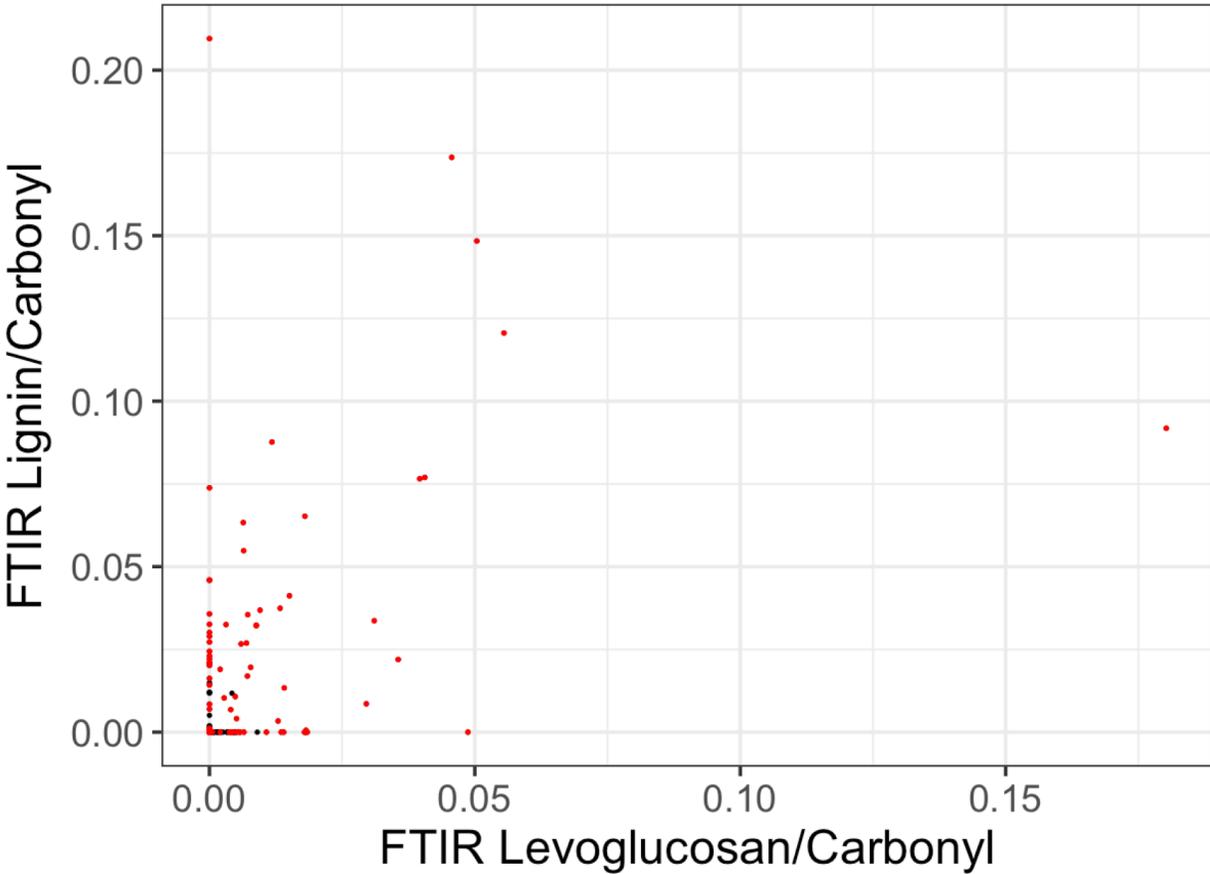
Questions ?

