

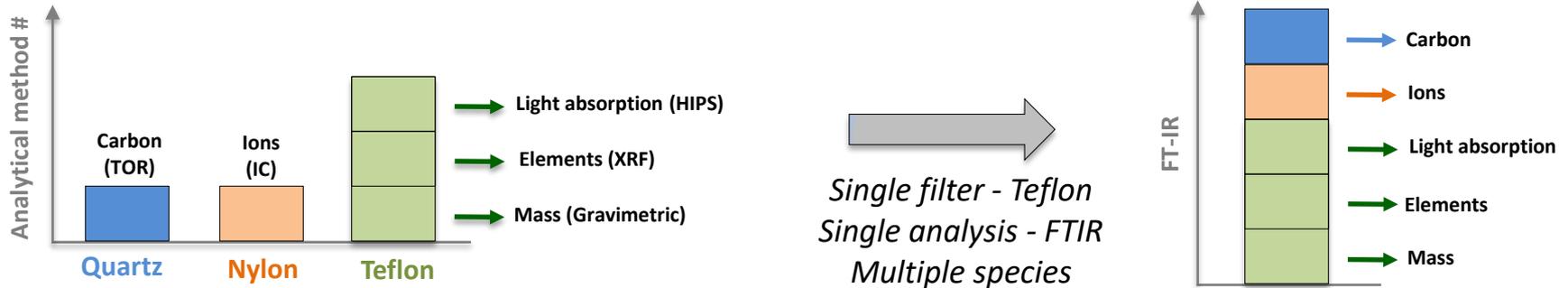
IMPROVE, CSN, FRM, ASCENT, SPARTAN, MAIA FTIR UPDATE – What is working, what we are working on, what doesn't work.

Ann M. Dillner, Bruno Debus, Andrew Weakly, Ana Amiri-Farahani,
Dominique Young, Na (Mona) Mao, Yiqiao (Chelsey) Li
Air Quality Research Center, UC Davis

IMPROVE Steering Committee, November 2, 2022, Plymouth, NH

IMPROVE

AIR QUALITY MONITORING - SAMPLING



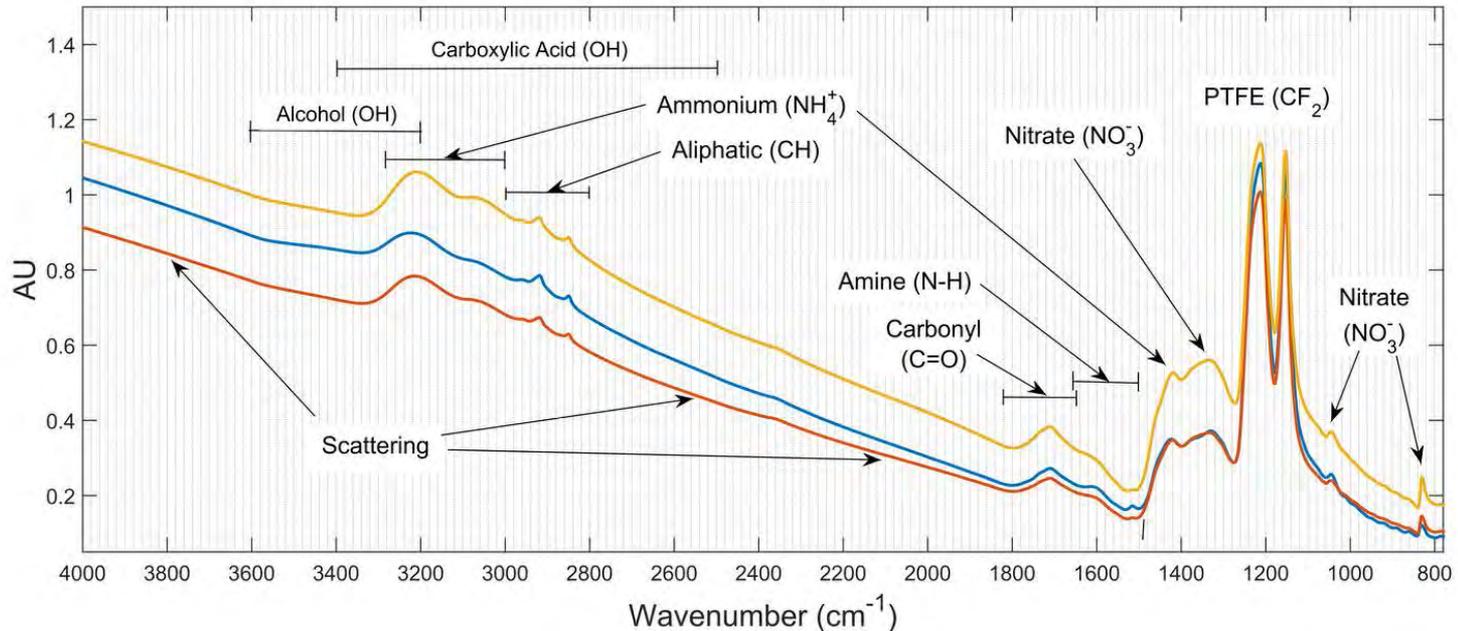
Aerosol signatures in FT-IR spectra



- Organics: C-H / O-H / N-H / C=O
- Ions: Nitrate, Sulfate, Ammonium
- Silicates and other soil related

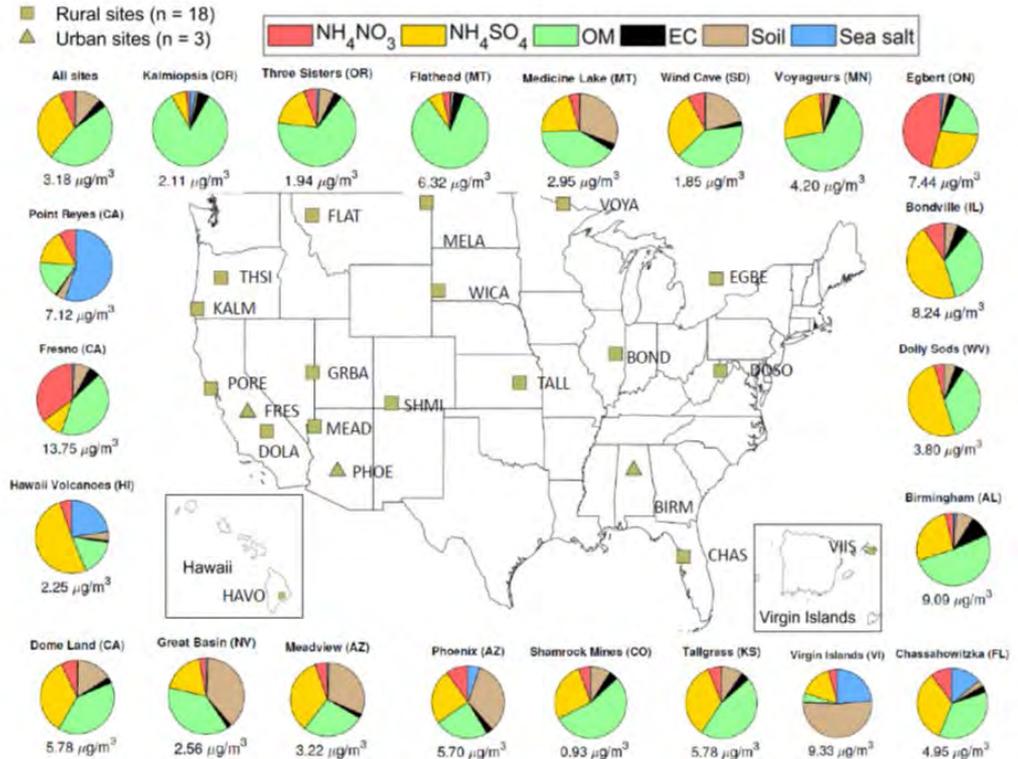


- Sea salt
- Trace elements (V, Sr ...)



