Lead Emission and Assessment

Image showing a filter sampler at the Grand Forks airport on August 19, 2025 with students Bryce Rickbeil and Jenna Post.

Learning Objectives

- Explain the sources and historical trends of atmospheric lead emissions.
- Describe the atmospheric chemistry and transport of lead particles/
- Assess the health and environmental impacts of lead exposure.
- Understand measurement techniques and monitoring networks for atmospheric lead.
- Evaluate the effectiveness of regulatory approaches to lead pollution control.

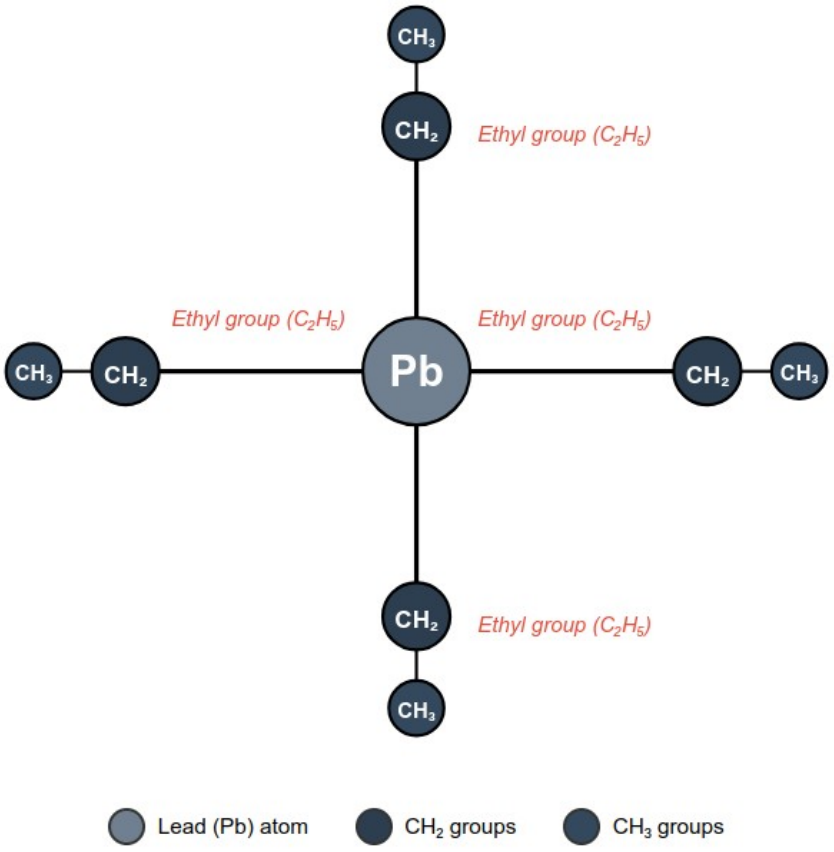
Image showing a high volume filter sampler on top of Clifford Hall and a filter sample obtained with the sampler.

Lead as an Air Pollutant

- Key Characteristics
  - Exists as particulate matter ($PM_{2.5}$)
  - Atmospheric lifetime of days to weeks
  - Does not degrade in the environment
  - Bioaccumulative and neurotoxic at low concentrations
- Common Forms of Lead
  - Lead oxides (PbO, PbO_2)
  - Lead sulfate ($PbSO_4$)
  - Lead chloride ($PbCl_2$)
  - Organometallic compounds

What are Organometallic Compounds?

