Overview of the last 30+ years of nanoparticle measurement and control

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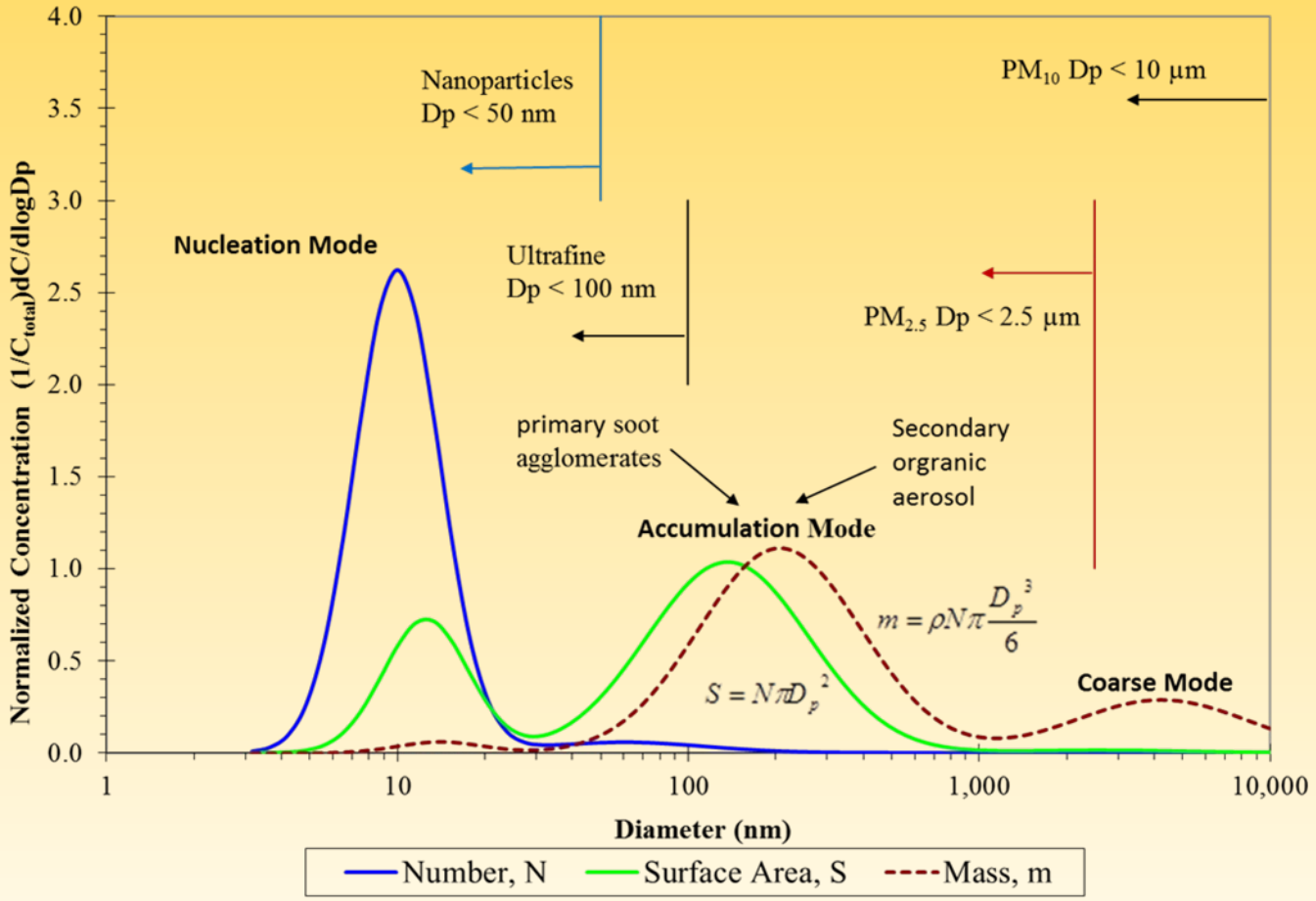
University of Minnesota

27th ETH Nanoparticles Conference
10-14 June 2024
ETH, Zurich

Most of you have seen this before, one of the first showings was at the 1997 ETH Naonoparticle meeting – but what came before?



Concentration proportional to area under curve in each size range

Events history – U of MN roadside trimodal distribution

- Whitby, K. T., Clark, W. E., Marple, V. A., Sverdrup, G. M., Sem, G. J., Willeke, K., Liu, B. Y. H., & Pui, D. Y. H. (1975). Characterization of California aerosols—I. Size distributions of freeway aerosol. Atmospheric Environment, 9(5), 463–482.
- Dolan D.F., K.T. Whitby, and D.B. Kittelson. 1975. "Measurement of Diesel Exhaust Particle Size Distribution," ASME Paper No. 75-WA/AC-5.
- Barnes, K.D., D.B. Kittelson, and T.E. Murphy. 1975. "Effects of Alcohols as Supplementary Fuels for Turbocharged Diesel Engines," SAE Paper No. 750469.
- Wilson, W.E., L.L. Spiller, T.G. Ellestad, R.J. Lamothe, T.G. Dzubay, R.K. Steven, E.S. Macias, J.D. Husar, R.B. Husar, K.T. Whitby, D.B. Kittelson, and B.K. Cantrell. 1977. "General Motors Sulfate Dispersion Experiment: Summary of EPA Measurement," J.A.P.C.A., 27, 1.
- Dolan, D.F. and D.B. Kittelson. 1979. "Roadway Measurements on Diesel Exhaust Aerosols," SAE Paper No. 790492.
- Kittelson, D.B., P.A. Kadue, H.C. Scherrer, and R. Lovrien. 1988. "Characterization of Diesel Particles in the Atmosphere," CRC project AP-1, Final Report, submitted to Coordinating Research Council, March 1988.

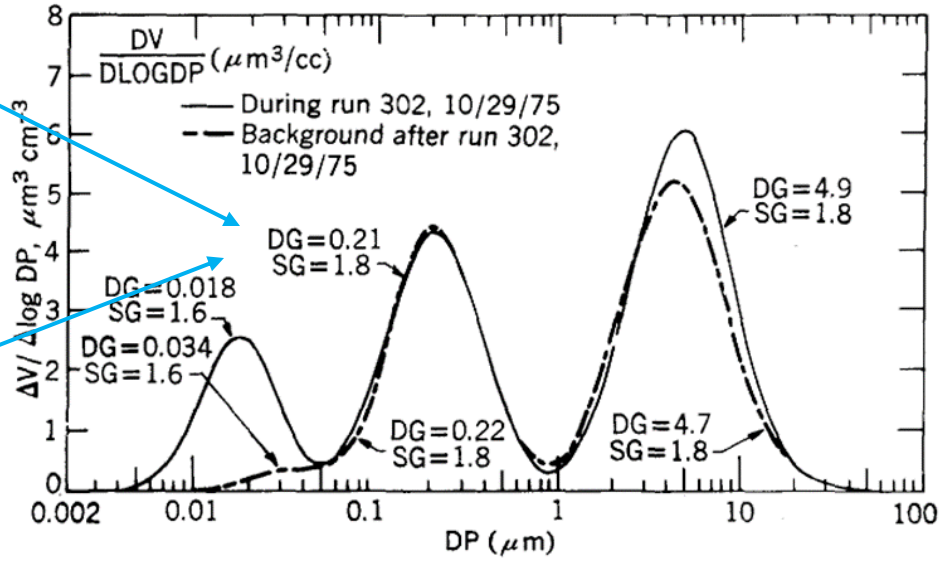


Figure 5. *Trimodal model distribution measured at the EPA trailer during run 302 on 10/29/75. The model distributions were obtained by fitting the data shown in Figure 5. Note that during the test the accumulation and coarse particle modes (center and right modes) have not changed significantly from the background conditions. On the other hand, practically all of the volume of the nuclei mode (left mode) is contributed by the cars on the roadway.*

Events history – On-road chase experiments MN CRC

- Whitby, K. T., Clark, W. E., Marple, V. A., Sverdrup, G. M., Sem, G. J., Willeke, K., Liu, B. Y. H., & Pui, D. Y. H. (1975). Characterization of California aerosols—I. Size distributions of freeway aerosol. Atmospheric Environment, 9(5), 463–482.
- Dolan D.F., K.T. Whitby, and D.B. Kittelson. 1975. "Measurement of Diesel Exhaust Particle Size Distribution," ASME Paper No. 75-WA/AC-5.
- Barnes, K.D., D.B. Kittelson, and T.E. Murphy. 1975. "Effects of Alcohols as Supplementary Fuels for Turbocharged Diesel Engines," SAE Paper No. 750469.
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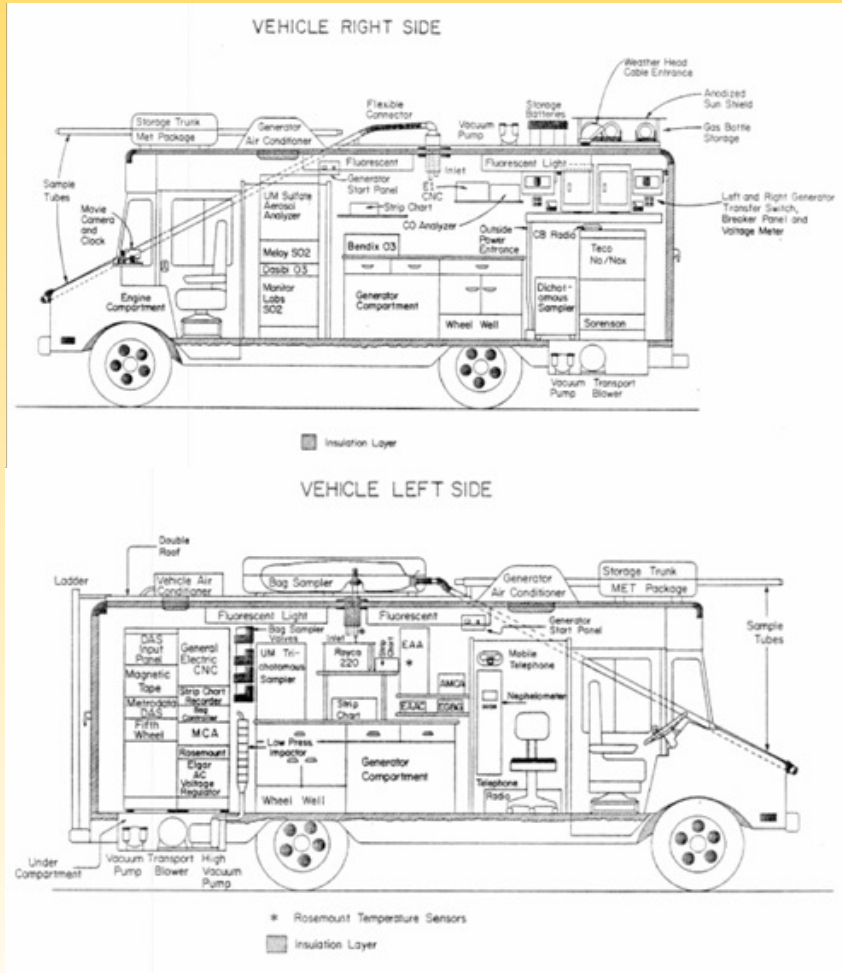