Select few sites to use as calibration standards

- Cluster all IMPROVE sites in 21 groups
- Select representative site per group
- Selected sites average composition
 - Across US
 - Three urban, rest rural
 - Composition varies from high OM to high sulfate to high soil
- Developed calibrations for each component (OC, EC, sulfate etc.) using these 21 sites
- Developed another set of calibrations for smoke samples

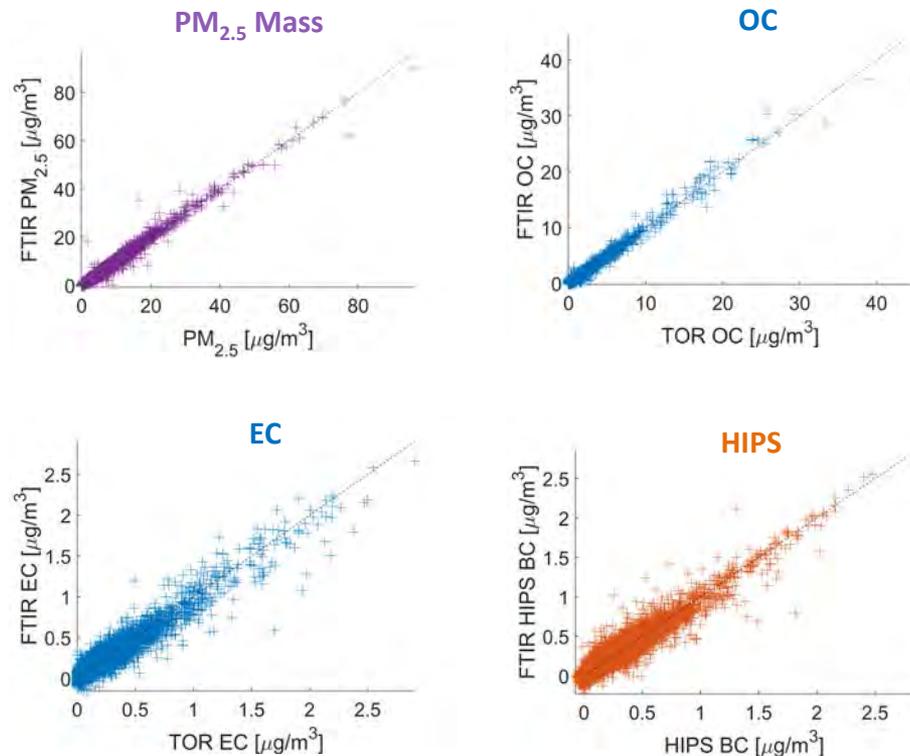


Carbon & PM_{2.5} Mass

Model performance

	R^2	Bias (%)	Error (%)	< MDL (%)
Mass (PM _{2.5})	0.984	0.4	6.7	0.8
OC	0.980	1.1	12.2	0.8
EC	0.911	1.6	31.0	22.4
HIPS	0.910	-1.3	25.0	21.7

- FT-IR predictions are in good agreement with known values

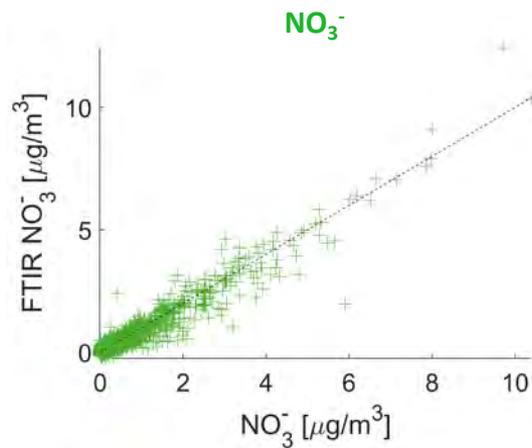
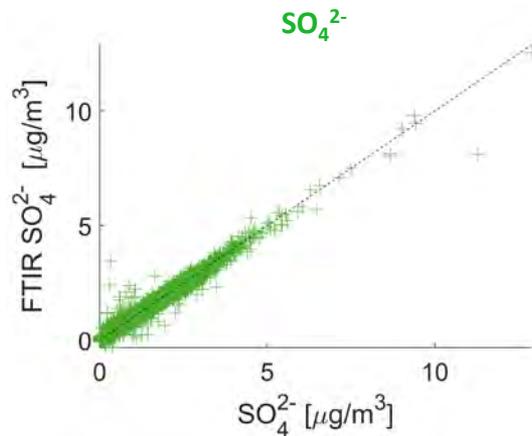


Ions

Model performance

	R^2	Bias (%)	Error (%)	< MDL (%)
SO_4^{2-}	0.983	-0.1	6.1	1.2
NO_3^- (Winter north)	0.927	10.7	48.6	25.1

- Sulfate is well quantified by FT-IR
- Nitrate poorly measured (error 50%)
 - Evaporation from Teflon filter (Temp. dependent)
 - Improvements made using lab standards but only to measure nitrate on Teflon not ambient nitrate
- Ammonium can be determined but no reference method is available for comparison in this data set



Soil elements

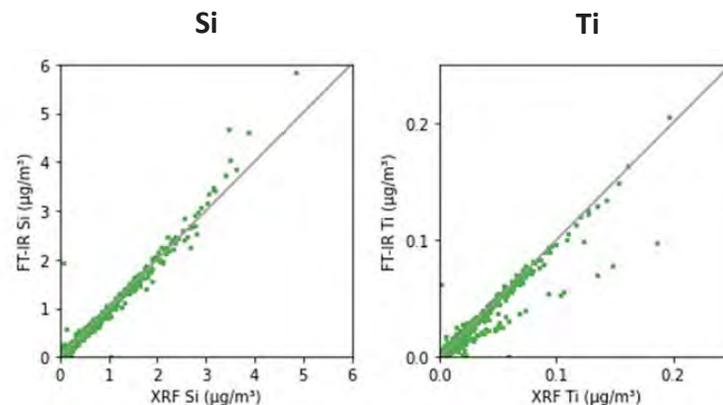
Model performance

	R^2	Bias (%)	Error (%)	< MDL (%)
Soil*	0.986	1.4	10	7
Al	0.985	2.2	12	6
Si	0.984	1.1	11	12
Ca	0.980	1.3	13	8
Ti	0.941	2.7	21	15

* based on the IMPROVE soil equation

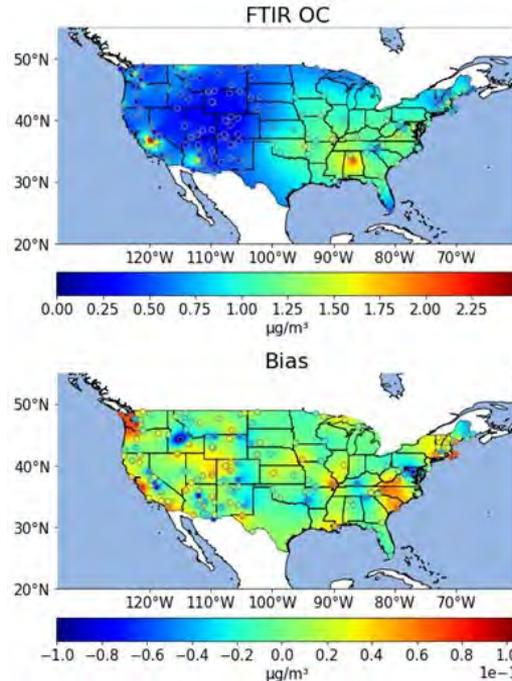
$$2.2*[Al] + 2.49*[Si] + 1.63*[Ca] + 2.42*[Fe] + 1.94*[Ti]$$

