ENV-167
Aerosol sensing

Satoshi Takahama

Laboratory for Atmospheric Processes and their Impacts

27.11.2024

About me

Formation

- BS Civil Engineering
- PhD Chemical Engineering
- Scripps Institution of Oceanography
- EPFL

Research in aerosol science and atmospheric chemistry

After this lecture, you will be able to answer the following questions

- Why do we care about atmospheric aerosols?
- What are some properties of atmospheric aerosols?
- Why do we need to measure chemical constituents?
- What are important light-matter interactions?
- What are the impediments to ubiquitous chemical measurements?

Related lectures:

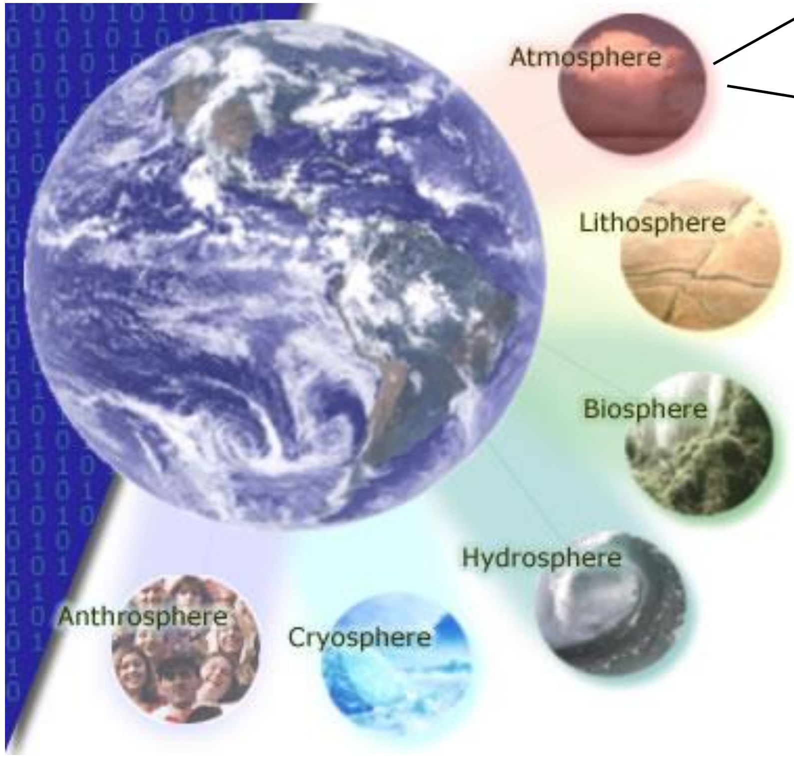
Outline

- Atmospheric composition
- Aerosols
- Aerosol impacts on climate and health
- Light-matter interactions
- Environmental monitoring via infrared

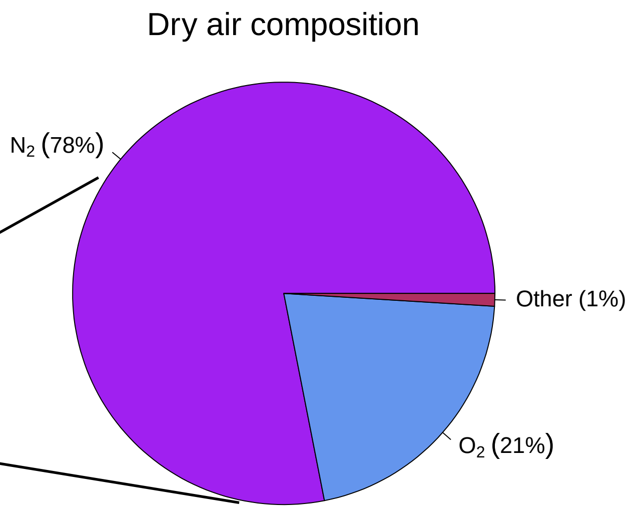
“To reduce pollution, you must first measure it”

“You can’t improve what you don’t measure”

Atmospheric composition



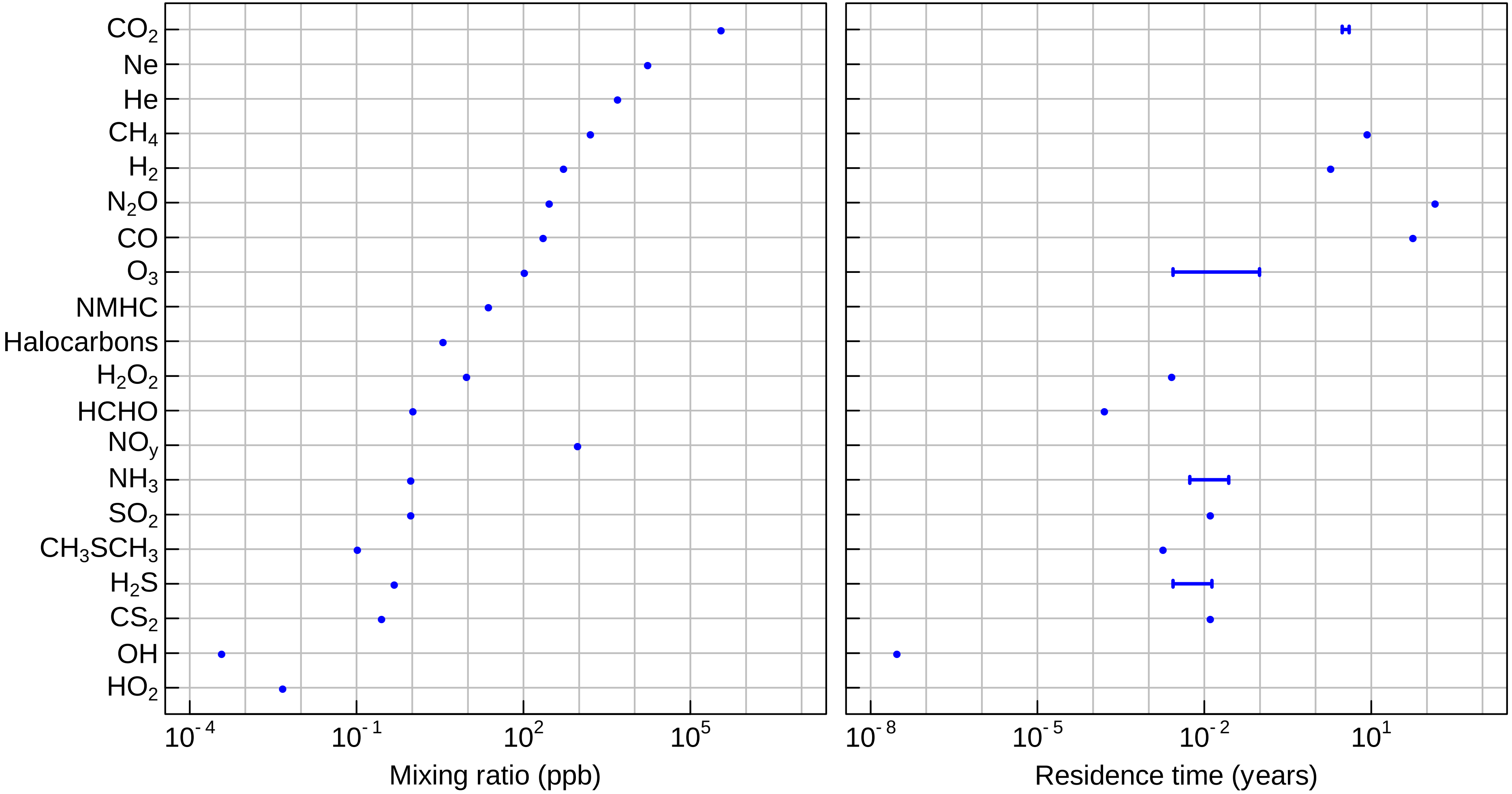
Source: Institute for Computational Earth System Science



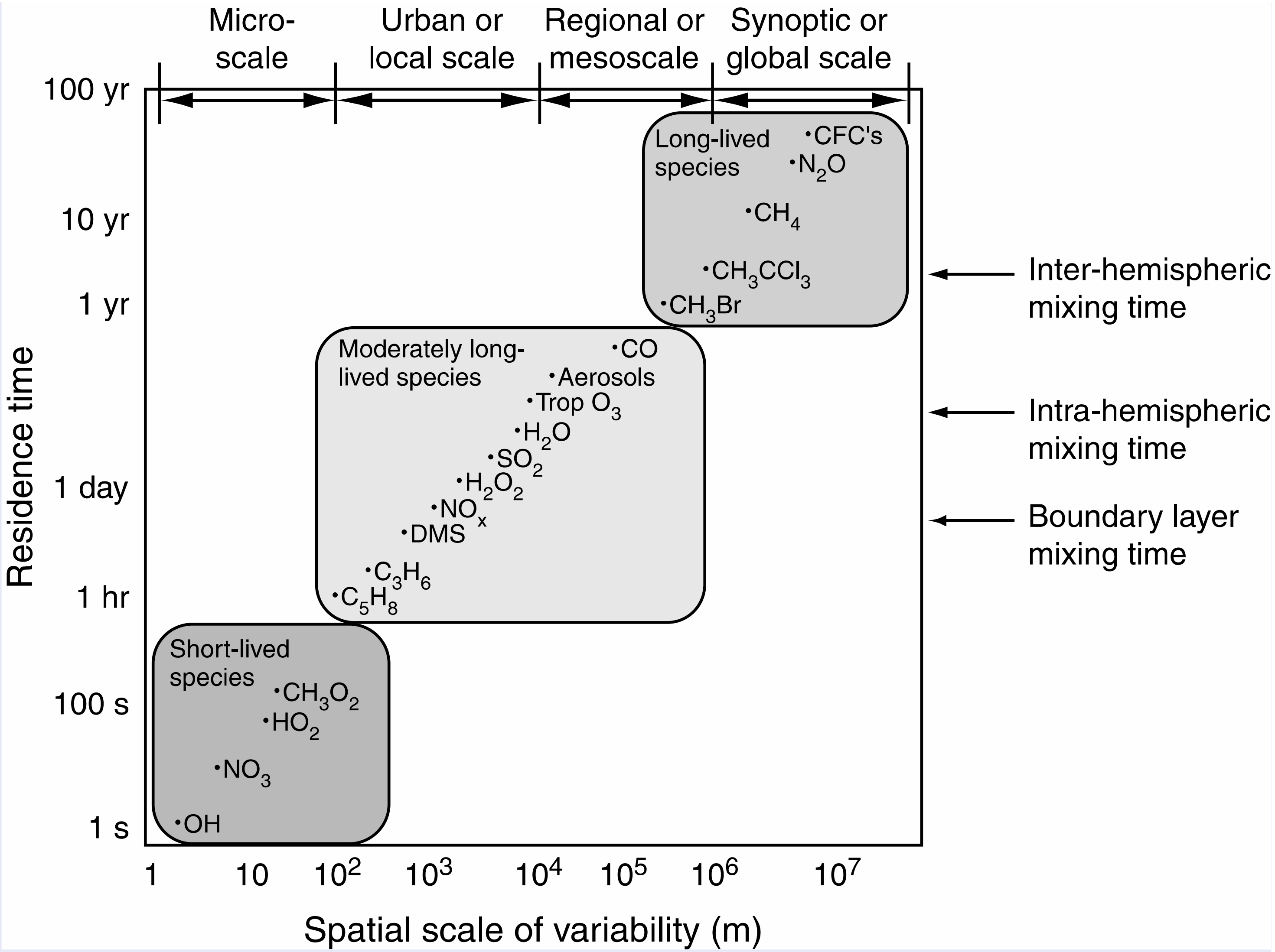
- Interest in trace compounds (in the 1%).
- Contribution of water to mass budget is also on the order of 1%.
- The atmosphere is a highly nonlinear system (magnitude of response is not proportional to its input)
- Elements additionally distributed throughout atmosphere, biosphere, lithosphere, hydrosphere, etc.