Events history – CRC, ETH, U of MN, ***other emission related..***

- October 1990 - First CRC-APRAC Vehicle Emissions Modeling Workshop
- 1990 – CRC EMA, U of MN, Michigan Tech, PM measurement variability study
  - Concern about meeting and measuring1994 PM emission Std
- November 1993 - CRC Workshop on Combustion Chamber Deposits
  - MN presentation on thermophoretic deposition and PM emission
- 1996 – HEI Study at Michigan Tech
  - Concerns - increased ultrafine/nanoparticle emissions from new technology engines
- 1997 Perkins, Chevron, EPA nanoparticle studies at U of MN
- 1997 First Annual ETH Zurich Nanoparticle meeting, founded jointly by ETH, U of MN
- 2007-2013 HEI Advanced Collaborative Emissions Study
- 2012 – IARC report on Carcinogenic Risks to Humans - Diesel and Gasoline Engine Exhausts and Some Nitroarenes
- 2014 Volkswagen NOx scandal (WVU ICCT 2014)

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Health concerns about diesel exhaust: IARC and HEI ACES studies

Lyon, France, June 12, 2012
After a week-long meeting of international experts, the International Agency for Research on Cancer (IARC), which is part of the World Health Organization (WHO), today **classified diesel engine exhaust as carcinogenic to humans (Group1)**, based on sufficient evidence that exposure is associated with an increased risk for lung cancer.

Boston, April 12, 2012
STUDY FINDS FEW HEALTH EFFECTS FROM NEW TECHNOLOGY DIESEL ENGINES: The first results of the most comprehensive study ever undertaken of the health effects of exposure to new technology diesel engines **has found no evidence of gene - damaging effects in the animals studied**, and only a few mild effects on the lungs, according to a report issued today by the Health Effects Institute (HEI) 1 . The study – the Advanced Collaborative Engine Study (ACES) – is exposing rats and mice for 16 hours a day to emissions from a heavy-duty diesel engine meeting stringent **2007 US EPA standards** that reduce emissions of fine particles and other pollutants by over 90% from levels emitted by older engines.

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Mainly due to NO_2, unforeseen future problem

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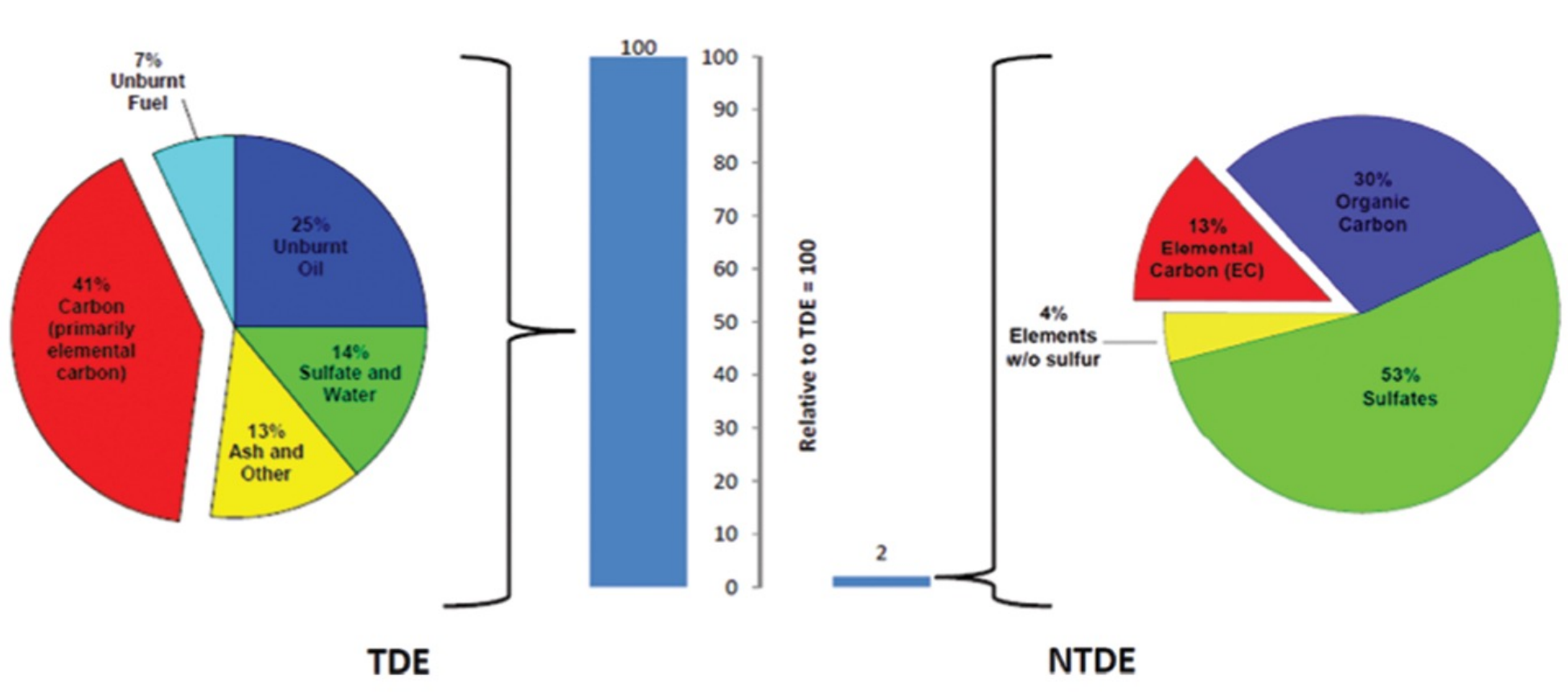
The IARC work based on tests old TDE, very different from modern NTDE used by ACES



Traditional Diesel Emissions

New Technology Diesel Emissions

Hesterberg, Thomas W.; Long, Christopher M.; Sax, Sonja N.; Lapin, Charles A.; Mcclellan, Roger O.; Bunn, William B.; Valberg, Peter A., 2011. Particulate matter in new technology diesel exhaust (NTDE) is quantitatively and qualitatively very different from that found in traditional diesel exhaust (TDE), Journal of the Air and Waste Management Association, v 61, n 9, p 894-913.

First? CRC APRAC Vehicle Emissions Modeling Workshop October 30-31, 1990, San Diego

- The main driving force for this meeting was recognition of the inconsistency between field laboratory field and laboratory measurements of the vehicle emissions and the existing models of California's EMFAC7 and EPA's MOBILE4 models.
- Tunnel studies show much higher measured than predicted emission rates of hydrocarbons (4x) and carbon monoxide (2.7x) while measured and predicted NOx emission rates agreed. Models were underpredicting, but the reasons were not understood.
- Early remote sensing identified CO high emitters, 10% emit 50%. Another study found 20% emit 65% BC. Concern about errors due to missing cold starts, enrichment events.
- A lot of talk about field studies, roadside dynamometer I/M combined with remote sensing.

- Papers presented in 4 sessions
  - EMFAC7 and MOBILE4 models
  - Model evaluations
  - Laboratory vehicle emissions
  - On road emissions studies

Nanoparticle Measurement
7. August 1997
ETH Zürich Laboratorium für Festkörperphysik

- Introduction and Welcomes
  - Siegmann H.C., AVL List Austria. 1997 - ***Introduction***
  - Mayer Andreas C., TTM. 1997 - ***VERT: Diesel Nano-Particulate Emissions***
  - Mayer Andreas C., VERT. 2023 - ***Millions of Soot Filters mitigating Climate Change***
  - 27 presentations 1997 - 2023
  - Filliger P. Automotive Plasma Technology GmbH, Graz. 1997 - ***VERT and PMIO in Switzerland***
- Particle Measurement
  - Ahlvik P., AB Svensk -Bilprovning. 1997 - ***Particle Size Distribution Activities at MTCU.***
  - 1 presentation 1997
  - Baltensperger U., Paul Scherrer Institut. 1997 - ***Measurement of the Hydrophilic Behavior of Soot***
  - Baltensperger U., Paul Scherrer Institut. 1997 - ***Analysis of Aerosols***
  - Baltensperger U., Paul Scherrer Institut. 2008 - ***Primary and Secondary Organic Aerosol from Diesel Engines***
  - 5 presentations 1997 - 2008

Nanoparticle Measurement
7. August 1997
ETH Zürich Laboratorium für Festkörperphysik

- Particle Measurement continued
  - Keskinen H., Tampere University of Technology, Finland. 1997 - ***Real Time Measurement of Combustion Aerosol Size Distribution***
  - Keskinen H., Jaatinen Antti, Miettinen Pasi, Romakkaniemi Sami, Joutsensaari Jorma, J. Smith, A. Laaksonen, Tampere University of Technology, Finland. 2010 - ***Water adsorption on silica nanoparticles***
  - 3 presentations 1997-2010 (co-author on many)

  - Kittelson David, University of Minnesota. 1997 - ***Engines and Nanoparticles***
  - Kittelson David, Myles D. Hicks, William F. Northrop, University of Minnesota. 2023 - ***Engine Crankcase Particulate Matter: Measurement Issues***
  - 33 presentations 1997-2023

  - Lüders H., Sächsisches Landesamt für Umwelt, Landschaft + Geologie, Dresden. 1997 - ***Effect of Measurement Conditions on Ultrafine Particle Emissions***
  - 1 presentation 1997

Nanoparticle Measurement
7. August 1997
ETH Zürich Laboratorium für Festkörperphysik