EPFL

UC DAVIS
UNIVERSITY OF CALIFORNIA

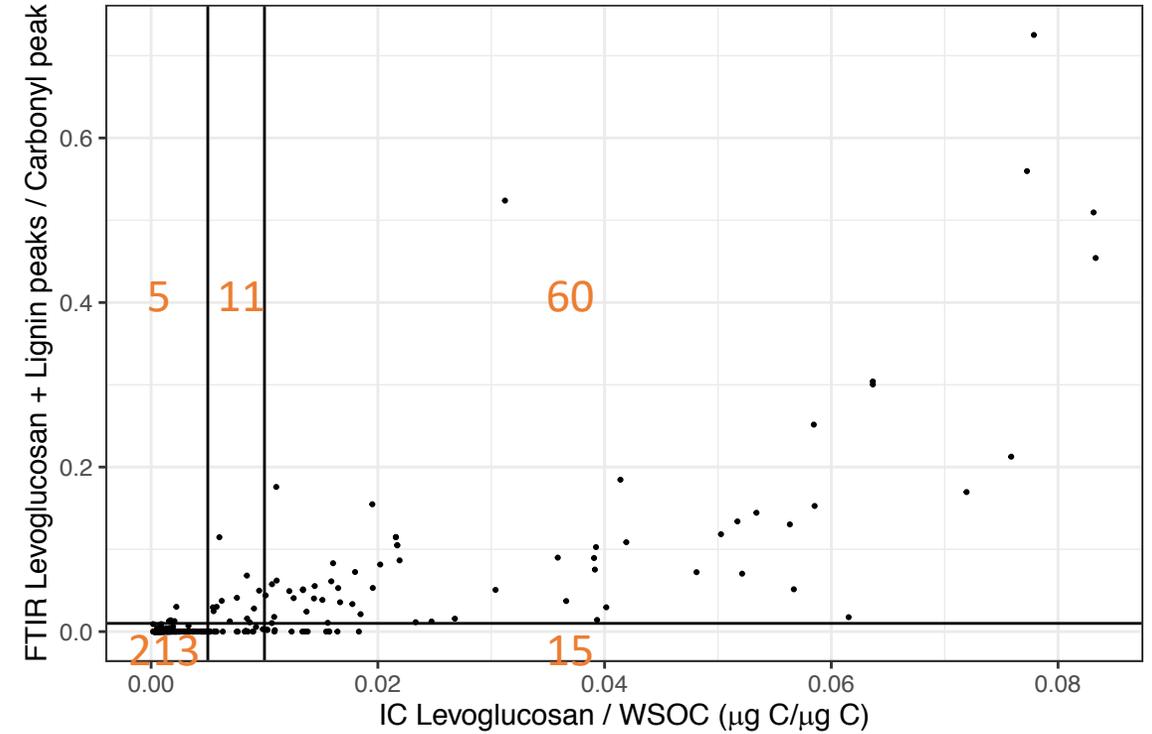
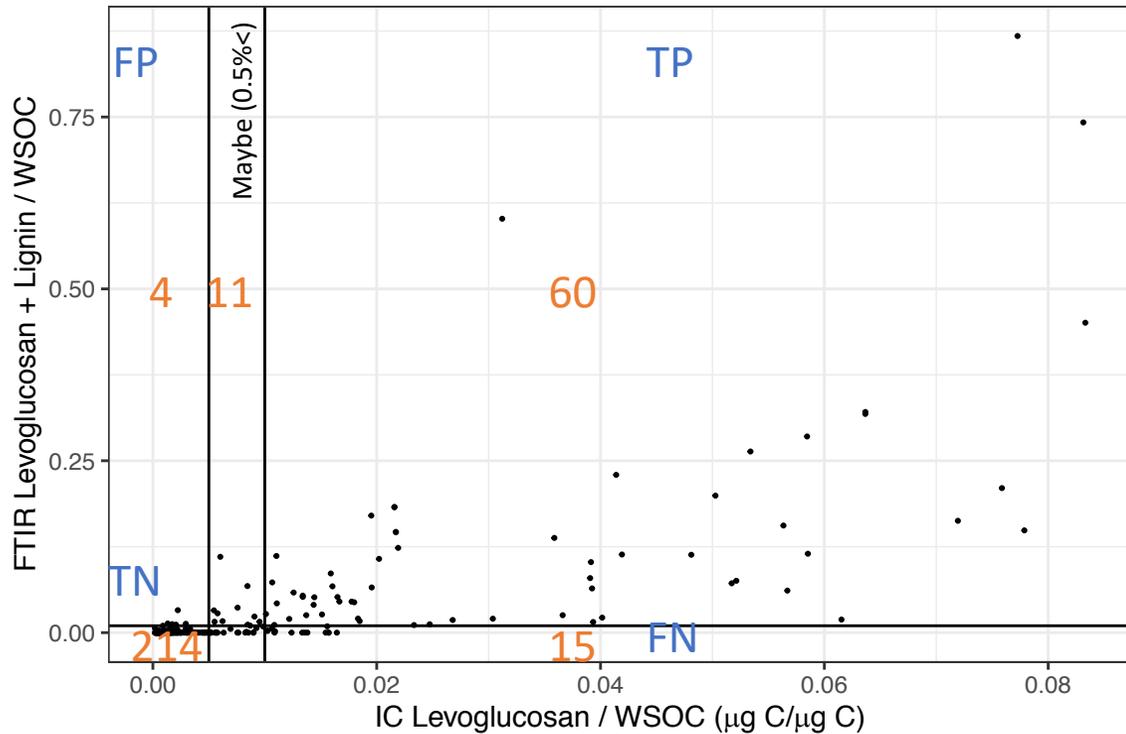