Tropospheric species in the gas phase

Data from Wallace and Hobbs, 2006



Residence Time and Spatial Scales of Variation of Chemicals in the Atmosphere

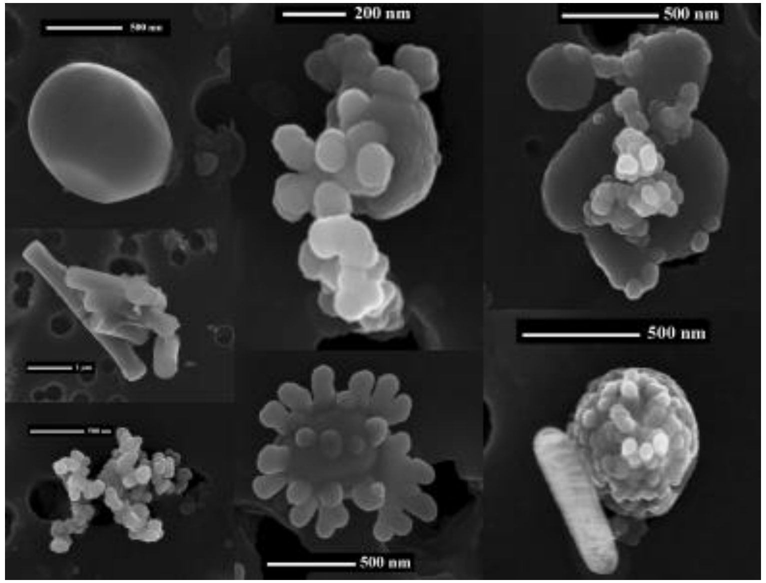


Wallace and Hobbs, Chapter 5.1

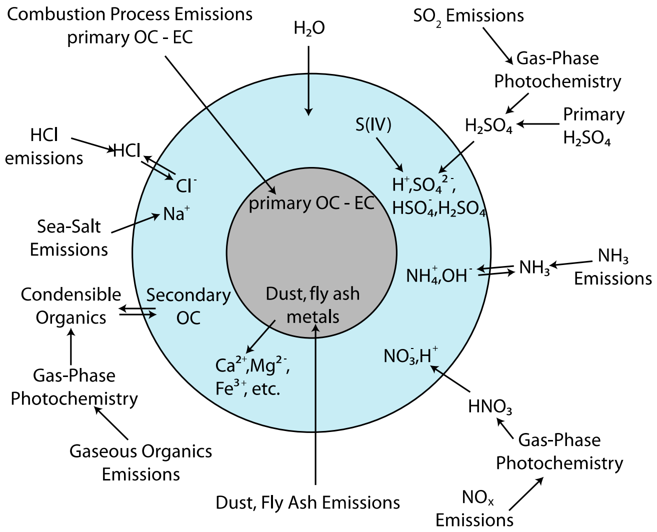
Atmospheric aerosols

Varies in
- size
- shape
- phase
- composition

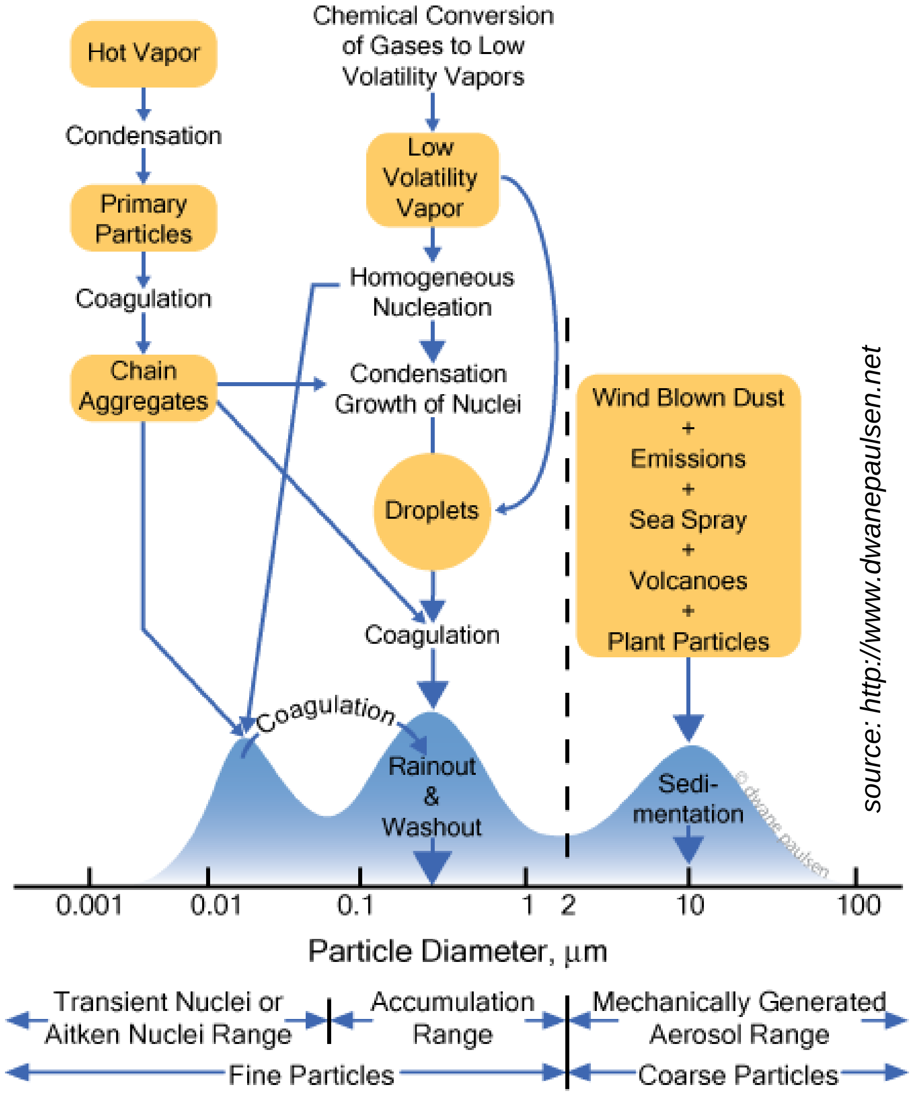
Scanning electron microscopy images



Coz et al., *Aerosol Sci. Tech.*, 2008

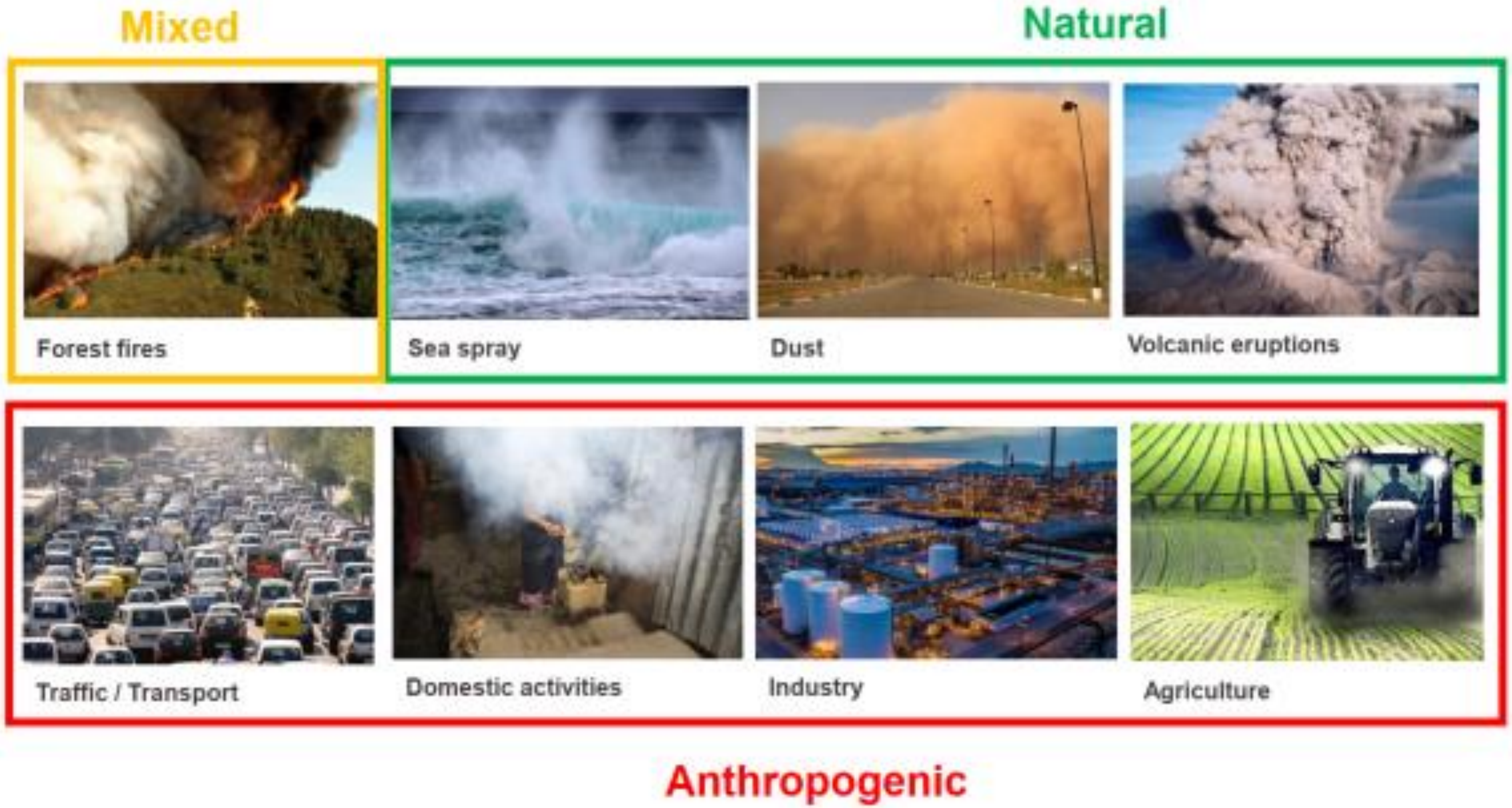


adapted from Pandis et al.,
J. Phys. Chem., 1995



source: http://www.dwanepaulsen.net

Aerosol sources



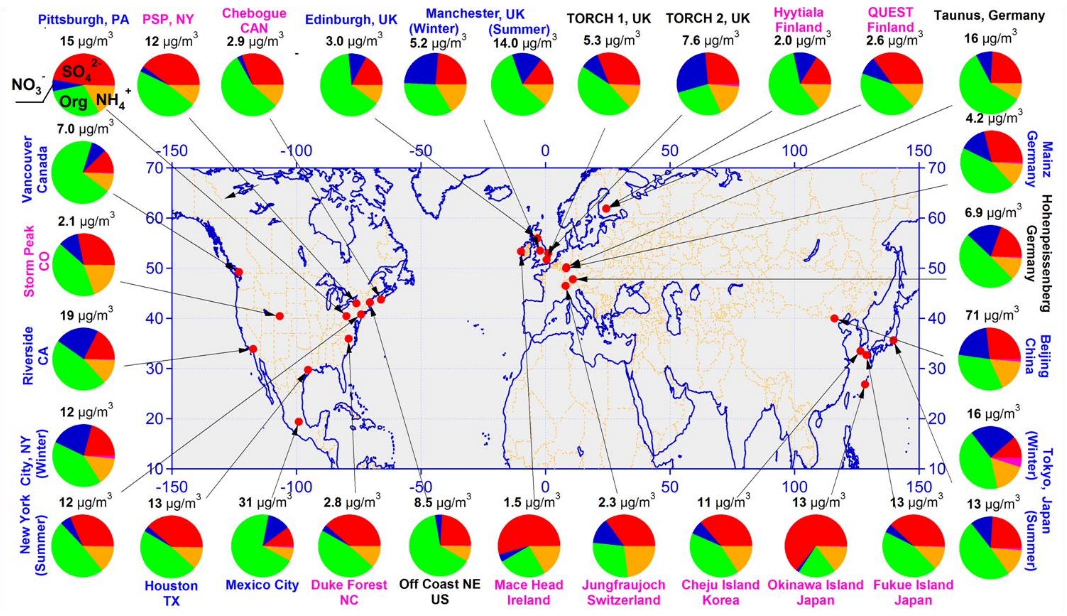
(Schmale lecture)

Aerosol composition

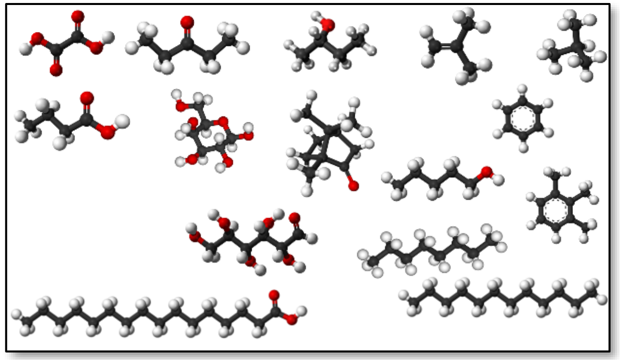
Major components:

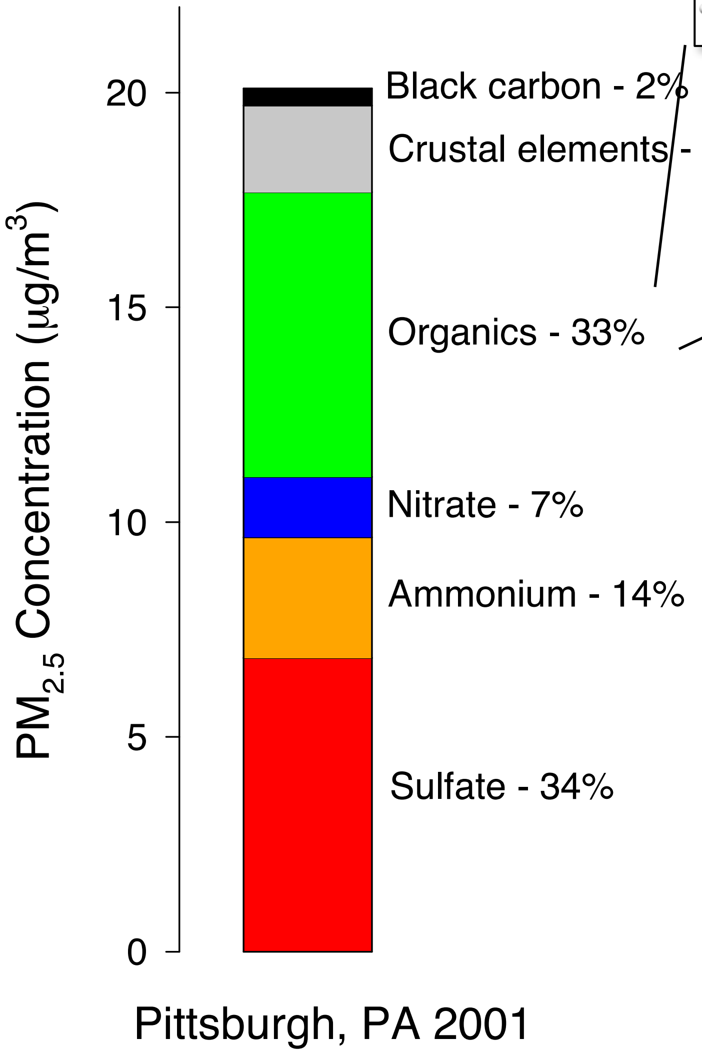
- Inorganic salts/ions
- Organic compounds (10,000+)
- Black carbon/soot
- Mineral dust

Occurs in different proportions over time and throughout the world

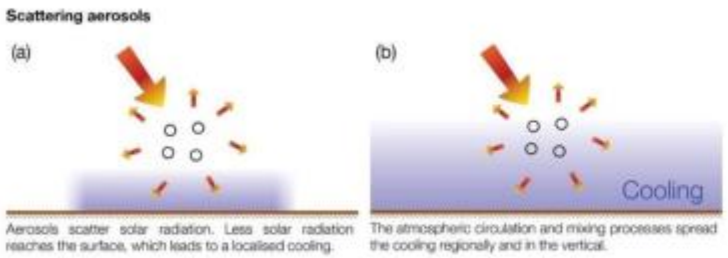


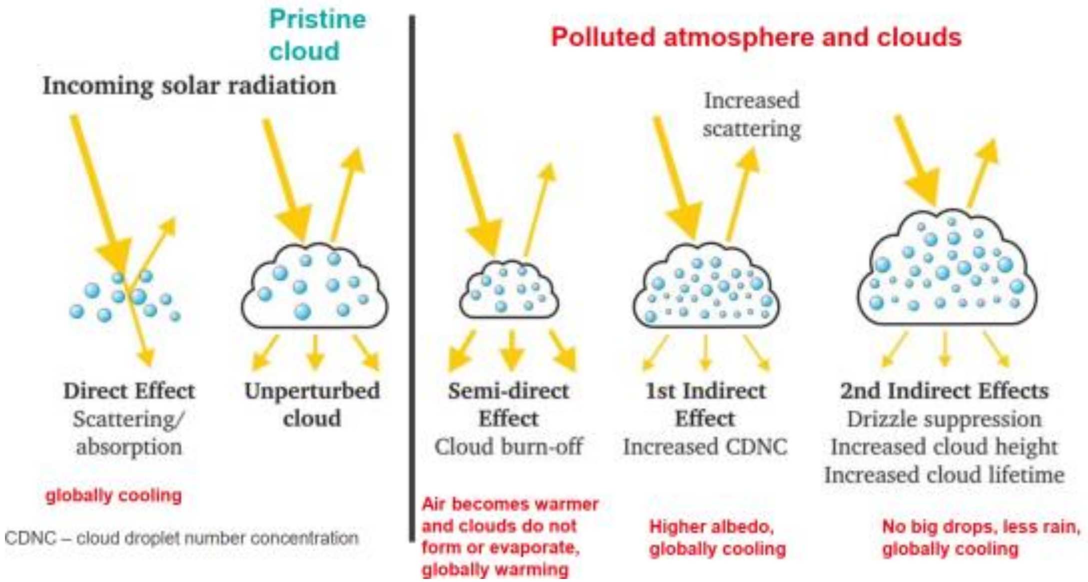
NR-PM$_1$: Zhang et al., *Geophys. Res. Lett.*, 2007

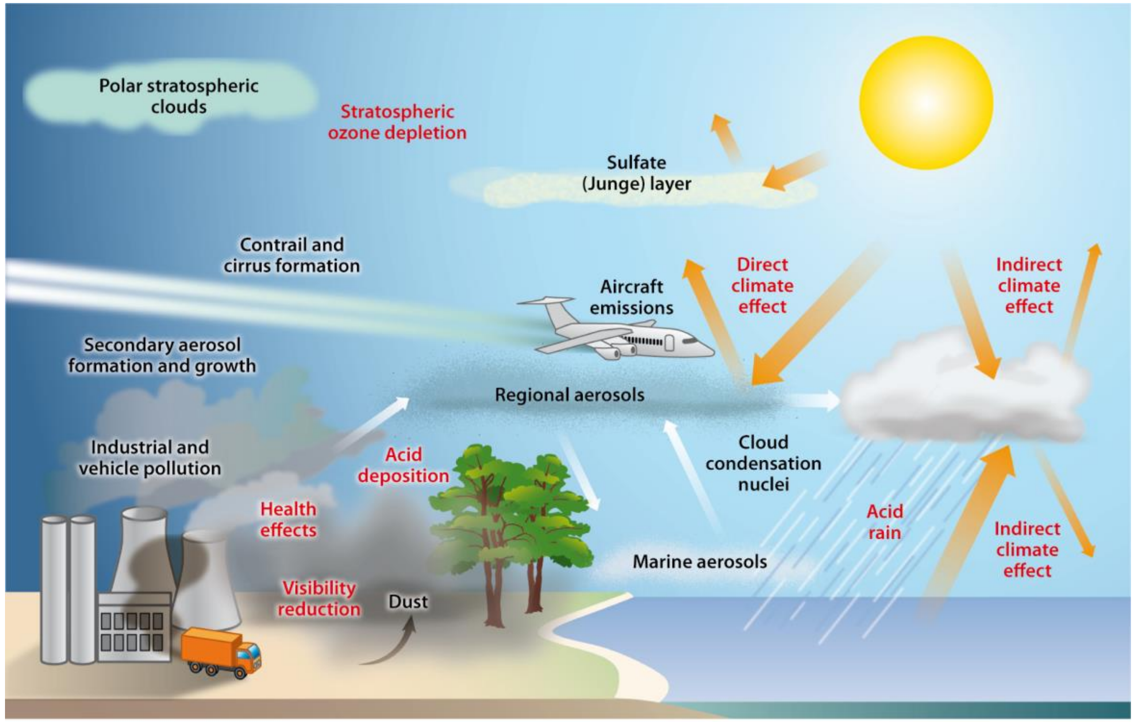




Aerosols and climate



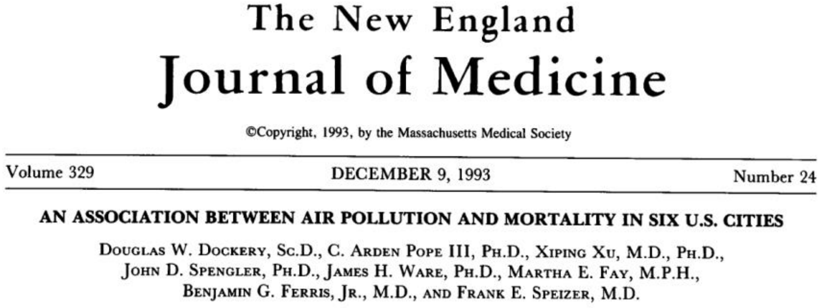




Kolb CE, Worsnop DR. 2012.
Annu. Rev. Phys. Chem. 63:471–91

(Schmale lecture)
IPCC 2013

Aerosols and health


The New England
Journal of Medicine
©Copyright, 1993, by the Massachusetts Medical Society
Volume 329 DECEMBER 9, 1993 Number 24
AN ASSOCIATION BETWEEN AIR POLLUTION AND MORTALITY IN SIX U.S. CITIES
Douglas W. Dockery, Sc.D., C. Arden Pope III, Ph.D., Xiping Xu, M.D., Ph.D., John D. Spengler, Ph.D., James H. Ware, Ph.D., Martha E. Fay, M.P.H., Benjamin G. Ferris, Jr., M.D., and Frank E. Speizer, M.D.

Cohort study of 8111 Americans

Medical history and lifestyle examined over 14-16 years

Association found between excess mortality and fine particulate matter pollution

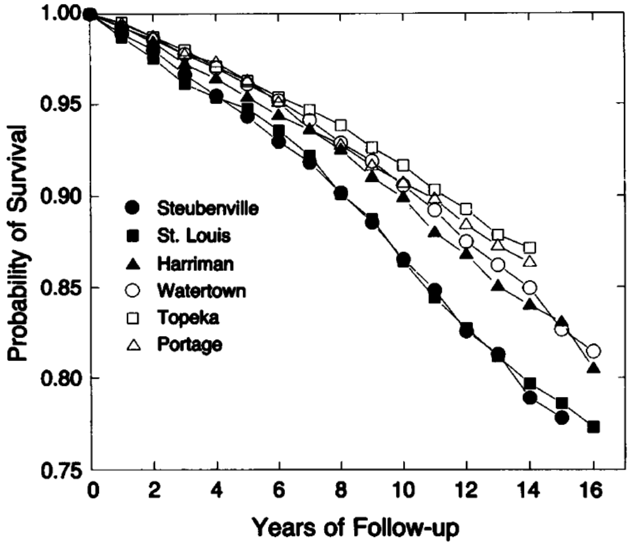


Figure 2. Crude Probability of Survival in the Six Cities, According to Years of Follow-up.

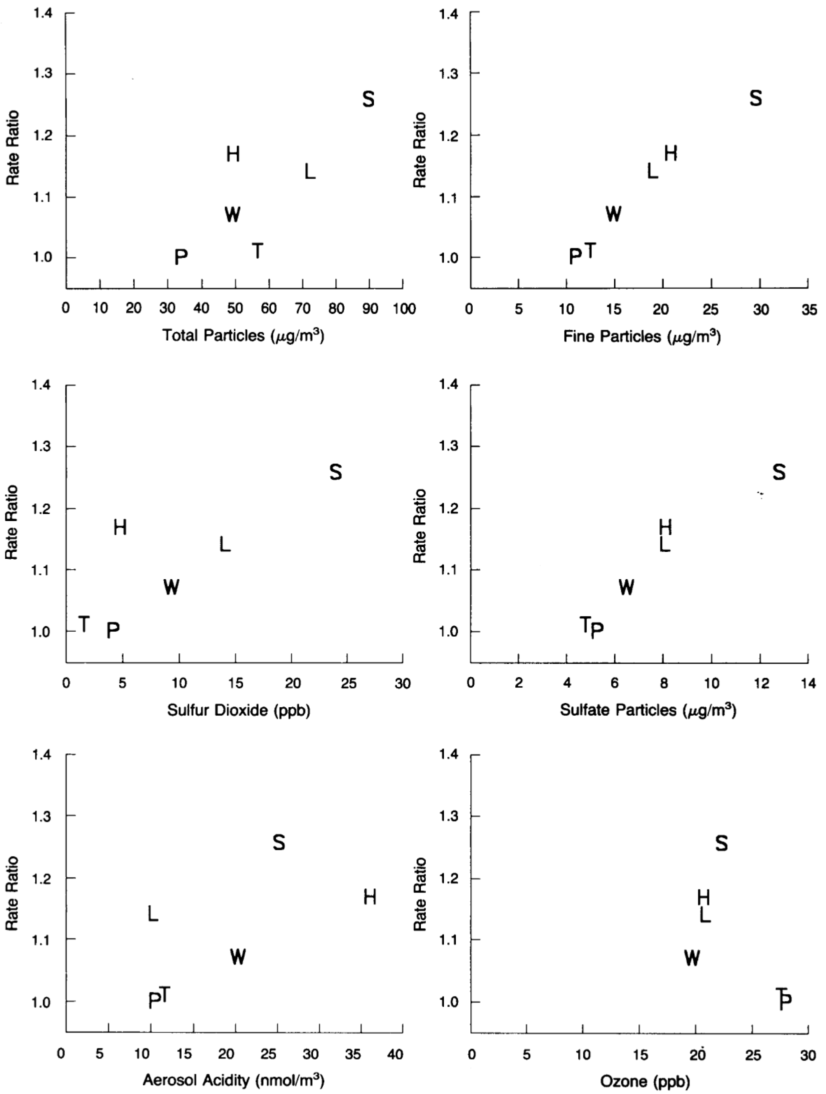


Figure 3. Estimated Adjusted Mortality-Rate Ratios and Pollution Levels in the Six Cities.
re shown for the measures of air pollution. P denotes Portage, Wisconsin; T Topeka, Kansas; W Watertown, Massachusetts; L St. Louis; H Harriman, Tennessee; and S Steubenville, Ohio.