- Particle Measurement continued
  - McAughey J., AEA. 1997 - ***Evaluation of Instruments for Vehicle Emission Particle Sizing***
  - McAughey J., AEA. 2001 - ***A Review of Recent Health Effects Research***
  - 7 presentations 1997 - 2001

  - Ji Ping Shi, University of Birmingham. 1997 - ***Measurement of Fine Particle Size Distribution in Diesel Exhaust and Ambient Air***
  - Ji Ping Shi, University of Birmingham. 2000 - ***Particle Number Emission from Diesel and Petrol Vehicles Driving on Road***
  - 3 presentations 1997 – 2000

- Combustion and Fuels
  - Czerwinski J., Laboratory for IC-Engines and Exhaust Emission Control (AFHB, Biel). 1997 - ***Combustion particles number concentrations with different engines and fuels***
  - Czerwinski J., D. Engelmann; P. Comte; A. Mayer; V. Hensel, Laboratory for IC-Engines and Exhaust Emission Control (AFHB, Biel). 2019 - ***PN Emissions of Passengers Cars – Potentials of GPF's***
  - 41 presentations 1997-2019

  - Mohr M., EMPA . 1997 - ***Formation of Carbon in Combustion: The Influence of Fuel Additives***
  - Mohr M., U. Lehmann, A.M. Forss, EMPA. 2005 - ***Measurement of post-trap emissions by a particle number count method developed for possible future type approval purpose***
  - 9 presentations 1997 – 2005

Nanoparticle Measurement
7. August 1997
ETH Zürich Laboratorium für Festkörperphysik

- Combustion and Fuels continued
  - Rickeard D.J., ESSO. 1997 - ***Fuel and Vehicle Effects on Particulate Emissions***
  - Rickeard D.J., ESSO. 2002 - ***CRC particle workshop, San Diego 21 October 2002***
  - 4 presentations 1997 - 2002

  - Siegmann H.C., AVL List Austria. 1997 - ***Formation of Carbon in Combustion: The influence of Fuel Additives***
  - Siegmann H.C., AVL List Austria. 2000 - ***Phys. And Chem. Properties of Particulate Air Pollution in Major Cities by Portable Sensors***
  - 3 presentations 1997 – 2000

- Ambient Measurements
  - Filliger P., Automotive Plasma Technology GmbH, Graz . 1997 - ***Ambient air quality measurements of TSP, PM10, PM2.5 and EC***
  - 2 presentations 1997

Nanoparticle Measurement
7. August 1997
ETH Zürich Laboratorium für Festkörperphysik

- Ambient Measurements continued
  - Weingartner E., Paul Scherrer Institut. 1997 - ***Aerosol Emission in a Road Tunnel***
  - Weingartner Ernest, Tobias Rüggeberg, Nadine Karlen, UASNW. 2023 - ***Physical properties of virus-containing aerosol particles***
  - 9 presentations 1997 - 2023

- Emission Standards and Aftertreatment
  - Lemaire J., AEEDA. 1997 - ***The Industry of Emissions Controls and the Ultrafine Particles***
  - Lemaire J., AEEDA. 1999 - ***What are the Ultimate Limits of Integrated Emission Controls Strategies?***
  - 2 presentations 1997 – 1999 (several as co-author)

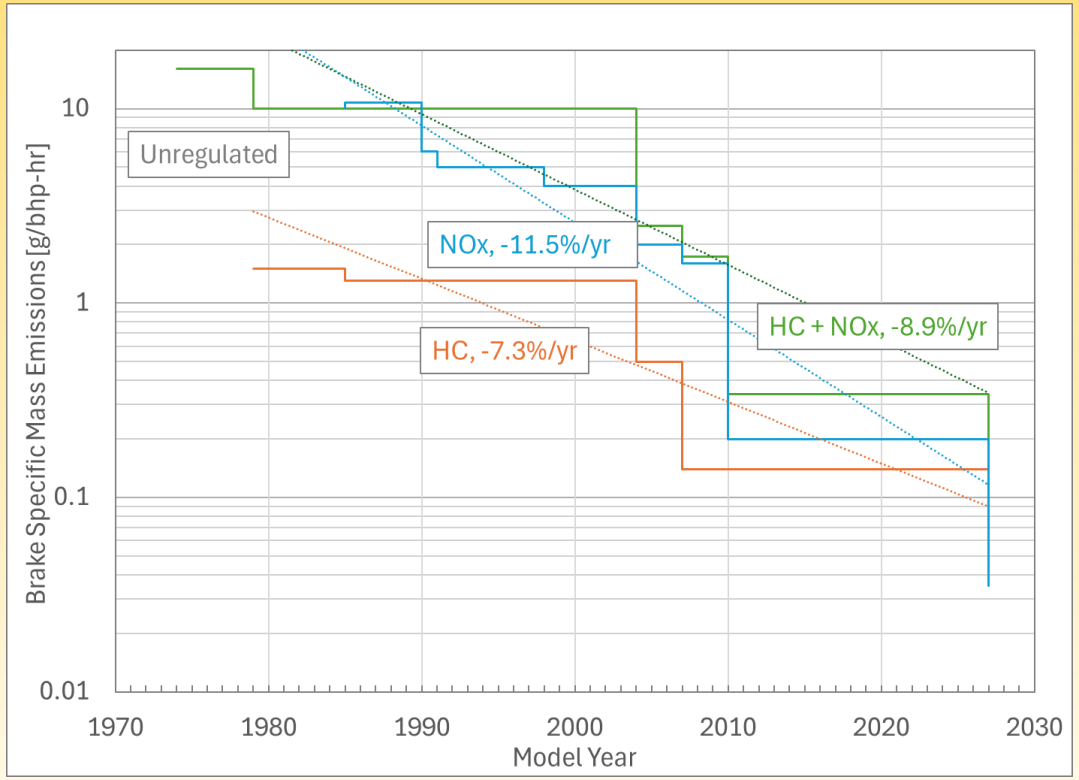
  - Matter U., ETH / Matter Engineering. 1997 - ***Penetration of Diesel Particle Filters Evaluated by Various Soot Analyzing Techniques***Matter U., ETH / Matter Engineering. 2001 - ***Influence of Sampling Conditions, Engine Load and Fuel Quality on Measurement of Ultrafine Particles from a Modern Diesel Vehicle – Sampling-Measuring- and Analyzing Methods***
  - 5 presentations 1997 - 2001

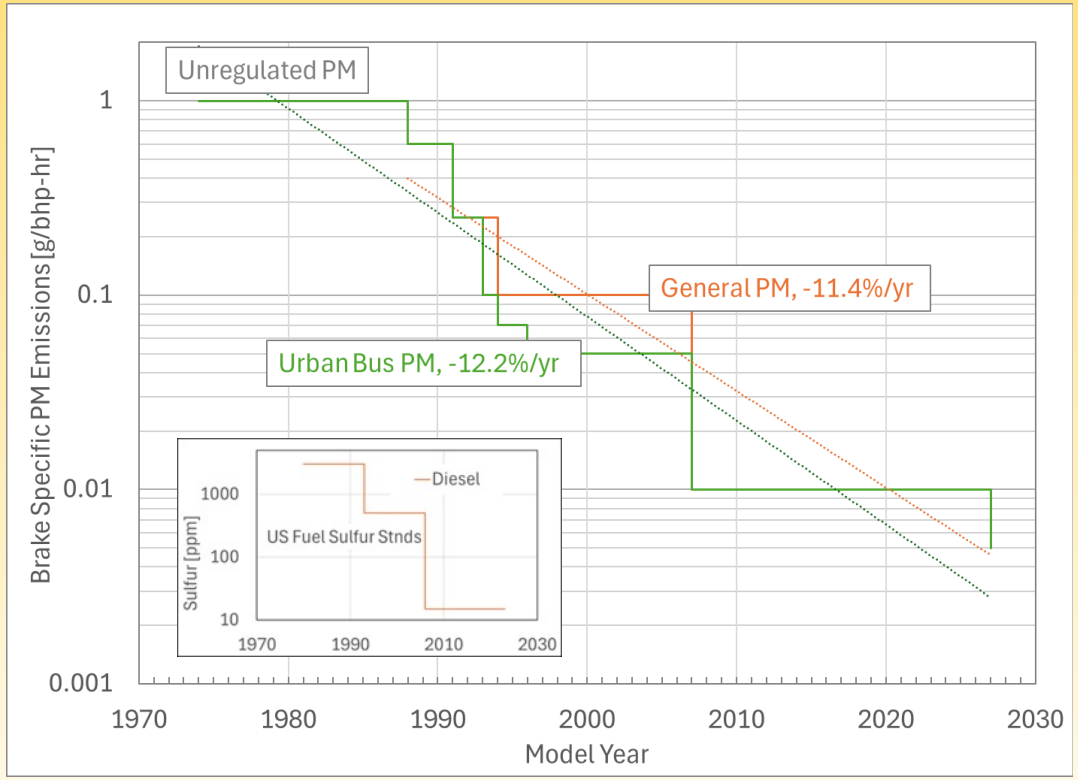
2024 topics not envisioned in 1997

- Aircraft, marine and other non-road sources
- Ambient air particles, secondary pollutants
- Biomass-, biofuel- and synfuel combustion
- Brake and tyre wear, non-combustion emissions
- Emission control of combustion engines
- Environmental effects
- Filtration of combustion and biogenic nanoparticles
- Health effects
- Impact on climate
- Indoor particles
- Legislation and enforcement
- Nanoparticle formation and transformation
- Nanoparticle metrology and chemical characterization
- Nanoparticle chemistry and toxicology
- Occupational exposure and prevention
- Periodical technical inspection for in-use vehicles

