FT-IR Updates

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IMPROVE Steering Committee, October 17, 2023
Glacier National Park, Kalispell, MT

IMPROVE, CSN, ASCENT, SPARTAN, MAIA FTIR UPDATE

Ann M. Dillner

Air Quality Research Center, UC Davis

IMPROVE Steering Committee, October 17, 2023

Glacier National Park, Kalispell, MT

Projects

- IMPROVE (collecting IR spectra at limited number of sites)
    - functional groups on Pall filters
    - functional group calibration on MTL filters – funded by ASCENT
    - organosulfates with RTI
    - DOE water uptake project
- CSN OC and EC (no longer analyzing filters by FT-IR)
- ASCENT
    - update on network
    - increasing chemical information from high time resolution instrument
- MAIA satellite update and OC and EC measurements
- SPARTAN functional group measurements at international sites

Functional groups in IMPROVE

Jan 2015- June 2018

- All IMPROVE samples analyzed by FTIR
- IMPROVE used Teflon filters by Pall (also sporadically since then)
- Functional group calibrations developed Ruthenburg et al., 2014
- Staff researcher on this project left AQRC - Project on hold

July 2018-current

- IMPROVE using MTL filters
- All samples analyzed through summer 2022, limited sites since then
- Calibration standards under development – funded by NSF ASCENT

IMPROVE – ORGANOSULFUR

RELEVANT TO MANY IMPROVE SITES

Marife Anunciado
former post-doc

Stability of Organosulfur and Organosulfates on IMPROVE filters

- RTI collaboration and funding
- Goal:
  - Assess stability on PTFE filters and
  - Assess suitability of non-destructive measurement by FT-IR
  - Using gravimetry, IC, ICP-OES and FT-IR
  - Timescales and storage relevant to IMPROVE

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https://doi.org/10.5194/amt-16-3515-2023

Atmospheric Measurement Techniques
Open Access
EGU

Stability assessment of organic sulfur and organosulfate compounds in filter samples for quantification by Fourier-transform infrared spectroscopy

Marife B. Anunciado[1], Miranda De Boskey[2], Laura Haines[2], Katarina Lindskog[2], Tracy Dombek[2], Satoshi Takahama[3], and Ann M. Dillner[1]

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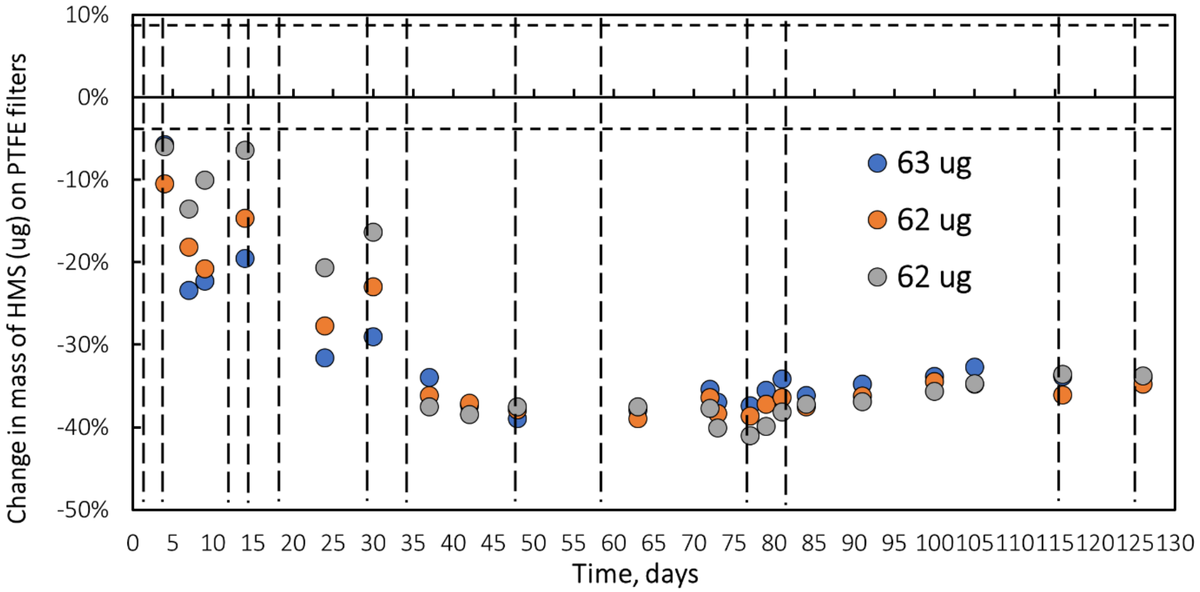
[3]Laboratory of Atmospheric Processes and their Impacts (LAPI), ENAC/IIE, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

Compounds evaluated

- Two organosulfur compounds, to measure specific compounds
  - Methanesulfonic acid (MSA)
    - Tracer for marine aerosol
  - Hydroxymethanesulfonate (HMS)
    - High haze conditions
    - Evidence of HMS in IMPROVE samples (Moch et al., 2020)
    - Difficult to measure (Moch et al., 2020)
- Two organosulfate compounds, measure organosulfate functional group
  - Methyl sulfate (MS) – small, commercially available
  - 2-methyltetrol sulfate (2-MTS) – highly abundant
    - Synthesized by Jason Surratt's group at UNC

HMS mass loss

- HMS loaded onto MTL PTFE filters with atomizer and IMPROVE sampler
- Weighed and scanned by FT-IR over 125 days
- Mass decreases but stabilizes after about a month



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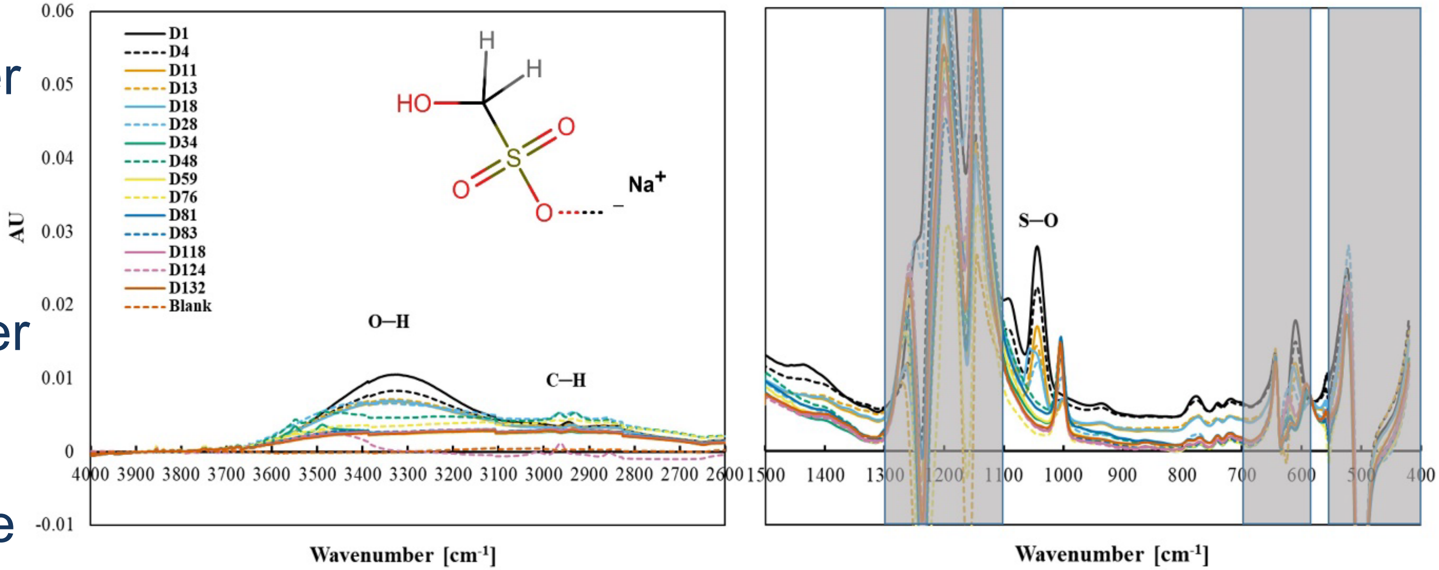
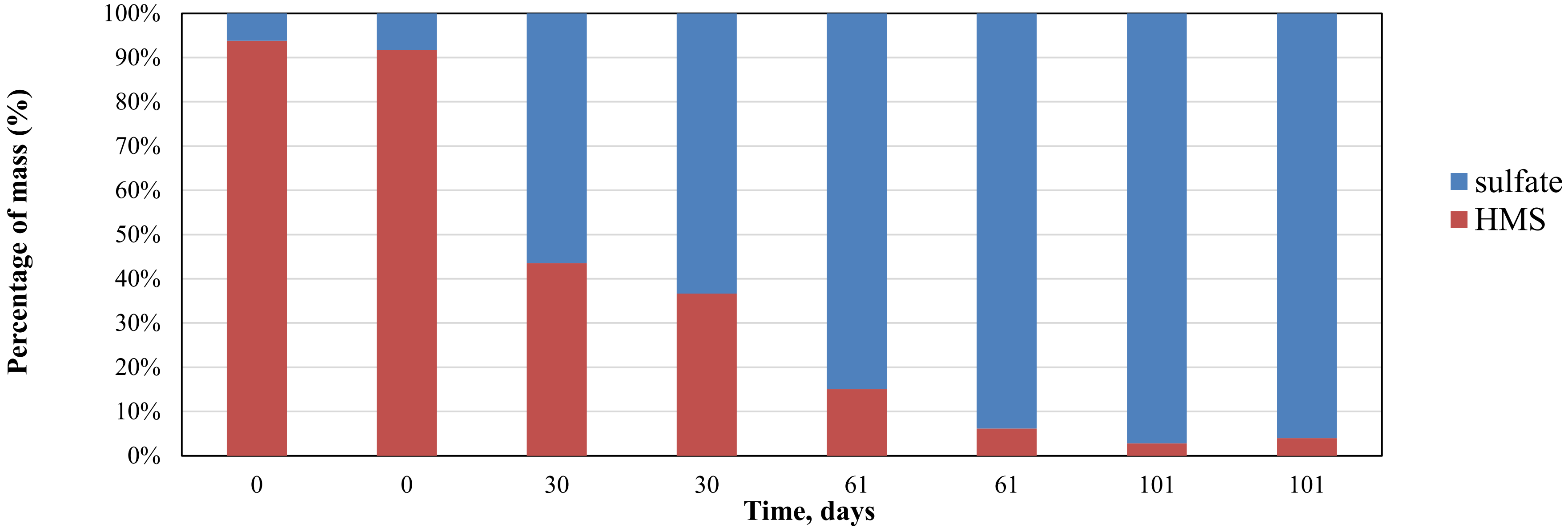
Infrared spectra changes over time in HMS particles

- OH and S-O decrease over time
- New peak appears and increases over time
- New peak likely bisulfate



Change in composition over time by IC



- Conversion from HMS to sulfate/bisulfate corresponds to 40% loss
- Can't measure HMS in IMPROVE filters

Results from other three compounds

- MSA
  - can be measured but all lower bound (some lost during storage)
- Methyl sulfate (organosulfate)
  - stable in mass and composition over time, can be measured
- 2-methyltetrol sulfate (organosulfate)
  - Mass loss (grav) and composition change (FTIR)
  - Likely converts into another organosulfate
  - Possible to measure organosulfates in IMPROVE filters
- Next steps
  - Influence of other compounds on measurements by FT-IR
  - Analyze additional organosulfates and calibrate

IMPROVE RELATED - DOE PROJECT ON WATER UPTAKE BY ORGANICS

Southern Great Plains and IMPROVE sites with high organic/inorganic mass

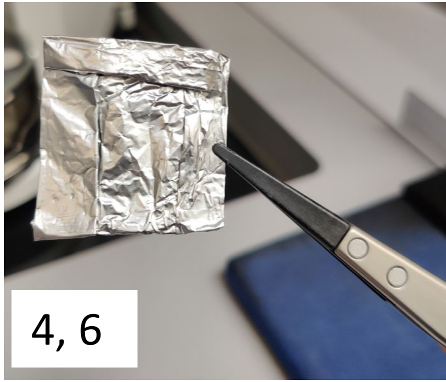
Post-doc Nagendra Raparthi

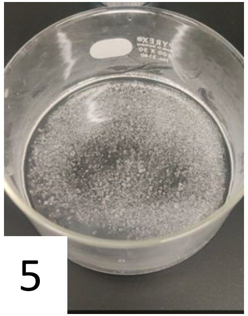
Hygroscopicity and CCN Potential of Organic Aerosol Functional Groups

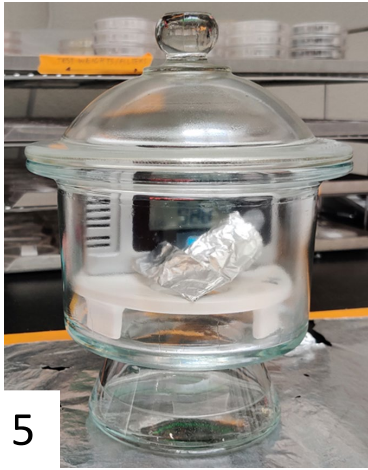
- Hygroscopicity formerly driven by inorganics
- Emission controls of SOx and NOx has increased organic fraction
- Tony Wexler - thermodynamic model for aqueous solutions
- Water uptake depends on functional groups
- Our goal is to validate model for sugars and carboxylic acids in laboratory, chamber and ambient samples at IMPROVE sites (including SOGP and some high organics/low inorganics sites)
- Add to DOE models and e-AIM (Tony's publicly available model that estimates gas/liquid/solid partitioning in aerosols)

Measuring water uptake as function of RH

1. Weigh blank filter
2. Collect organic compound on filter
3. Dry and weigh filter to obtain chemical mass
4. Place filter in open foil pouch, dry and weigh
5. Place filter in pouch in RH controlled dessicator (saturated solutions)
6. After 24 hours, seal pouch and weigh