Tetraethyl Lead (TEL)
$Pb(C_2H_5)_4$ or $(CH_3CH_2)_4Pb$



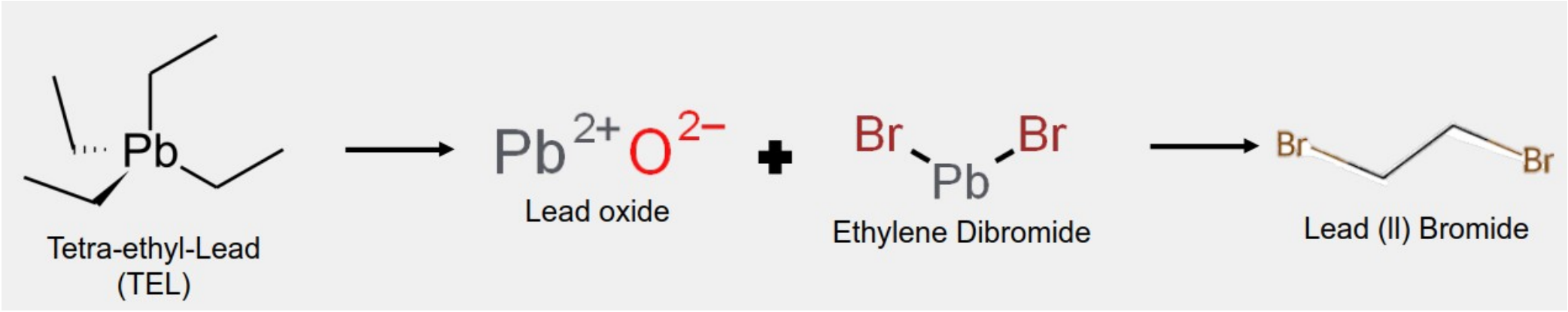
Tetraethyl Lead Usage

- In 1921, Thomas Midgley Jr. discovers that tetraethyl lead (TEL), which eliminates engine knock.
- Peak United States Usage:
  - Lead usage peaked in the 1970s.
  - Gasoline had 2-3 grams of lead per gallon.
  - The United States used over 200,000 metric tons/year of tetraethyl lead.
  - The urban concentrations of lead was over 2 $\mu g/m^3$.

Image showing portrait Thomas Midgley, Jr. (1889-1944). Image is courtesy of Science History Institute.

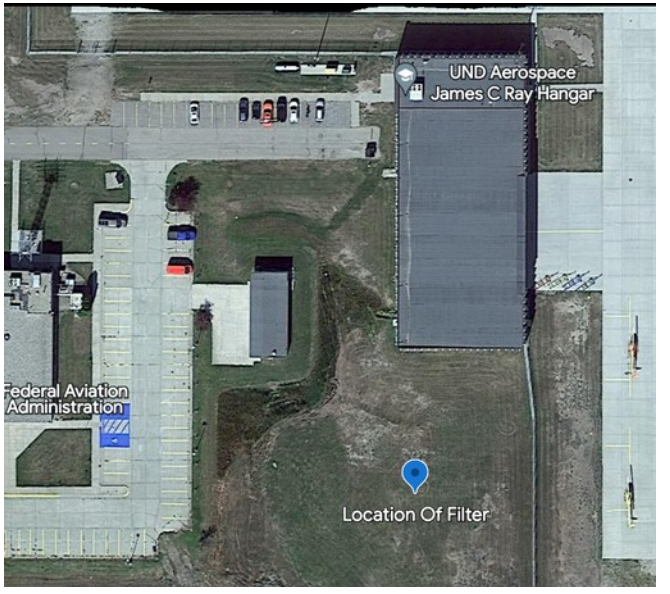
Tetraethyl Lead (TEL) in LL100 Fuel (Avgas)

- As LL100 fuel burns, TEL naturally degrades to lead oxide which is what increases the octane rating.
- Deposits are formed due to lead oxides high melting point.
  - These deposits are electrically conductive and is corrosive.
- To prevent deposits forming, ethylene dibromide is used to react with lead oxide to form lead bromide which is a more volatile and a gas around a lower temperature to ensure that lead will be fully exhausted from the engine.



Tetraethyl Lead (TEL) in LL100 Fuel (Avgas)

- Exhausted gas cools to the solid phase in the atmosphere where the lead exists/evolves into different leaded compounds and ions.
- Leaded compounds travel long distances in the air before going into the soil and possibly groundwater.
- Exposure to these lead sources will lead to disruptions of tightly regulated processes due to lead stronger a binding affinity compared to these metal ions (Ca2+, Mg, Zn, Fe, et…) which are known to be involved within functions in biological systems.