Heavy-Duty Diesel Emission Standards

Light trend lines show annual % decrease

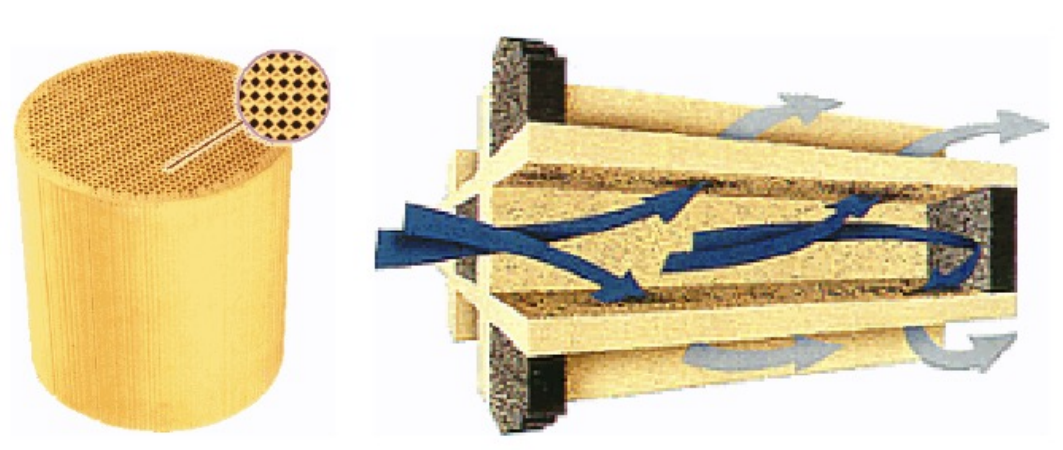




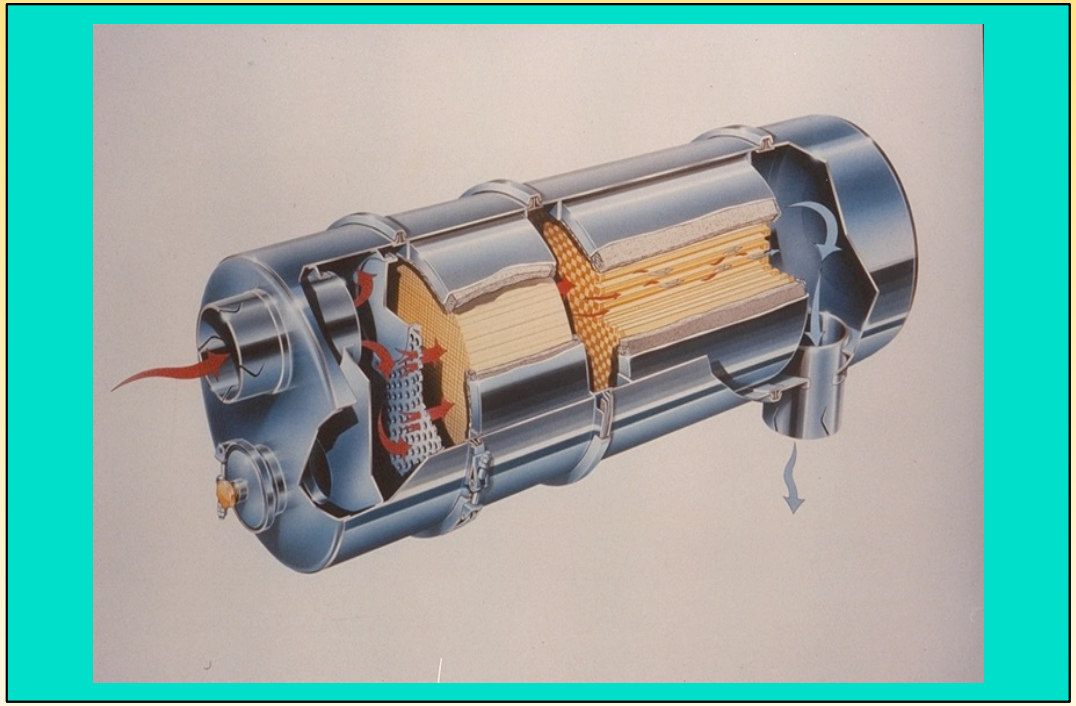
Engine changes to meet increasingly stringent emission standards, local and global (GHG)

- Reducing engine-out emissions while improving efficiency
  - ***Getting the time-temperature-mixing history right***
  - Spark ignition and diesel technologies are converging, both incorporating more aspects of low temperature combustion
- Improved aftertreatment
  - Diesel (compression ignition)
    - Diesel oxidizing catalysts (DOC)
    - Diesel Particle filters (DPF), passive and active regeneration
    - Lean NOx traps (LNT), selective catalytic reduction (SCR)
    - Various combinations of above
  - Gasoline (spark ignition)
    - Oxidizing catalysts
    - Ever improving 3-way catalysts, multiple, close coupled, preheated
    - Gasoline particle filters, GPF
- All this facilitated by improved fuels, reduced sulfur, aromatics, etc.

More than anything filtration, DPF, GPF has had the largest impact

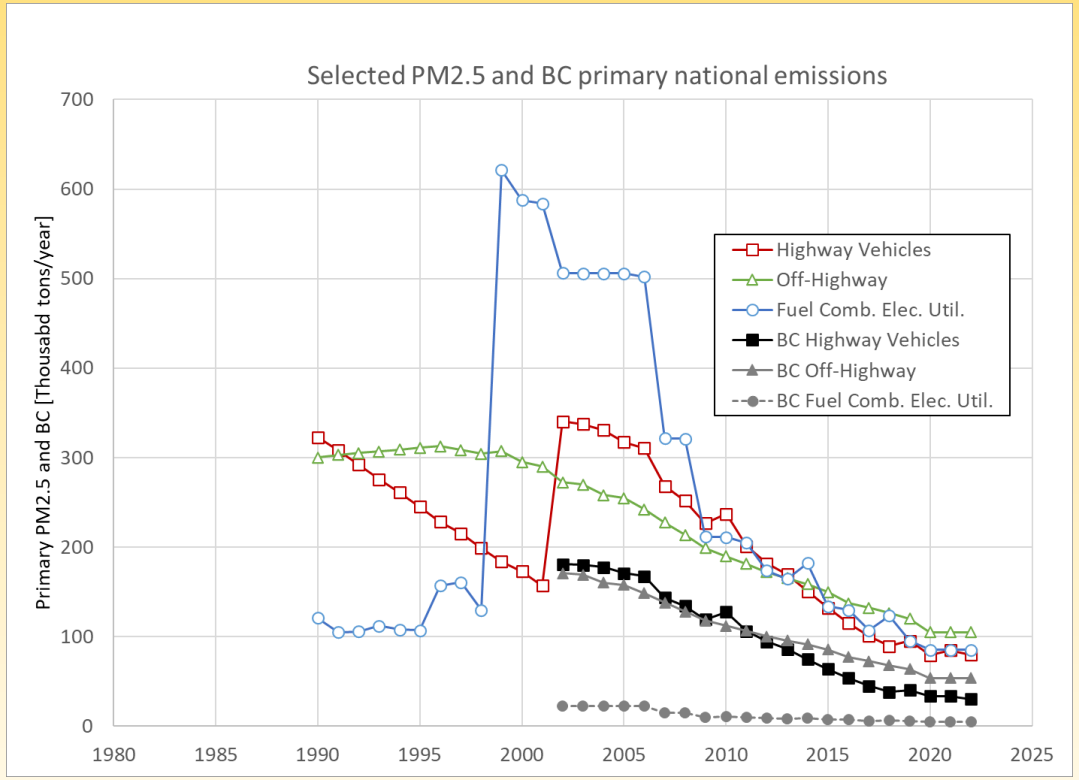


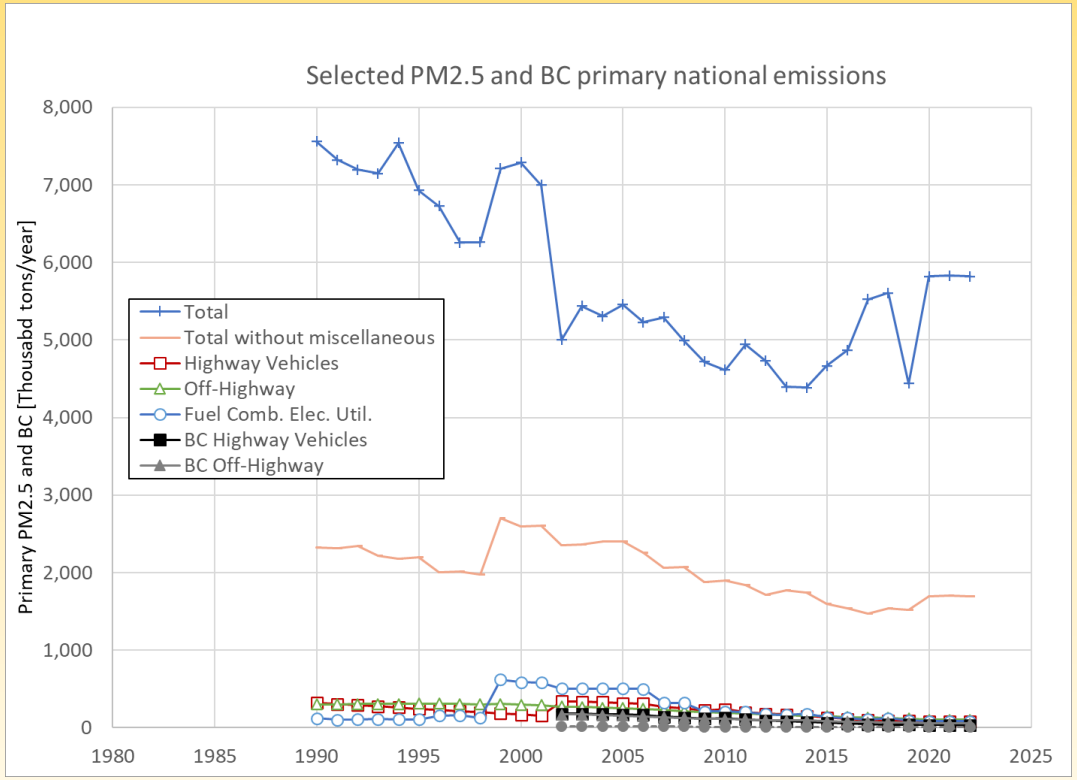
Figures courtesy Corning and Johnson-Matthey