- Soil related elements are well quantified
- Ti has low predictions for one site in Oregon



Maps of FT-IR predictions compared to routine data

- FTIR OC and TOR OC maps look very similar
- Bias and norm. bias show regions of very low bias and regions with higher bias
- Additional maps of error, MDL differences and R^2



Uses and Limitations

- OC, EC, sulfate, Si, Al, Ca, Fe, Ti, Fabs, mass work!
 - QC of IMPROVE data – updating site list
 - New IMPROVE sites - Teflon only samples (cheaper)
 - Replace subset of measurements at existing sites
- Limitations – not going to work
 - Nitrate poorly measured, Na, Cl and trace elements not measured
 - Not necessarily transferrable to other networks
- 2022-2023
 - Measuring spectra on only ~30 sites

Atmos. Meas. Tech., 15, 2685–2702, 2022
<https://doi.org/10.5194/amt-15-2685-2022>
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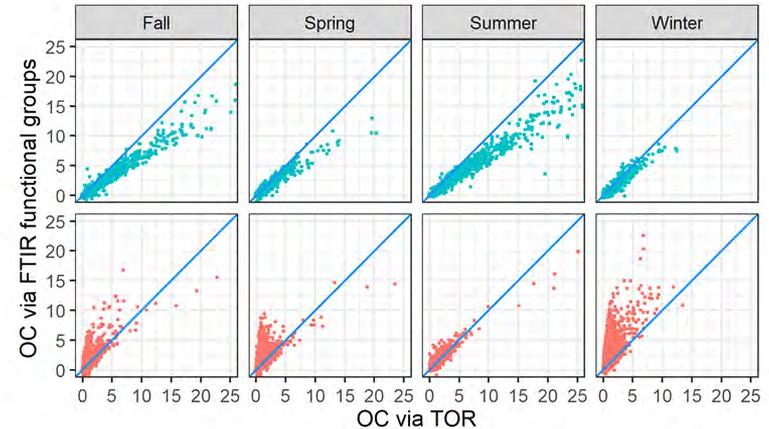
Atmospheric
Measurement
Techniques
Open Access
EGU

Quantification of major particulate matter species from a single filter type using infrared spectroscopy – application to a large-scale monitoring network

Bruno Debus¹, Andrew T. Weakley¹, Satoshi Takahama², Kathryn M. George^{1,3}, Anahita Amiri-Farahani¹, Bret Schichtel⁴, Scott Copeland⁵, Anthony S. Wexler^{1,6,7,8}, and Ann M. Dillner¹

Functional group Measurements for IMPROVE

- 2015-18 (Pall filters) using 2011 calibrations
 - selecting model parameters (harder than we thought)
- 2018-2021 (MTL filters)
 - calibrations developed for different project
- Working on it



$\text{Ammonium}_{\text{est}} / \text{TOR OC} > 0.3$ or $\text{Ammonium}_{\text{est}} \geq 1 \mu\text{g}/\text{m}^3$

• False • True

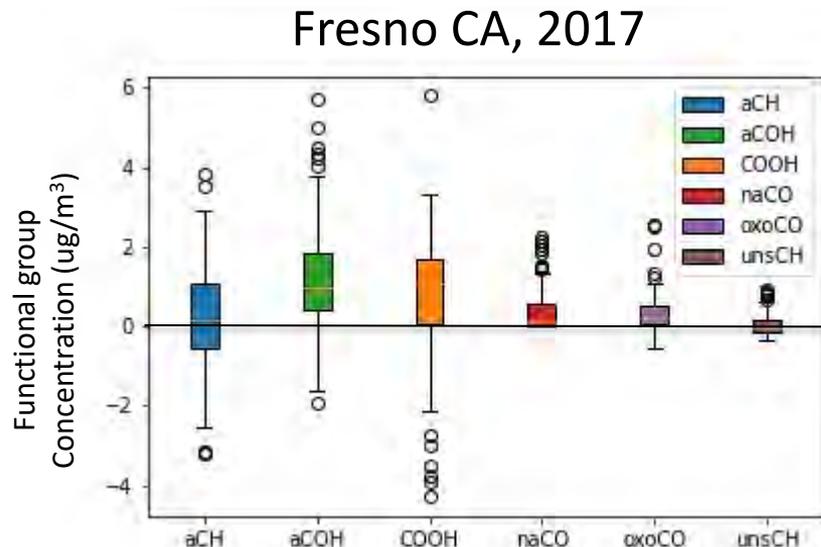
Concentration in $\mu\text{g}/\text{m}^3$

CSN

- Lower aerial density of PM on the filter than IMPROVE
 - Larger filters
 - Lower flow rate
- Filters are optically thicker in FTIR than IMPROVE – more interference
- Aerosol more complex and variable in urban environments
 - Different mixtures of primary aerosols
 - EC of diesel soot near source different from aged EC
- Requires grouping sites with similar carbonaceous, inorganic and elemental composition
- Currently using 7 calibrations with varying quality and MDLs to predict whole network
- Working on this for QC in the network or to replace some existing data

Functional groups measured from CSN filters

- Calibrations for functional groups developed for SEARCH network
 - 47mm
 - Optical thick Teflon, same as CSN
 - 16.7 lpm
 - Southeast which has high OM
- Very low FG concentrations
 - Negative CH for ~1/2 of samples
- Stopped here for now, hope to revisit
- 25 mm inserts for CSN samplers
 - Optically thinner filters
 - Increase likelihood of success
- Currently **not working**



FRM

PM2.5 network

Predict species using CSN data and functional groups

11 sites in 2016

- Bakersfield, CA
 - Boston, MA
 - Elizabeth, NJ
 - Fresno, CA
 - Indianapolis, IN
 - Los Angeles, CA
 - New York, NY
 - Providence, RI
 - Riverside, CA
 - Seattle, WA
 - Washington DC
- Measure species and functional groups at FRM sites
 - Use CSN data and FRM spectra to develop species calibrations – OC, EC, sulfate, Si etc.
 - 11 sites in 2016
 - Flowrate 16.7 lpm (6.7 lpm for CSN)
 - 47 mm MTL filters