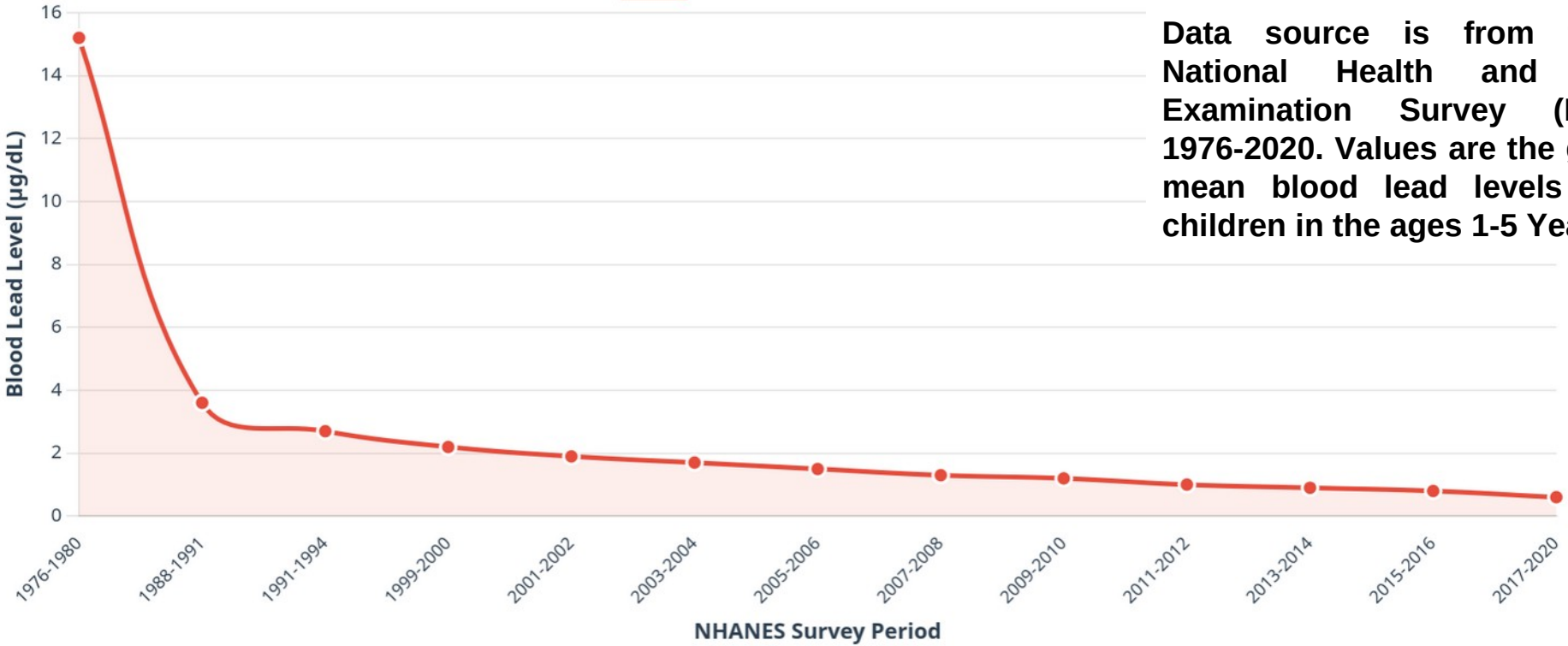
UND Aerospace general aviation airport was chosen for the location of high-volume sample. Daily and weekly samples have been collected.

Overview of Health Effects of Lead

- No safe threshold for lead exposure in children
- Bioaccumulation
  - 99 % of blood lead is bound to red blood cells.
  - Lead accumulates in bone with a half-life of years to decades.
  - Children absorb 50 % compared to 10-15% in adults.
- Children
  - Developing Nervous Systems
- Pregnant Women
  - Lead Crosses Placental Barrier
- Occupational Exposure
  - Industrial Workers

Tetraethyl Lead Health Impacts

- Had a massive population exposure.
- Resulted in elevated levels of lead in the blood of people.
- Had neurodevelopmental effects on people.