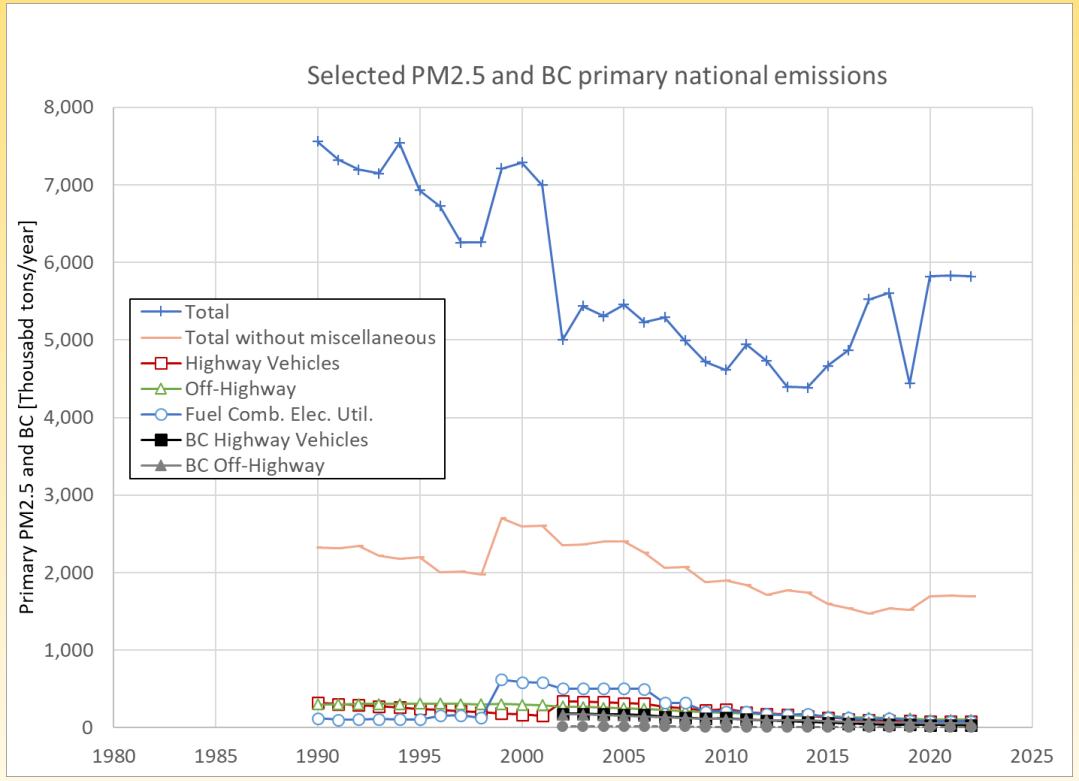
What has all this done to emissions and air quality?

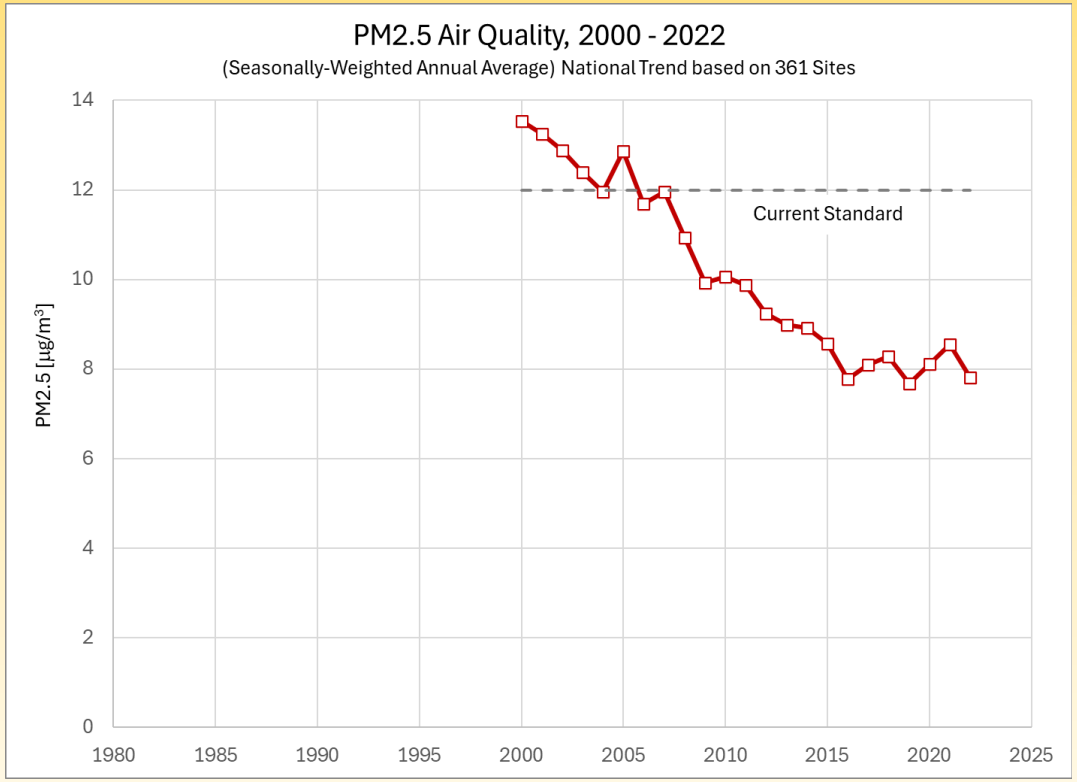
PM2.5 Emissions from vehicles and electric power are small fraction of total



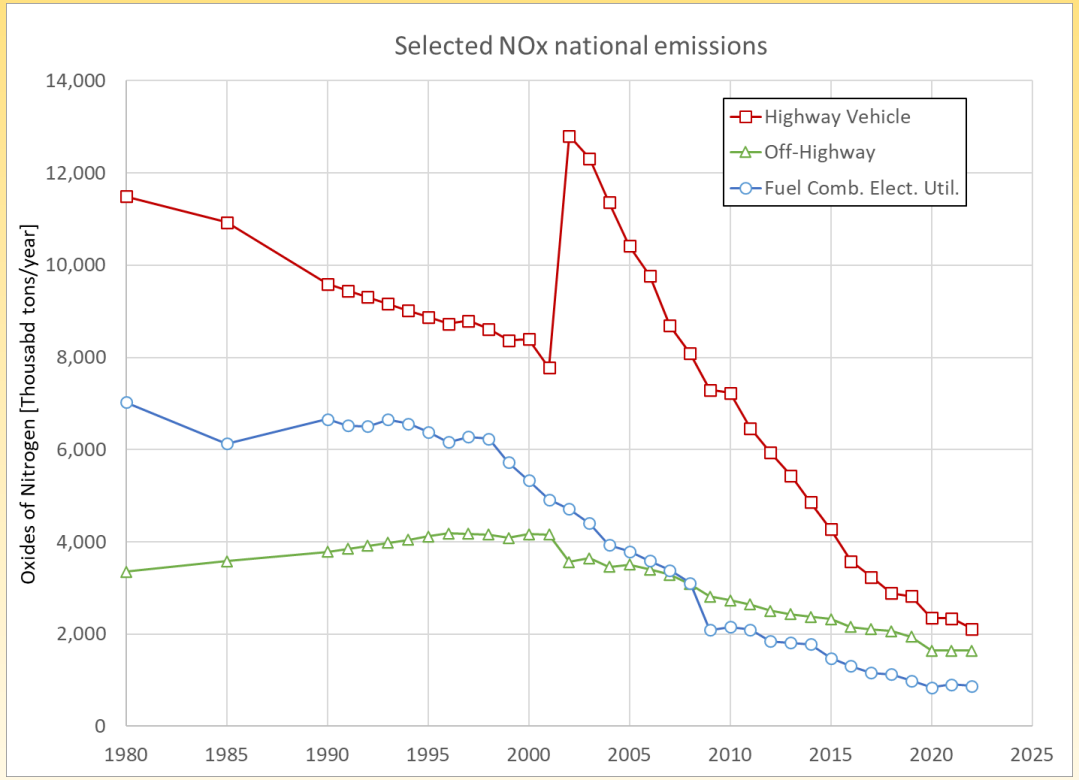


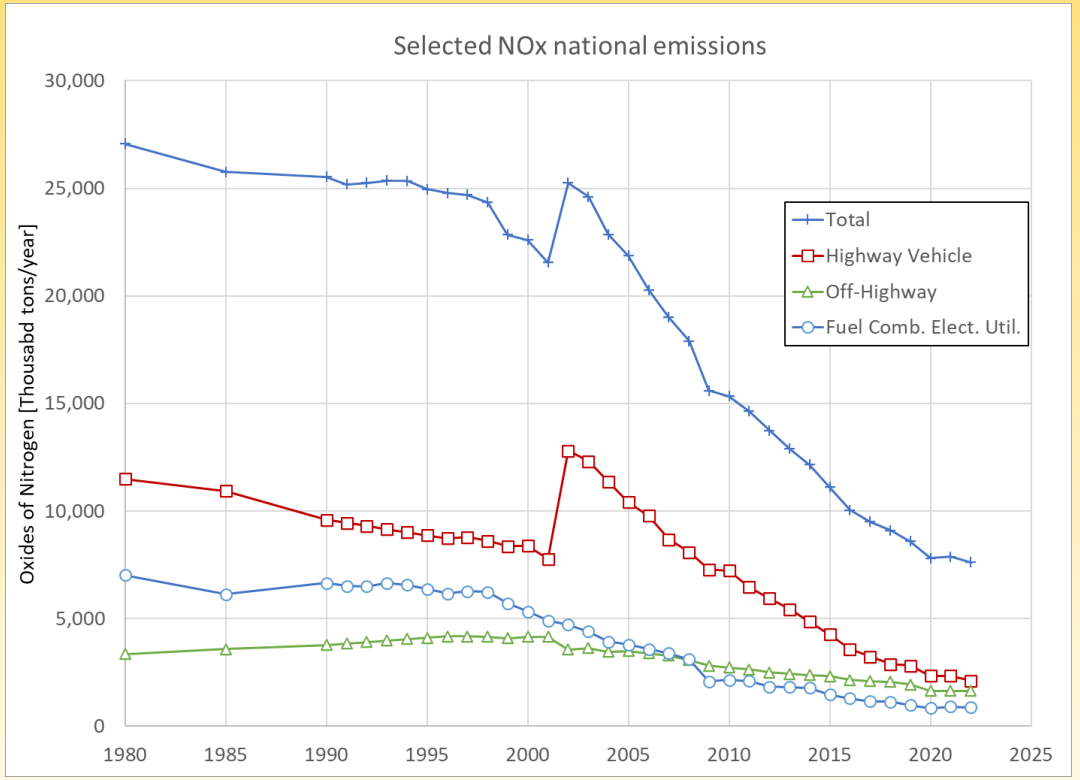
Ambient PM2.5 dropping much faster than total PM2.5 emissions