Survival analysis

Cox proportional hazards model

$$\lambda_{\mathrm{A}}(t) = -\frac{d}{dt}\ln S(t)$$

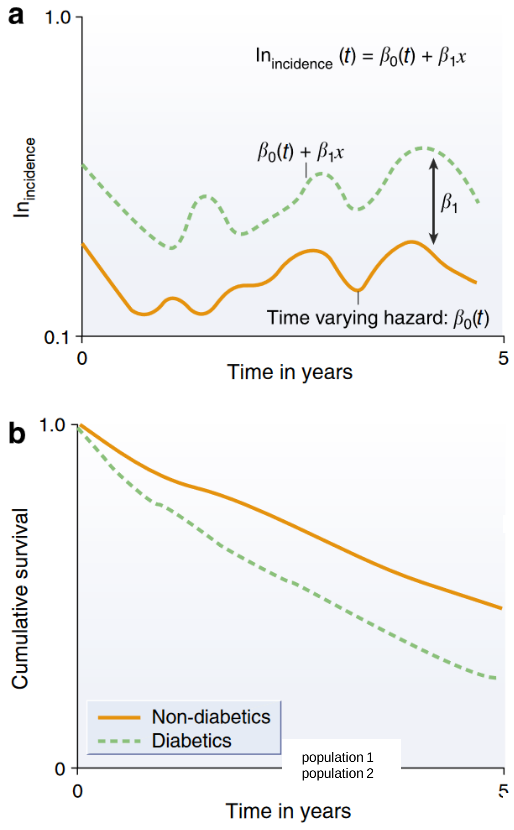
survival probability

Incidence rate — Baseline incidence rate — Confounders — Exposure

$$\lambda_A(t) = \lambda_B(t) \times \exp\left(\sum_{i=1}^{k} \beta_i X_i + \gamma E\right)$$

Log-linear relation to exposure

$$\ln \lambda_A(t) = \beta_0(t) + \sum_{i=1}^{k} \beta_i X_i + \gamma E$$



adapted from van Dijk et al., 2008

Confounders

- Stratified by age group and sex

- Smoking
- Education level
- BMI
- Exposure to local sources (occupational exposure)

Improvements in estimates (1993 – present)

- Larger cohorts
- Better exposure estimate
  - combine ground-based measurements, satellite remote sensing, and air quality model simulations
  - high resolution
  - capture microenvironments
- More confounding variables
  - environmental variables
  - behavioral, social, and economic variables
  - demographic variables
- Specific chemical constituents

Global urban temporal trends in fine particulate matter ($PM_{2\cdot5}$) and attributable health burdens: estimates from global datasets

Veronica A Southerland, Michael Brauer, Arash Mohegh, Melanie S Hammer, Aaron van Donkelaar, Randall V Martin, Joshua S Apte, Susan C Anenberg

Lancet Planet Health 2022; 6: e139–46

Published Online
January 5, 2022
https://doi.org/10.1016/S2542-5196(21)00350-8

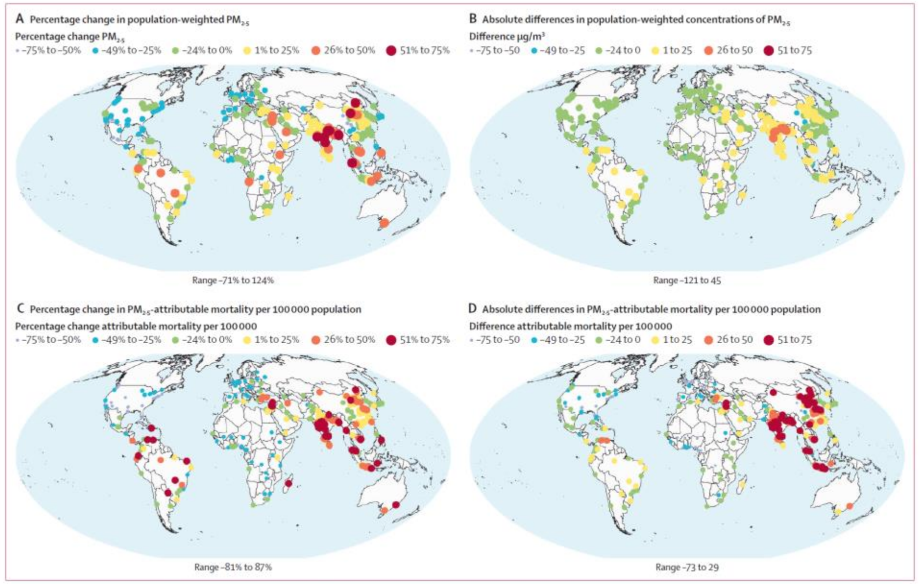


Figure 3: Change in population-weighted $PM_{2\cdot5}$ concentrations and $PM_{2\cdot5}$-attributable mortality rates between 2000 and 2019 for the top 250 most populated urban areas based on 2019 WorldPop estimates
(A) Percentage change in population-weighted $PM_{2\cdot5}$ concentrations. (B) Absolute differences in population-weighted concentrations of $PM_{2\cdot5}$. (C) Percentage change in $PM_{2\cdot5}$-attributable mortality per 100000 population. (D) Absolute differences in $PM_{2\cdot5}$-attributable mortality per 100 000 population.

Summary

Background With much of the world's population residing in urban areas, an understanding of air pollution exposures at the city level can inform mitigation approaches. Previous studies of global urban air pollution have not considered trends in air pollutant concentrations nor corresponding attributable mortality burdens. We aimed to estimate trends in fine particulate matter ($PM_{2\cdot5}$) concentrations and associated mortality for cities globally.

Methods We use high-resolution annual average $PM_{2\cdot5}$ concentrations, epidemiologically derived concentration response functions, and country-level baseline disease rates to estimate population-weighted $PM_{2\cdot5}$ concentrations and attributable cause-specific mortality in 13 160 urban centres between the years 2000 and 2019.

Findings Although regional averages of urban $PM_{2\cdot5}$ concentrations decreased between the years 2000 and 2019, we found considerable heterogeneity in trends of $PM_{2\cdot5}$ concentrations between urban areas. Approximately 86% (2·5 billion inhabitants) of urban inhabitants lived in urban areas that exceeded WHO's 2005 guideline annual average $PM_{2\cdot5}$ (10 µg/m³), resulting in an excess of 1·8 million (95% CI 1·34 million–2·3 million) deaths in 2019. Regional averages of $PM_{2\cdot5}$-attributable deaths increased in all regions except for Europe and the Americas, driven by changes in population numbers, age structures, and disease rates. In some cities, $PM_{2\cdot5}$-attributable mortality increased despite decreases in $PM_{2\cdot5}$ concentrations, resulting from shifting age distributions and rates of non-communicable disease.

Interpretation Our study showed that, between the years 2000 and 2019, most of the world's urban population lived in areas with unhealthy levels of $PM_{2\cdot5}$, leading to substantial contributions to non-communicable disease burdens. Our results highlight that avoiding the large public health burden from urban $PM_{2\cdot5}$ will require strategies that reduce exposure through emissions mitigation, as well as strategies that reduce vulnerability to $PM_{2\cdot5}$ by improving overall public health.

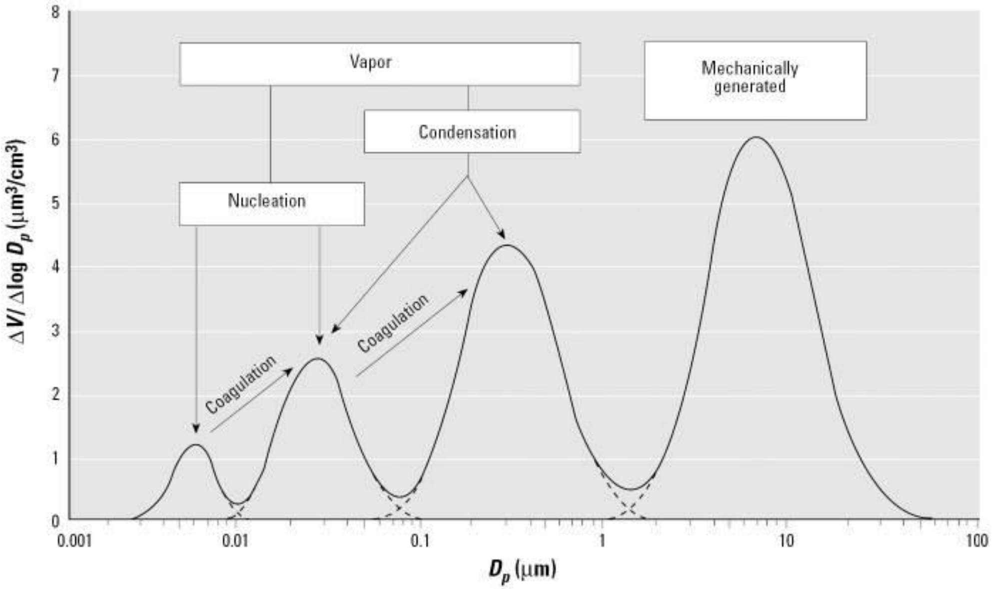
A pollutant is a substance detectable in the environment, at least partially due to human activity, and that may induce adverse effects on the living organisms.

Moriarty 1983

(Breider lecture)

Guideline levels for each pollutant ($\mu g/m^3$):		
$PM_{2.5}$	1 year	~~10~~ **5** (reduced in 2021)
	24 h (99th percentile)	25
PM_{10}	1 year	20
	24 h (99th percentile)	50
Ozone, O_3	8 h, daily maximum	100
Nitrogen dioxide, NO_2	1 yr	40
	1 h	200
Sulfur dioxide, SO_2	24 h	20
	10 min	500

Mechanisms



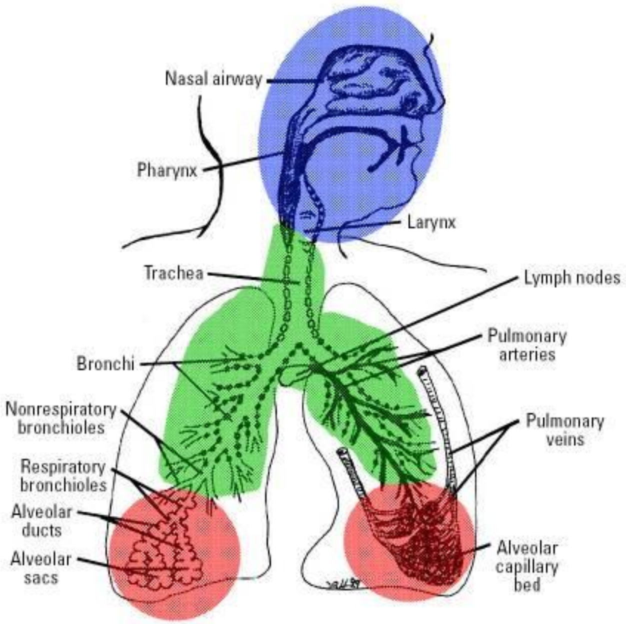
Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles

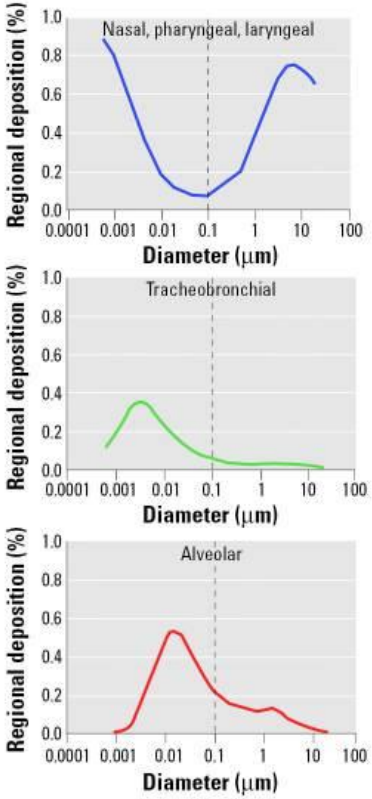
Günter Oberdörster,[1] Eva Oberdörster,[2] and Jan Oberdörster[3]

[1]Department of Environmental Medicine, University of Rochester, Rochester, New York, USA; [2]Department of Biology, Southern Methodist University, Dallas, Texas, USA; [3]Toxicology Department, Bayer CropScience, Research Triangle Park, North Carolina, USA

Deposited particles

- mucocilliary clearance
- dissolution and blood stream
- translocation





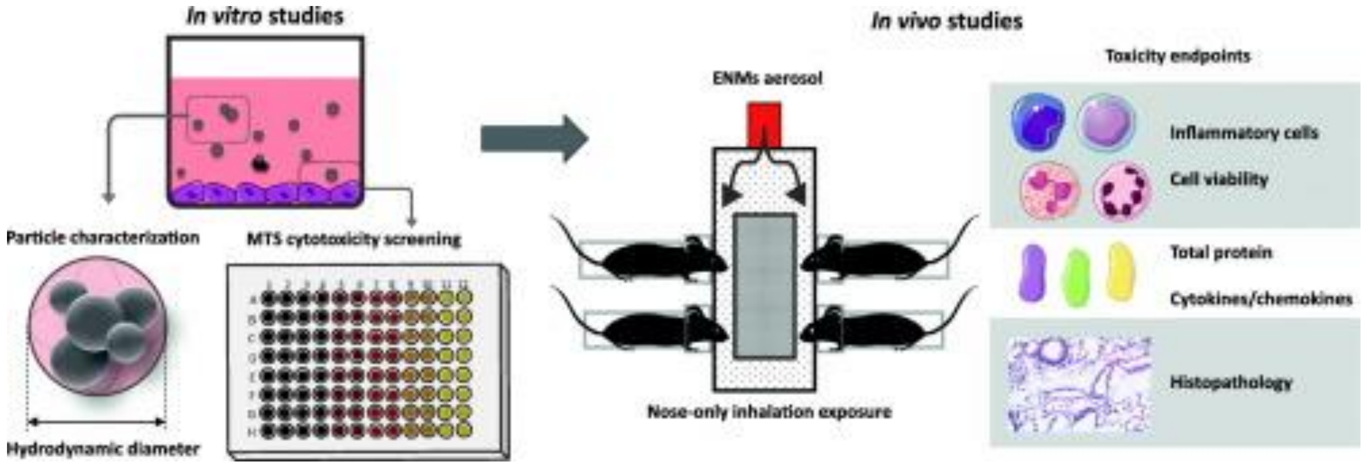
Toxicity studies

in vitro

- acellular / chemical assays
- cellular / biological assays

in vivo

- human subjects
- other animal subjects



Areecheewakul et al., *Nanoimpact*, 2020

Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles

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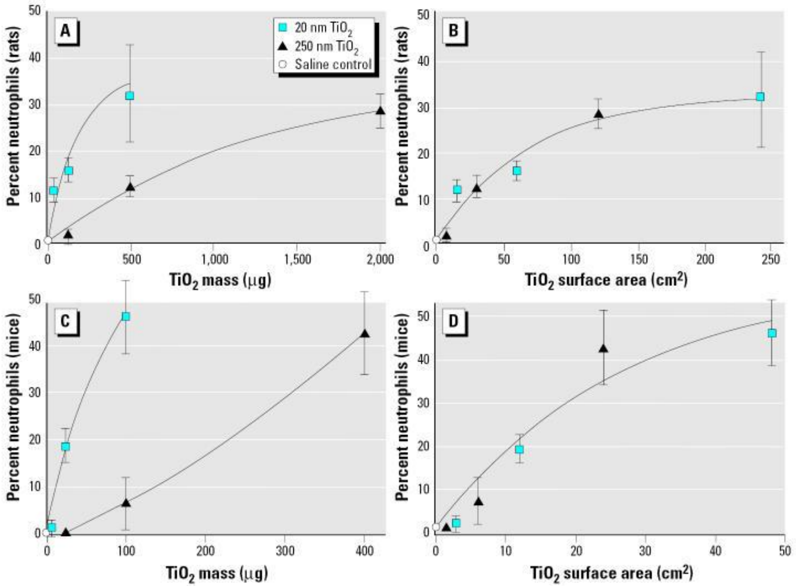
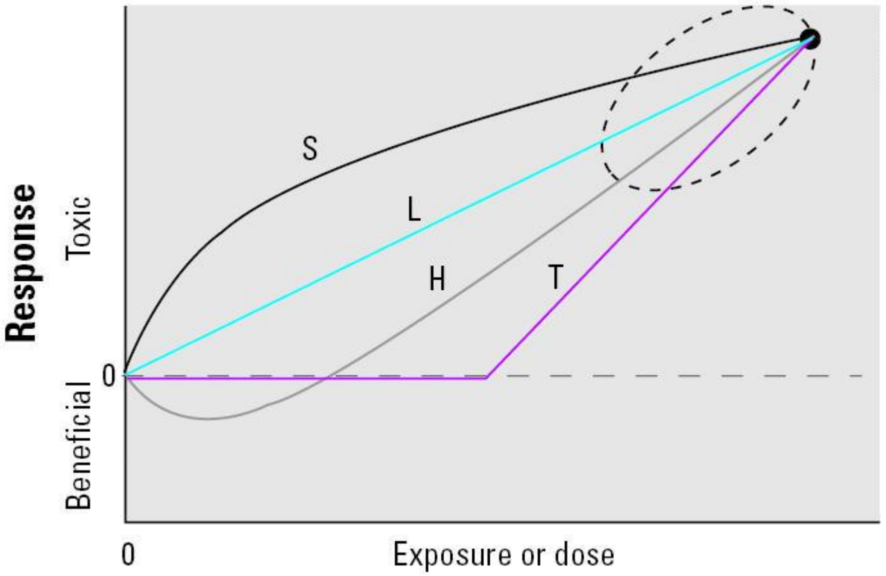
[1]Department of Environmental Medicine, University of Rochester, Rochester, New York, USA; [2]Department of Biology, Southern Methodist University, Dallas, Texas, USA; [3]Toxicology Department, Bayer CropScience, Research Triangle Park, North Carolina, USA



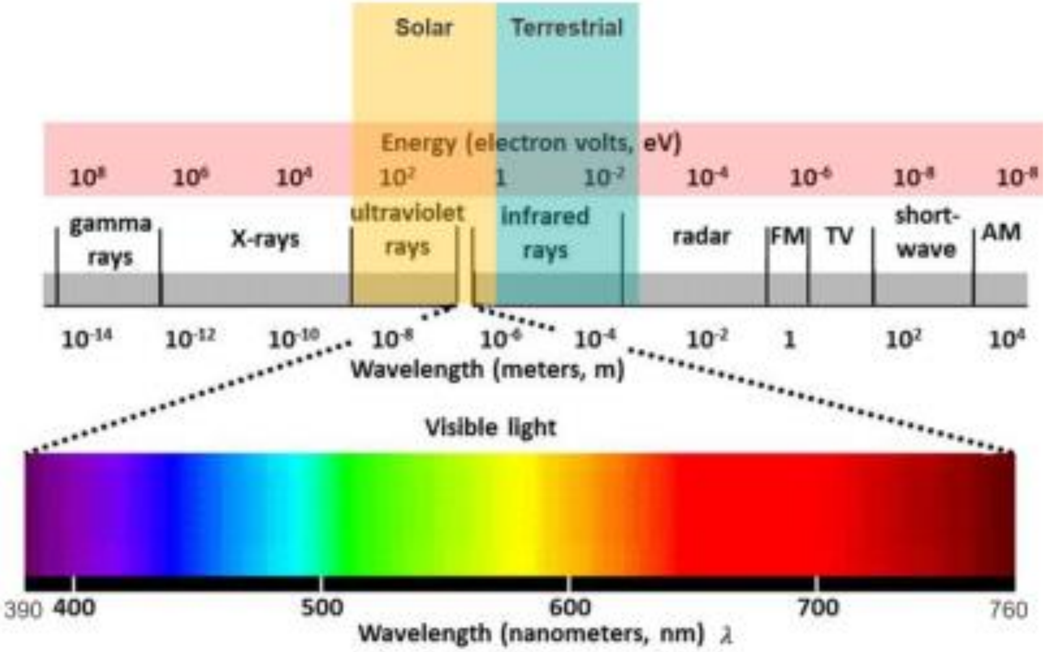
- High dose and exposure concentrations
- Short timescale of experiments
- Interpolation to low concentrations

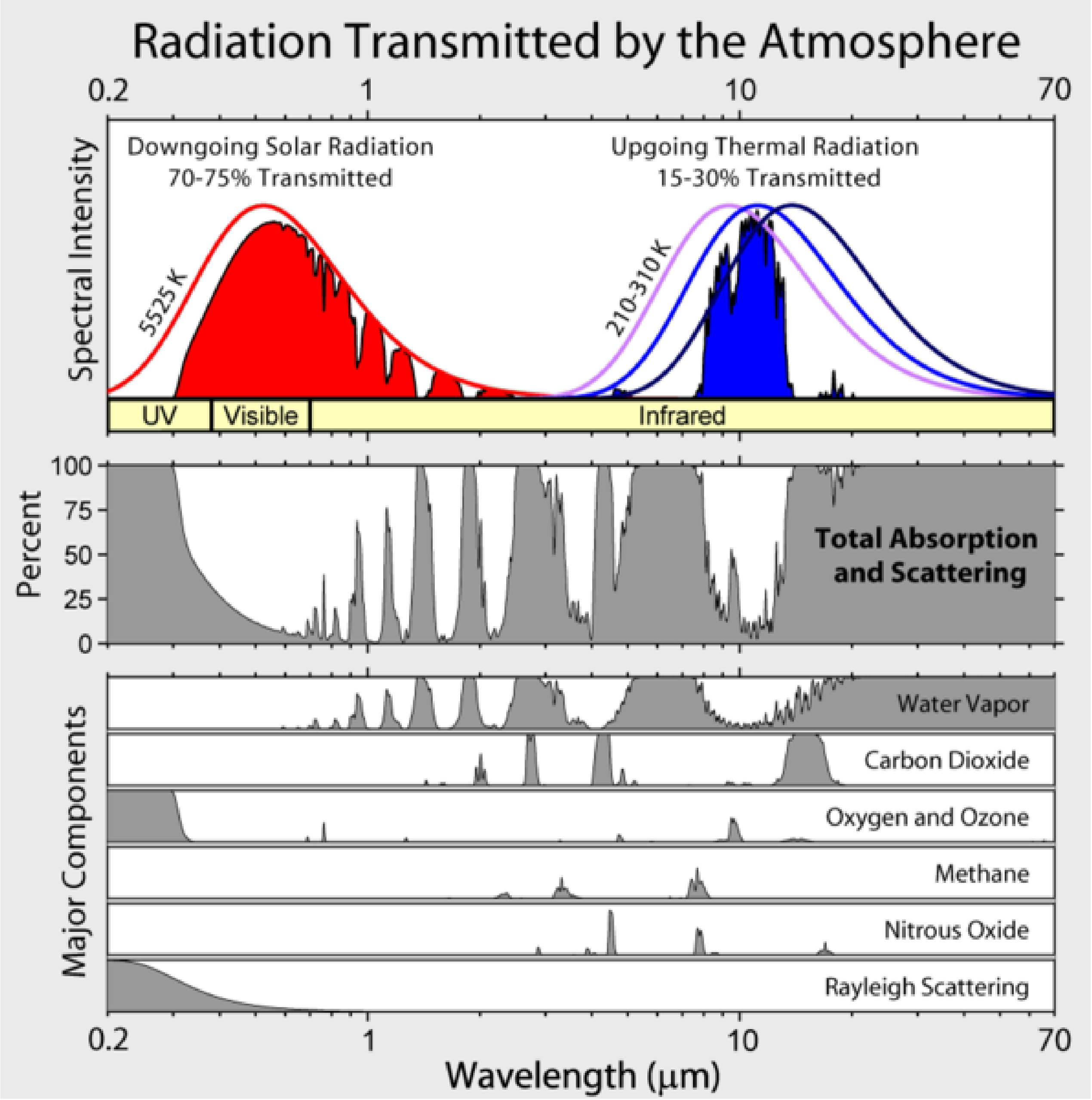


Measuring chemicals with infrared (thermal / mid-infrared)

light-matter interactions

Electromagnetic spectrum





Wikimedia
https://ozonedepletiontheory.info/what-is-radiation/

Absorption

An oscillating dipole can absorb energy from an oscillating electric field if the field also oscillates at the same frequency.