Fewer species predicted well in FRM than IMPROVE

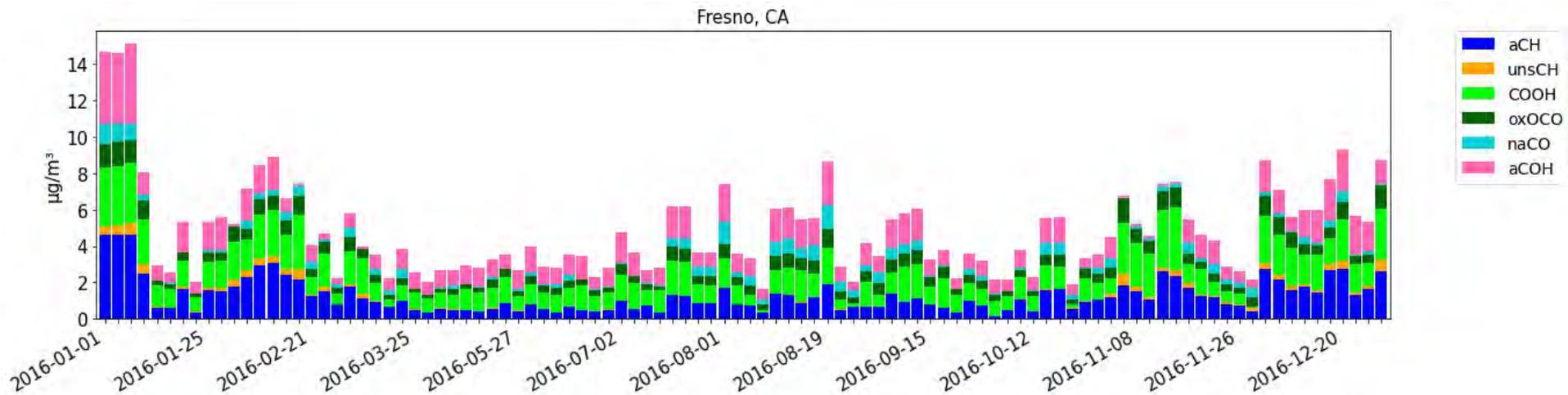
Species	R ²	Normalized Bias (%)	Normalized Error (%)
OC	0.74	-6	17
EC	0.68	-4	25
Nitrate	0.84	-20	51
Sulfate	0.73	-7	20
S	0.77	-4	17
Si	0.46	-9	86
K	0.35	-12	41
Ca	0.07	-11	50

Nitrate volatilizes off PTFE filter

Likely sources of Si, Ca other than soil at FRM sites

Only used small, non-optimized subset of sites

Functional groups



Measured at each site

Used calibrations developed for SEARCH network

2016 last year this is possible – Filters currently used in network have QR code on filter

ASCENT

New US network

ASCENT: A new long-term, ground-based high time-resolution air quality monitoring network

- Atmospheric **S**cience and **C**hemistry **mE**asurement **NeT**work
- Long-term
 - 3 year NSF Infrastructure grant (\$12M) + 10+ year from NSF
- Ground-based
 - 12 sites measuring PM_{2.5} (map on following page)
 - Use sites in existing networks
 - Leverage existing measurements, infrastructure, personnel
 - Provides additional data for these sites
 - IMPROVE, CSN, SCAQMD, NEON (NSF National Ecological Observatory Network), HNET (Houston)



ASCENT: Atmospheric Science and Chemistry mEasurement NeTWork

IMPROVE sites:

Cheeka Peak/Makah, WA
Joshua Tree NP, CA
Yellowstone NP, WY
Great Smoky Mountain NP, NC

CSN sites:

Rubidoux, CA
La Casa, Denver, CO
Queens College 2, NYC, NY

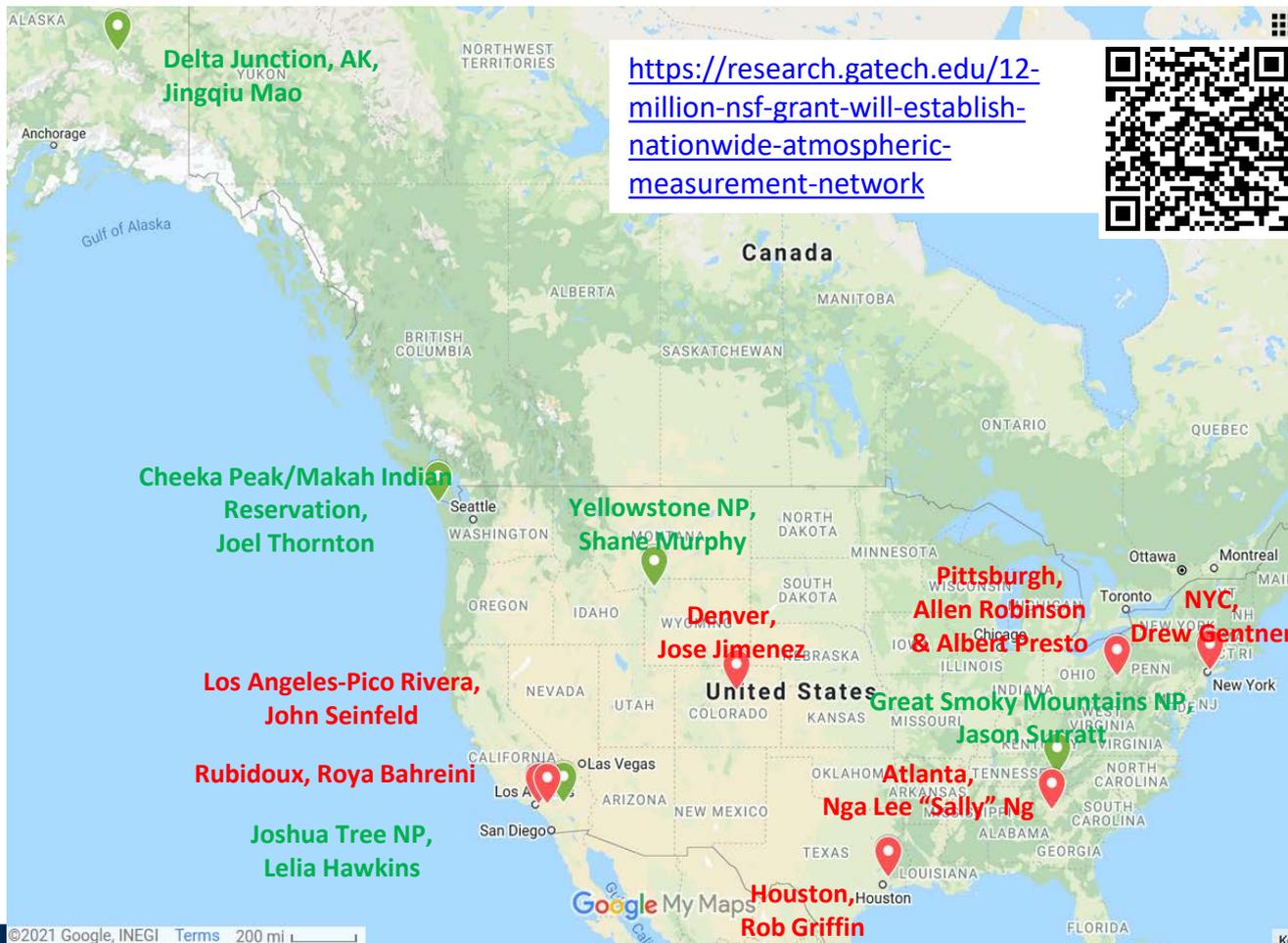
IMPROVE/CSN:

Lawrenceville, Pittsburgh, PA
South DeKalb, Atlanta, GA

NEON: Delta Junction, AK

SCAQMD: Los Angeles - Pico Rivera, CA

HNET: Houston, TX

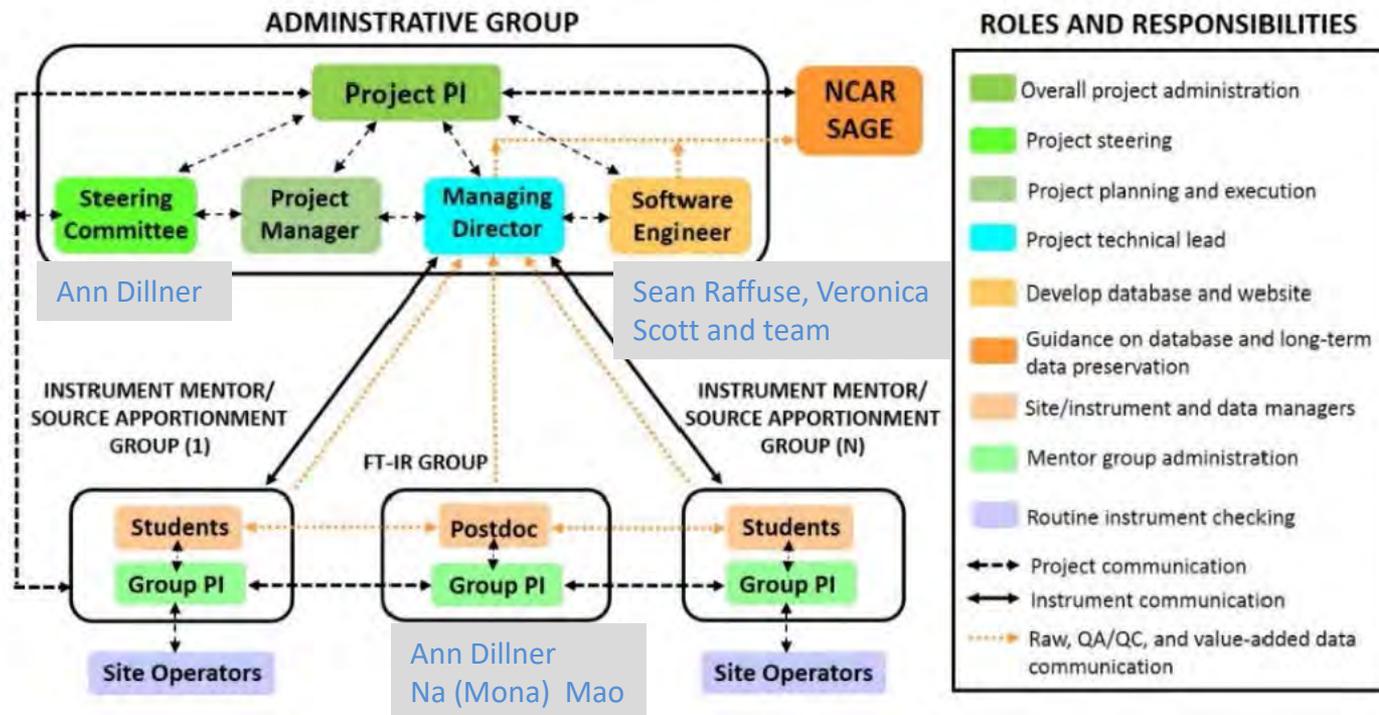


Test bed for other researcher

- Lots of interest by aerosol researchers at recent conference
- collaborations
 - Instrument comparisons
 - New methods
 - New sites (Barbados)
 - Modeling
- NSF provide research support for these collaborations through grant proposal process



ASCENT organizational chart



UC Davis AQRC researchers and staff involved with ASCENT

High Time-Resolution Aerosol Instrumentation

Instrument	Model and Manufacturer	Measurements
Aerosol Chemical Speciation Monitor (ACSM)	ToF-ACSM, Aerodyne Research	Organics, sulfate, nitrate, ammonium, chloride
Xact	625i, Cooper Environmental	Trace metals: Sb, As, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Hg, Mn, Ni, Se, Ag, Sn, Ti, Tl, V, Zn, more available
Aethalometer	AE33, Magee Scientific	Wavelength-dependent absorption; black and brown carbon
Scanning Mobility Particle Sizer (SMPS)	3938L89, TSI	Particle number size distribution, number concentration

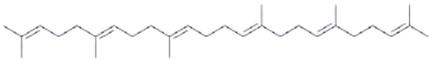
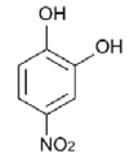
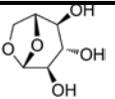
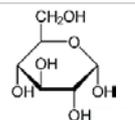
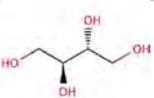
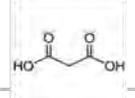
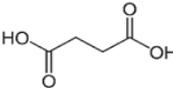
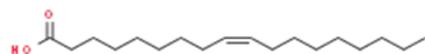
Year 1 goal: Have all instruments established at all 12 sites

Current Status: Yellowstone next May, Rubidoux needs power, ACSMs delayed for several sites

FT-IR to enhance organics information from ACSM

- Parallel ACSM and FT-IR functional groups for
 - Single compounds and mixtures, including highly functionalized
 - Chamber studies at Ga Tech
 - IMPROVE ASCENT sites (not CSN)
- Year 1:
 - Begun developing FT-IR calibrations for MTL filters
 - 3 day training on ACSM at Aerodyne – ACSM in lab by years end
- Goal:
 - Develop parameterizations of ACSM data to increase the chemical resolution of OA from the ACSM
- FT-IR functional group calibrations can be used at all IMPROVE sites since 2018

Working on it

Category	Functional Group	Chemical Name	Chemical structure	Molecular Formula	O: C	Source
HOA	Unsaturated hydrocarbon	Squalene		C ₃₀ H ₅₀	0.00	
BBOA	Nitrated phenols	4-Nitrocatechol		C ₆ H ₅ NO ₄	0.67	Representative of phenols, typical of biomass burning emissions
BBOA, COA in the condensed phase	Sugars	Levoglucosan		C ₆ H ₁₀ O ₅	0.83	Biomass burning OA (BBOA)
Carbohydrates	Sugars	Glucose		C ₆ H ₁₂ O ₆	1.00	Representative of carbohydrates
isoprene SOA oxidation product	Sugars	meso-Erythritol		C ₄ H ₁₀ O ₄	1.00	Abundant product of isoprene oxidation
SOA. COA in the gas phase	Carboxylic	Malonic Acid		C ₃ H ₄ O ₄	1.33	COA O/C ranging from 0.1 to 1.3
SOA. COA in the condensed phase	Carboxylic	Suberic acid		C ₈ H ₁₄ O ₄	0.50	
COA in the condensed phase	Carboxylic	Succinic acid		C ₄ H ₆ O ₄	1.00	cooking aerosol
COA in the condensed phase	Carboxylic	oleic acid		C ₁₈ H ₃₄ O ₂	0.11	cooking aerosol

SPARTAN

International Monitoring Network

SPARTAN

SPARTAN: Surface PARTiculate mAtter Network

Sites located worldwide in densely populated cities

PM filter samples – PTFE (teflon) only

PM_{2.5} speciation

PM₁₀ speciation

Light scattering (in-situ nephelometer)

Mission:

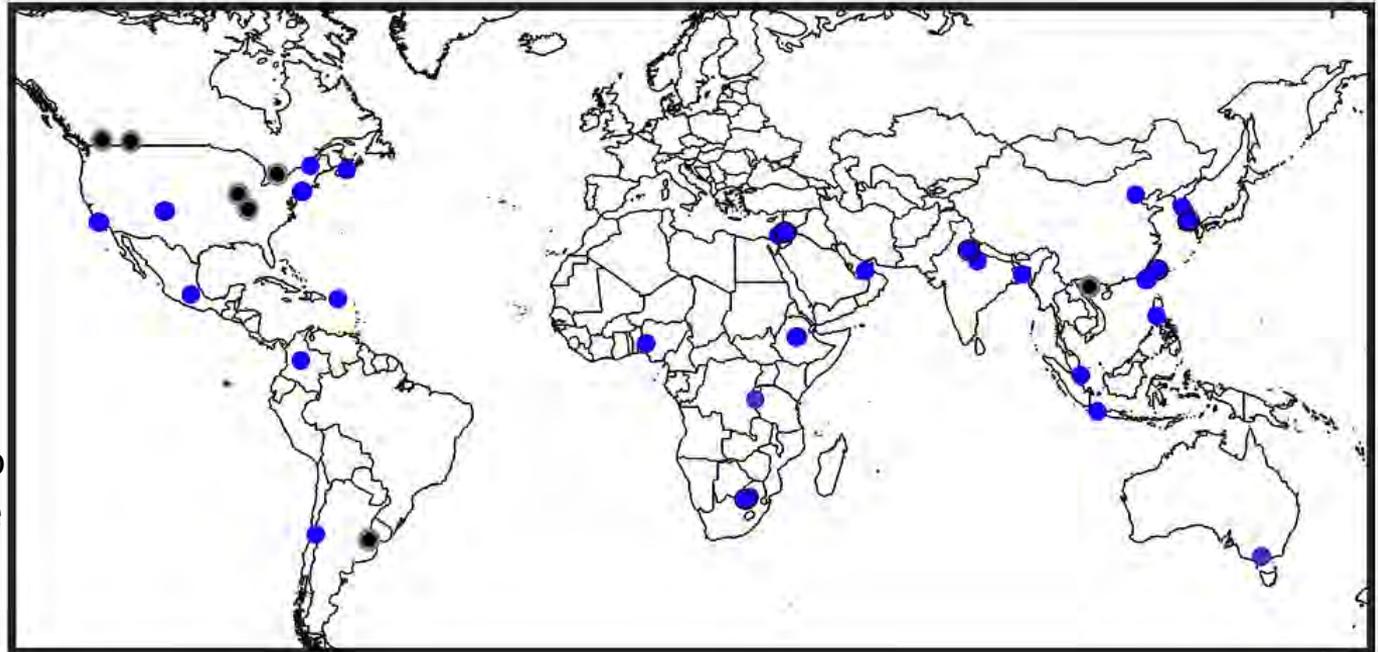
Enhance satellite remote sensing estimates of PM_{2.5} to connect PM_{2.5} composition to health outcomes worldwide

Publically available data (www.spartan-network.org)

Operated by Washington Univ. in St. Louis and Dalhousie, Univ. in Canada

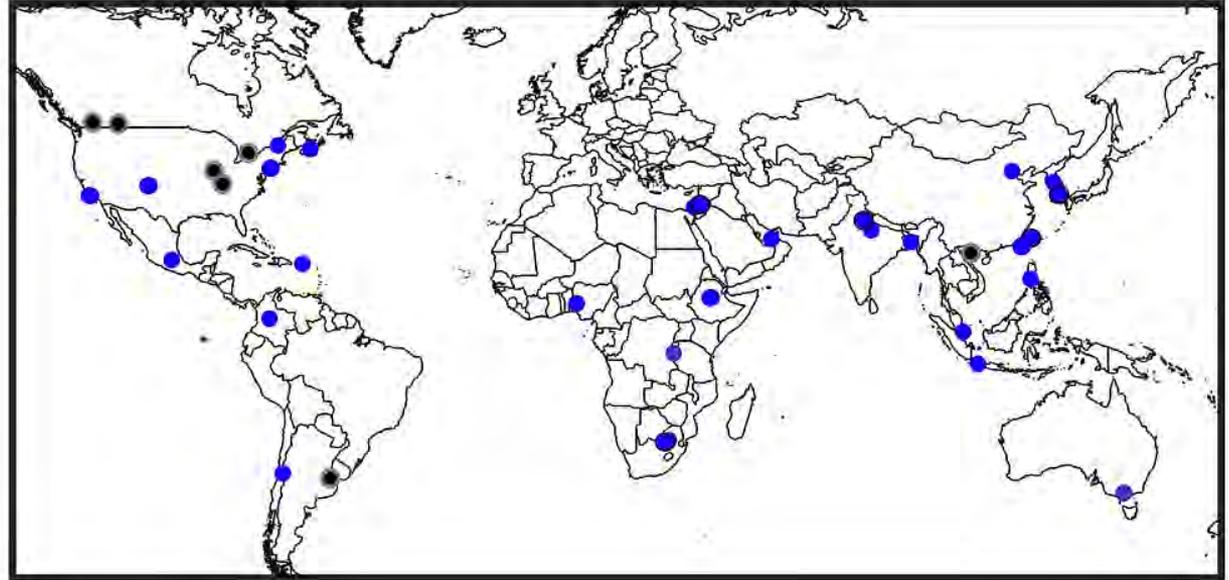
SPARTAN map – 18 active sites

AEAZ Abu Dhabi, UAE
BDDU Dhaka, Bangladesh
CAHA Halifax, Canada
CASH Sherbrooke, Canada
CHTS Beijing, China
CLST Santiago Chile
IDBD Bandung, Indonesia
INKA Kanpur, India
ILNZ Rehovot, Israel
KRUL Ulsan, South Korea
KRSE Seoul, South Korea
MXMC Mexico City, Mexico
SGSU Singapore, Singapore
TWTA Taipei Taiwan
USPA Pasadena, CA, USA
VNHN Hanoi, Vietnam
ZAPR Pretoria, South Africa



SPARTAN map – 7 new (or recently started) sites

ETAD Addis Ababa, Ethiopia
INDH Dehli, India
ILHA Haifa, Israel
ITXX Rome, Italy
TWTA Taipei, Taiwan
USXX Atlanta, GA
ZAPB Johannesburg, SA



Sampling

AirPhoton Sampler – typical operation

PM2.5 – collected intermittently over 9 days

PM10 – collected over 54 days

filter cartridge stays in field for 54 days

6 PM2.5 filters

1 PM10 filter

1 travel blank

5 lpm

MTL PTFE 25 mm

same filters used by
IMPROVE



PM2.5 speciation

Grav mass - MTL chamber (like AQRC)

OC and EC - FTIR at AQRC

Light absorption - by HIPS at AQRC

Elements - Panalytical Epsilon 4 (bench-top instrument at Wash. U.)

Ions - IC analysis (destructive to sample at Wash. U.)

Analyses by ICPMS, advanced MS analysis for organics and others on select samples for research purposes

AQMT and SPARTAN

Filter analysis by FTIR and HIPS

50 filters/month and increasing
~1400 samples analyzed to date

New “Networks” database

FTIR spectra and HIPS (soon) routinely ingested

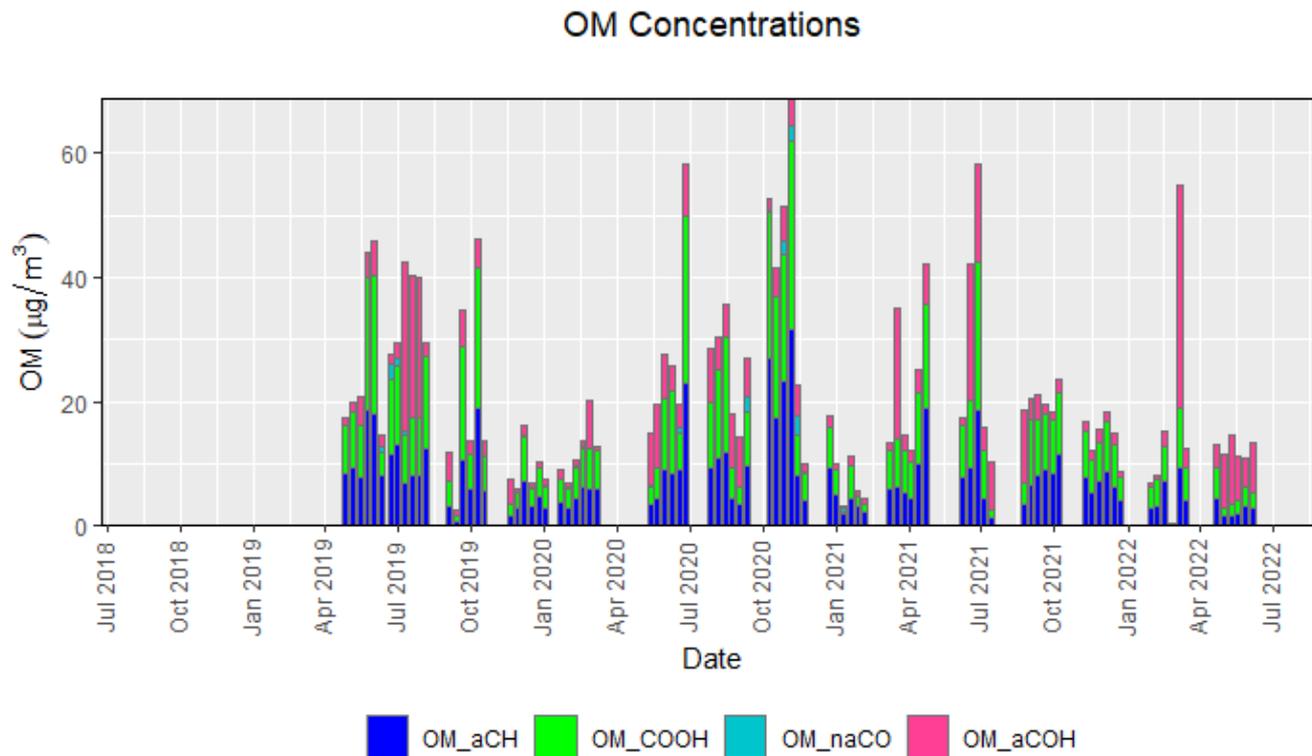
Level 0 validation on data files from SPARTAN and put into database