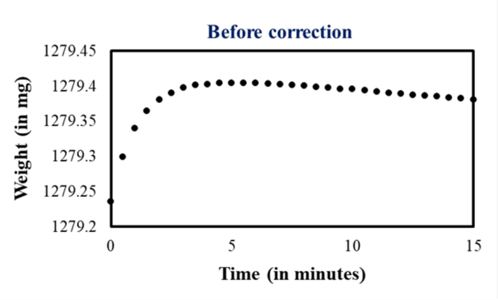


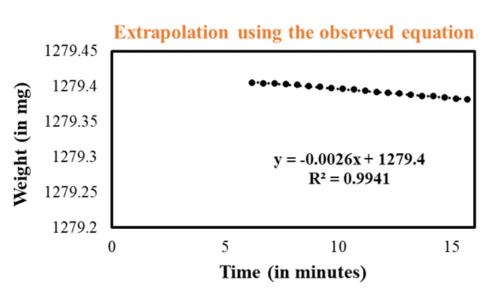


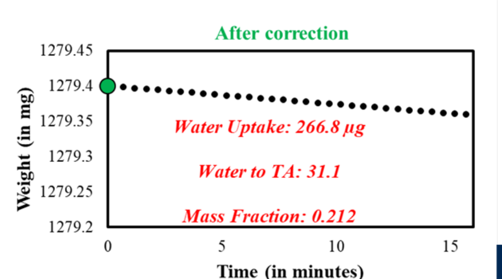


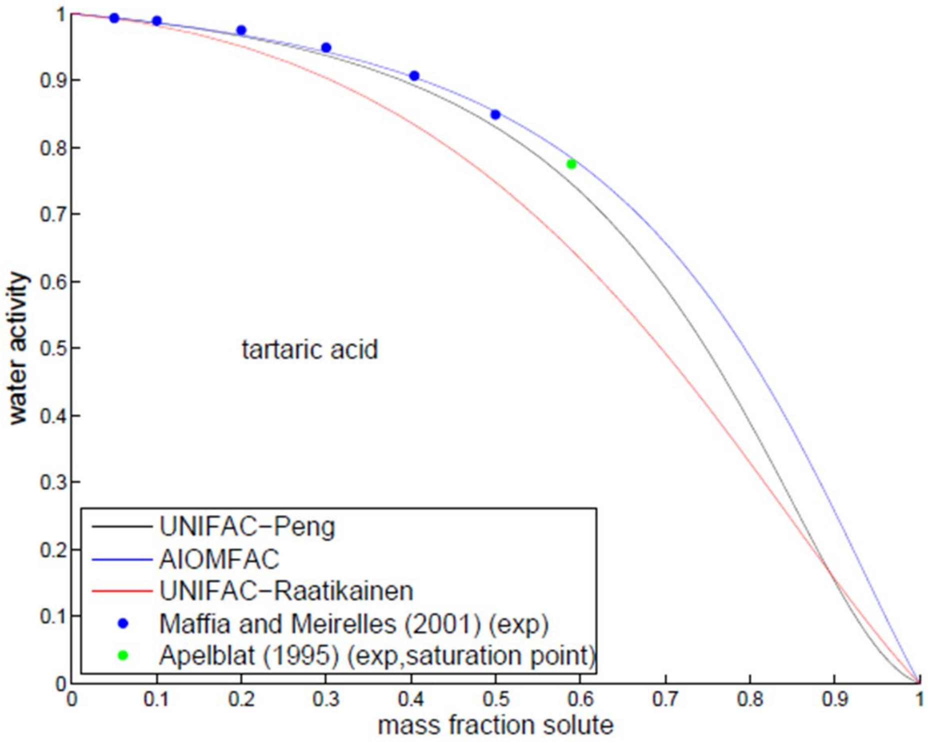
Method validation

Tartaric Acid – 71.6µg (RH: 97%)









Maffia & Meirelles, 2001:

RH = 97.5%, models give 0.19-0.25

Next Steps

Measure water uptake for additional compounds

Collect mixtures in the lab

- FTIR to measure functional group mass
- Measure water uptake at 3 RHs
- Compare to model for individual compounds – revise or validate model

Chamber (PNNL) and ambient IMPROVE samples

- use FTIR to measure functional group mass,
- inorganic mass from IMPROVE
- Measure water uptake in lab at 3 RHs
- Compare/update/validate model

CSN OC AND EC

Post-doc Ana Amiri Farahani

CSN OC and EC

- 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
- Recently identified samples with black dust on quartz filter and samples with no OP removed from data set
    - Number of atypical models decreased from 7 to 3

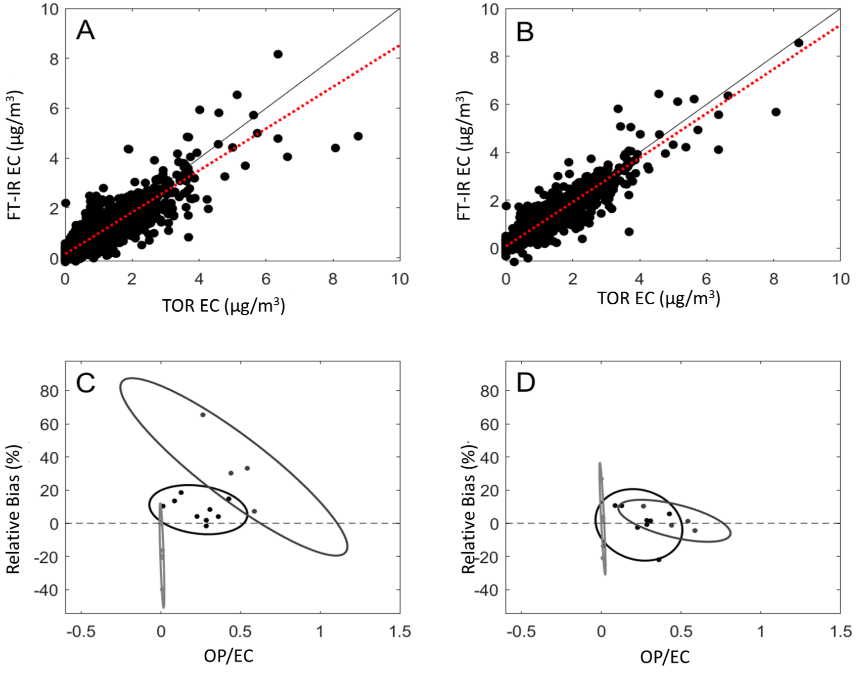
Methods – 1 of 2

- Used data from October 2018 to May 31, 2021
- Split into pre-COVID, COVID and post-COVID time periods
- Identified 18 (~15% of CSN sites) "atypical sites" - those with poor EC prediction

#	SiteName	SiteID	State	3 Clusters	Color Coded
1	Charleston NCore	54-039-0020	WV	2	Pre-COVID, COVID, Post-COVID
2	Rome - Elementary School	13-115-0003	GA	1	Pre-COVID & Post-COVID
3	Birmingham - North Birmingham	01-073-0023	AL	1	COVID & Post-COVID
4	South Alleghany (Liberty)	42-003-0064	PA	3	Post-COVID
5	Sacramento - Del Paso Manor	06-067-0006	CA	1	
6	Zampieri State (Burlington)	50-007-0012	VT	1	
7	Riverside - Rubidoux	06-065-8001	CA	2	
8	Butte-Greeley School	30-093-0005	MT	3	
9	South Dekalb	13-089-0002	GA	1	
10	Johnstown	42-021-0011	PA	1	
11	San Jose - Jackson Street	06-085-0005	CA	1	
12	Los Angeles - North Main Street	06-037-1103	CA	1	
13	Elizabeth Lab	34-039-0004	NJ	1	
14	Parklane (Columbia)	45-079-0007	SC	2	
15	Augusta	13-245-0091	GA	2	
16	Tallahassee Community College	12-073-0012	FL	3	
17	Garinger High School	37-119-0041	NC	3	
18	Gary	18-089-0022	IN	3	

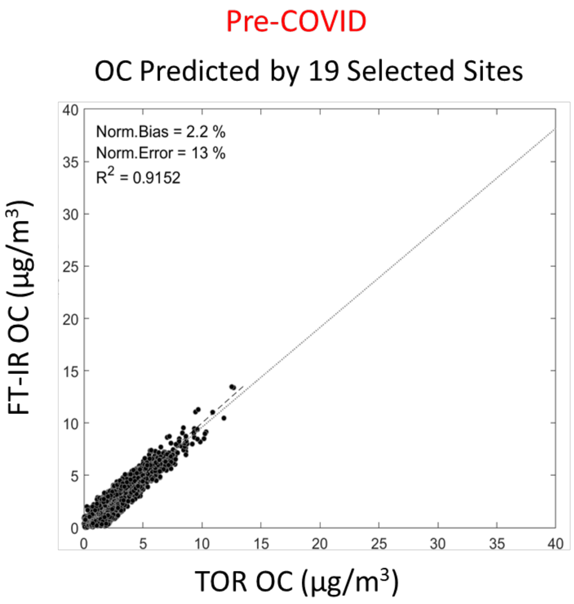
Methods – 2 of 2

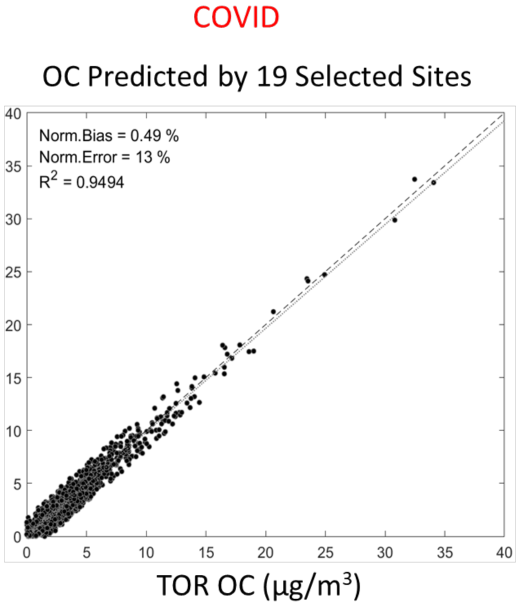
- For EC atyipical sites, developed 3 models
  - 6 calibration sites selected
  - Decreases relative bias
- For EC typical sites, selected 13 calibration sites after grouping by composition
- For OC, used 13 typical and 6 atypical sites to predict all sites

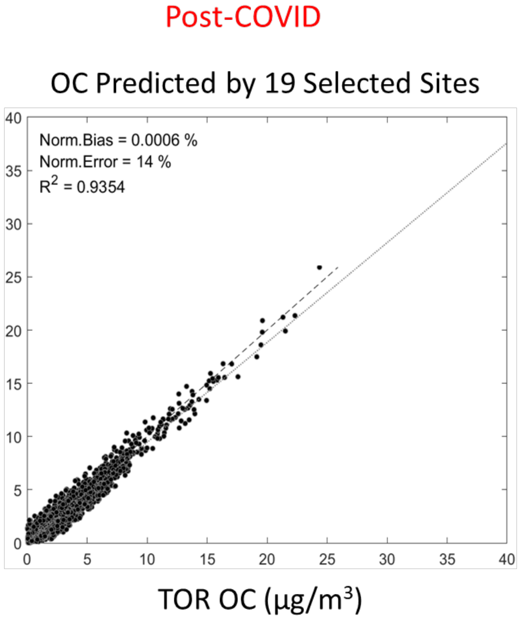


Atypical samples predicted by all atypical sites (A), by 3 atypical models (B). C and D show relative bias for 3 groups for A and B.

OC predictions for all 3 time periods







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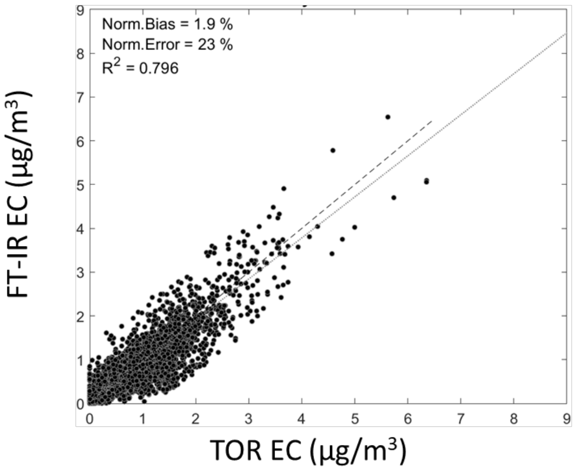
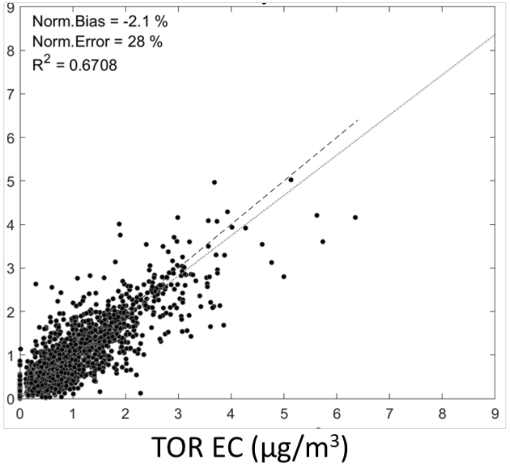
EC

Post-COVID

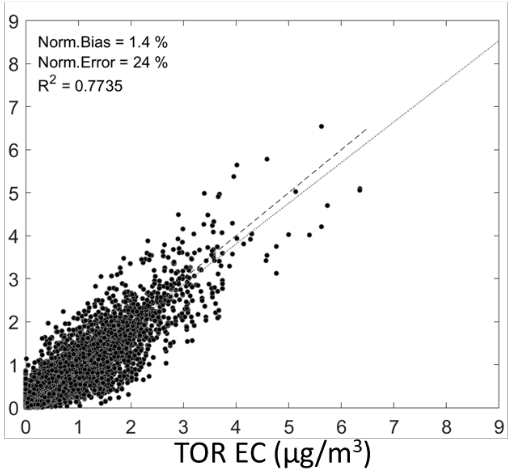
Typical Samples Predicted by 13 Selected Sites