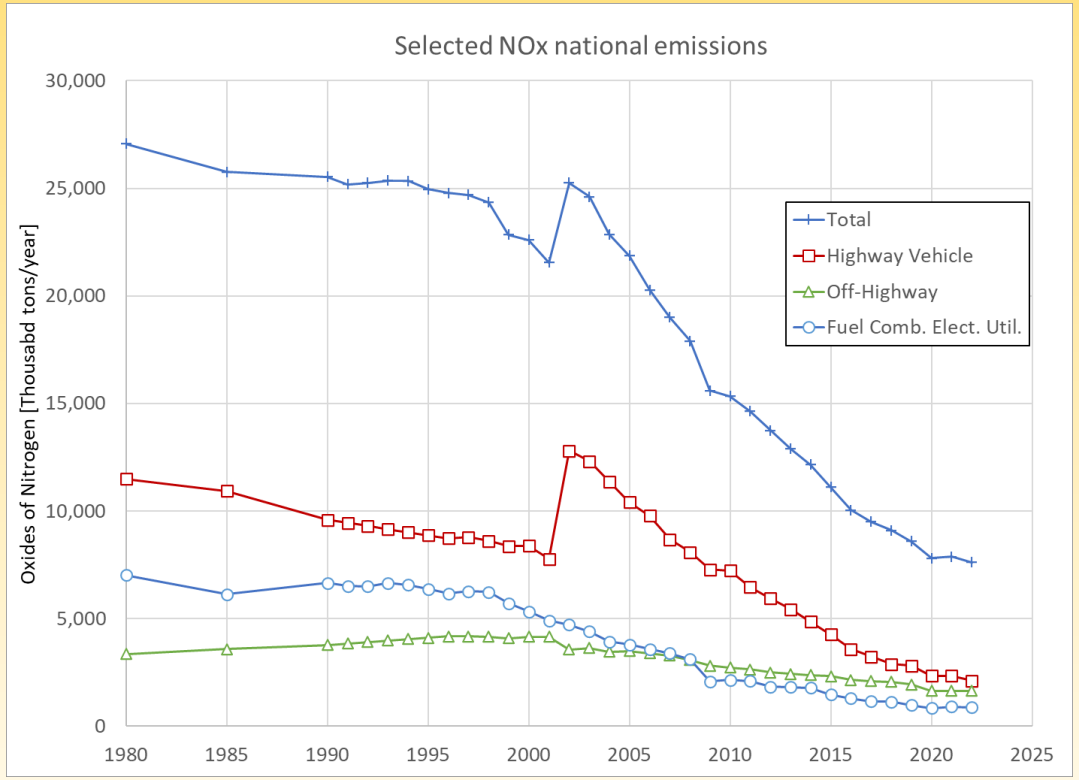


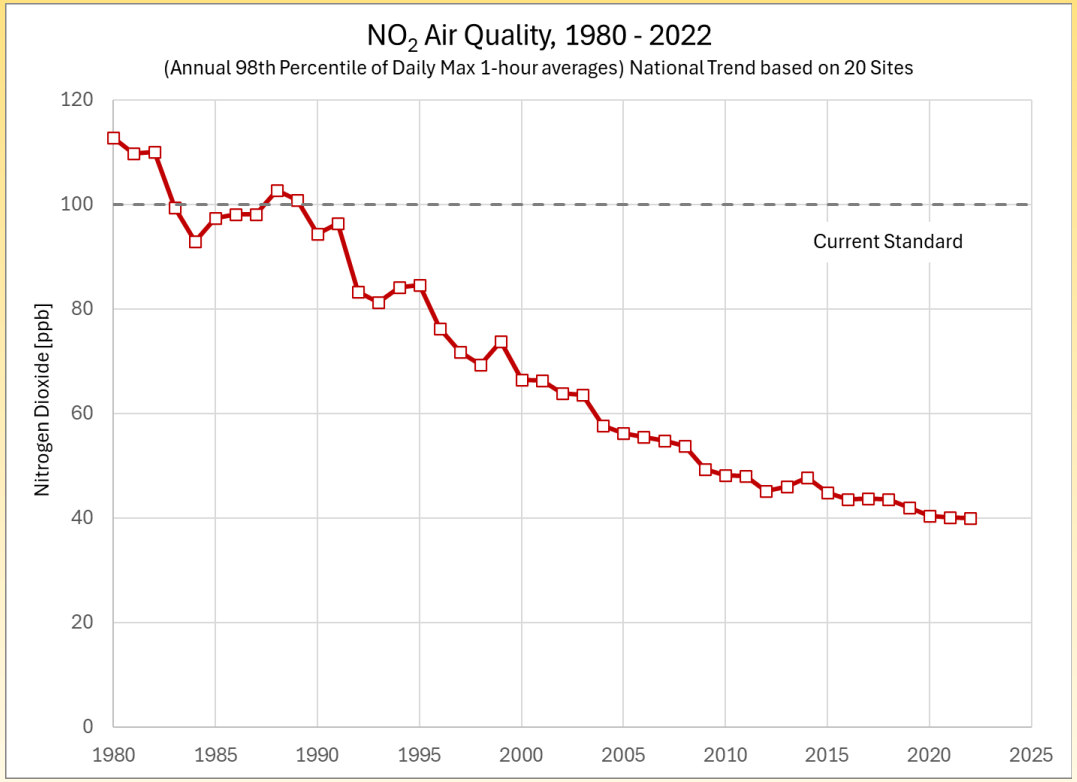
Total national NOx emissions larger than from vehicles but tracks with them



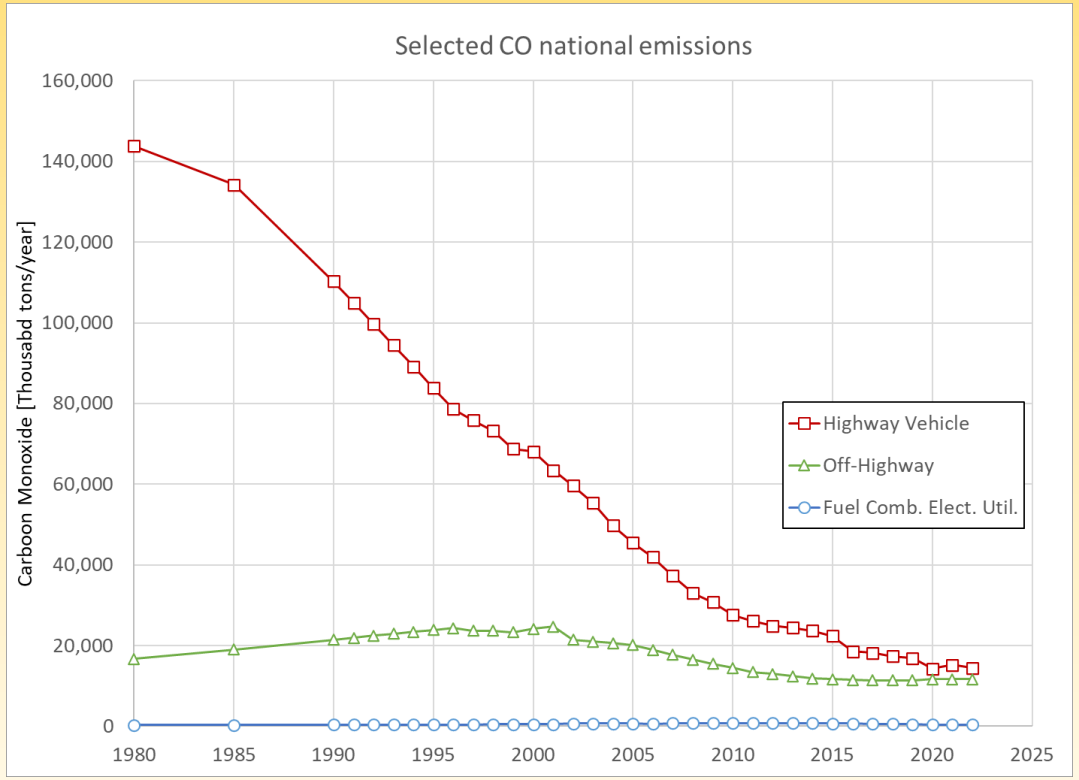


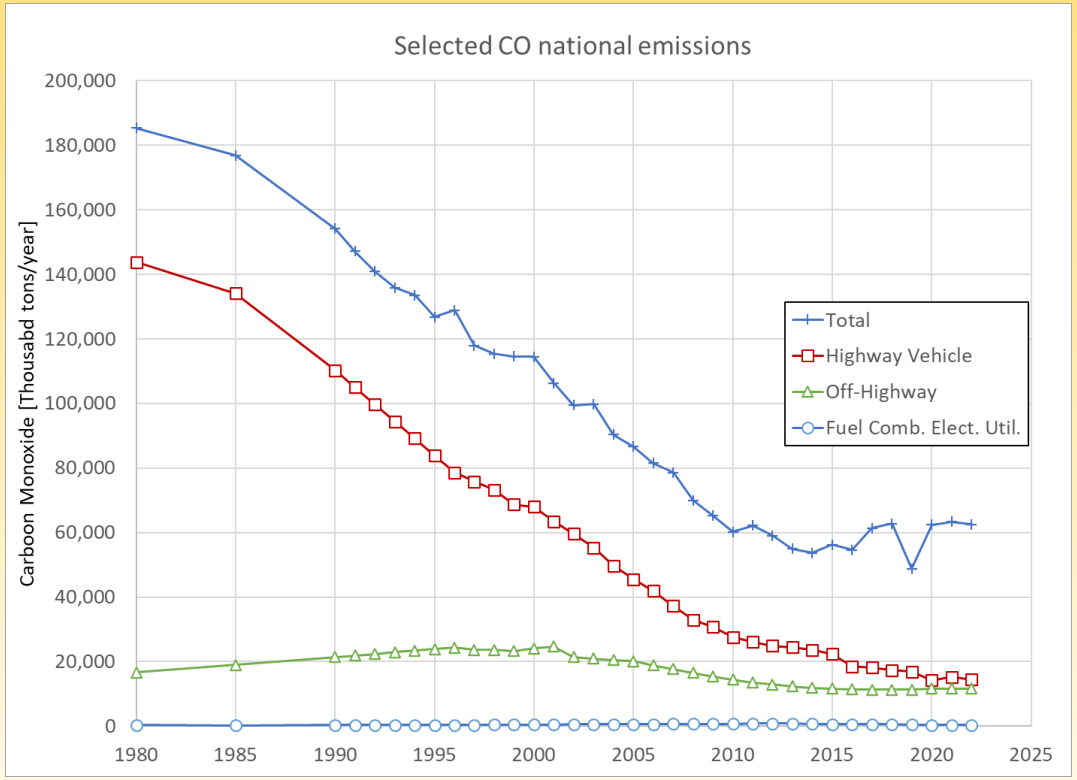
Ambient NO_2 tracks well with total NOx emissions