Naveed Anwar – Fulbright Scholar from Pakistan

PhD student in the Atmospheric Science Department

seasonal and longer term trends in PM composition (functional groups, elements, ions) and sources at some of the SPARTAN sites

AEAZ Abu Dhabi, UAE

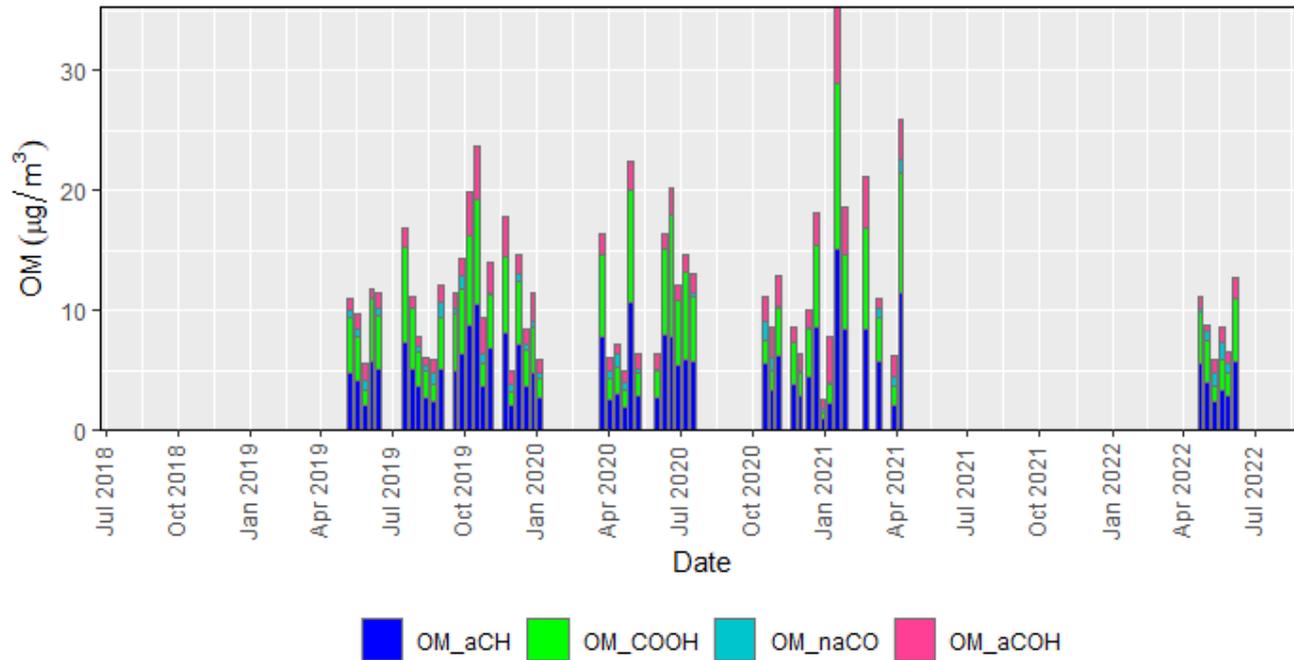


FTIR measurements

- July 2018-July 2022 and ongoing
- Measured using **peak fitting** due to lack of calibration on MTL filters
- Will **resubmit** data based on ASCENT calibration (MTL)
- Also predicting **OC and EC** using IMPROVE data
- Will resubmit OC and EC with data from MAIA