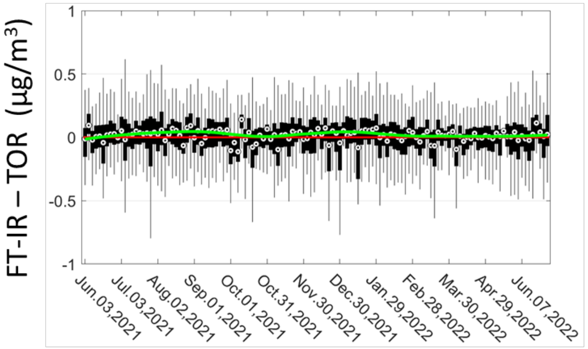


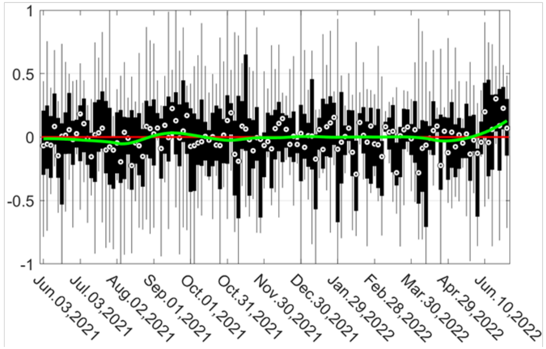
Atypical Samples Predicted by 3 Models

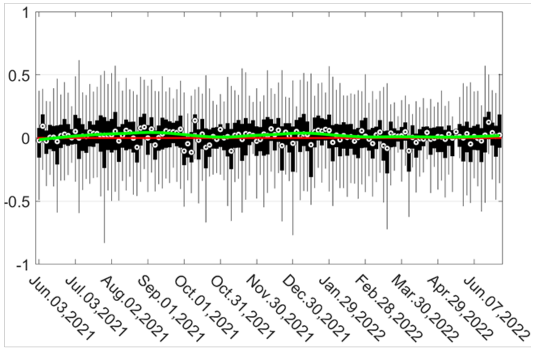


Aggregated (Typical + Atypical)









CSN OC and EC next steps

- Compare to IMPROVE results (published last year)
- Extrapolate to next month with most recent one year of data to mimic network operations
- Document method for possible future use

ASCENT – NEW NETWORK AT IMPROVE AND CSN SITES

Ann Dillner – ASCENT Steering Committee, PI of organics data enhancement sub project

Na Mao – post-doc on organics data enhancement sub project

Sean Raffuse – ASCENT data management lead,

Veronica Scott and Rudi DeMarco – Sean's team members contributing to data management project

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

- **A**tmospheric **S**cience and **C**hemistry m**E**asurement **N**e**T**work
- Long-term
  - 3 year NSF infrastructure grant - October 2021
  - 10+ year NSF funding to NCAR - October 2025
- Ground- based
  - 12 sites (map on following page)
  - Leverage existing measurements, infrastructure, personnel
- High-time resolution
  - Four instruments with minutes to hours resolution
- Air Quality Monitoring Network
  - Focused on PM2.5

ASCENT
Atmospheric Science and Chemistry mEasurement NeTwork

ASCENT: Atmospheric Science and Chemistry mEasurement NeTwork

IMPROVE sites:
Joshua Tree NP, CA
Yellowstone NP, WY
Great Smoky Mountain NP, NC

CSN/NCORE sites:
Rubidoux, CA
La Casa, Denver, CO
Queens College 2, NYC, NY

IMPROVE/CSN:
Lawrenceville, Pittsburgh, PA
South DeKalb, Atlanta, GA
Cheeka Peak/Makah, WA

NEON: Delta Junction, AK
SCAQMD: Los Angeles - Pico Rivera, CA
HNET: Houston, TX

ASCENT Instrumentation

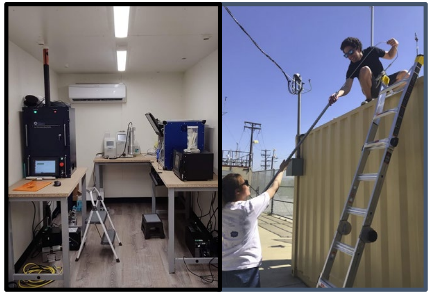
Instrument	Model and Manufacturer	Measurements
Aerosol Chemical Speciation Monitor (ACSM), $PM_{2.5}$	ToF-ACSM, Aerodyne Research	Organics, sulfate, nitrate, ammonium, chloride
Xact, $PM_{2.5}$	625i, Cooper Environmental	Trace metals: Sb, As, Ba, Cd, Ca Cr, Co, Cu, Fe, Pb, Hg, Mn, Ni, Se, Ag, Sn, Ti, Tl, V, Zn, more available
Aethalometer, $PM_{2.5}$	AE33, Magee Scientific	Wavelength-dependent absorption; black and brown carbon
Scanning Mobility Particle Sizer (SMPS), PM_1	3938W89, TSI	Particle number size distribution, number concentration

Slide courtesy of Sally Ng, AAAR 2023 presentation

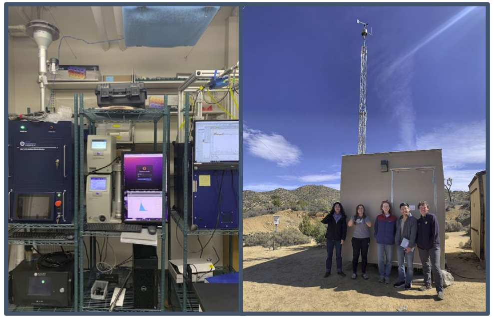
Instrument Delivery and Installation

- All instruments delivered to universities by Jan 2023
- All instruments running at 10 sites since Spring/Summer 2023, Joshua Tree and Houston this fall
- Also deployed low-cost sensors (PurpleAir, QuantAQ MODUAIR-PM) @ all ASCENT sites and MODUAIR at selected sites

Above: South DeKalb Atlanta; Below Rubidoux

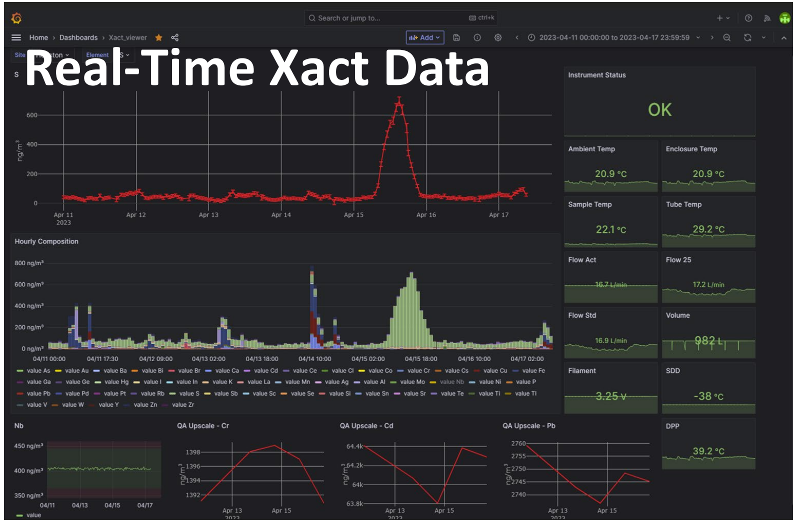


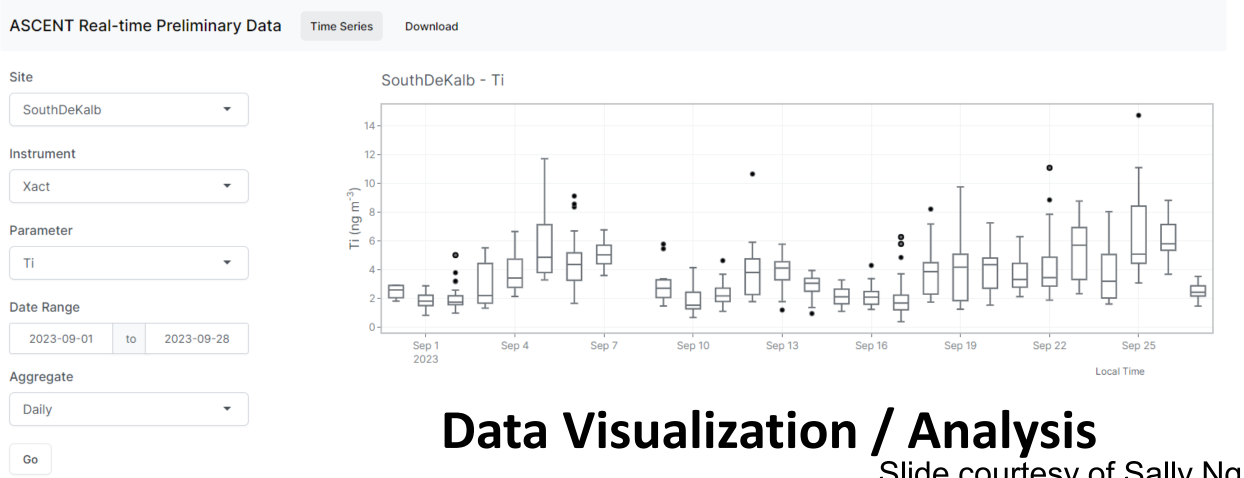
Above: Pittsburgh Lawrenceville;
Below: Queens College



Above: Joshua Tree NP; Below: Great Smoky Mountains NP

Slide courtesy of Sally Ng, AAAR 2023 presentation



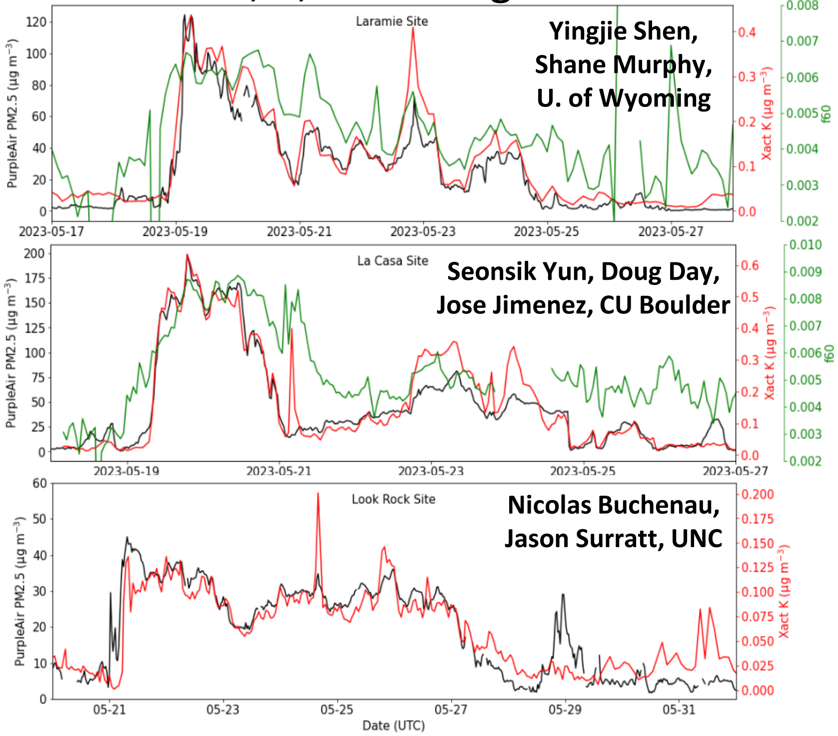


Data Visualization / Analysis

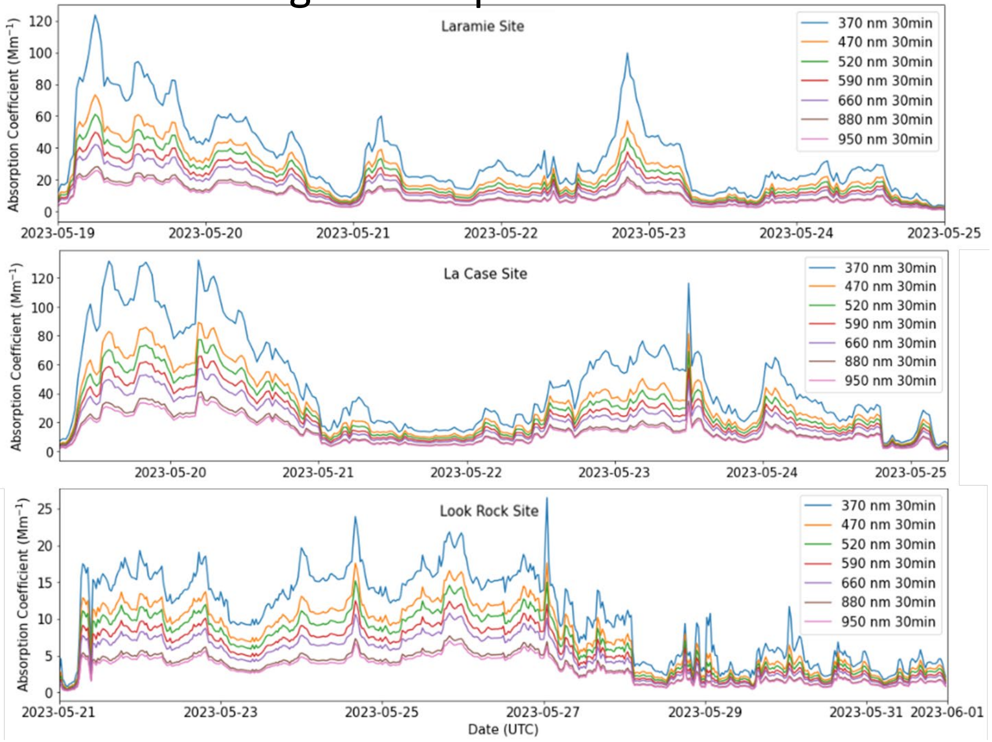
Slide courtesy of Sally Ng, AAAR 2023 presentation

Wildfire Event – Wyoming, Colorado, North Carolina

PM, K, ACSM organics



Light absorption



Slide courtesy of Sally Ng, AAAR 2023 presentation

Collaborations

- ASCENT annual meeting (5/22-23) and workshop (5/24-25), > 100 attendees, AAAR

- **Instrument comparison**
  - **TCA-08** (CARB) @ Pico Rivera and Rubidoux
  - **TARTA** metals instrument (Tony Wexler, UC Davis, San Diego State University; Hanyang Li) @Pico Rivera

- ASCENT-like sites
  - Wilmington, CA - SCAQMD (**Payam Pakbin; Mohammad Sowlat**): EPA Enhanced Air Quality Monitoring for Communities grant
  - Barbados - NSF MRI Cassie Gaston (U. of Miami),
  - Great Smokies site NSF MRI Bob Swarthout and James Sherman (Appalachian State U.)