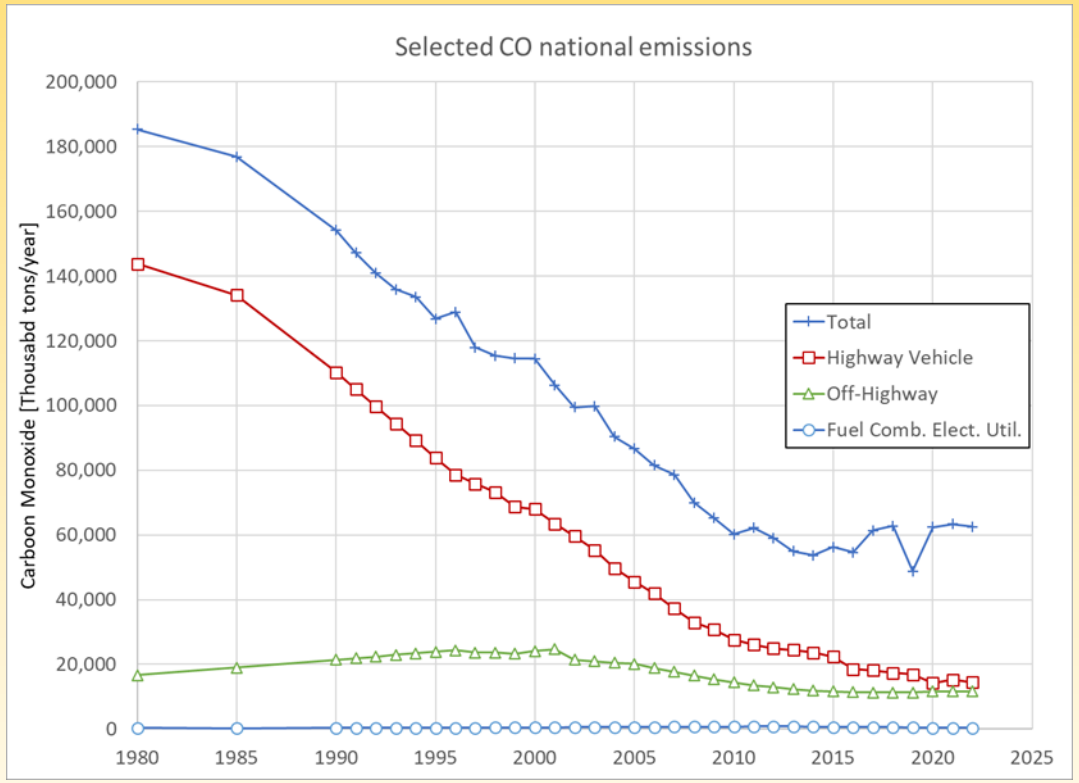


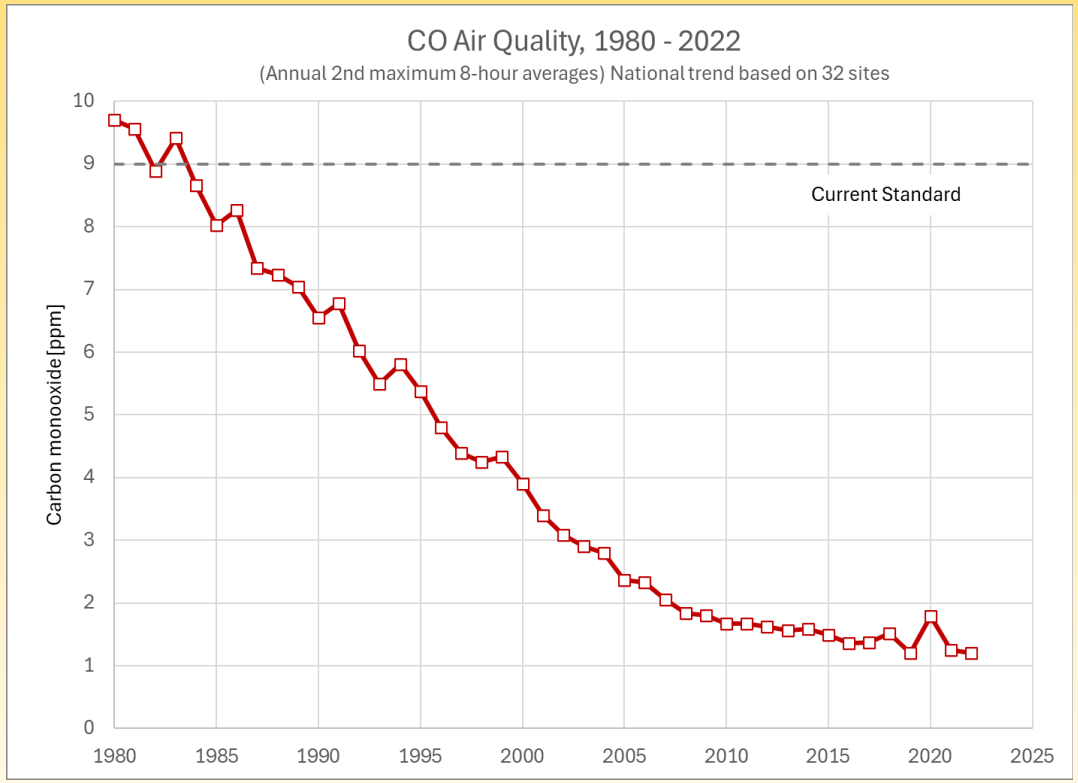
CO Emission Trends, mainly driven by on-highway vehicle emissions



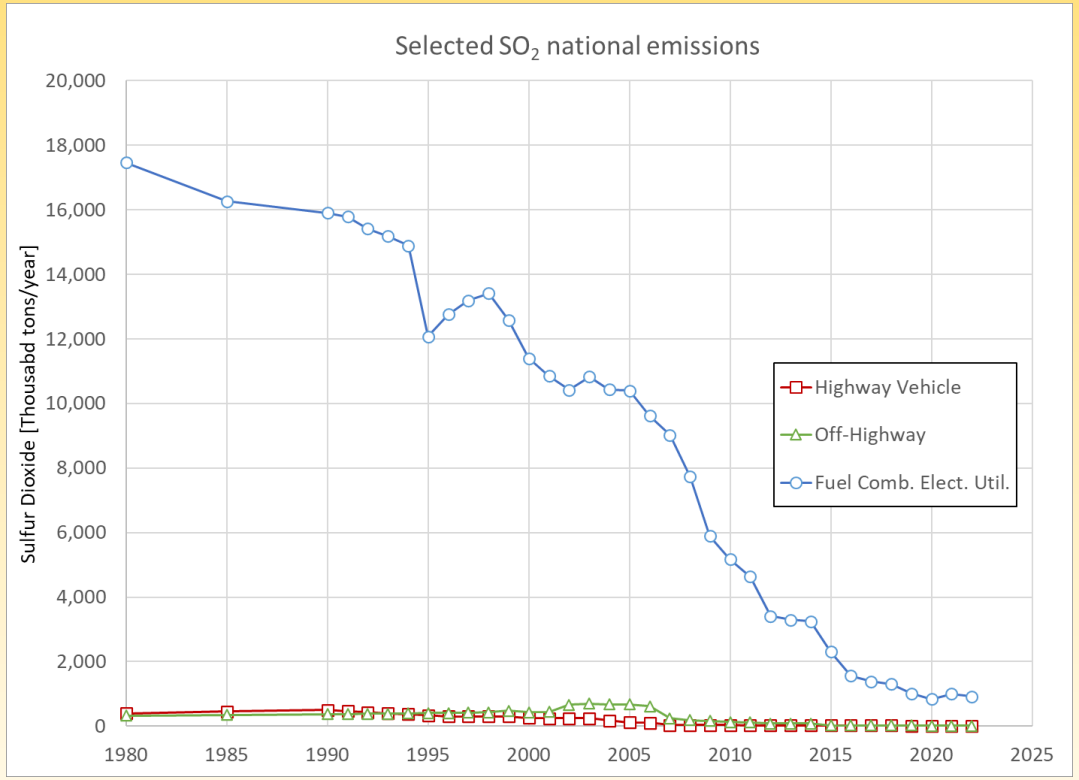


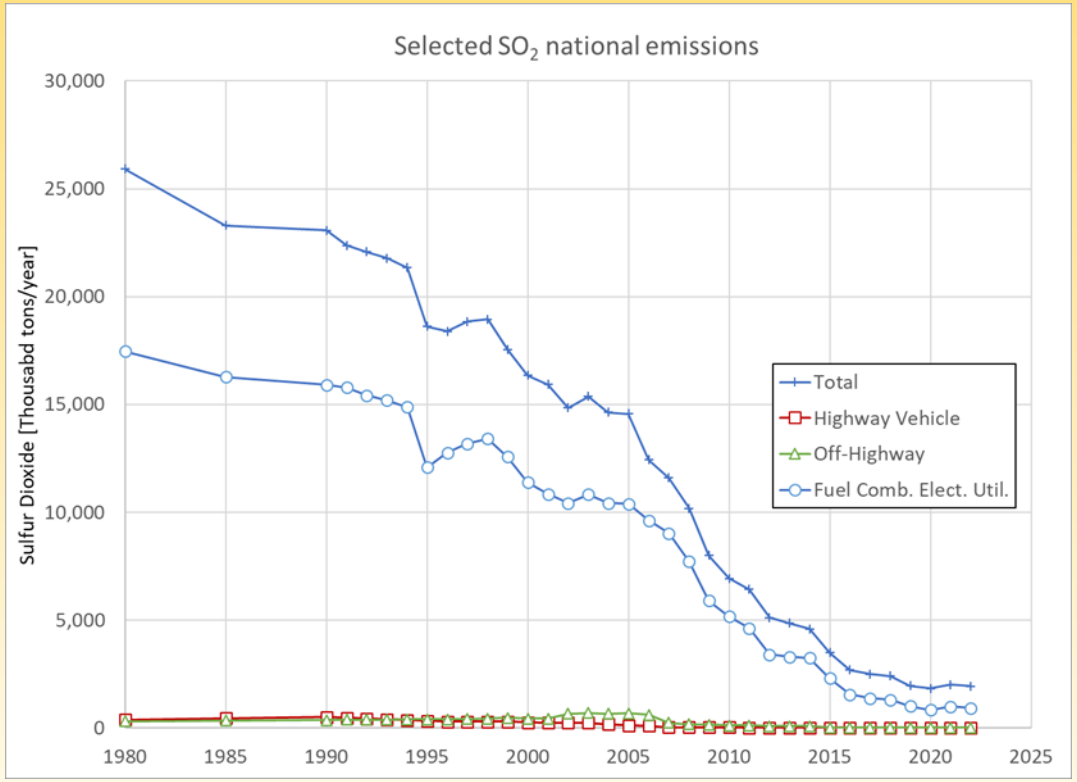
CO Emission Trends, air quality and emissions track well