- a molecular dipole moment occurs because of unequal sharing of electrons
- electron densities of molecules are often approximated by point charges on atoms

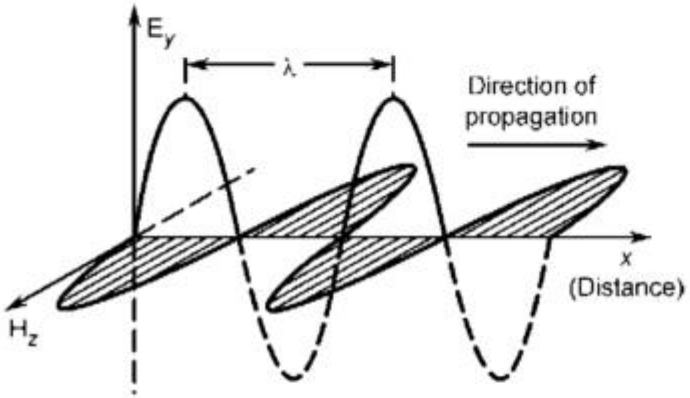
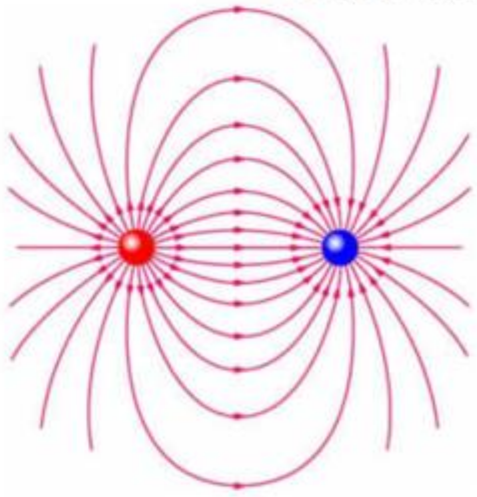


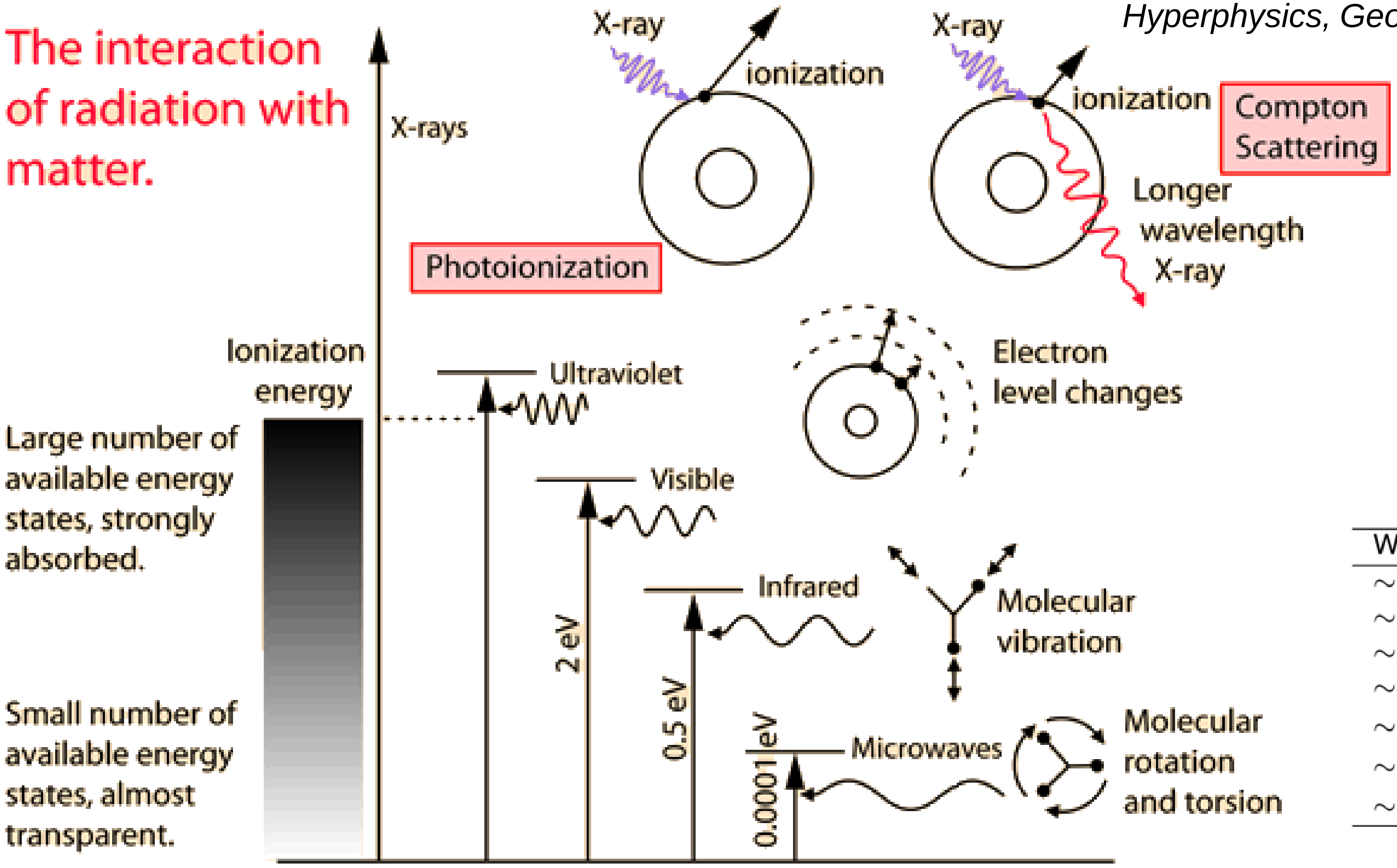
FIGURE 3.10 The instantaneous electric (E_y) and magnetic (H_z) field strength vectors of a plane-polarized light wave as a function of position along the axis of propagation (x) (from Calvert and Pitts, 1966).

Finlayson-Pitts and Pitts, 1999



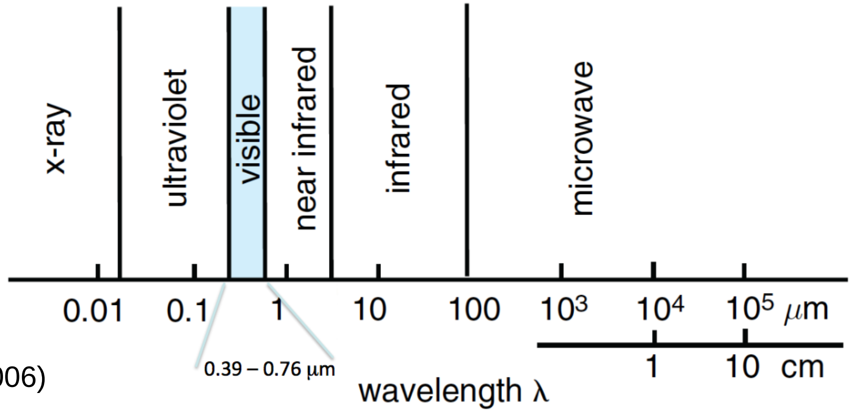
http://www.chem.ox.ac.uk/

The interaction of radiation with matter.



Hyperphysics, Georgia State Univ.

Wavelength (nm)	Description	Transition
$\sim$0.0003–0.03	γ-rays	nuclear
$\sim$0.03–10	X-rays	core electrons
$\sim$30–400	UV	valence electrons
$\sim$400–800	Visible	valence electrons
$\sim 1000–3 \times 10^5$	Infrared	molecular vibration
$\sim 3 \times 10^7–3 \times 10^{11}$	Microwave	molecular rotation
$\sim 3 \times 10^{11}–3 \times 10^{13}$	Radio	nuclear spin

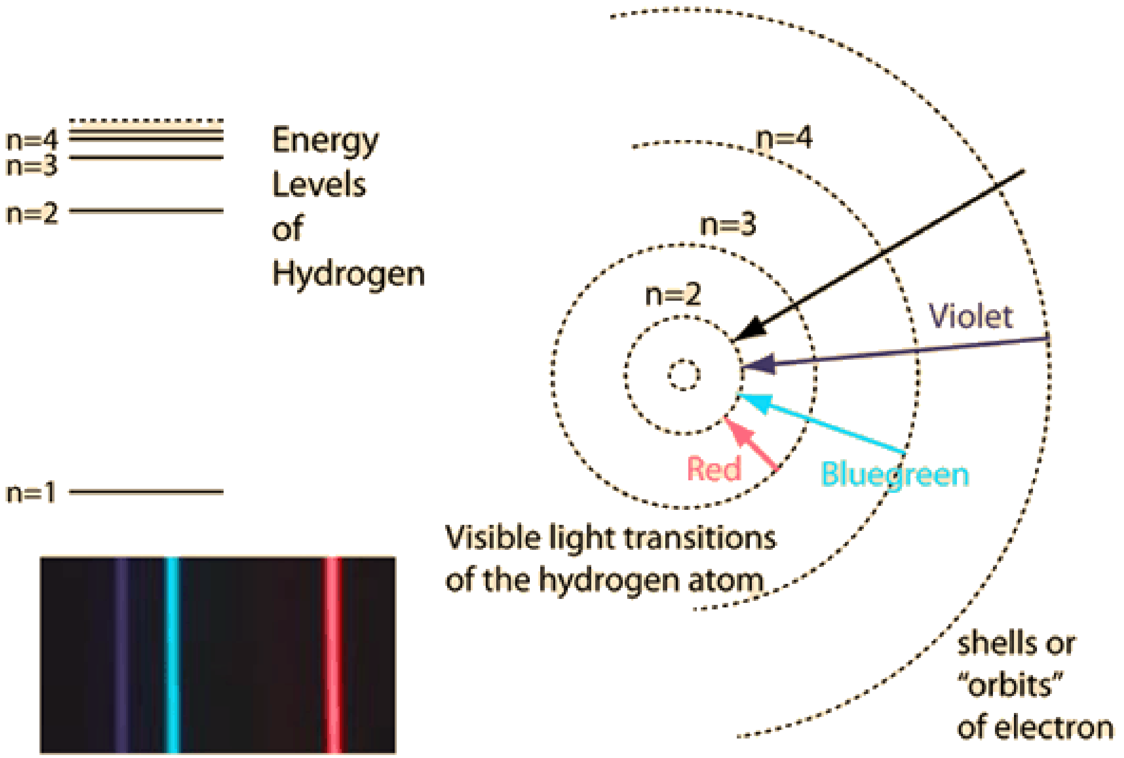


Wallace and Hobbs (2006)

Relationship between wavelength, energy, and frequency:

$$E = \frac{hc}{l} = hu$$

Conceptual model 1:
Bohr's model of the atom



Hyperphysics, Georgia State Univ.

Ultraviolet radiation

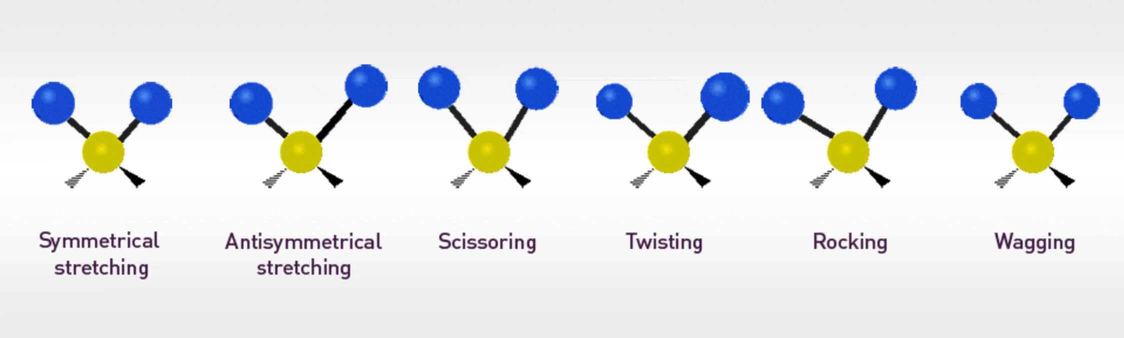
- electronic transitions (non-ionizing) induce excited states
- Ionizing at higher energies (*sunburn and skin cancer*)

Visible radiation

- electronic transitions induce excited states

Conceptual model 2: (an)harmonic oscillators

Infrared radiation induces changes in vibrational and rotational motion



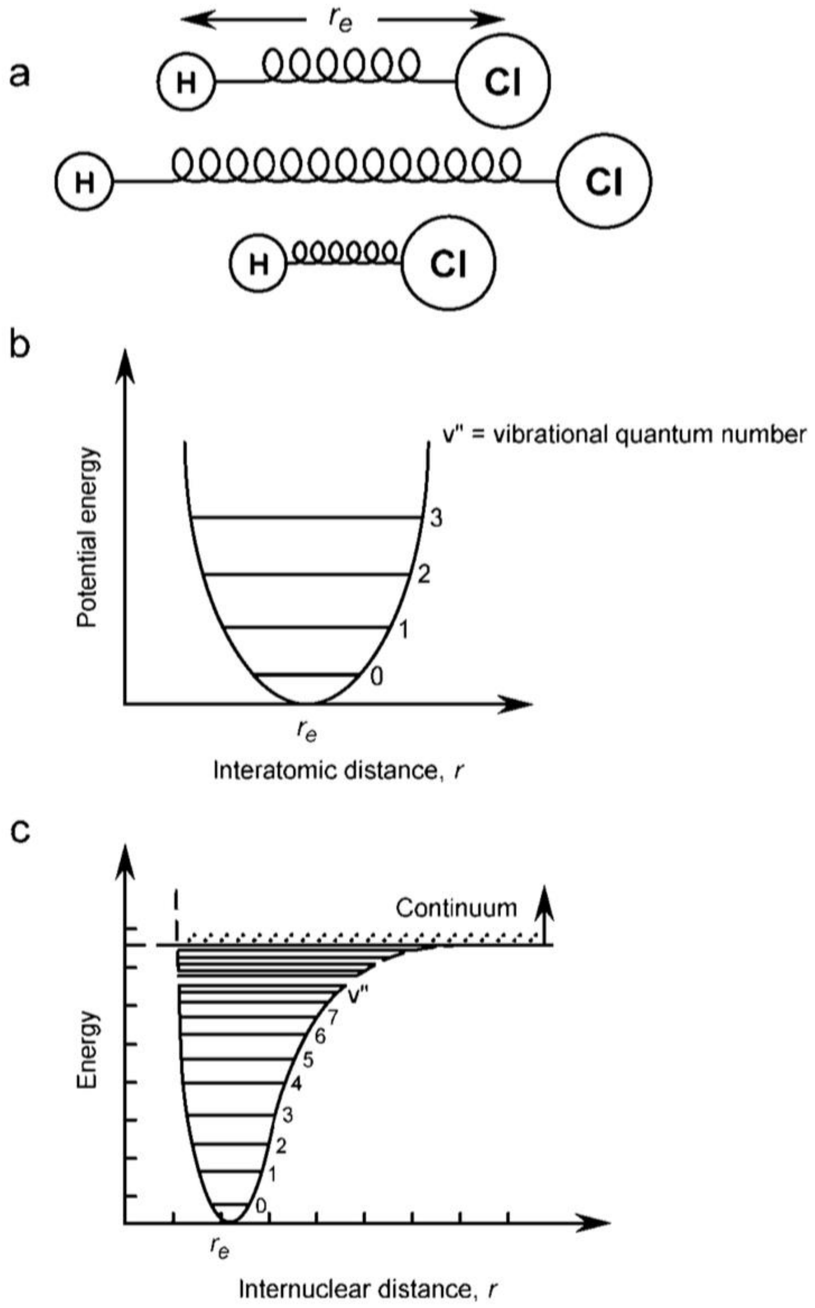


FIGURE 3.2 (a) Vibration of diatomic molecule, HCl, (b) potential energy of an ideal harmonic oscillator, and (c) an anharmonic oscillator described by the Morse function.

Finlayson-Pitts and Pitts, 1999
https://www.analyticon.eu/en/nir.html

Most major constituents of atmospheric aerosols have absorption bands in the mid-infrared

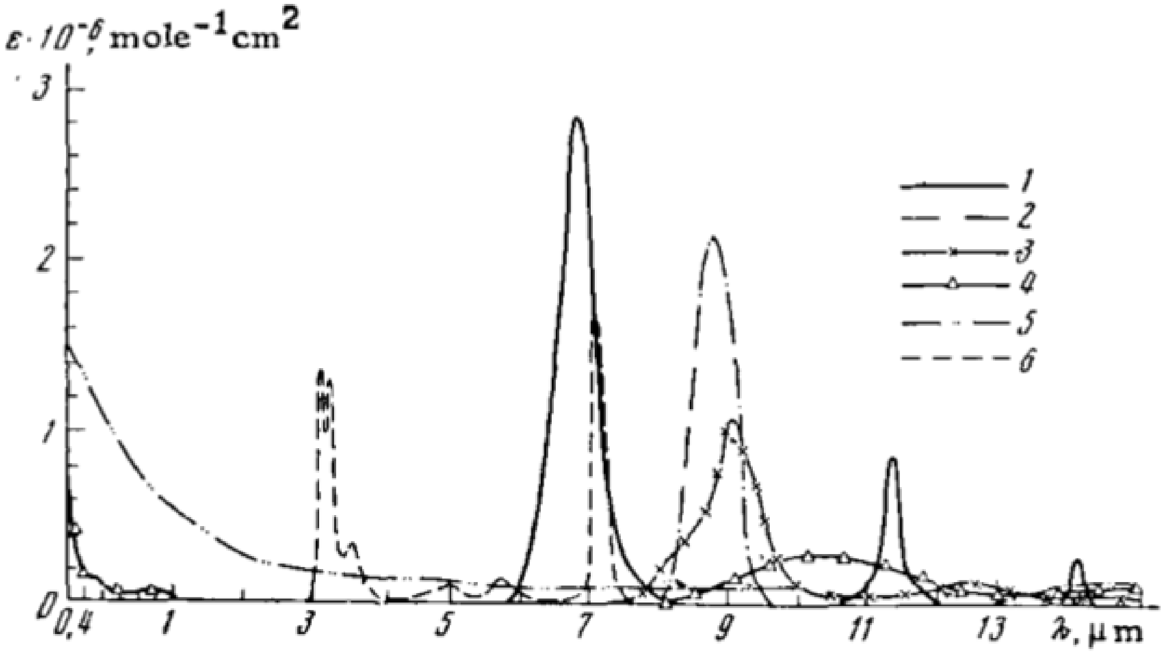
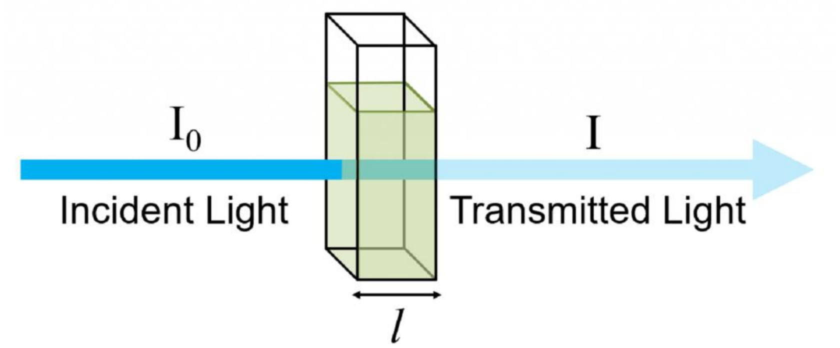


Fig. 5. Molar coefficients of absorption of the most important constituents of the atmospheric aerosol: 1) carbonate class; 2) sulfate class; 3) silicates; 4) amorphous hematite; 5) carbon black; 6) ammonium group.