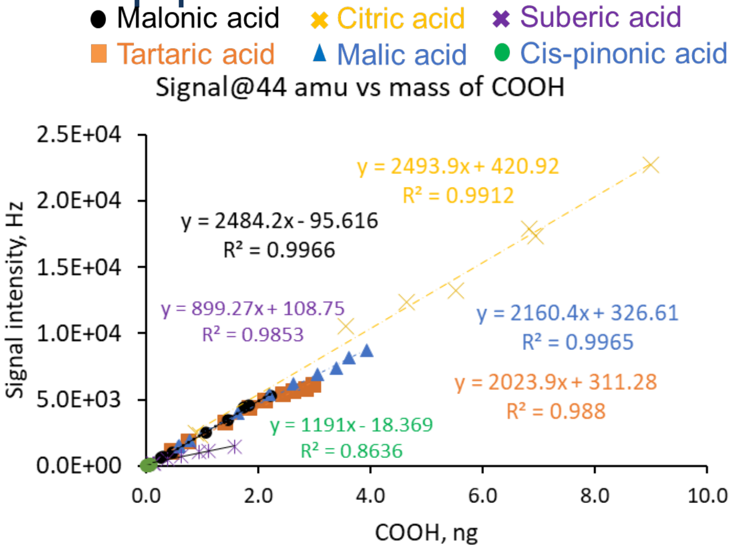
- Ongoing discussions with ACTRIS (European network), MAIA, SPARTAN, DOE AMF3 deployment at SIPS teams

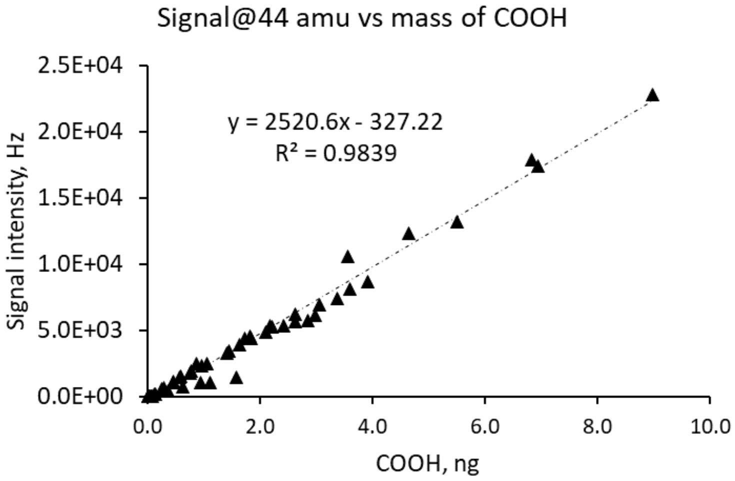
Slide courtesy of Sally Ng, AAAR 2023 presentation

FT-IR ASCENT projects

- Goal: increase chemical resolution of ACSM
- Measure organic functional groups by FT-IR in parallel with ACSM for laboratory mixtures, chamber samples and ASCENT ambient samples
- Develop parameterizations of ACSM data

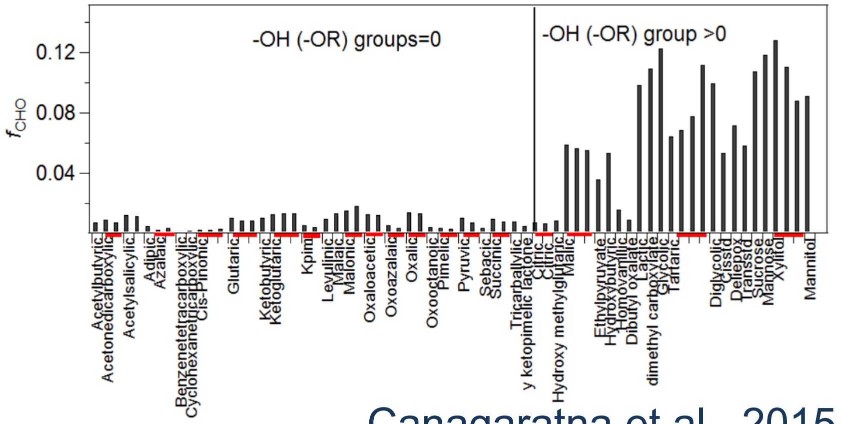
Post-doc Na Mao



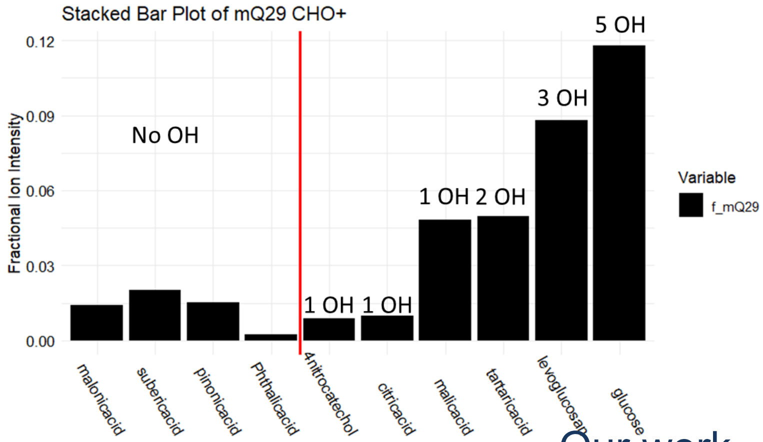


Quality Assurance of ACSM data

- Compounds with increasing OH have increasing fraction of CHO ion in MS
- Standards analyzed by ACSM at UC Davis show same pattern
- Next Steps
    - Analyze mixtures
    - Chamber and ambient samples at ASCENT sites – measure FGs with FTIR
    - Develop parameterizations to relate FGs to MS, building on Yazdani, Takahama et al., 2022



Canagaratna et al., 2015



Our work

SPARTAN AND MAIA

International Monitoring Network

Graduate student and Fulbright Scholar
Naveed Anwar

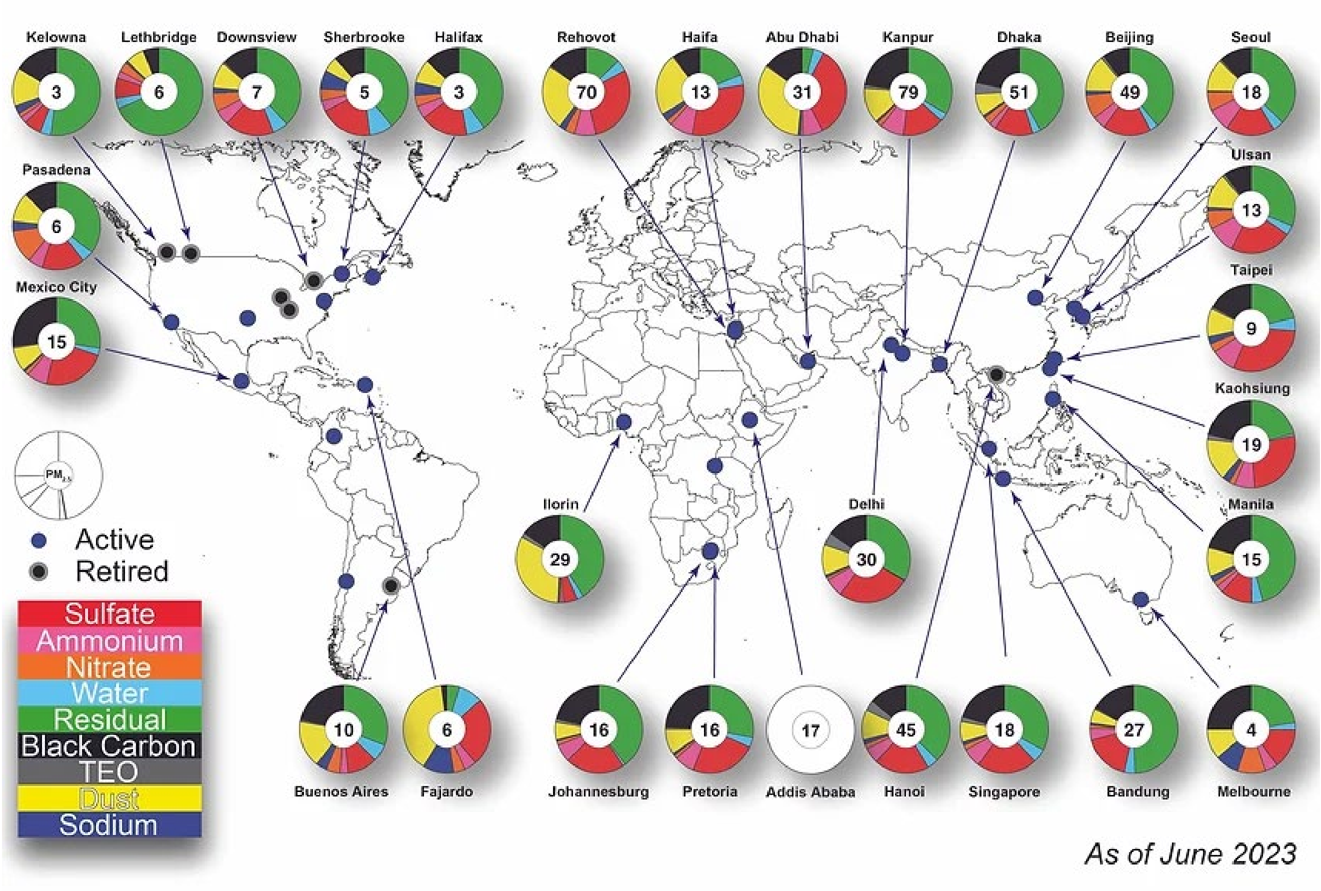
MAIA – Multi-Angle Imager for Aerosols

- MAIA's objective is to link exposure to different PM types with human health around the globe.
- Project began: 2016; Satellite launch: ~2025
- Baseline flight mission duration: 3 years
- Italian Space Agency (ASI) provides host spacecraft, launch, and complementary science.
- Additional PM sampling: AMOD (CSU) and SPARTAN
- UC Davis provides OC, EC, organic functional groups using FTIR and light absorption by HIPS

SPARTAN: Surface PARTiculate mAtter Network

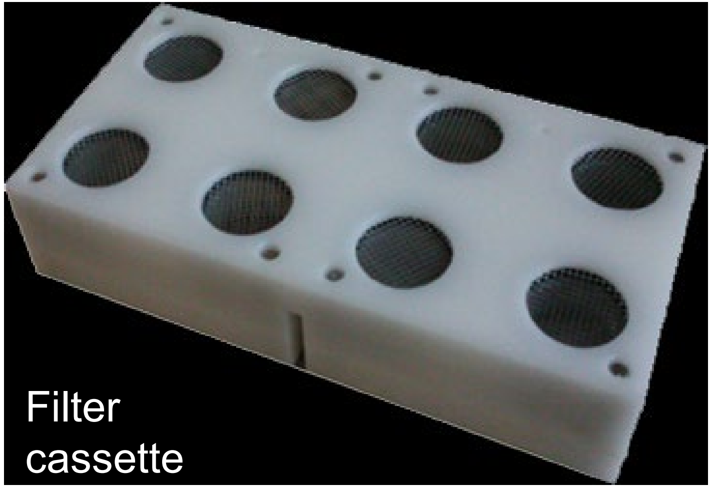
- Existing international network
- Sites located worldwide in densely populated cities
- PM filter samples – PTFE (teflon) only
  - Gravimetry for mass, XRF for elements, FTIR for carbon, HIPS for absorption, IC for ions
- Light scattering (in-situ nephelometer)
- Mission:
  - Enhance satellite remote sensing estimates of PM2.5 to connect PM2.5 composition to health outcomes worldwide
- Publically available data (www.spartan-network.org)
- Operated by Washington Univ. in St. Louis

SPARTAN map


Kelowna
3
Lethbridge
6
Downsview
7
Sherbrooke
5
Halifax
3
Rehovot
70
Haifa
13
Abu Dhabi
31
Kanpur
79
Dhaka
51
Beijing
49
Seoul
18
Pasadena
6
Mexico City
15
Ulsan
13
Taipei
9
Kaohsiung
19
Manila
15
Ilorin
29
Delhi
30
PM2.5
Active
Retired
Sulfate
Ammonium
Nitrate
Water
Residual
Black Carbon
TEO
Dust
Sodium
10
Buenos Aires
6
Fajardo
16
Johannesburg
16
Pretoria
17
Addis Ababa
45
Hanoi
18
Singapore
27
Bandung
4
Melbourne
As of June 2023

Sampling

- AirPhoton Sampler
- PM2.5
  - collected intermittently over 9 days
  - collected 1 in 3 days with MAIA satellite
- PM10
- Cassette
  - 6 PM2.5 filters
  - 1 PM10 filter
  - 1 travel blank
- 5 lpm
- MTL PTFE 25 mm
  same as IMPROVE