SO_2 Emission Trends, mainly driven by electric power generation





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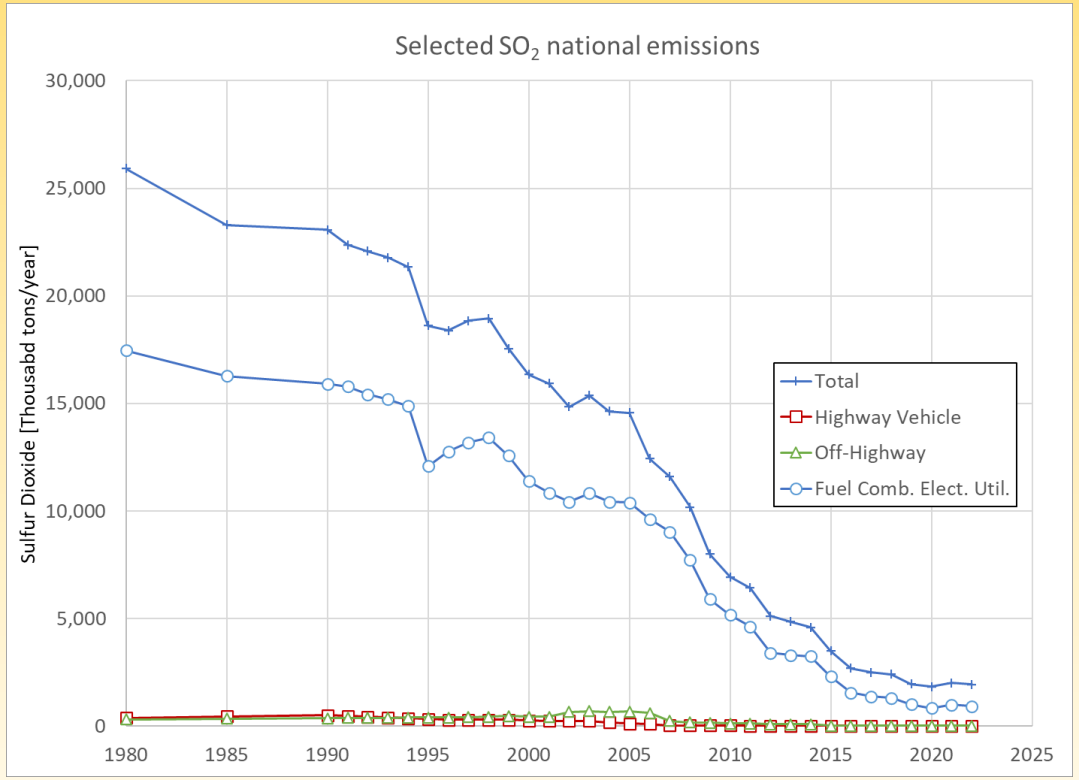
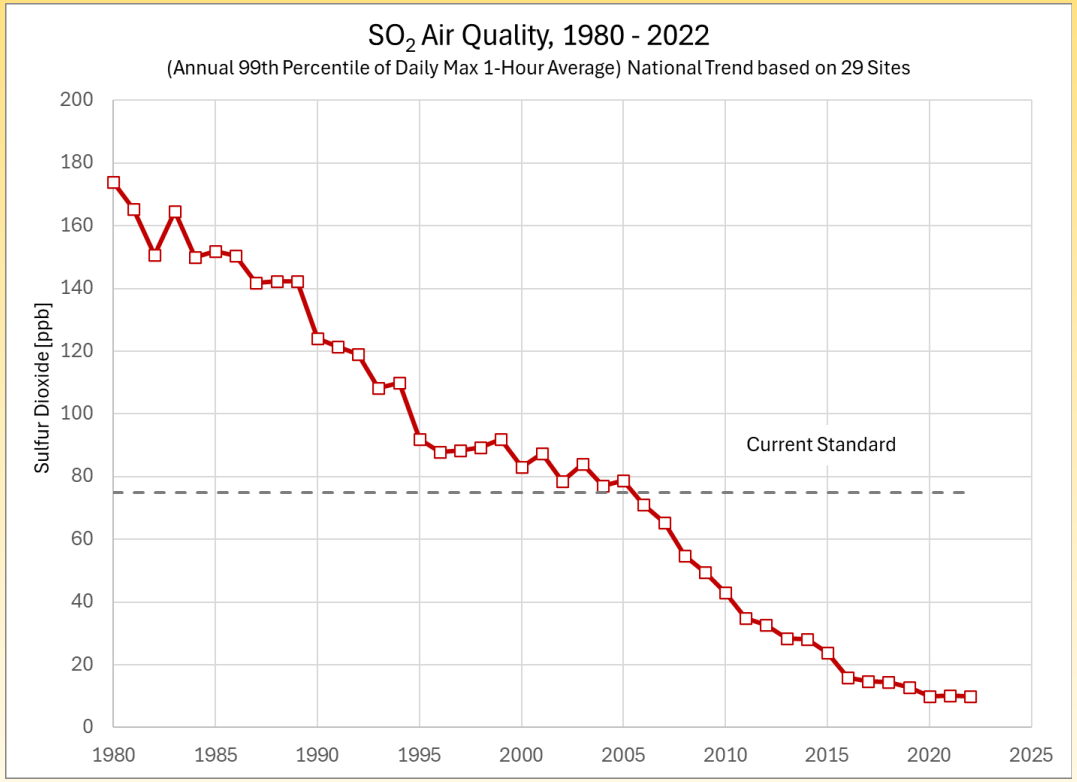
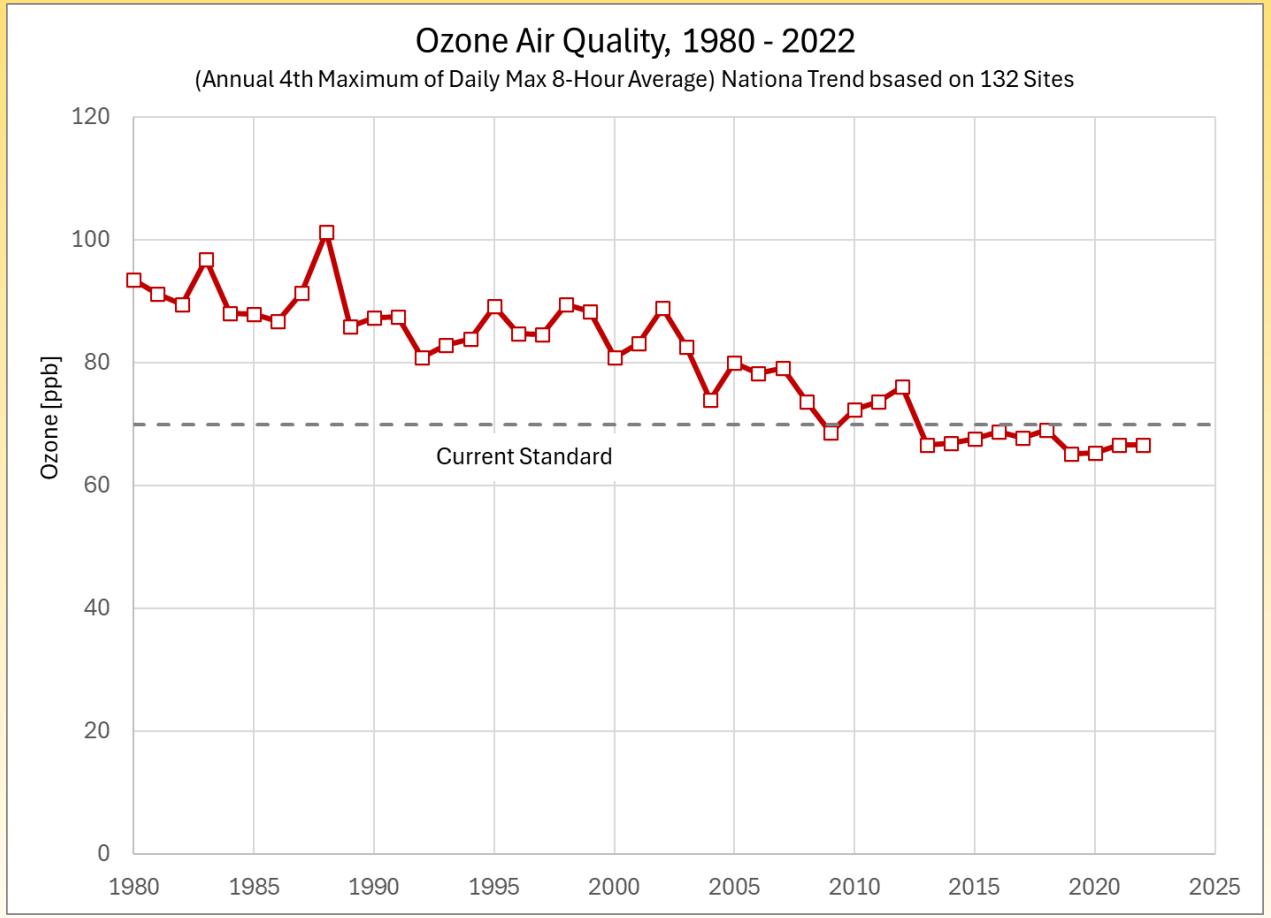




Not everything is going so well – these are national averages, many sites are worse



DPFs and GPFs are making it difficult for those of use who love particles, but you can’t filter this

Courtesy autoevolution.com

Thank you for listening, questions?