Ivlev and Popova, *Izv. Atmos. Ocean. Phys.*, 1973

Radiative transfer models

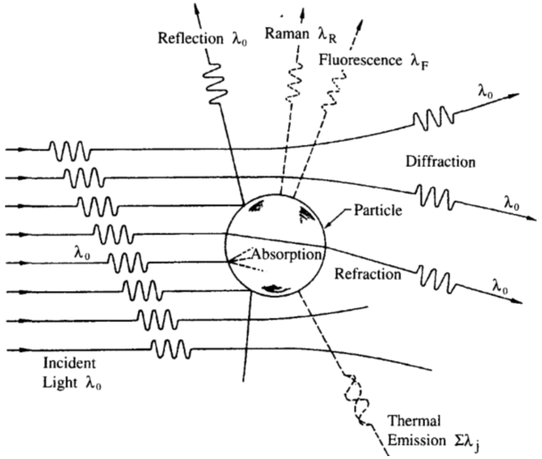


Bouguer-Lambert-Beer law of absorption

$$dI = -N\sigma I d\ell \quad \mathrm{I} = I_0 \text{ at } \ell = 0$$

$$T = \frac{I}{I_0} = e^{-N\sigma\ell}$$

$$A = -\log T = N\sigma\ell$$



Particles scatter radiation

$$\sigma \rightarrow \sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{sca}}$$

Atmosphere is a mixture of multiple phases

$$A = \ell \left(\sum_{i \in \text{gases}} N_i \sigma_{\text{ext},i} + \sum_{i \in \text{particles}} N_i \sigma_{\text{ext},i} + \sum_{i \in \text{hydrometeors}} N_i \sigma_{\text{ext},i} \right)$$

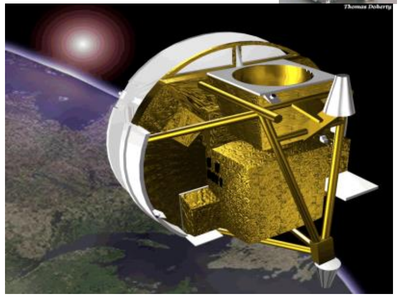
https://www.edinst.com/blog/the-beer-lambert-law/

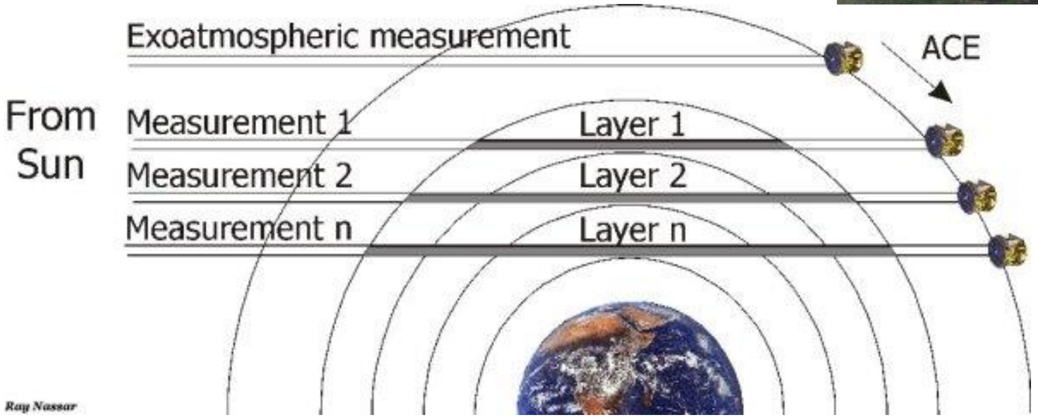
Pandis and Seinfeld (2006)

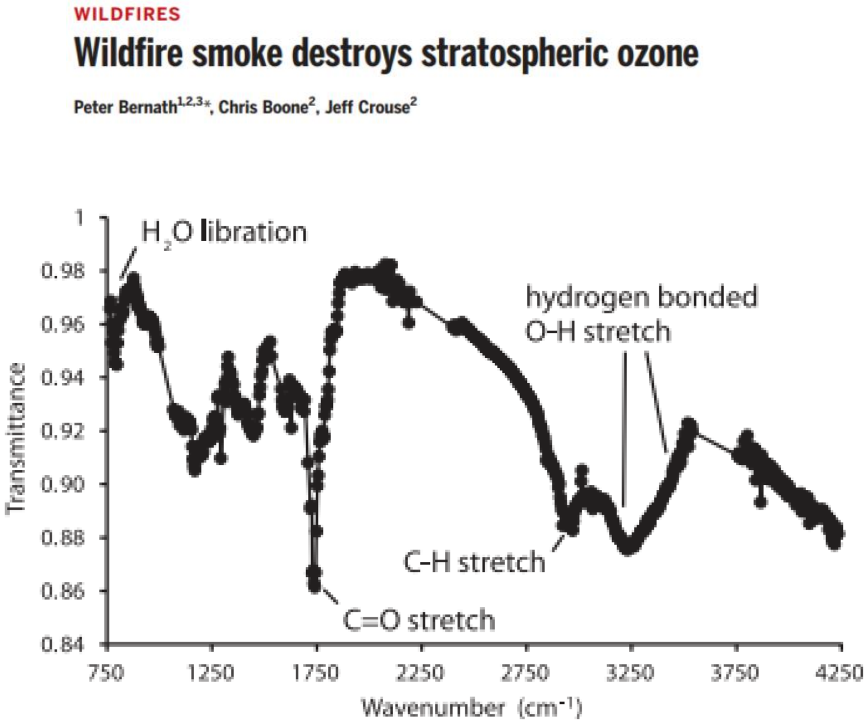
Applications to environmental monitoring / Earth Observation

ACE-FTS aboard the SCISAT-1

Atmospheric Chemistry Experiment – Fourier Transform Spectrometer





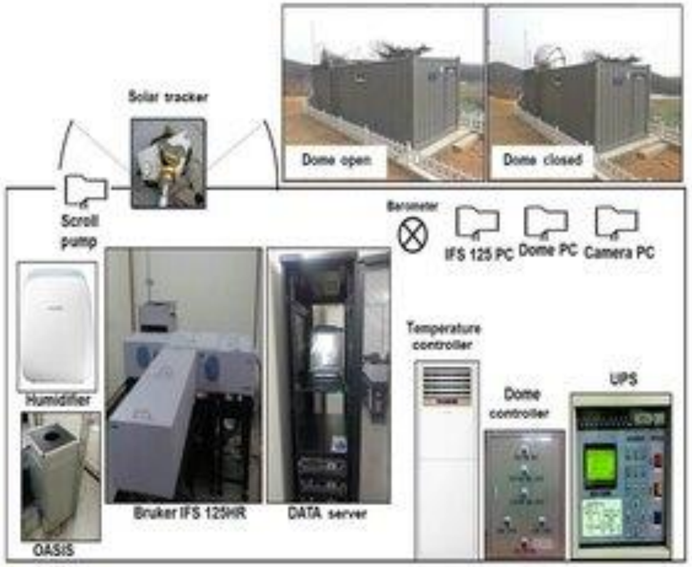


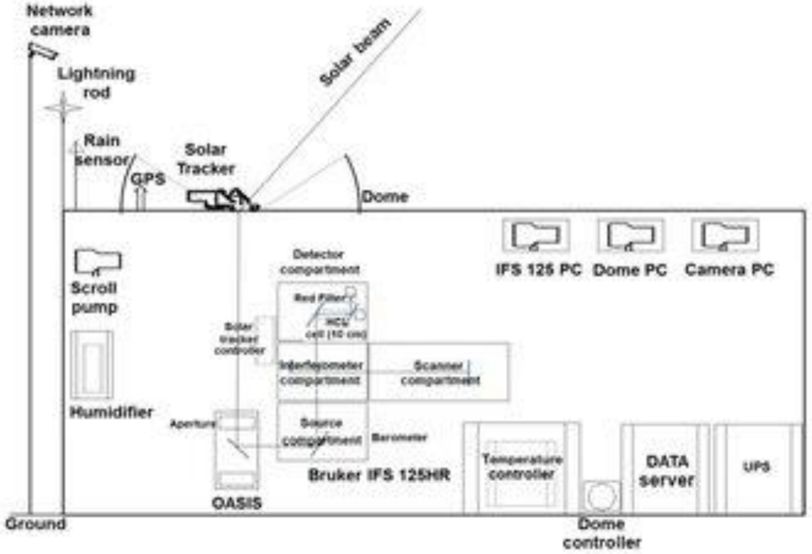
Wavenumber $\tilde{\nu} = \frac{1}{\lambda}$

https://uwaterloo.ca/atmospheric-chemistry-experiment/mission/solar-occultation-orbit
https://uwaterloo.ca/atmospheric-chemistry-experiment/instruments/ace-fts
https://www.nasa.gov/image-article/scientific-satellite-atmospheric-chemistry-experiment-1-scisat-1/

Solar-viewing FTS in the NDACC

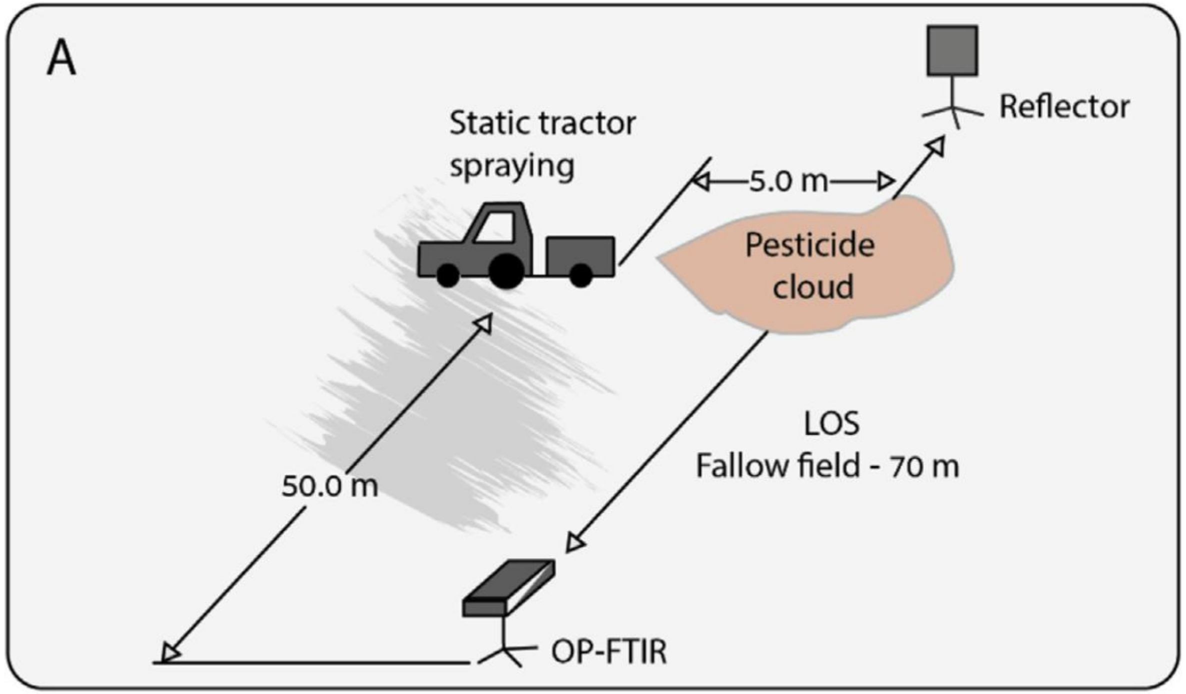
Network for the Detection of Atmospheric Composition Change

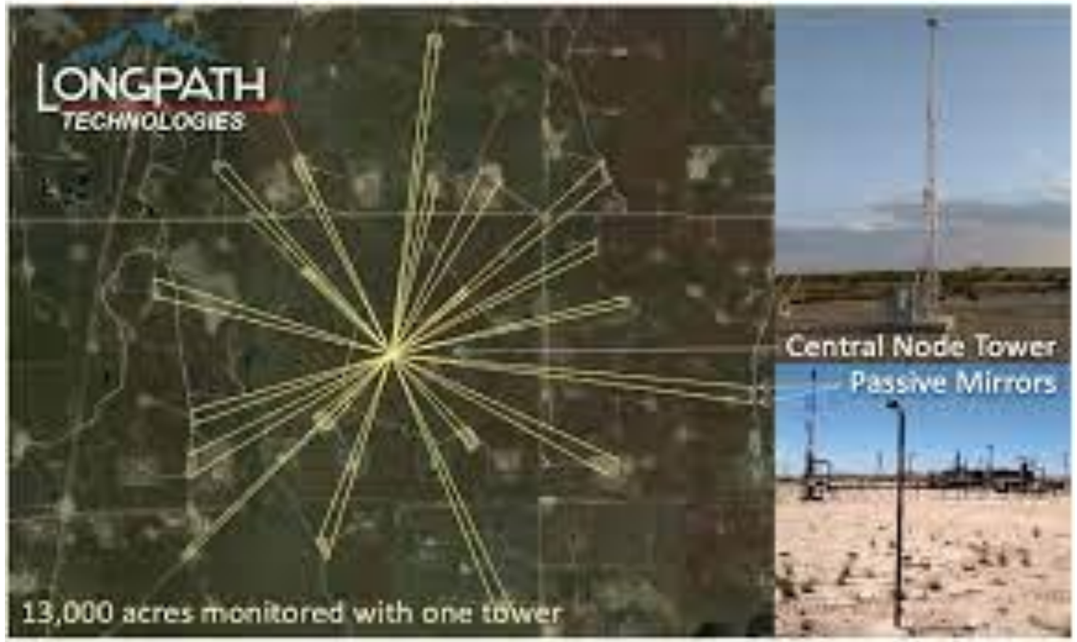




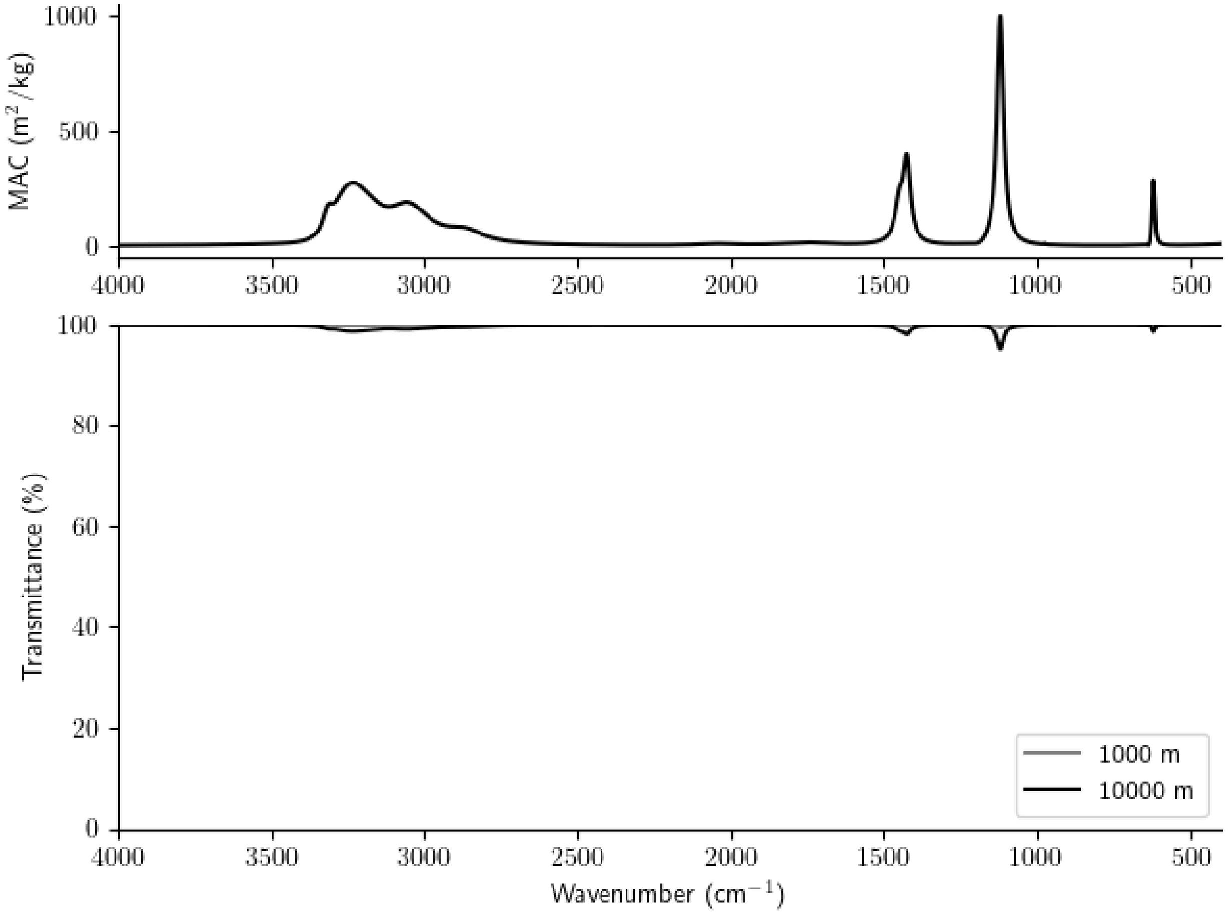
Oh et al., doi:10.5194/amt-11-2361-2018, 2018

Open-path infrared ("standoff detection")



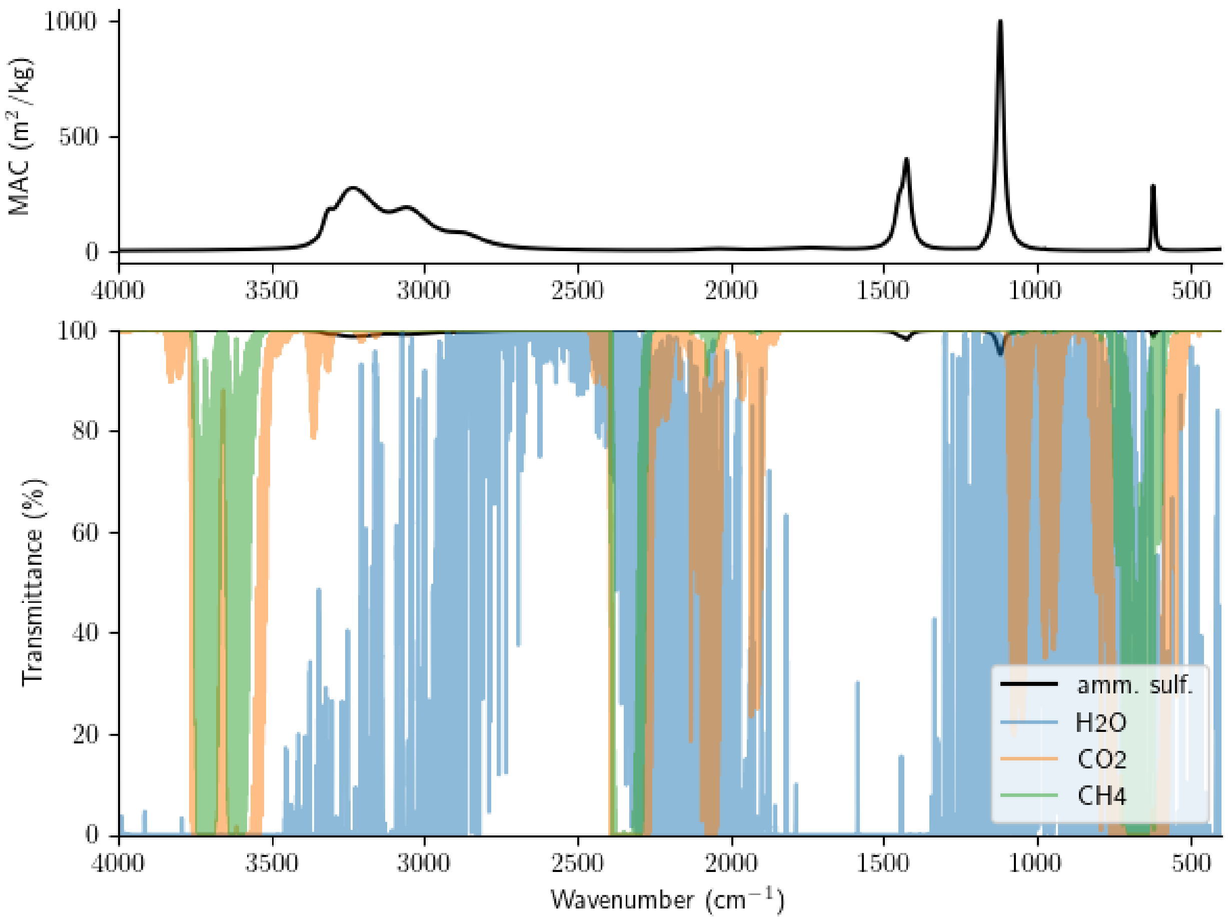


Kira et al., *Atmos. Environ.*, 2016



virtual experiment

- ammonium sulfate 5 µg/m^3
- path lengths 1 and 10 km



virtual experiment

- ammonium sulfate 5 µg/m^3
- path length 10 km
- H_2O: 50%RH at 25 deg.C (11 g/m^3)
- CO_2: 420 ppm (0.8 g/m^3)
- CH_4: 1911 ppb (1 mg/m^3)