Filter cassette

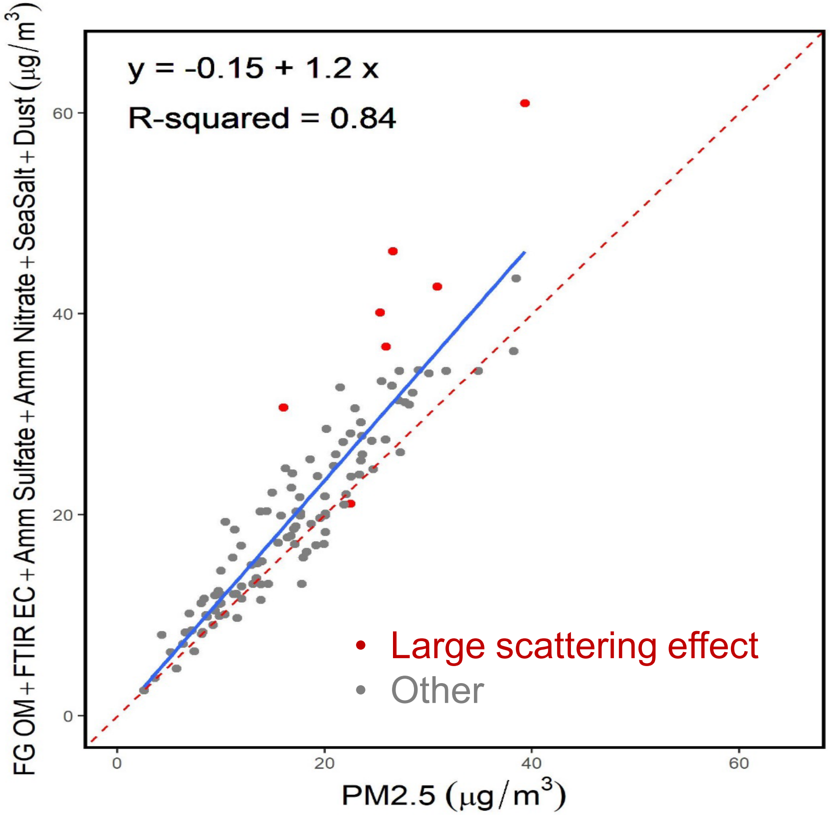
AirPhoton Sampler

FT-IR research conducted for SPARTAN

1. Measure OC and EC using IMPROVE filters and collocated AMOD samples at international sites as calibration
2. Evaluate and improve FT-IR functional group measurements for international sites
3. Evaluate chemical composition and sources of PM at Pretoria, South Africa SPARTAN site

Quality Assurance of Functional Groups

- Evaluate OM measurements by comparing RCFM to gravimetric for Pretoria data
- Correlation reasonable but biased high
- Identified 7 samples with high sulfate/mass ratios and key spectral features suggesting that the spectra are anomalous (scattering)



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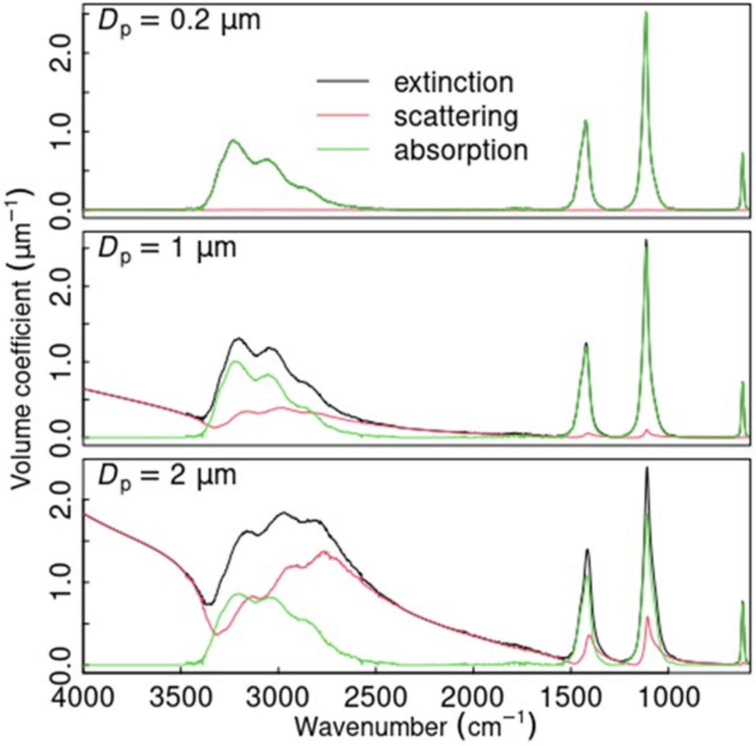
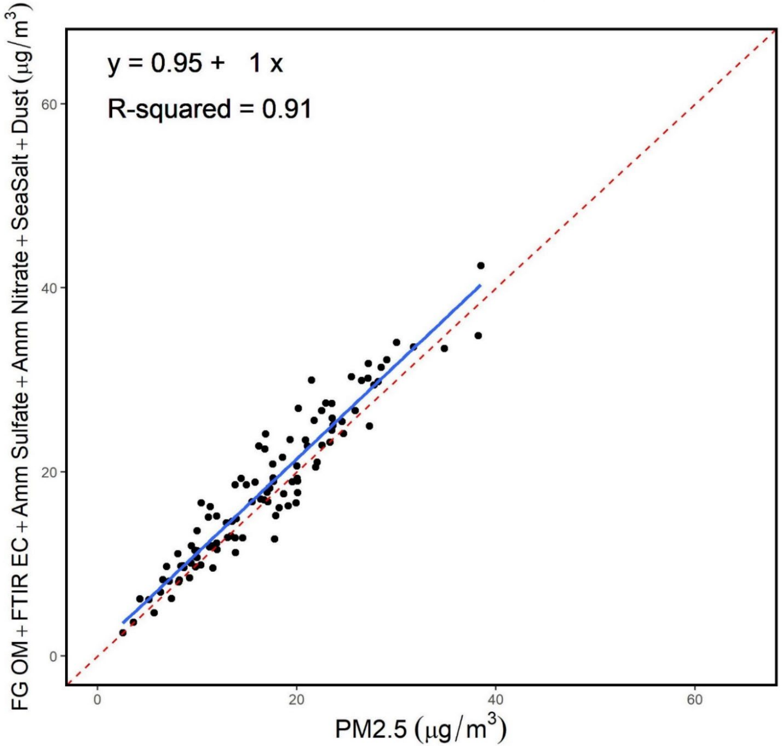
Scattering effects



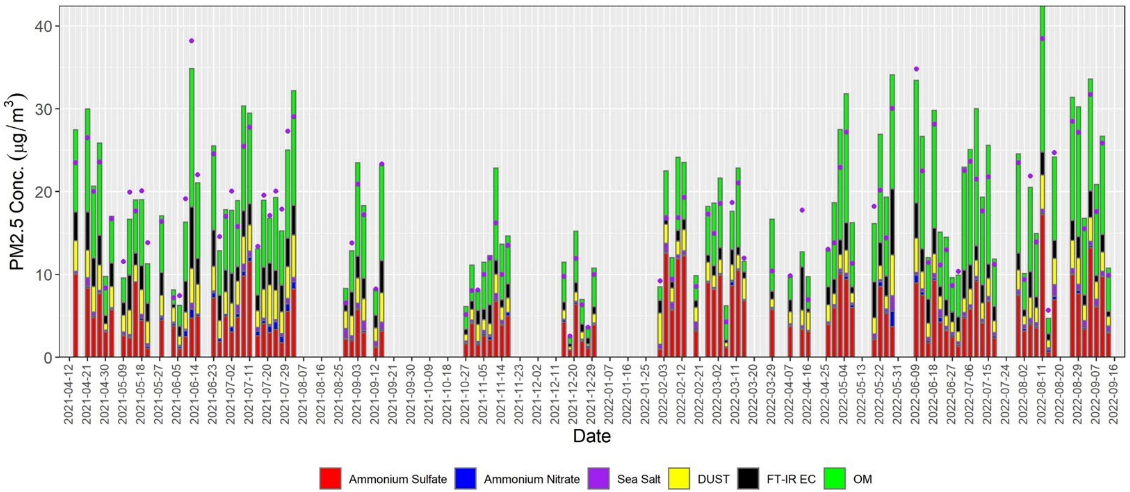
Identified C=O as minimally impacted



Samples with mild impacts – use C=O not cOH to measure COOH

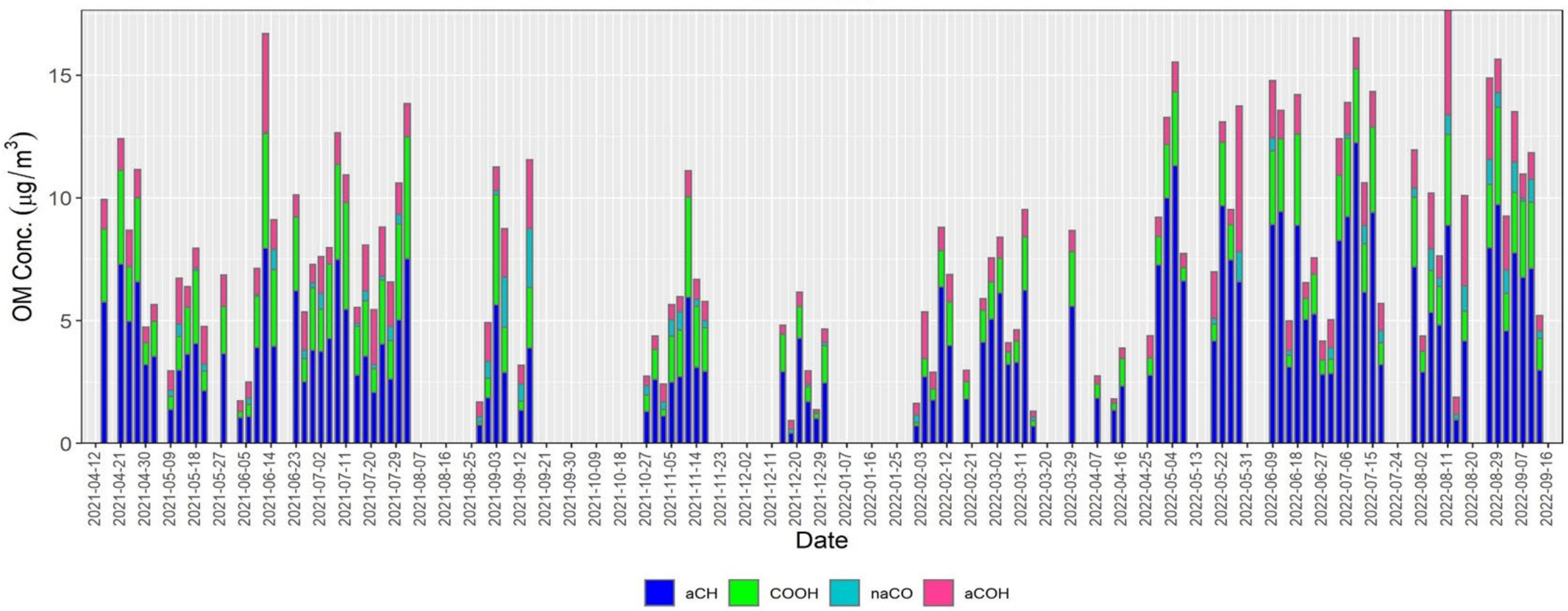
Pretoria, South Africa

- 3.3 million people
- Middle income country
- Data set from 4/21 to 9/22
- Sampling 1 in 3 days for MAIA



- Fairly complete data set
- Sulfate and OM dominated

Functional group data for Pretoria



- Dominated by aCH (primary aerosol) and COOH (highly oxidized)
- Next steps: evaluate seasonality of composition and source apportionment

Projects

- IMPROVE (collecting IR spectra at limited number of sites)
    - functional groups on Pall filters – staff person left, on hold
    - functional group calibration on MTL filters – funded by ASCENT
    - organosulfates with RTI – published, further work to measure
    - DOE water uptake project – just beginning
- CSN OC and EC (no longer analyzing filters by FT-IR) – network ops
- ASCENT
    - update on network – instruments installed, data flowing
    - increasing chemical information from high time resolution instrument – QC of data, prelim results
- MAIA – satellite to launch 2025
- SPARTAN – functional group measurements, international, Pretoria

Funding

NPS Cooperative Agreements

EPA

DOE

NSF

SPARTAN

NASA/JPL

USAID

Measuring carbon with FTIR – updates

Toward “universal” calibrations with infrared spectroscopy

Satoshi Takahama
Laboratory for Atmospheric Processes and their Impacts
Ecole Polytechnique Fédérale de Lausanne (EPFL)

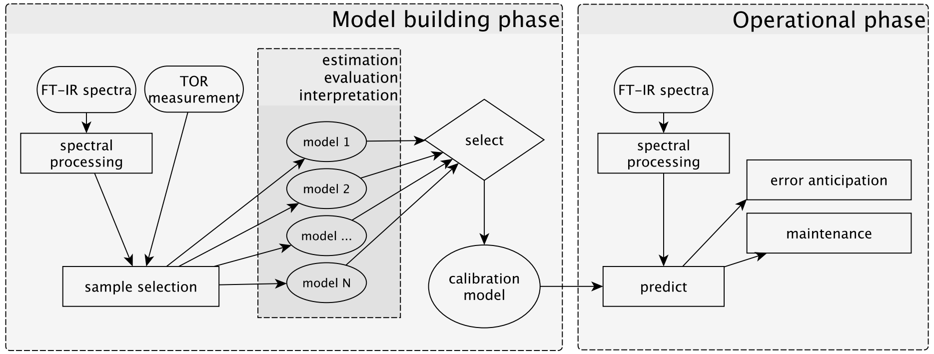
IMPROVE Steering Committee Meeting
Oct 17, 2023