FTIR smoke identification assessment – IC carbohydrate measurements



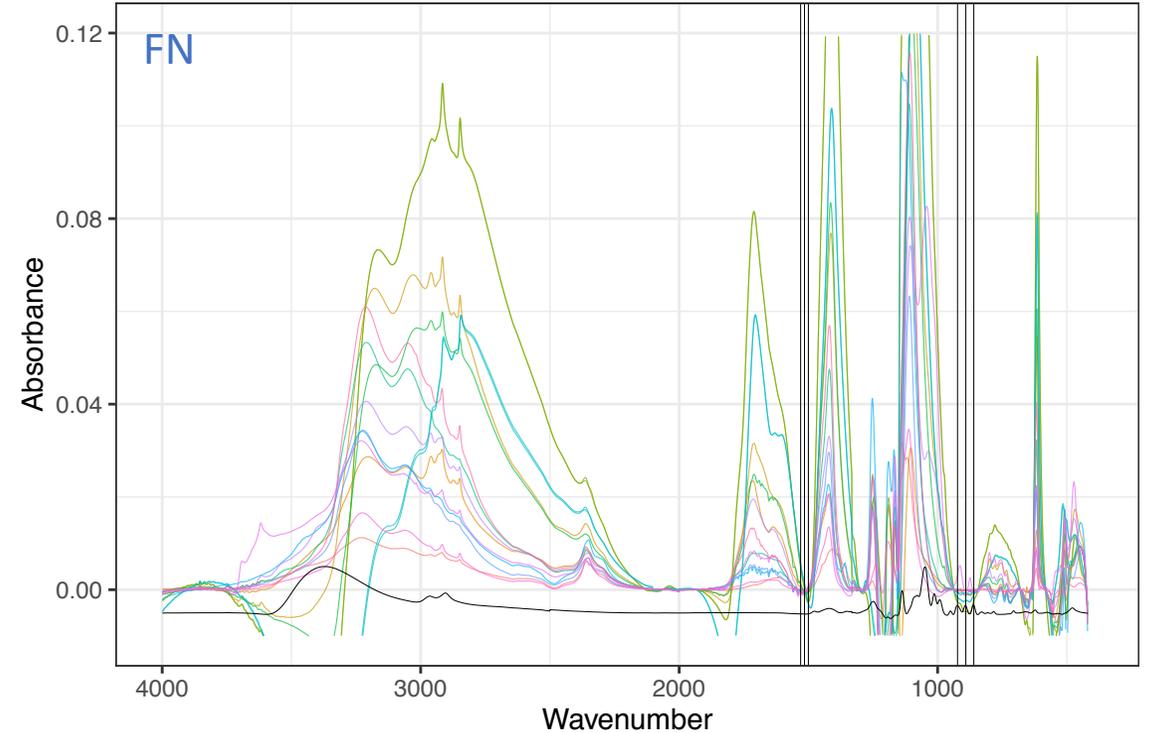
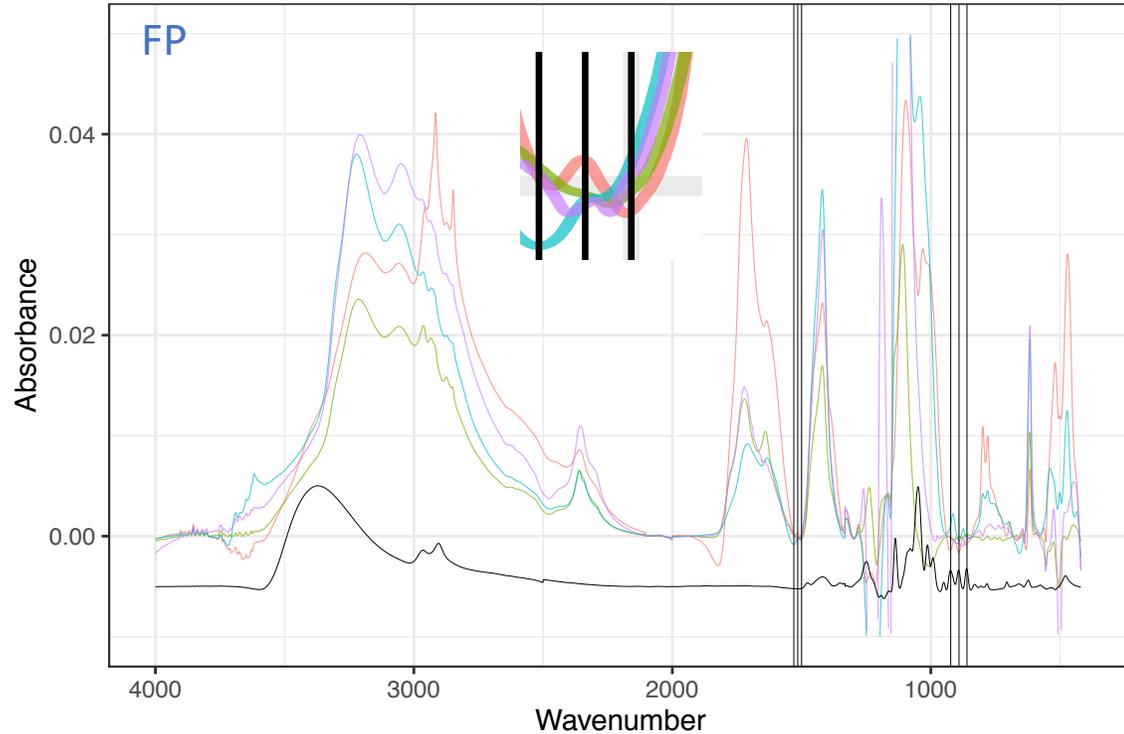
- Logistic regression (assuming three possibilities) results a similar identification.