Advances in open path technologies

- High intensity source
- High spectral resolution (remove gas phase)
- Stable baseline
- Select applications

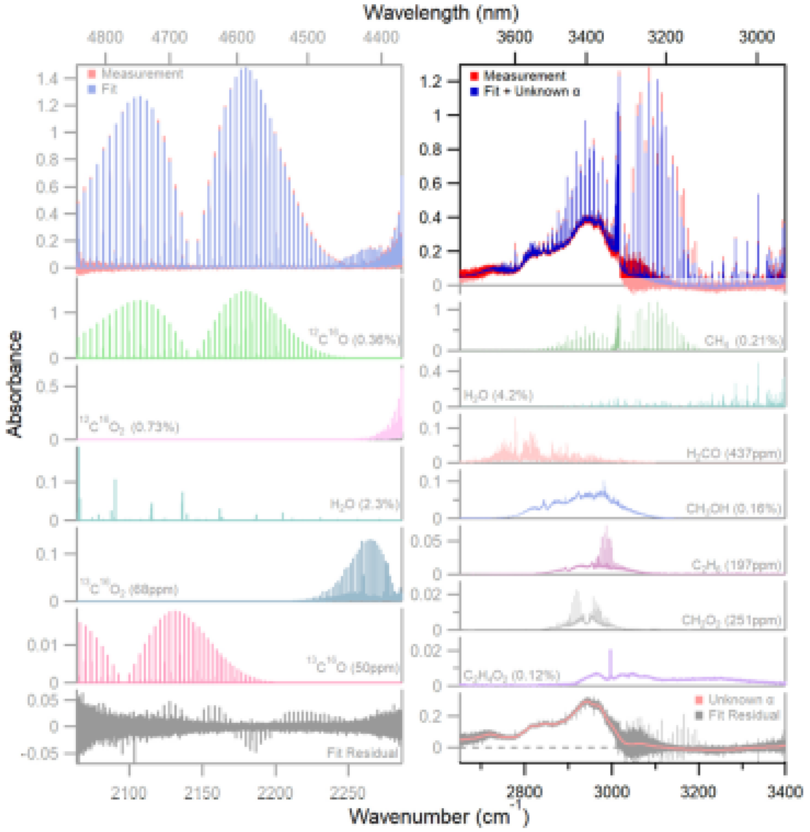
Proceedings of the Combustion Institute

Mid-infrared dual frequency comb spectroscopy for combustion analysis from 2.8 to 5 µm

Amanda S. Makowiecki[a], Daniel I. Herman[b], Nazanin Hoghooghi[a], Elizabeth F. Strong[a], Ryan K. Cole[a], Gabe Ycas[c], Fabrizio R. Giorgetta[c], Caelan B. Lapointe[a], Jeffrey F. Glusman[a], John W. Daily[a], Peter E. Hamlington[a], Nathan R. Newbury[c], Ian R. Coddington[c], Gregory B. Rieker[a,*]

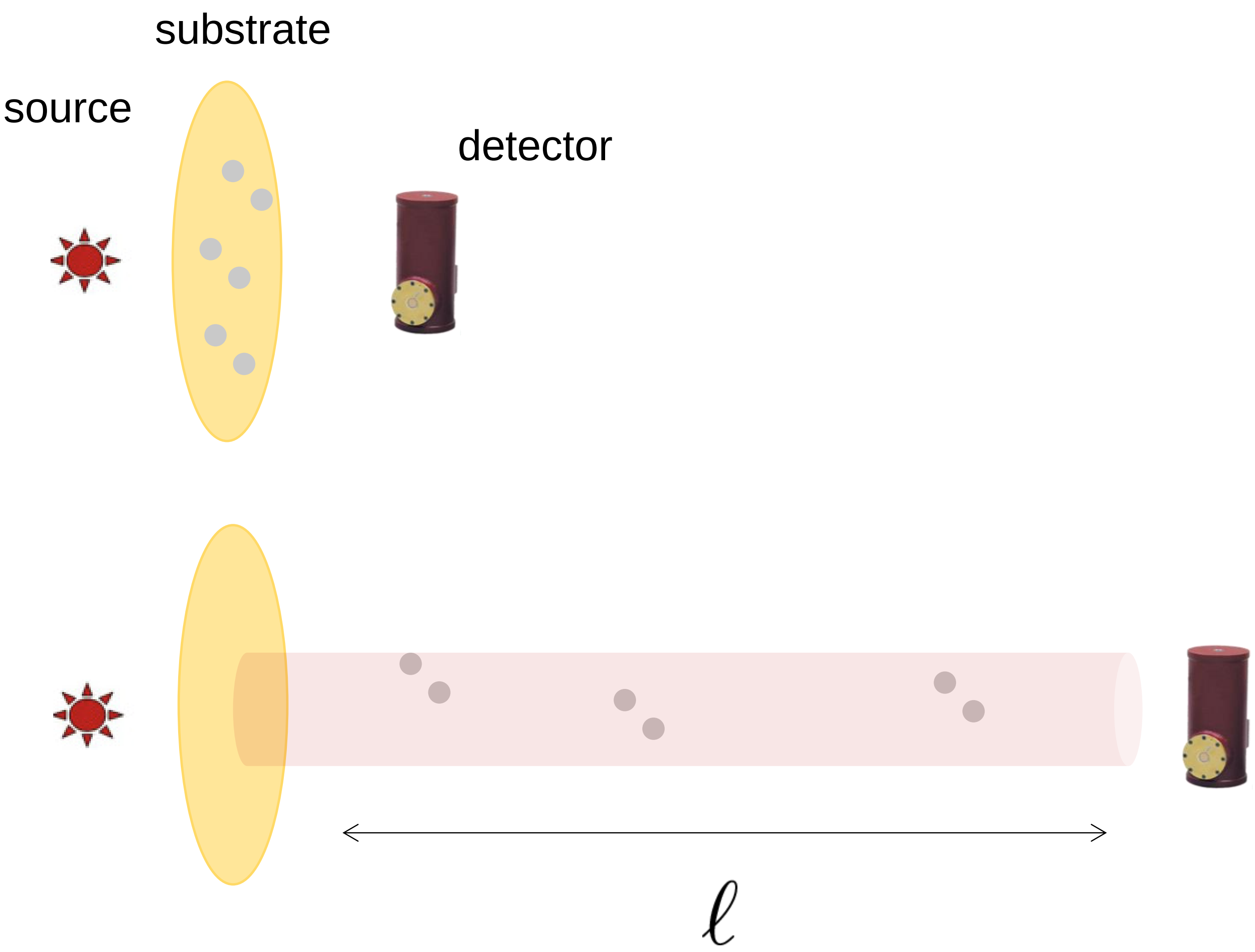
[a] Department of Mechanical Engineering, University of Colorado Boulder, Boulder, CO 80309, USA
[b] Department of Physics, University of Colorado Boulder, Boulder, CO 80309, USA
[c] National Institute of Standards and Technology, Boulder, CO 80305, USA

Received 7 November 2019; accepted 7 June 2020
Available online 29 September 2020



Mid-infrared in aerosol chemical monitoring

Particle collection for infrared sensing



areal number density

$$A = N^{(\mathrm{area})}\sigma_{\mathrm{ext}}$$

$$N^{(\mathrm{area})} = N\ell$$

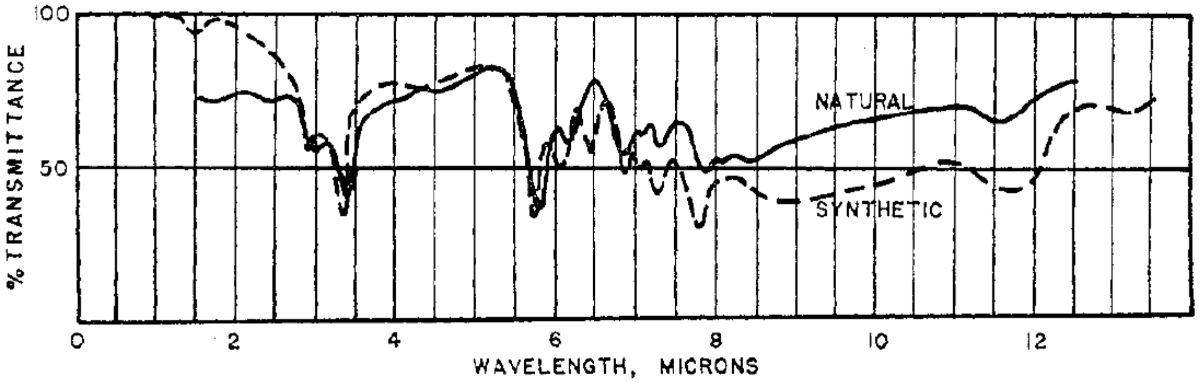
$$\ell = v_f t$$

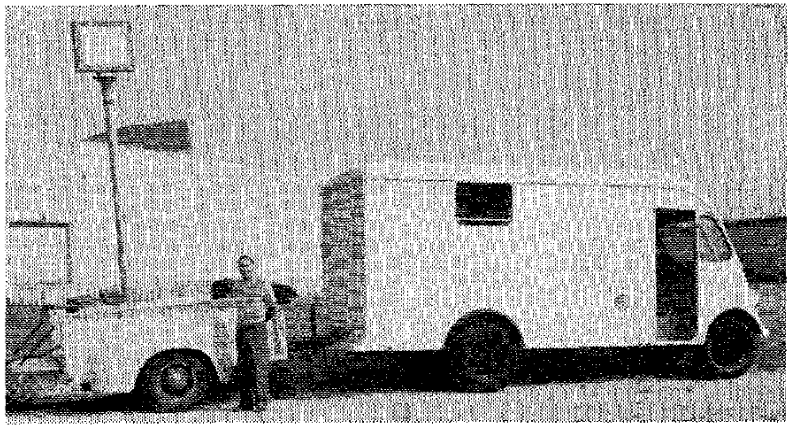
substrate face velocity

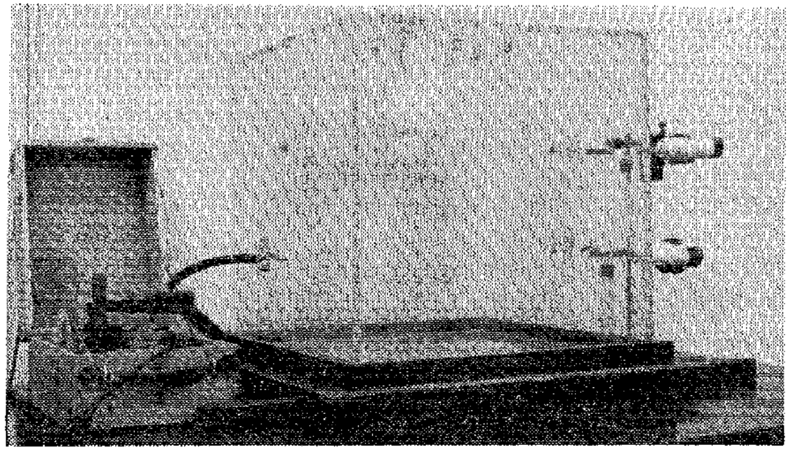
Composition of Organic Portion of Atmospheric Aerosols in the Los Angeles Area

PAUL P. MADER, ROBERT D. MACPHEE,
ROBERT T. LOFBERG, AND GORDON P. LARSON
Los Angeles County Air Pollution Control District, Los Angeles, Calif.

June 1952 INDUSTRIAL AND ENGINEERING CHEMISTRY





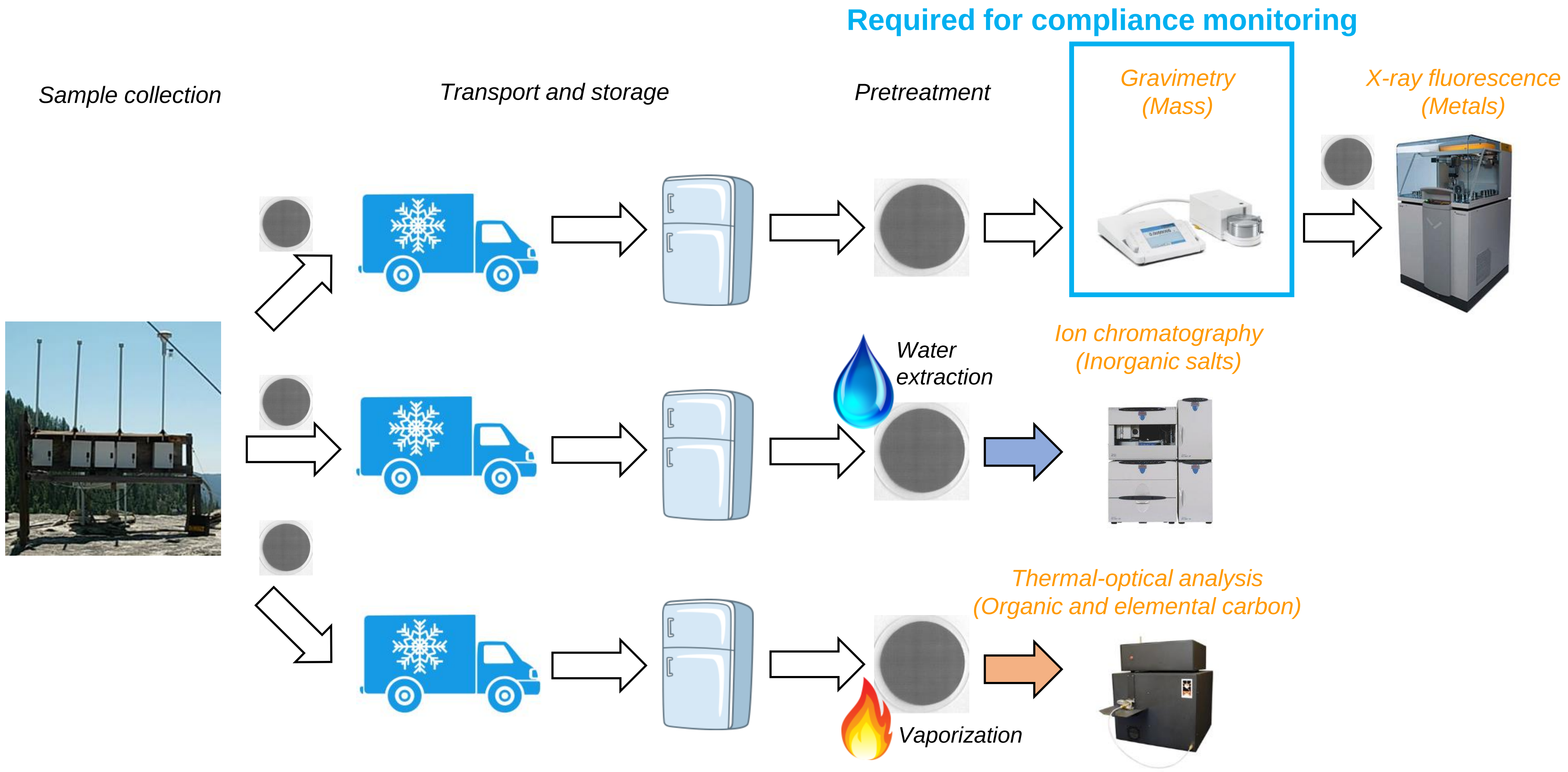


…~45 years later →

Chemical measurement technology tradeoffs

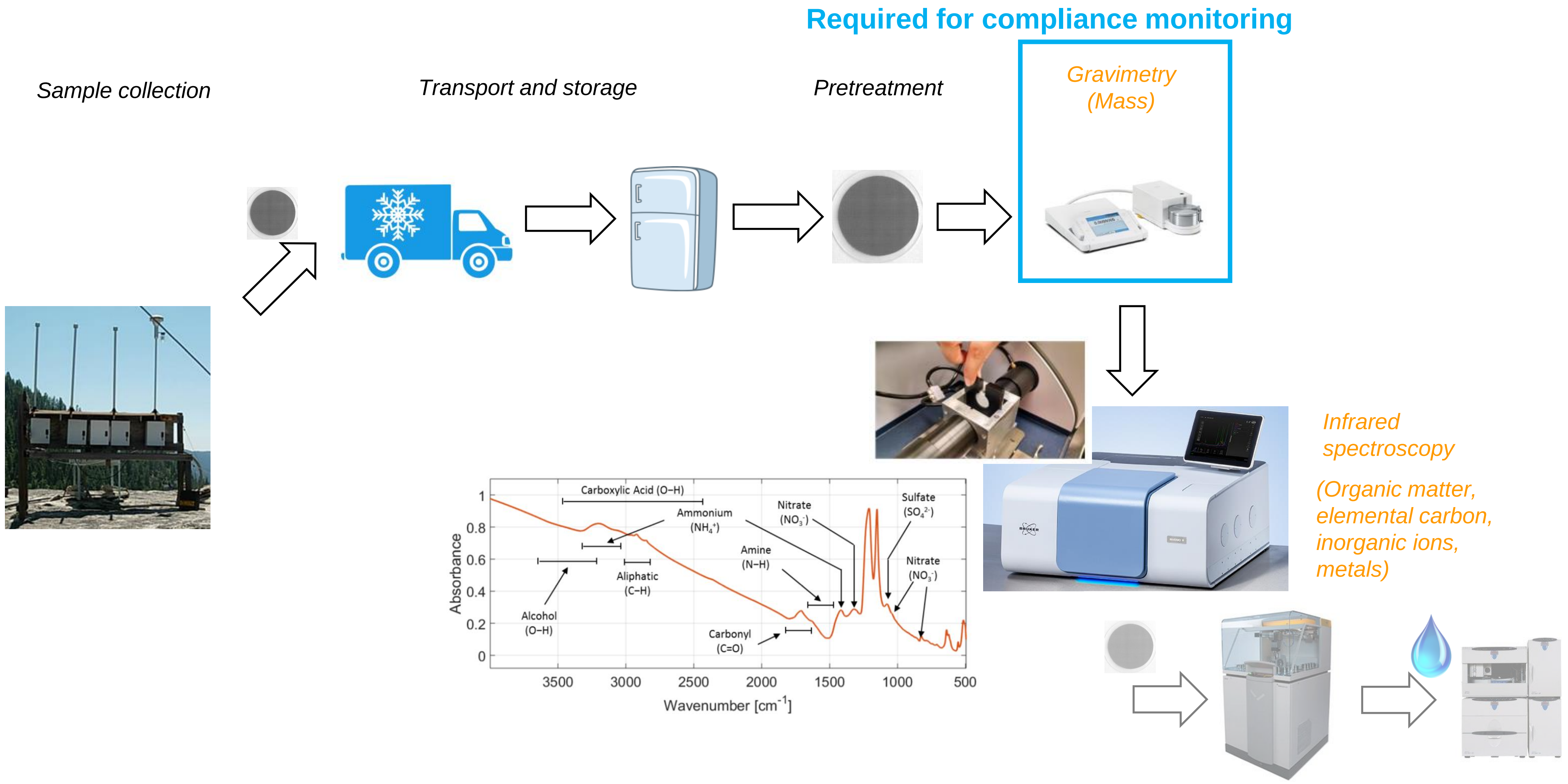
- offline / online
- time resolution
- chemical resolution (number of species)
- quantitative / qualitative
- physical / chemical separation vs algorithmic separation
- scalability – labor and cost