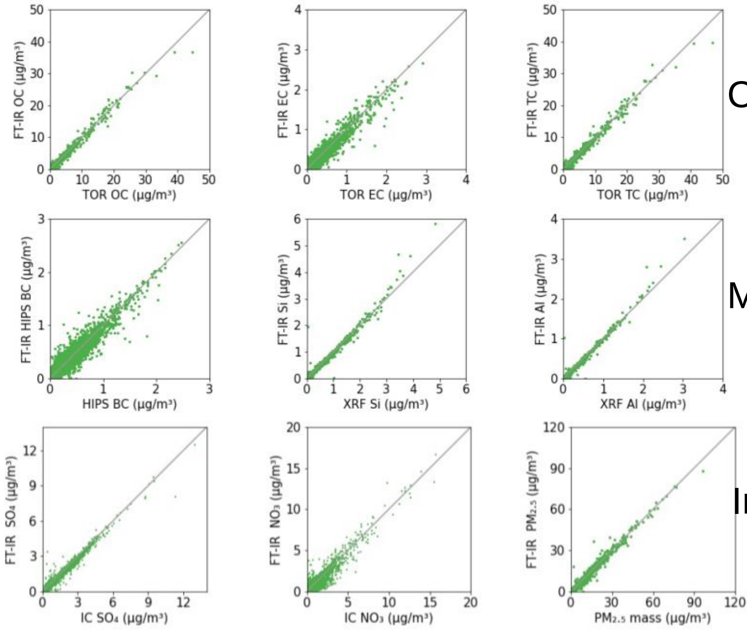
Spectroscopic methods for ground-based atmospheric monitoring (non-exclusive)

	UV/Vis/NIR	mid-IR
Gas-phase	DOAS [differential optical absorption spec.] CRDS [cavity ringdown spec.] CAPS [cavity attenuation phase shift spec.] Standard gas measurements Passive FTIR (TCCON)	DIAL [differential infrared absorption lidar] TDLAS [tunable diode laser absorption spec.] Open Path FTIR Long-path IR Passive FTIR (NDACC) Extractive FTIR (EPA Method 320)
Particle phase	MAAP [multi-angle absorption spectrometer] SP2 [single particle soot photometer] CAPS Nephelometer (IMPROVE) Aethalometer (ASCENT) Lidar (AERONET)	FTIR of $PM_{2.5}$ (SPARTAN, MAIA, ASCENT…)

FTIR of $PM_{2.5}$

Collocated measurements





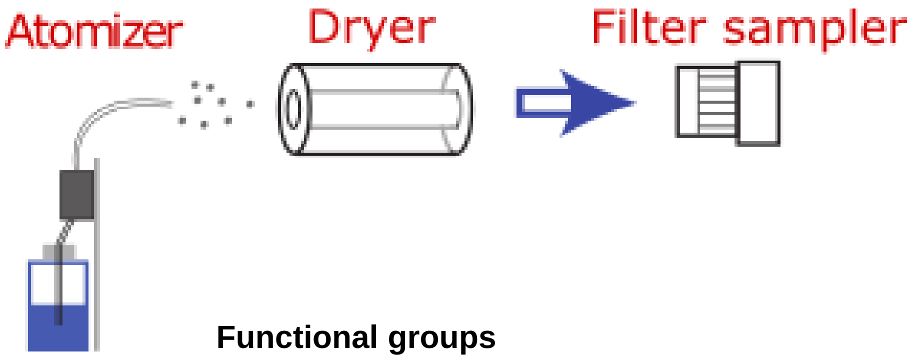
Carbon

Mineral dust

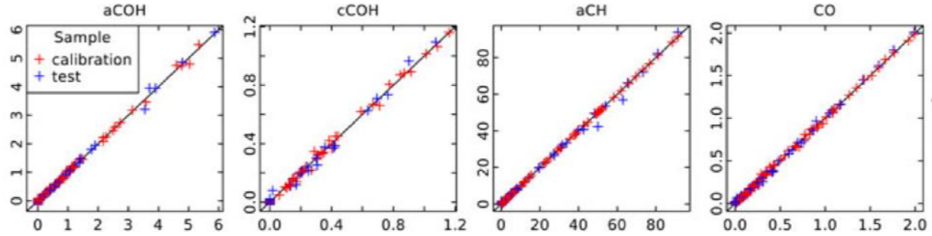
Inorganic salts, $PM_{2.5}$

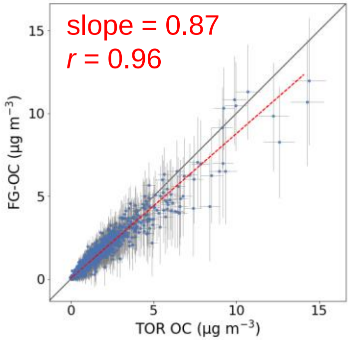
Takahama et al., *Atmos. Meas. Tech.*, 2019
Debus et al., *Atmos. Meas. Tech.*, 2021

Laboratory calibrations



Functional groups





Ambient OC

Ruthenburg et al., *Atmos. Environ.*, 2014
Takahama and Dillner, *J. Chemometrics*, 2015
Bürki et al., *Atmos. Meas. Tech.*, 2020

Current challenges

- Many calibration models, specialized for each task
  - Separate models built with
    1. laboratory standards
    2. ambient samples
  - Separate models for each species
  - PTFE interference handled ad hoc
- Need to address limitations in generalizability

Solution

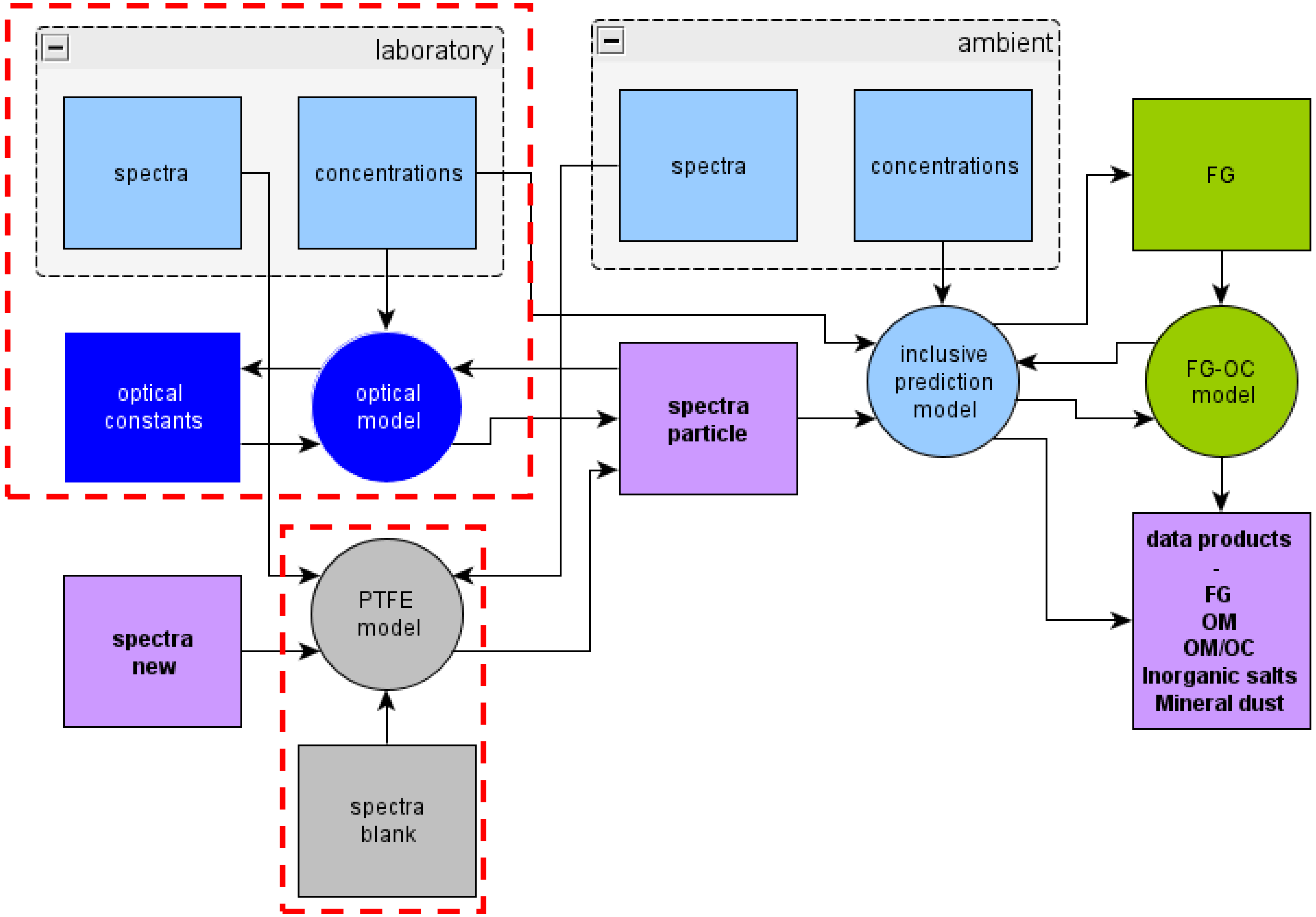
- Model for PTFE
- Single model for multiple calibrations

Project *CHEMSPEC*
with Ann Dillner, Athansios Nenes
and
the Swiss Data Science Center

SDSC

Francois Kamper
Ekaterina Krymova
Guillaume Obozinski

Making use of available data



Available data (spectra from Dillner group)

- Several hundred laboratory spectra with reference measurements
- Analytical and field blanks
- 170,000+ spectra with collocated measurements

Overall scope

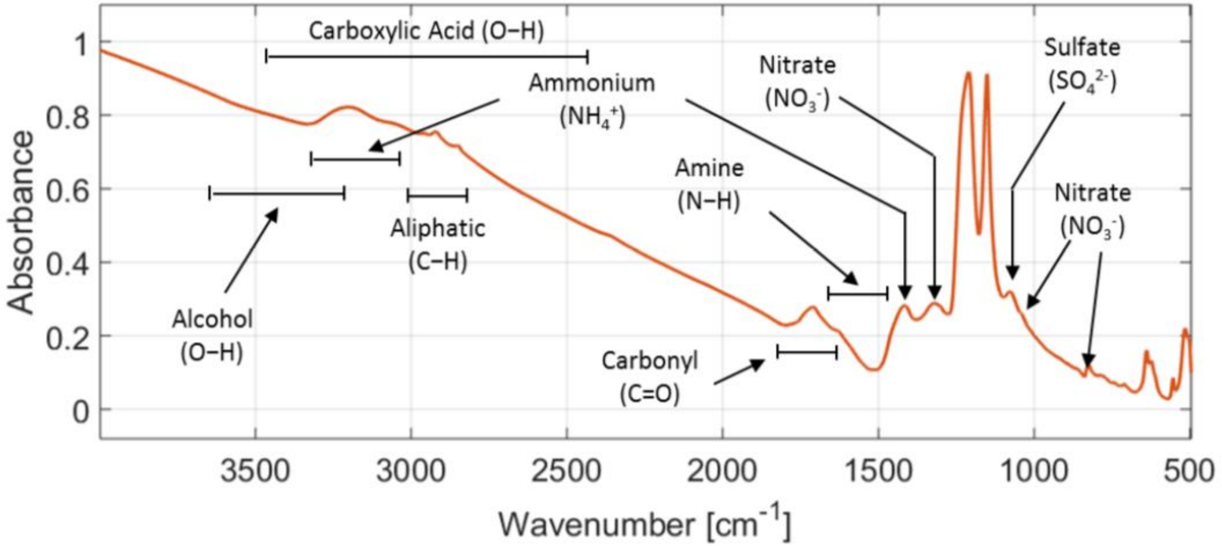
- same model for laboratory and ambient
- same model for all species
- enable use of external data for calibrations

Focus today on red boxes

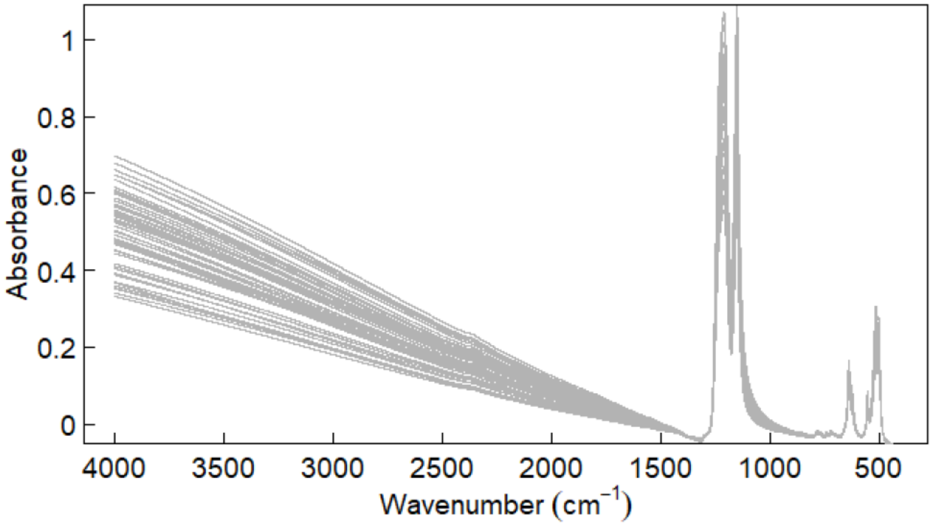
- obtaining particle spectra
- relating to mid-infrared optical constants

Obtaining particle spectra
Eliminating PTFE (polytetrafluoroethylene) interference