FTIR smoke identification assessment – IC carbohydrate measurements



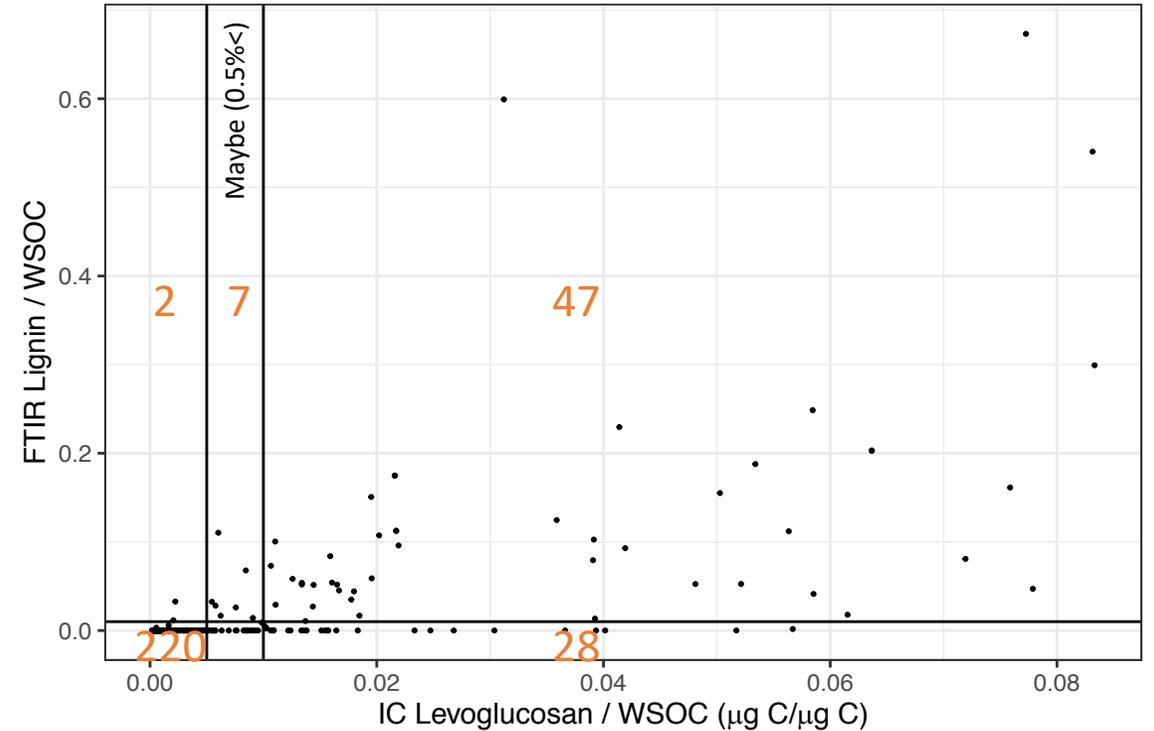
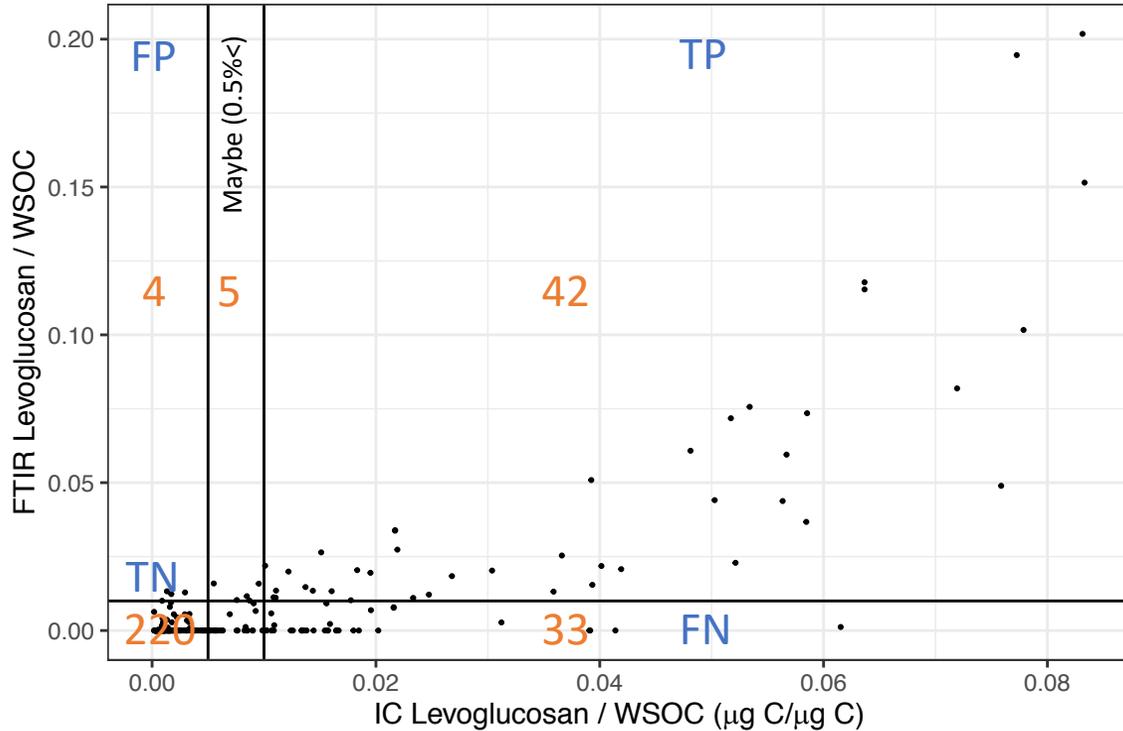
- Combining levoglucosan and lignin reduces the false negatives.
- FTIR carbonyl can be used as a proxy to WSOC.

FTIR smoke identification assessment – IC carbohydrate measurements



- Two of the true false positive samples have visible lignin peaks.
- Two of the false negative samples have high acid abundance (a common burning profile).

FTIR smoke identification assessment – IC carbohydrate measurements (omit)



- Levoglucosan and lignin can be used separately for identification.
- True false positive results are few but false negative results are considerable.