Conventional chemical speciation methods
Laborious and costly



Mid-infrared spectrometry

Single analytical technique for chemical speciation



Challenges for quantitative analysis of atmospheric aerosols with infrared

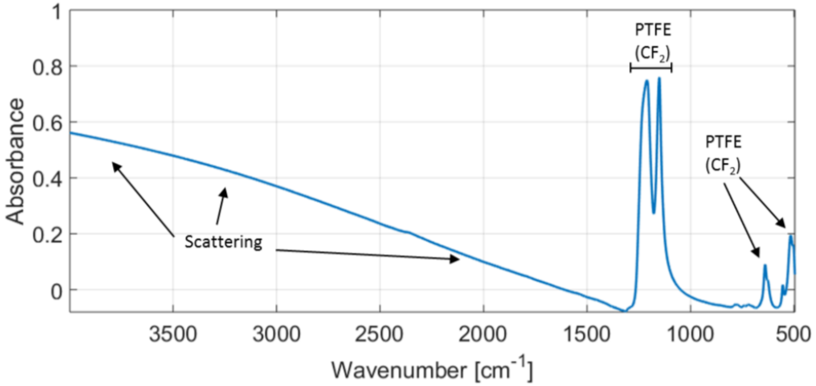
Environmental infrared spectra is especially complex

- heterogeneous media leading to scattering and other phenomena
- mixtures leading to overlapped peaks
- interference from substrate

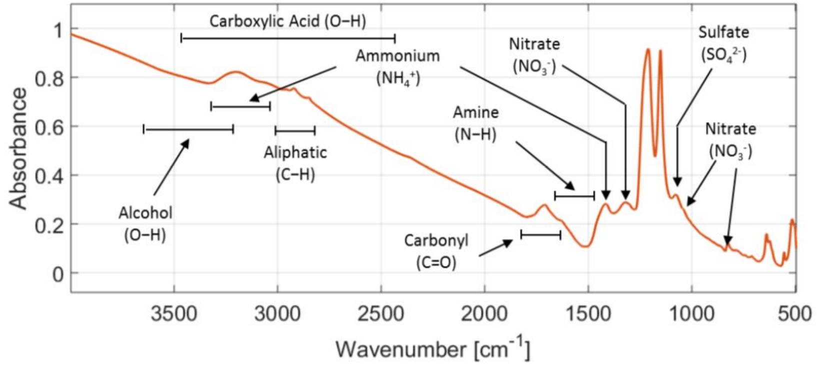
Algorithmic approach
for quantitative analysis of atmospheric aerosols:

- ensure reliability across diverse samples in measurement network
- expert systems (first wave of AI)
- data-drive modeling (machine learning)

blank Teflon filter

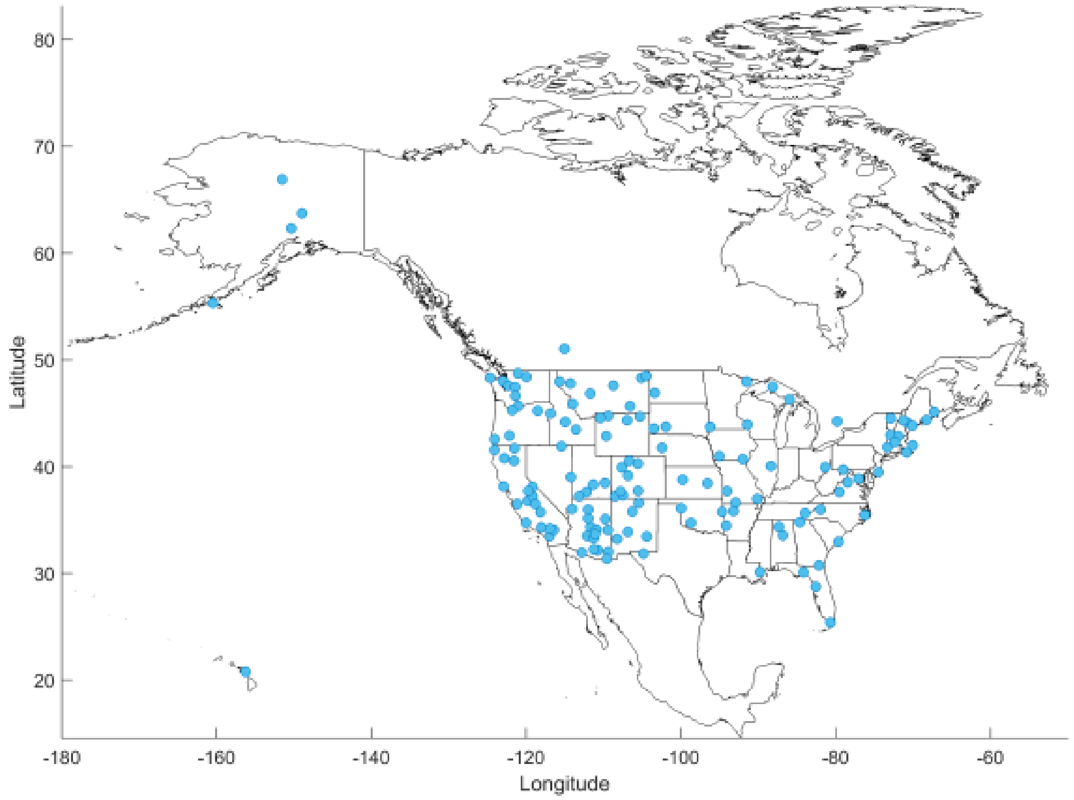


particle-loaded filter

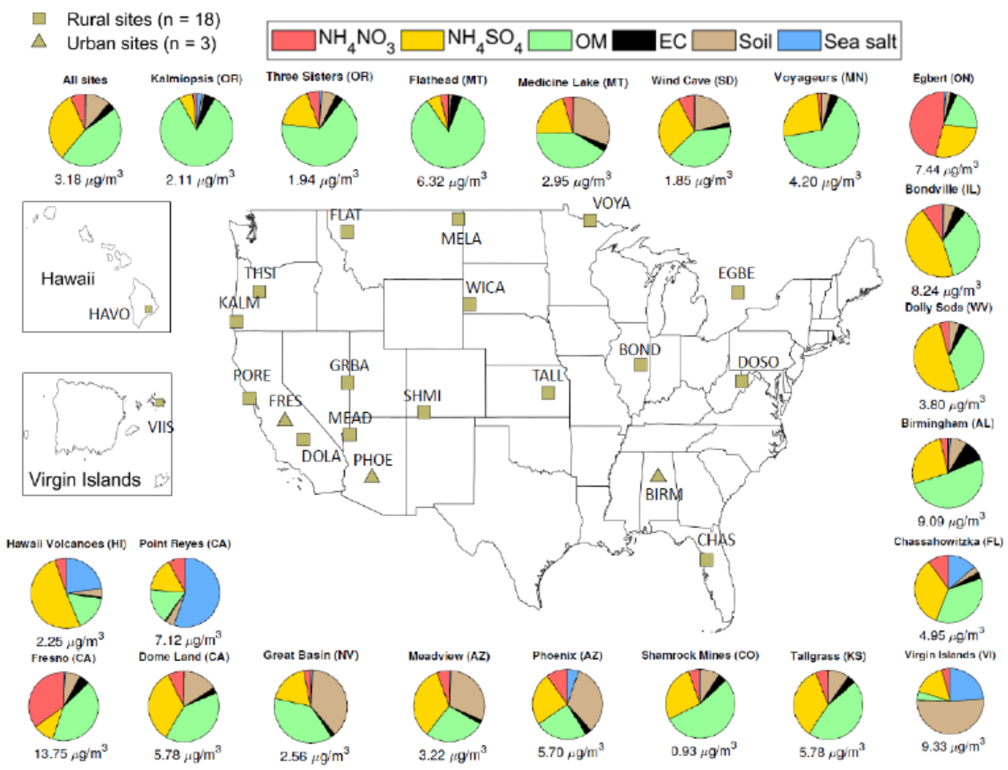


Debus, Takahama et al., *Appl. Spectroscopy*, 2018

Example demonstration in IMRPOVE
Interagency Monitoring of Protected Visual Environments

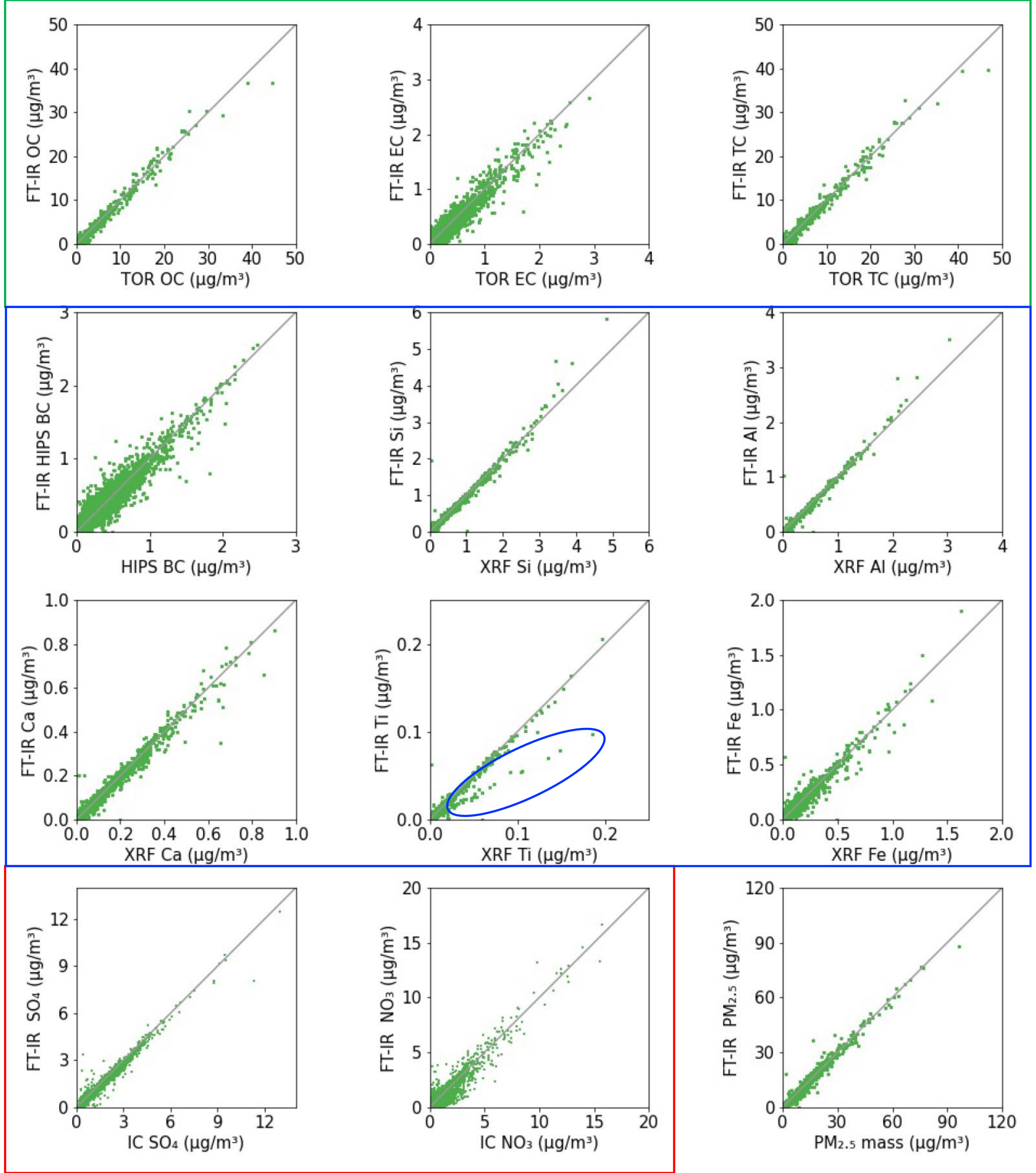


IMPROVE network, 161 sites



21 sites selected based on abundance of spectral types

Debus et al., *Atmos. Meas. Tech. Discuss*, 2021



carbon

metals

inorganic salts
and $PM_{2.5}$

Predictions for ~61,500 samples from 2015-2017

Prediction accuracy compared against collocated precision of reference

Error for Ti in Sycamore Canyon (AZ)

Editorials

nature

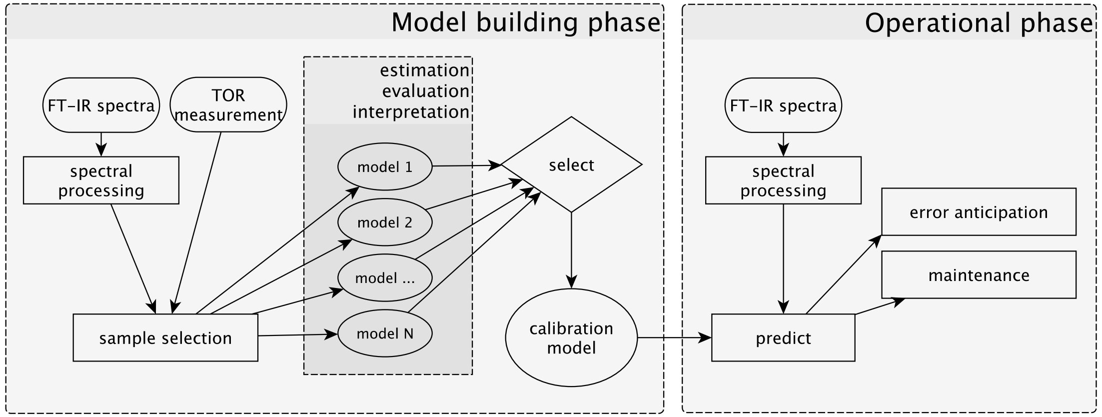
| Nature | Vol 617 | 18 May 2023

For chemists, the AI revolution has yet to happen

Machine-learning systems in chemistry need accurate and accessible training data. Until they get it, they won't achieve their potential.

"The best possible training sets would also include data on negative outcomes."

Network implementation

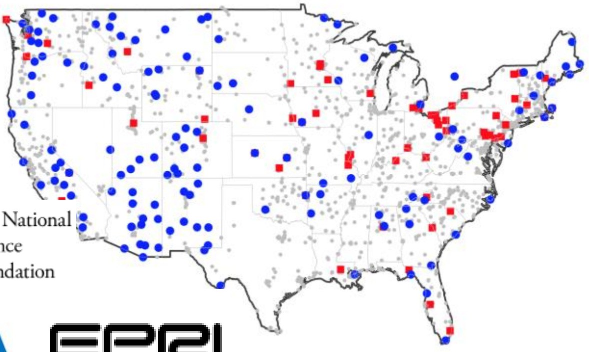


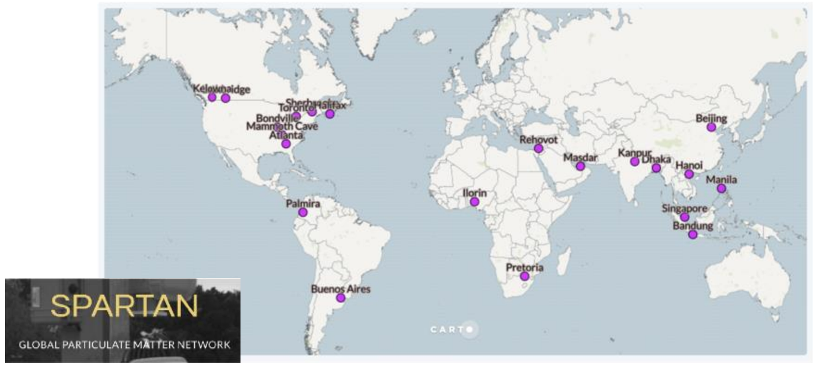
Takahama et al., *Atmos. Meas. Tech.*, 2019
Debus et al., *Atmos. Meas. Tech.*, 2022

Quantification of major species:

- Organic and elemental carbon
- Organic matter
- Inorganic salts
- Mineral dust

~200,000 samples
over 8 years across 5 separate monitoring networks



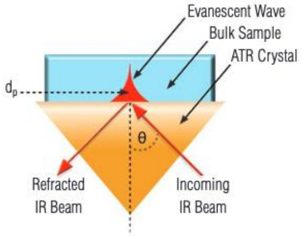


Toward an automated infrared monitor

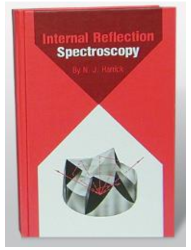
Methods for particle collection

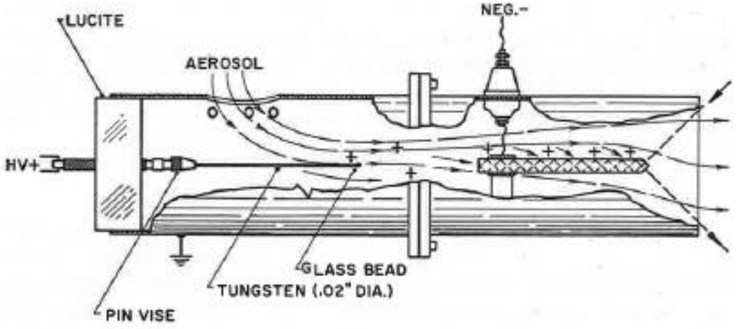
- Passive sedimentation
- Filtration
- Impaction
- Electrostatic deposition
- Thermophoresis

Past designs proposed

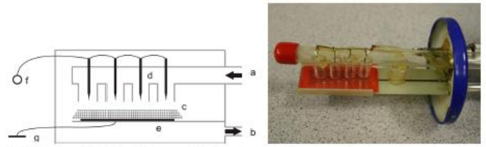


Harrick 1979
(1st printing 1967)

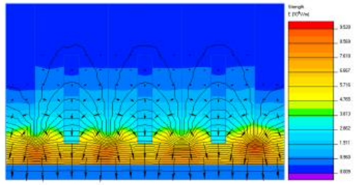




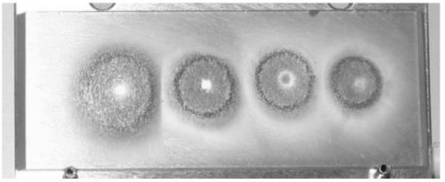
Ofner et al. 2008
Tech. Univ. Vienna

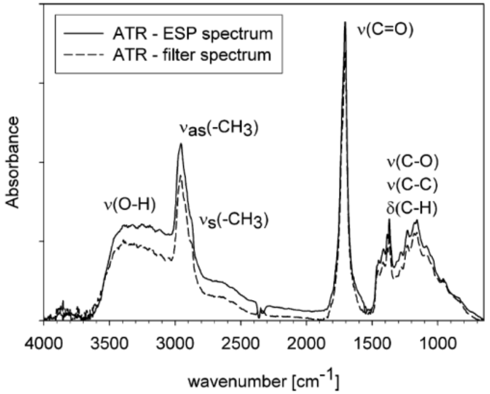


(a) Concept: a–inlet, b–outlet, c–crystal, d–needles, e–copper plate, f–high voltage supply, g–electric ground (b) Experimental setup: ESP version 1 with a KRS-5 ATR crystal on the deposition plate

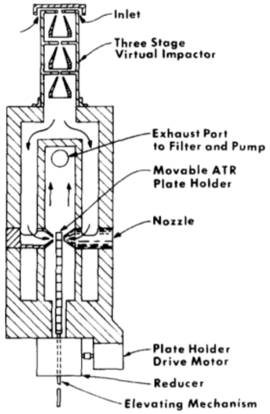


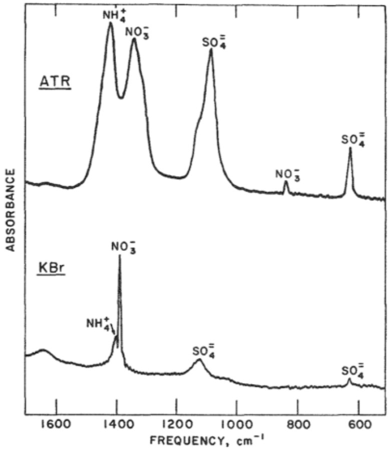
(c) Calculation: The maximum of the electric field strength is directed towards the crystal surface where deposition of the charged particles takes place.