Example sample filter



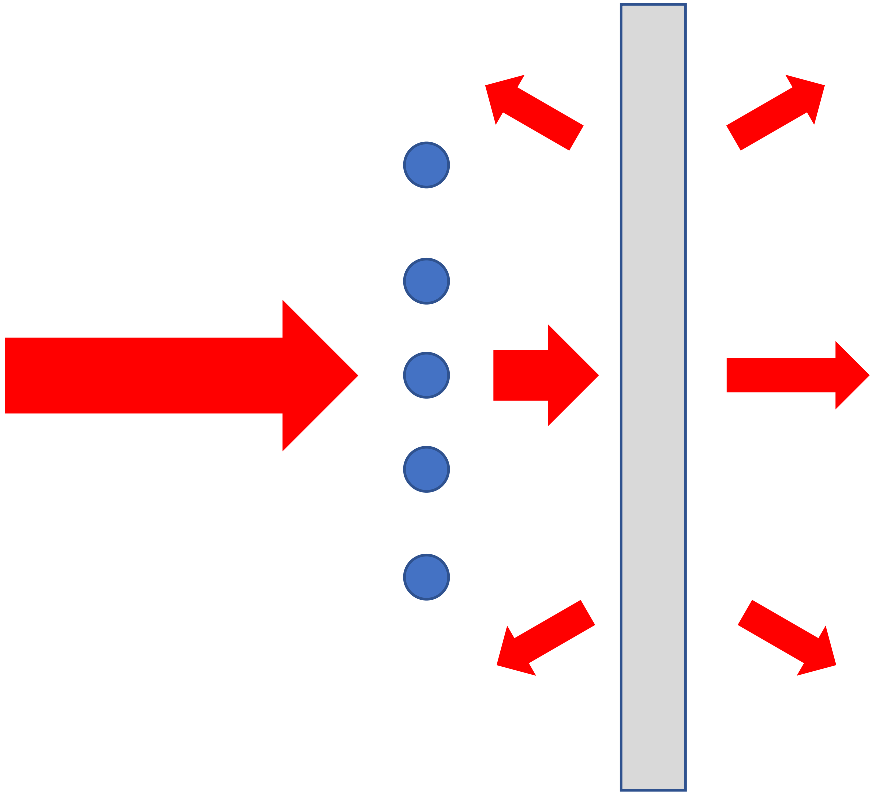
Example blank filters



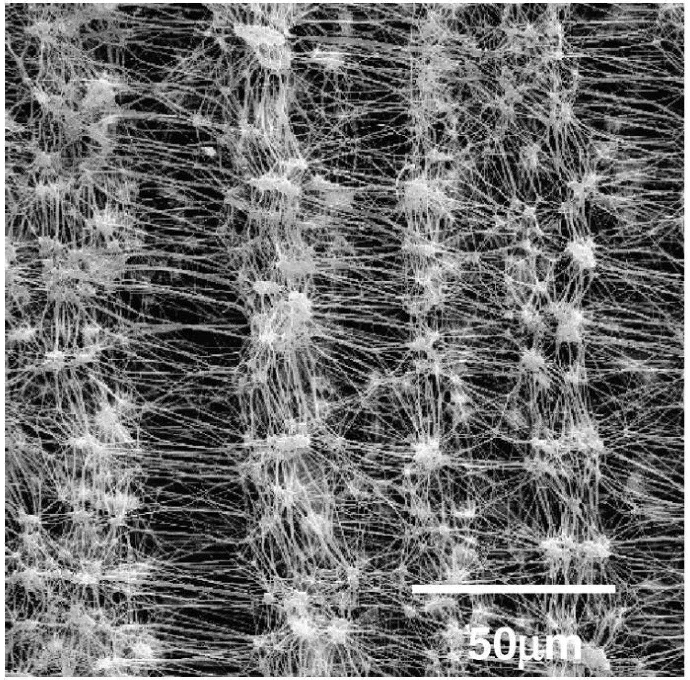
Debus et al., *Appl. Spectroscopy*, 2019

Modeling substrate interactions

For optically small particles (Rayleigh regime),
assume independent interactions between substrate and particles
(Dudani and Takahama, *Atmos. Meas. Tech.*, 2022)



Blank PTFE membrane filter
(Casuccio et al., *Fuel Process. Tech.*, 2004)

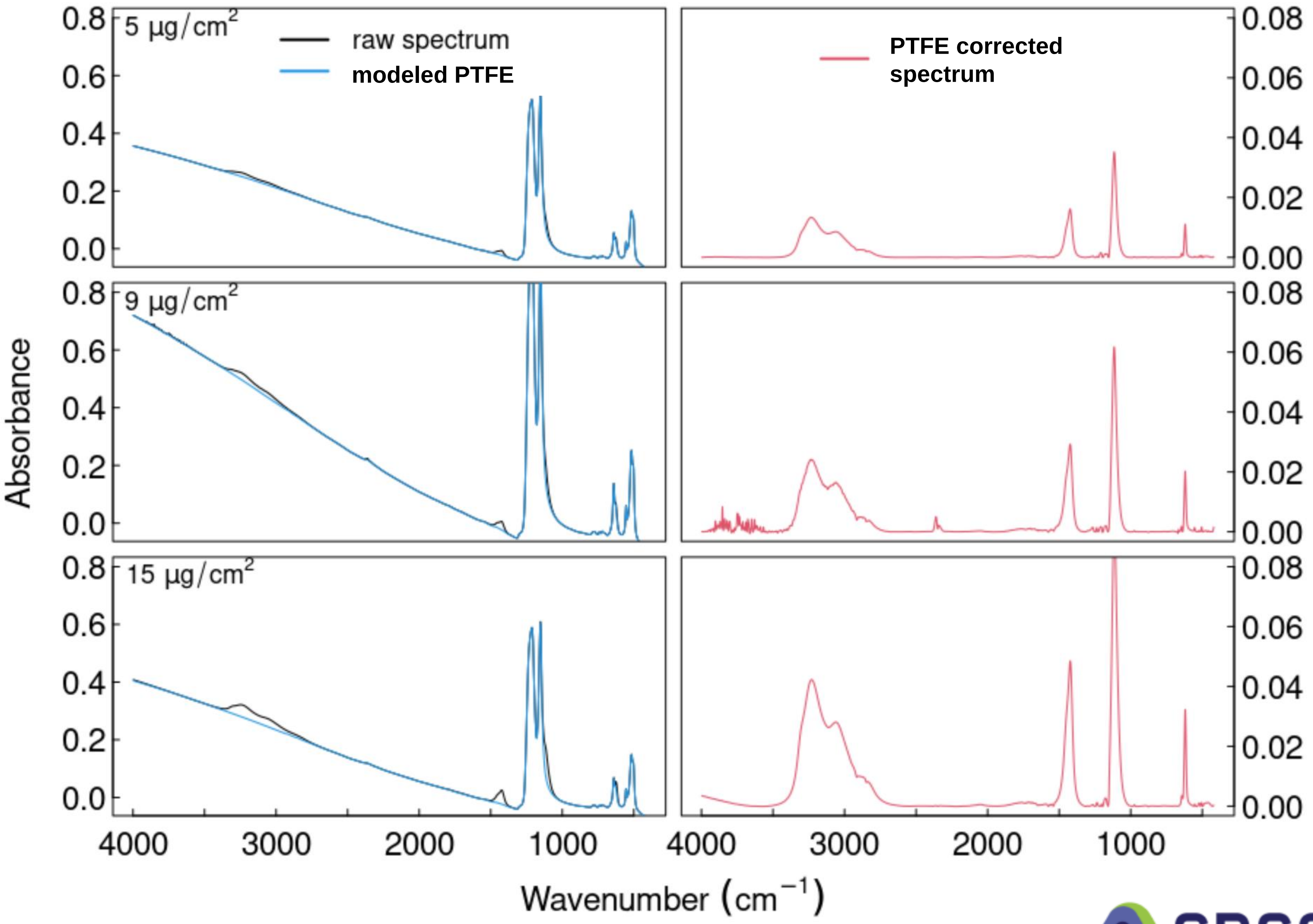


Build statistical model for PTFE spectrum trained on blanks

Statistical model trained on blank filters

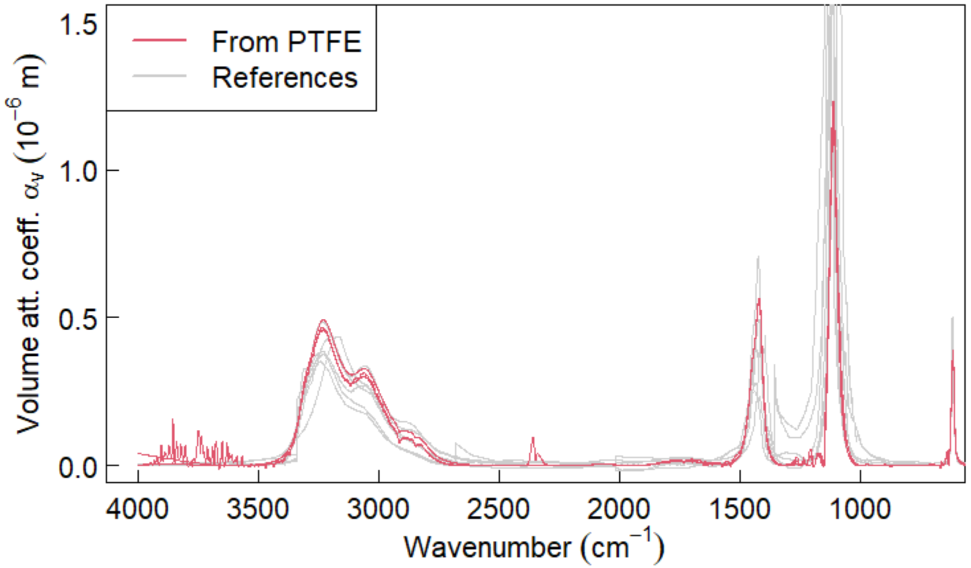
Applied to laboratory standards of ammonium sulfate

IMPROVE-equivalent ambient concentrations of 0.5-1.6 ug/m³

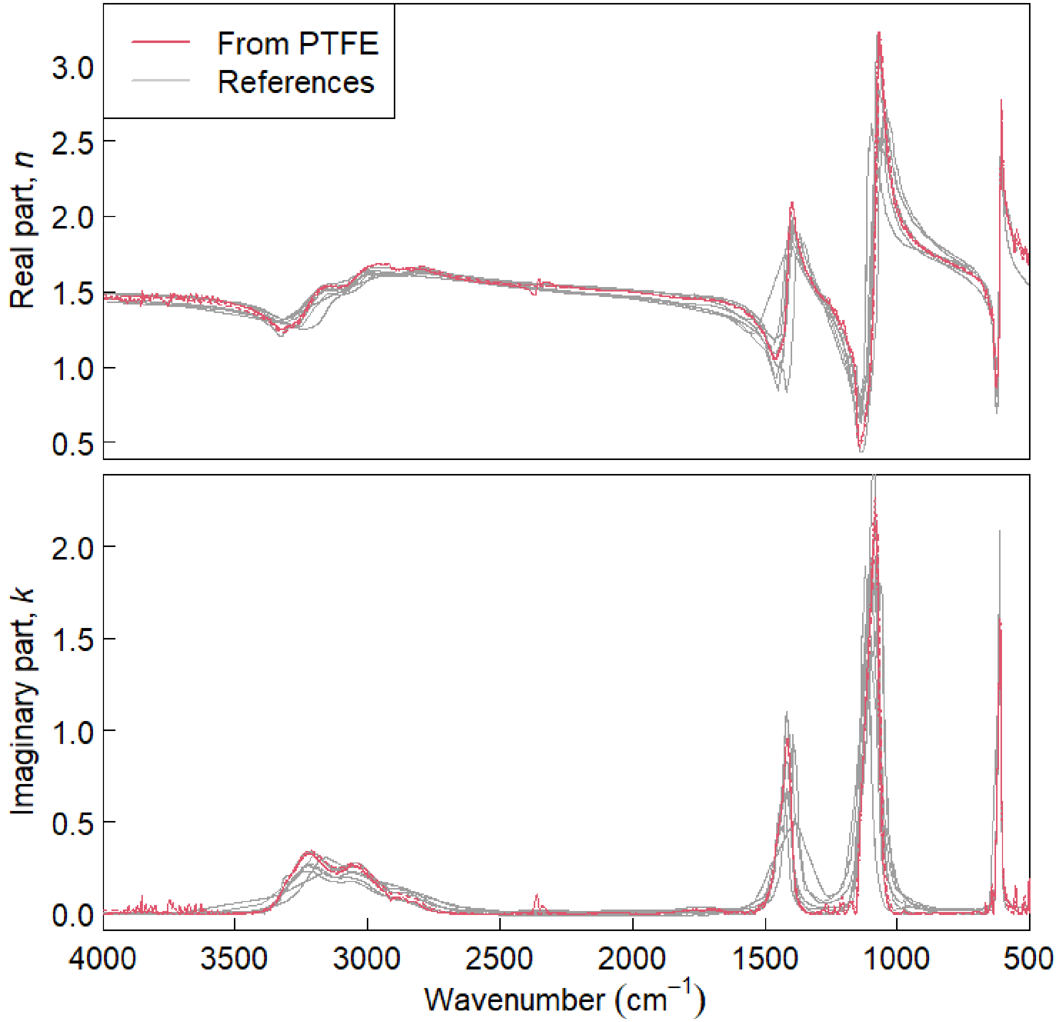


Spectra from Ruthenburg et al., *Atmos. Environ.*, 2014

Optical property
(volume attenuation coefficient)



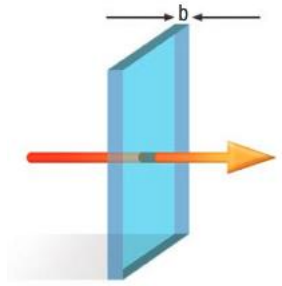
Optical constants
(complex refractive index)



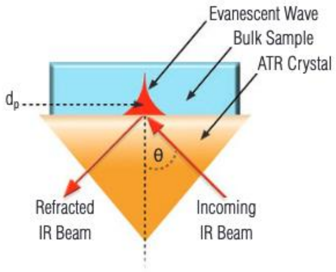
<u>References</u>

Toon et al. 1976 – single crystal
Shettle and Volz 1977 – halide pellet
Weis and Ewing 1996 – suspended particles
Earle et al. 2006 – suspended particles
Segal-Rosenheimer et al. 2009 – suspended particles
Laskina et al. 2014 – suspended particles