CHTS – Beijing, China

OM Concentrations

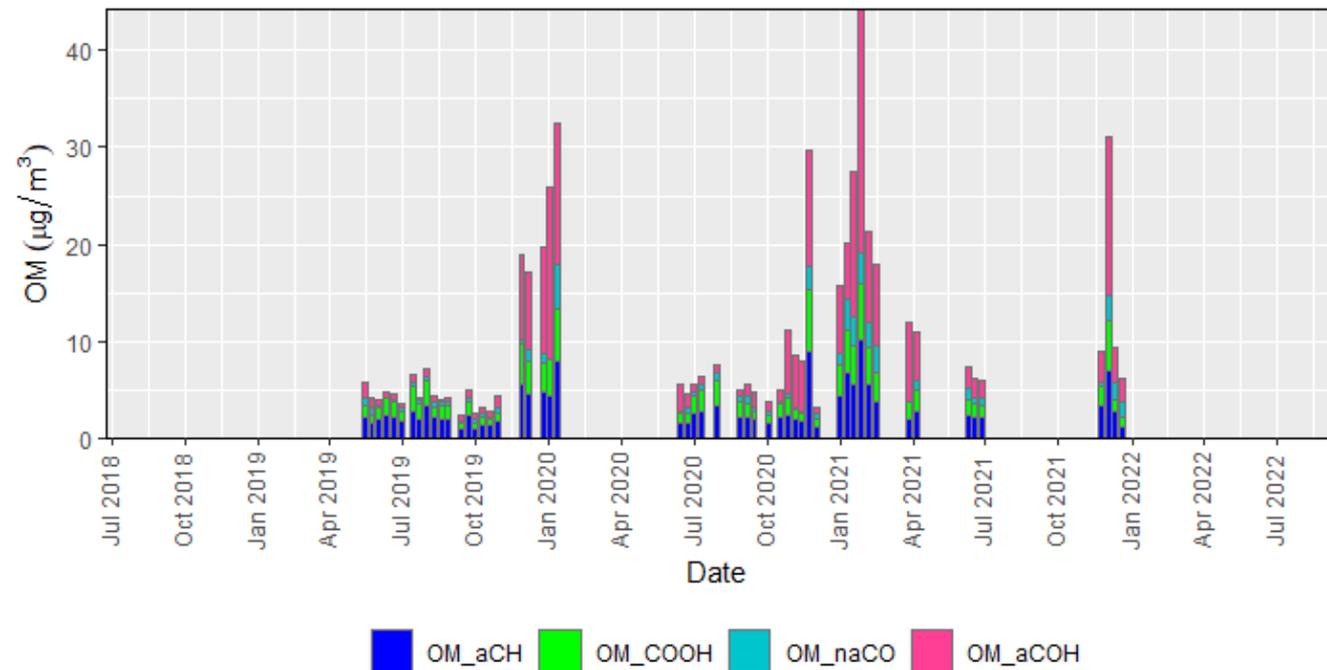


Missing data

- COVID lockdown
- Instrument issues
- Political issues between US and China

NGIL Ilorin, Nigeria

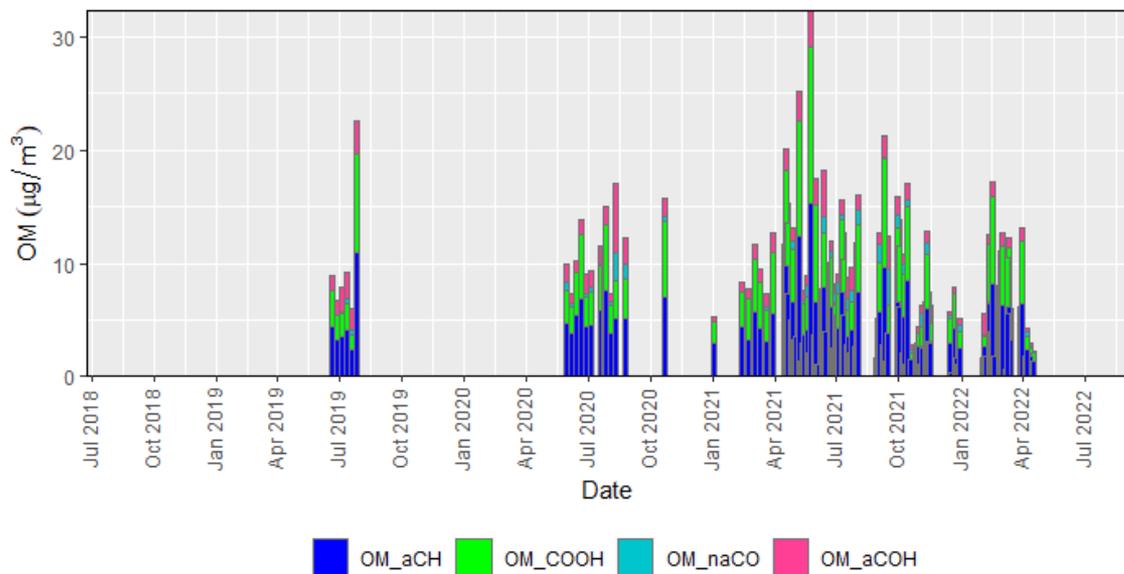
OM Concentrations



- Data from Africa – cool
- High concentrations
- Large seasonal swings
- Lots of missing data

ZAPR Pretoria, South Africa

OM Concentrations



- More data from Africa
- Took sometime to get started
- Now running pretty smoothly

MAIA

NASA Satellite for aerosol composition and health

MAIA – Multi-Angle Imager for Aerosols

- Project began: 2016
- MAIA's objective is to link exposure to **different PM types** with **human health**.
- MAIA applies and extends satellite-based methods to **map speciated PM** in selected cities
- Satellite launch: **~2024**
- Baseline flight mission duration: **3 years**
- Abbey Nastan, JPL - IMPROVE SC in 2019
- Science meeting next week in Pasadena



Hasheminassab, Diner, Dillner et al., AAAR, 2022

Key Elements of MAIA Investigation

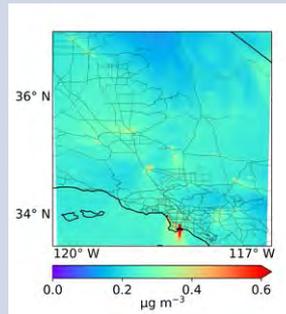


Satellite instrument

(To be completed at
end of October
2022)



Surface monitor network



Chemical transport model



Health records

Public
products

Privacy
protected



Daily concentration maps of PM_{10} , $\text{PM}_{2.5}$,
speciated $\text{PM}_{2.5}$ at 1-km spatial resolution

Epidemiological
studies

Birth, death, and
hospitalization data

Sulfate

Nitrate

OC

EC

Dust

Selected Cities - Current MAIA Target Areas

Primary Target Areas

- USA-LosAngeles
- USA-Atlanta
- USA-Boston
- ESP-Barcelona
- ITA-Rome
- ZAF-Johannesburg
- ISR-TelAviv
- ETH-AddisAbaba
- IND-Delhi
- CHN-Beijing
- TWN-Taipei

Secondary Target Areas

- USA-Hilo
- PAC-OceanStCu
- USA-SanFrancisco
- USA-Phoenix
- USA-Denver
- MEX-MexicoCity
- CAN-Toronto
- PER-Lima
- CHL-Santiago
- PRI-SanJuan
- BRA-SãoPaulo
- SEN-Dakar
- GHA-Accra
- ATL-OceanStCu
- NGA-Lagos
- ZAF-CapeTown
- SRB-Belgrade
- KEN-Nairobi
- ETH-Harar
- KWT-KuwaitCity
- PAK-Karachi
- IND-Chennai
- BGD-Dhaka
- THA-Bangkok
- VNM-Hanoi
- MNG-Ulaanbaatar
- RUS-Yakutsk
- KOR-Seoul
- AUS-Sydney

Calibration/Validation Target Areas

- USA-RailroadValley
- MRT-Mauritania1
- NAM-Gobabeb
- LBY-Libya4

MAIA Investigation is Target Based



Target area dimensions: 360 km x 480 km

Primary Target Areas (PTAs) are chosen for conducting and supporting the MAIA health studies
Secondary Target Areas (STAs) are areas of interest (e.g., cities with major pollution, aerosol source regions, climatically important cloud regimes), but where health studies are not mandated

MAIA Surface PM Monitoring Sites

AirPhoton SS5i PM_{2.5} Sampler (SPARTAN Network)

Haifa, Israel

*Technion Israel Institute
of Technology*



Rehovot, Israel

Weizmann Institute



New Delhi, India

*Indian Institute of
Technology*



Kaohsiung, Taiwan

*Kaohsiung Medical
University*



Taipei, Taiwan

NTUNHS



Johannesburg, S. Africa

*University of
Johannesburg Kingsway
Campus*



MAIA Surface PM Monitoring Sites

Aerosol Mass and Optical Depth (AMOD) Sampler from Colorado State University

Gurugram, India
Amity University



Noida, India
Amity University



Sonipat, India
Indian Institute of Technology



Taichung, Taiwan
Taiwan EPA Station



MAIA at AQRC at UC Davis

- Two IMPROVE sites converted to full IMPROVE sites in 2019 for MAIA
 - Pittsburgh and Atlanta
- Filter analysis by FTIR and HIPS beginning now
 - 50 filters/batch
 - Sampling with AMODs beginning, slow start up
- In first year, collocated quartz/TOR and PTFE filters for FTIR OC and EC calibration
- New “Networks” database
 - FTIR spectra and HIPS will be routinely ingested
 - Level 0 validation on data files from GITHUB
 - Data to be delivered to GITHUB

Summary

Not working

- Ambient nitrate (volatility), Na, Cl, trace elements (not in IR spectra)
- CSN functional groups (flowrate low, thick filters)
- FRM functional groups and species 2017 to current (QR code on filter)

Working on it

- CSN OC and EC
- IMPROVE functional groups
- Higher quality functional groups and OC and EC for SPARTAN and MAIA

Working

- Measuring OC, EC, sulfate, soil elements in IMPROVE
- Functional groups in SEARCH and FRM networks
- Preliminary functional groups and OC and EC for SPARTAN

Funding

NPS Cooperative Agreements

EPA

NSF

SPARTAN

NASA

USAID

EPRI