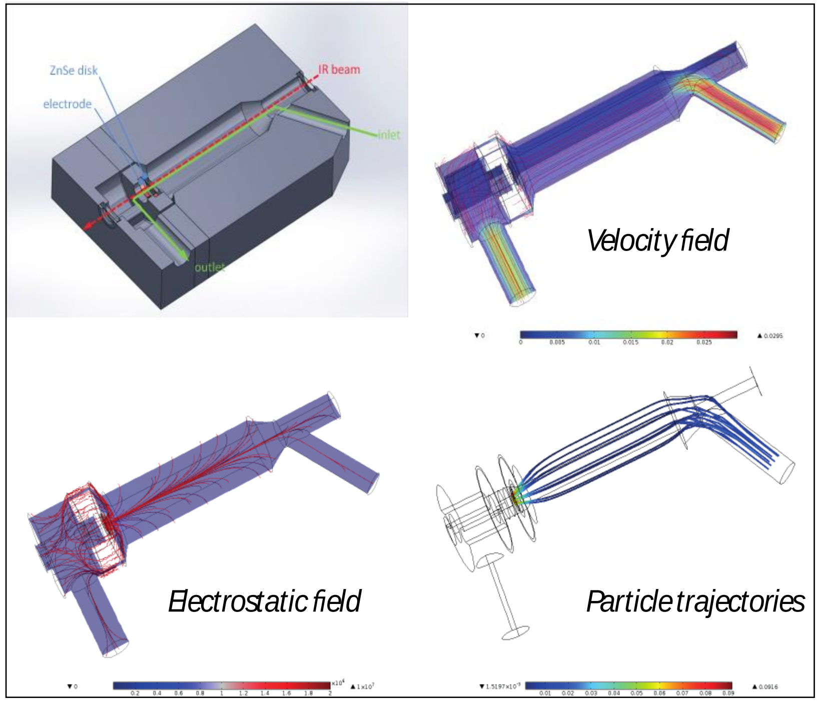
Johnson 1981
Argonne National Lab





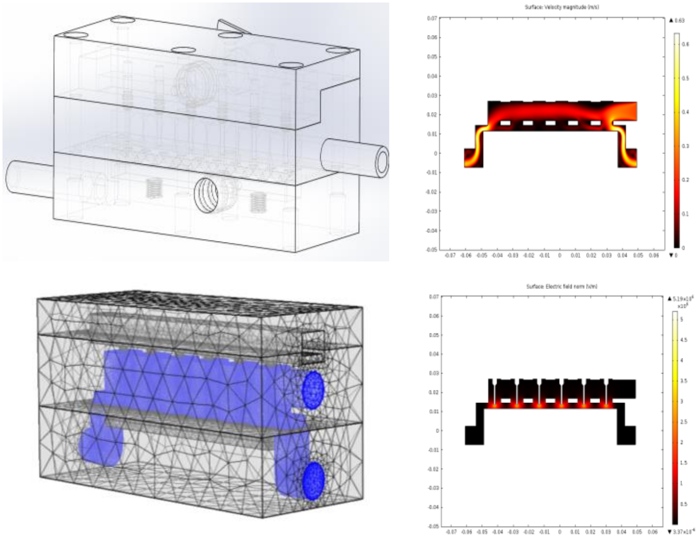
Evolution in design at EPFL

2012-2013

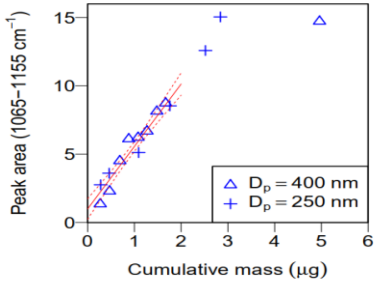


Florian Breider

2014-2017

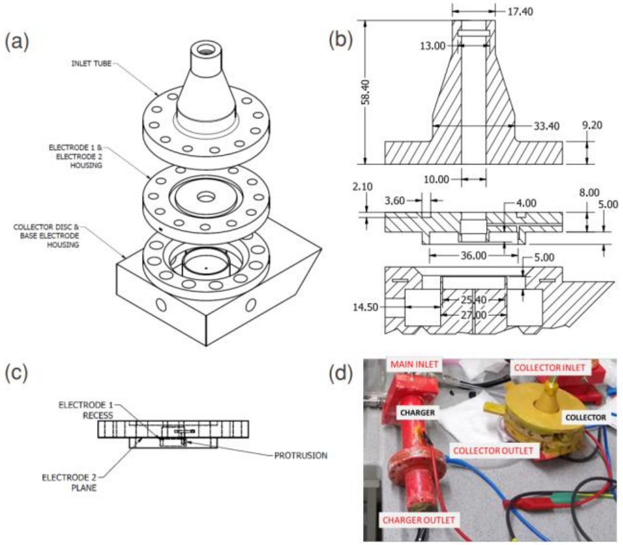


Rob Modini
Christophe Delval

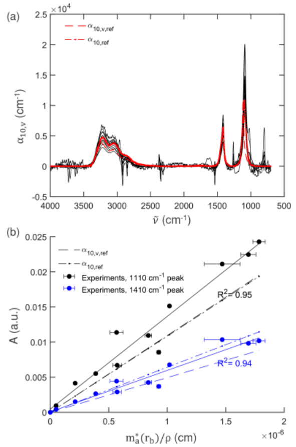


European
Commission

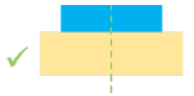
2017-2019



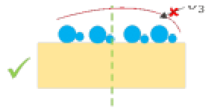
Nikunj Dudani



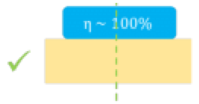
Core innovation in particle collection



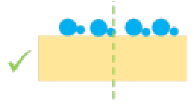
Uniform deposition



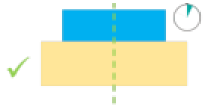
Minimal chemical modification



High collection efficiency



Low particle size dependence



High throughput

$$r_f/R_c = \Omega\left(\frac{r_i^*}{r_{lim}^*}\right)\sqrt{r_{geo}^{\dagger\,2}+3\alpha\beta\left(\frac{2-\Omega^2 r_i^{*2}}{2-r_{lim}^{*\,2}}\right)}$$

$$\Omega = \frac{r_0^*}{r_i^*} = f\left(r_i^*, \frac{H}{R}, \frac{R}{R_c}, \alpha, \beta\right) ;\ r_{geo}^\dagger = \left(r_{lim}^* \frac{R}{R_c}\right) ;\ \alpha = \frac{Q_a\mu}{eE_0R_c} ;\ \beta=\frac{D_p}{nC_cR_c} ;\ r_0^*=\frac{r_0}{R} ;\ r_{lim}^*=\frac{r_{i,\max}}{R}$$

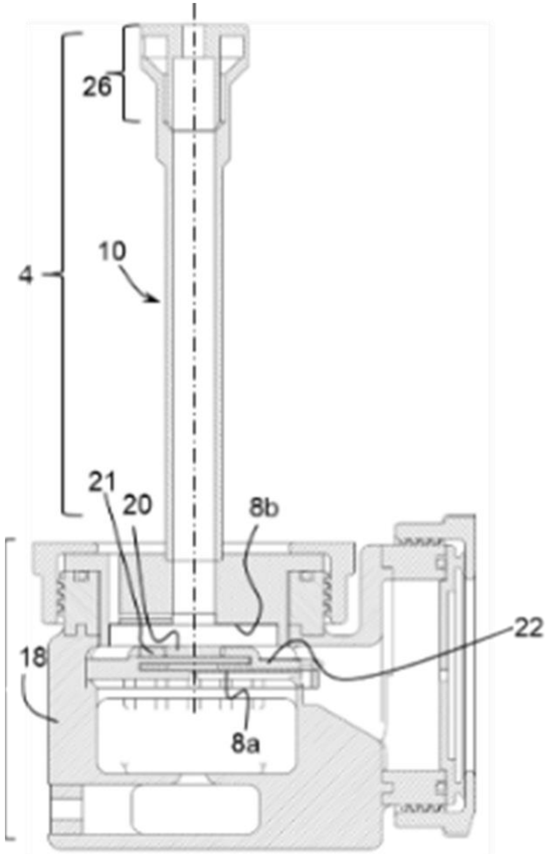
$$0\le r_i \le r_{lim}^* ;\ 0\le\Omega\le1$$

$$\Omega^3 - \frac{3}{r_i^{*2}}\left(1+\frac{v_{\mathrm{elec},r}}{2v_{\mathrm{in}}}\right)\Omega - \left\{1-\frac{3}{r_i^{*2}}\left(1+\frac{v_{\mathrm{elec},r}}{2v_{\mathrm{in}}}\right)+\frac{3}{r_i^{*3}}\left(\frac{v_{\mathrm{elec},r}}{2v_{\mathrm{in}}}\right)\right\}=0$$

$$\text{where } v_{\mathrm{in}}/v_{\mathrm{elec}} = \frac{1}{E_{\mathrm{corr}}}\frac{3\alpha\beta}{r_{lim}^{*\,2}(2-r_{lim}^{*\,2})}\left(\frac{R}{R_c}\right)^{-2} ;\ E_{\mathrm{corr}}=f(H/R)$$

Geometric variables	Operating variables	Inlet variables	Performance variables
R_c: Collection disc radius R: Inlet radius H: Electrode separation distance	Q_a: Aerosol flow rate E: Electric field strength V_0: Voltage difference between $z=0$ and $z=H$	D_p: Particle diameter n: no. of elementary charges on the particle r_{lim}^*: Sheath position r_i^*: Inlet position	$\frac{r_f}{R_c}$: Dimensionless final position of deposition

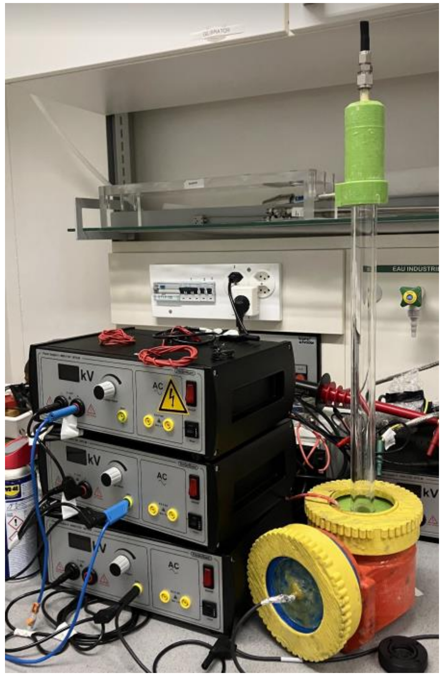
Dudani, PhD thesis, 2021



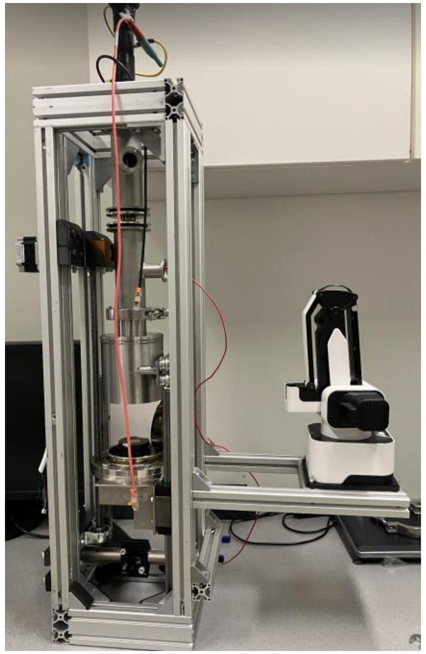
Dudani and Takahama (US patent) filed 2020; granted 2024

Toward automated measurement

Prototype collector
3-D printed
2019-2021

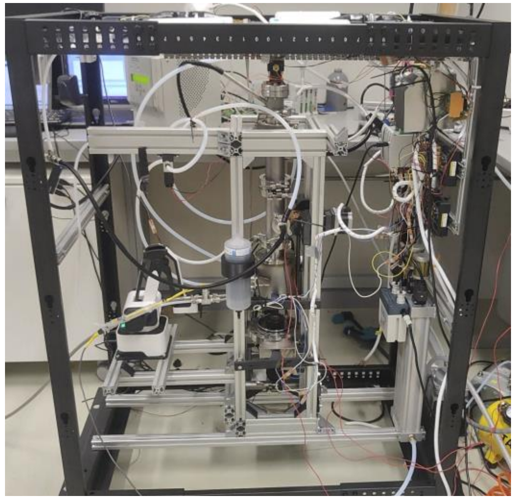


Sample collector
machine fabrication
2023



Fully-integrated
online monitor
2023-2024

Prototype v1

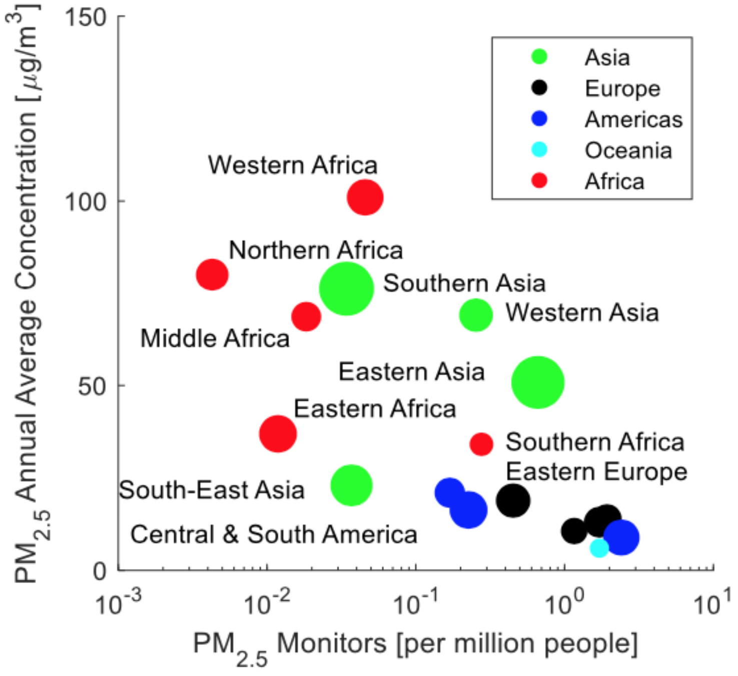


Prototype v2

Aerospec

FNSNF · Innosuisse · EPFL Innogrants · Venture Kick · Wissenschaft. Bewegen Gebert Rüf Stiftung · FIT Fondation pour l'innovation et la technologie

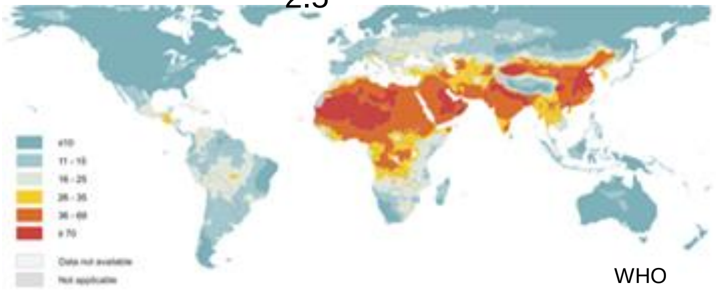
Need for cost-effective monitoring of air pollution



Lack of monitors in high population areas

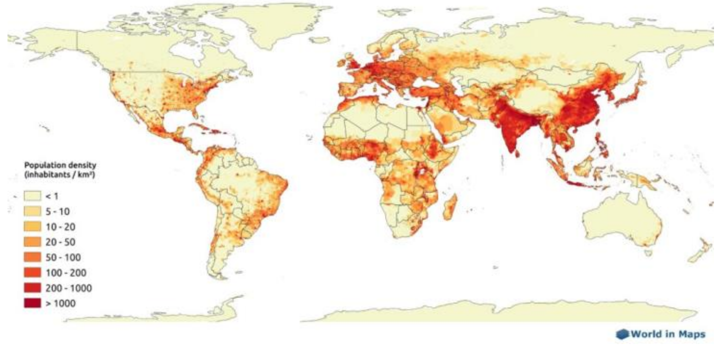
Malings et al., 2020

Estimated $PM_{2.5}$ concentrations

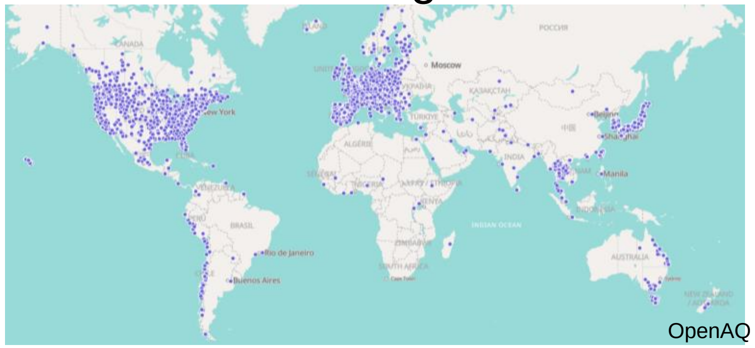


WHO

Population density



Available monitoring data



OpenAQ

Ground-based aerosol measurements

Advanced scientific instruments

- High chemical resolution
- Deploy in short, intensive campaigns
- Expensive

Low-cost sensors

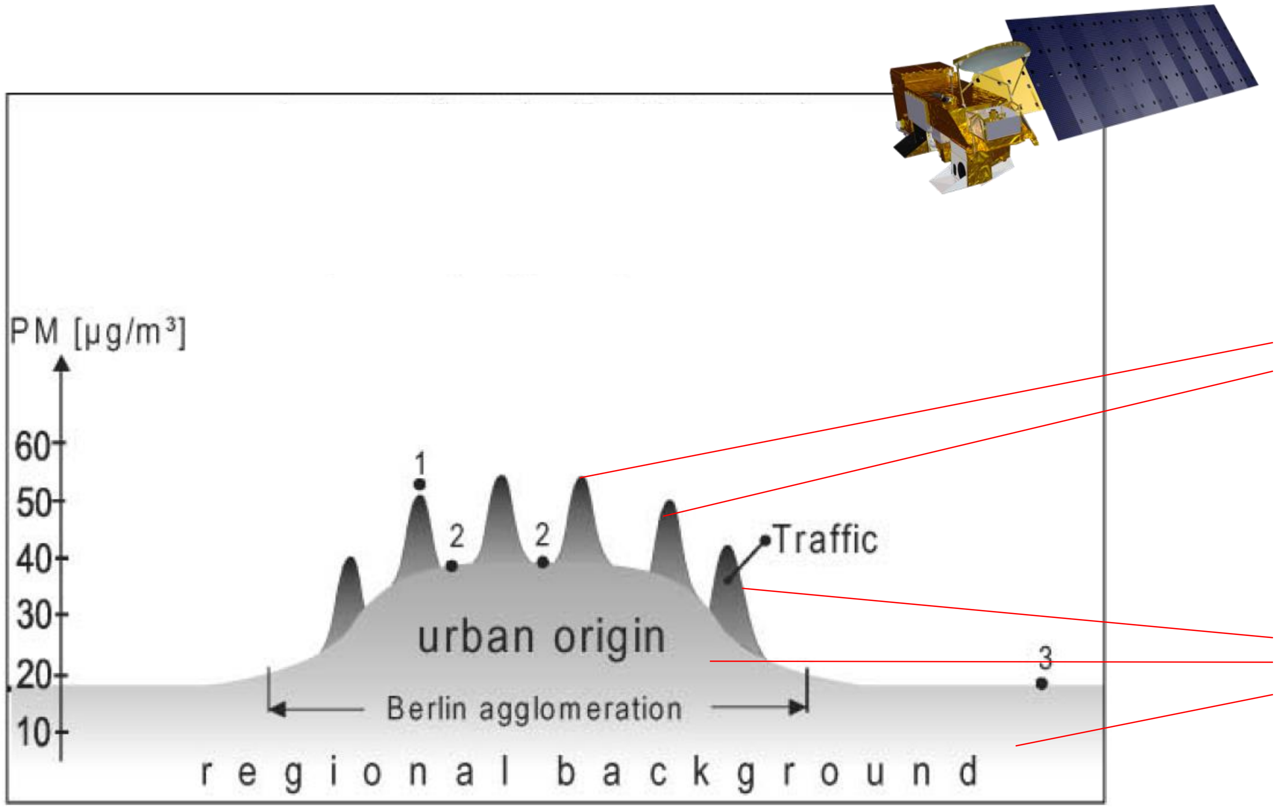
- High spatial (and time) resolution
- Personalized information (“citizen science”)
- No chemical information, low accuracy

Regulatory monitors

- Reliable, standardized
- Accurate
- Cost-effective
- Chemical speciation

Complementary monitoring strategies

Aerosol concentration



Spatial extent of urban city

Satellite observation
(*intermittent, clear-sky coverage)*

Low-cost sensors
(*high spatial coverage, low data quality)*

Reference monitors
(*high data quality,*
*"chemical fingerprint" of sources***)**

Figure from Lenschow et al., *Atmos. Environ.*, 2001