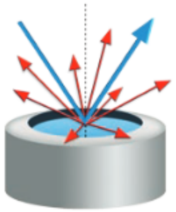
Refractive indices for liquid, solids, compressed powders, suspended particles can be used to constrain aerosol calibrations



transmission

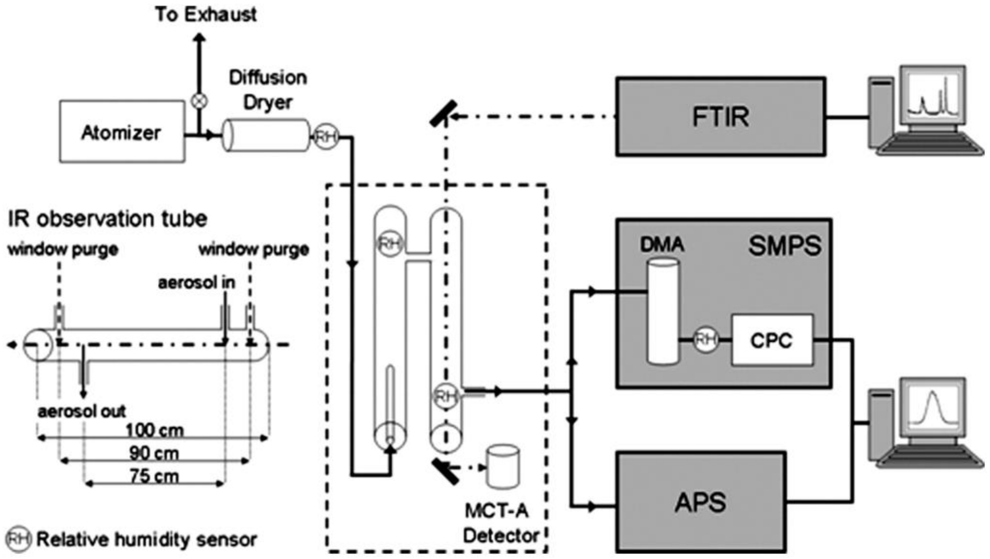


internal reflection

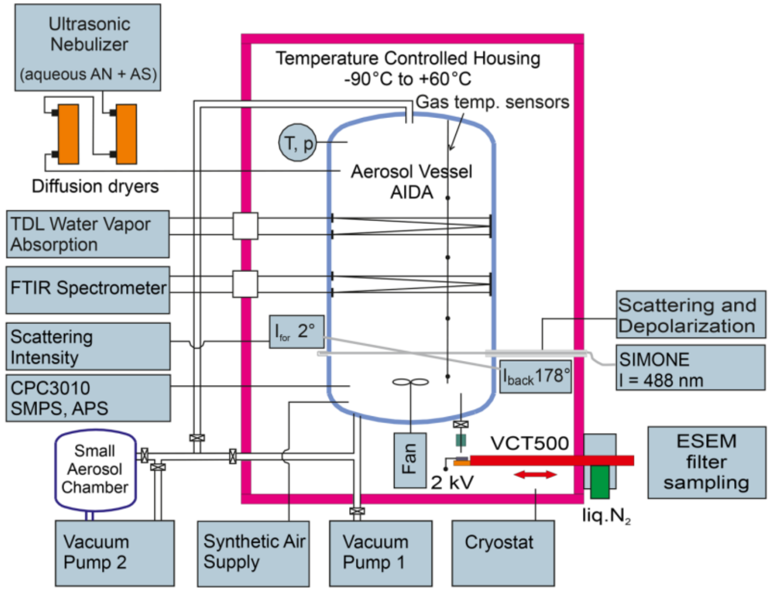


external reflection

PIKE Technologies



Hudson et al., *Aerosol Sci. Tech.*, 2007



Wagner et al., *Atmos. Chem. Phyis.*, 2021

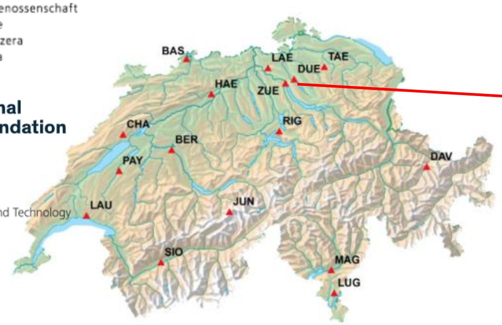
Application to calibrations

Samples from Zürich on quartz filters

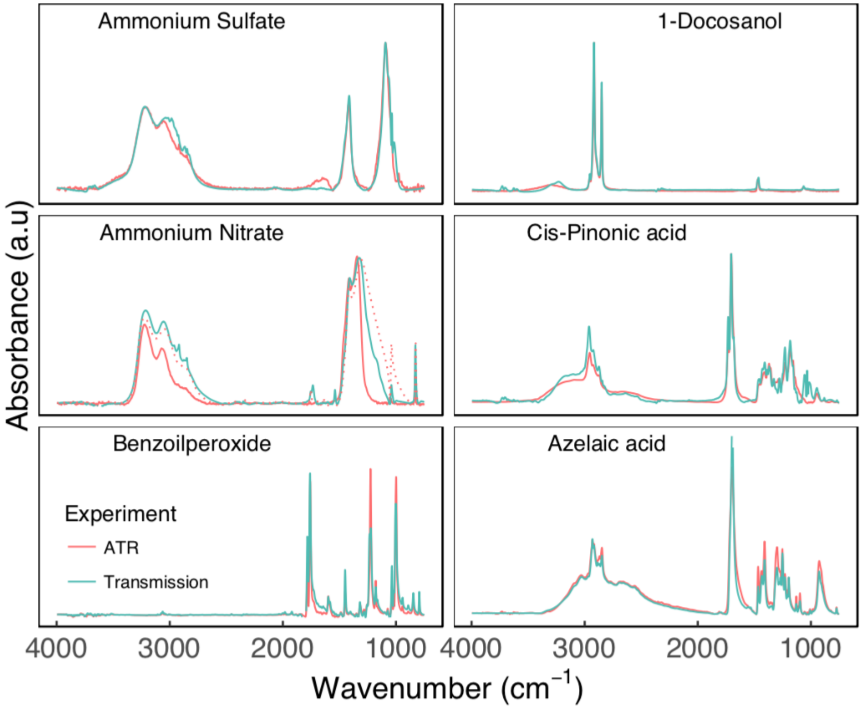
Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss National Science Foundation

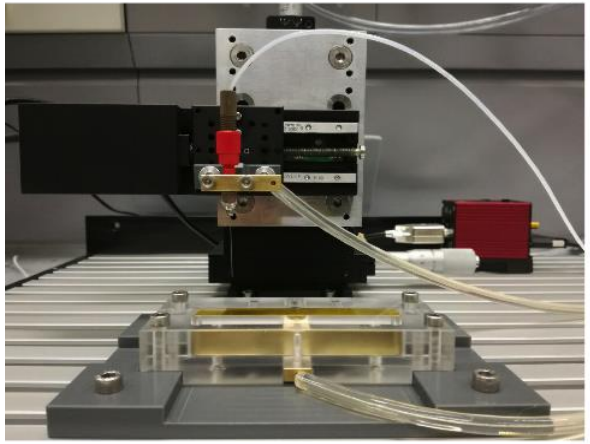
Empa
Materials Science and Technology

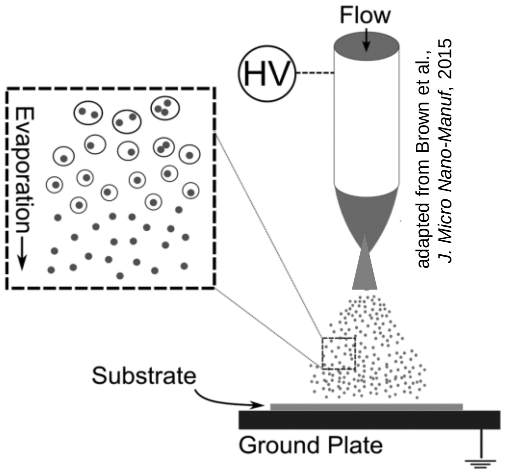


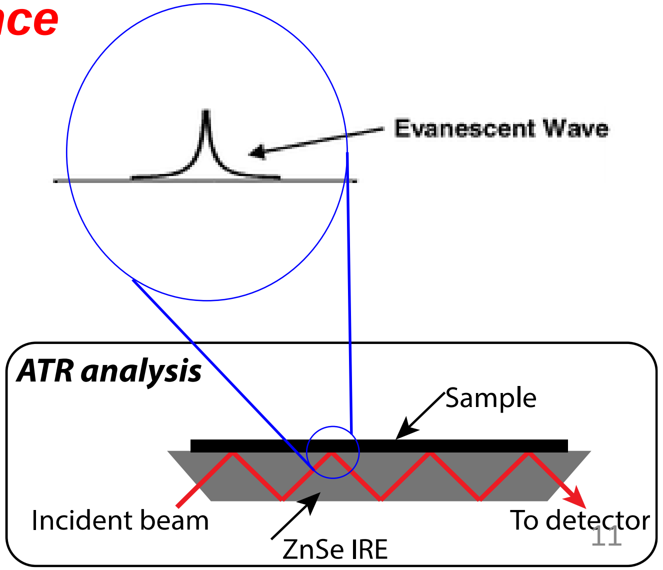
Zürich –Kaserne
(urban site)
2015-2016



Extracted solution electrosprayed onto crystal – no PTFE interference







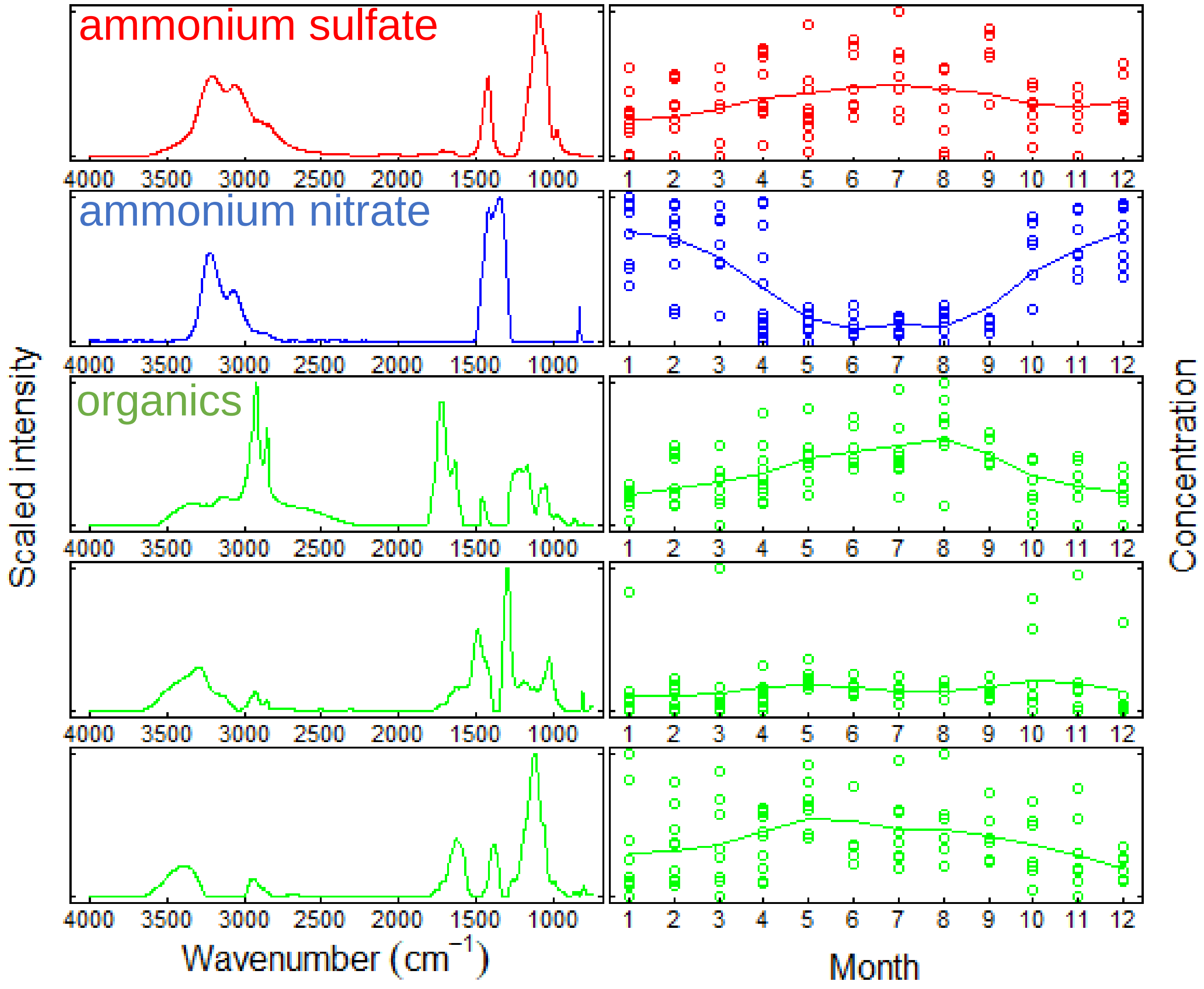
Arangio et al., *Appl. Spectroscopy*, 2019

Matrix Factorization with partially-constrained factor profiles

- Apply constrained matrix factorization with ammonium sulfate and ammonium nitrate profiles fixed to linear absorption coefficient

- Other factors mostly organic

- Can be applied to constrain contributions of fixed components



Arangio et al. *in prep*

Summary

Until present day

- Demonstrated quantitative information can be extracted from FTIR spectra
- Identified important calibration bands used by calibration models to reduce possibility that correlation is used
- Many models to maintain

Current work

- Generate suite of data products from single, shared representation
- Constrain models with fundamental optical properties