Data source is from the CDC National Health and Nutrition Examination Survey (NHANES), 1976-2020. Values are the geometric mean blood lead levels for U.S. children in the ages 1-5 Years.

Neurological Effects of Lead

- **Children**
  - Decreased Intelligence
  - Impaired Cognitive Function
  - Reduced Academic Achievement
  - Behavioral Problems
  - Effects at Blood Lead <10 µg/dL
- **Adults**
  - Peripheral Neuropathy
  - Cognitive Decline

Mechanisms

- Interferes with Neurotransmitter Function
- Disrupts Calcium Homeostasis
- Impairs Synaptogenesis
- Alters Myelination
- Induces Oxidative Stress

Reduction of Lead in the Environment

- 1970: US Clean Air Act passed
- Mid-1970s: US Phase-down begins
- 1996: Complete elimination from on-road gasoline in the US.
- In 2021 Algeria is the last country to eliminate leaded from gasoline.

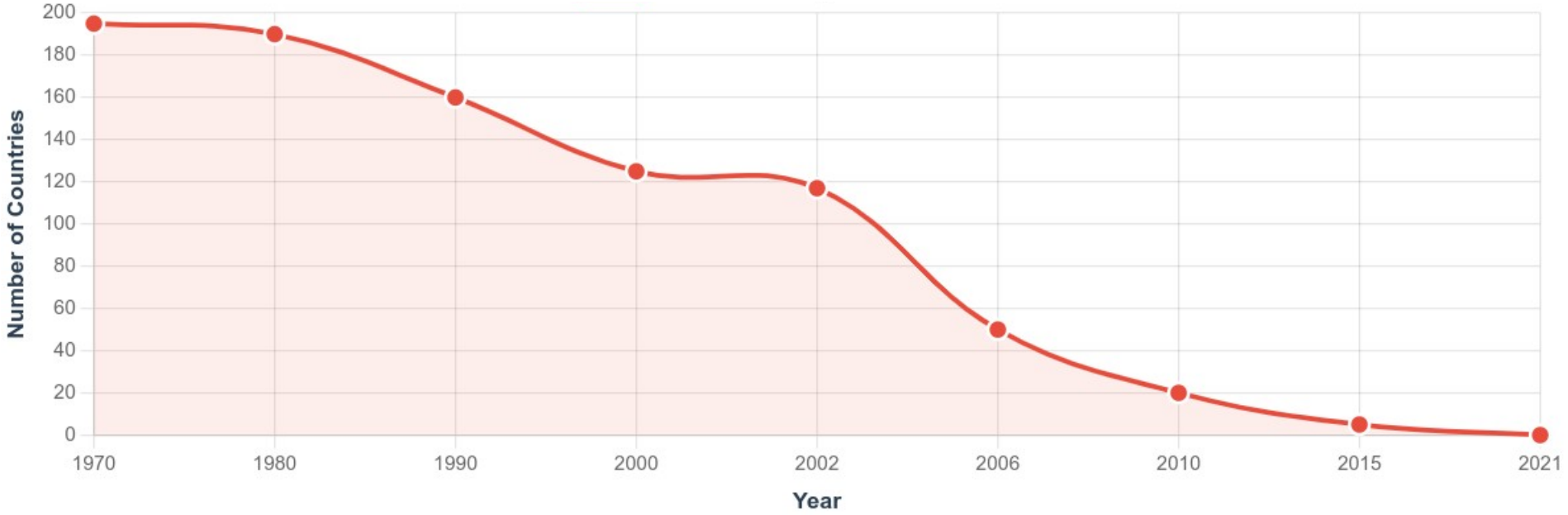


Image showing the reduction of countries using leaded gasoline. Data source is the United Nations Environment Programme (UNEP), 2011 & 2021.

Contemporary Sources of Lead

- **Industrial**
  - Lead Smelters and Refineries
  - Battery Manufacturing
  - Non-ferrous Metal Smelting
- **Aviation**
  - Piston-engine Aircraft use Leaded Avgas
  - Elevated Lead near Small Airports.
- **Other Sources**
  - Waste Incinerators
  - Coal Combustion
  - Resuspended Legacy Contamination

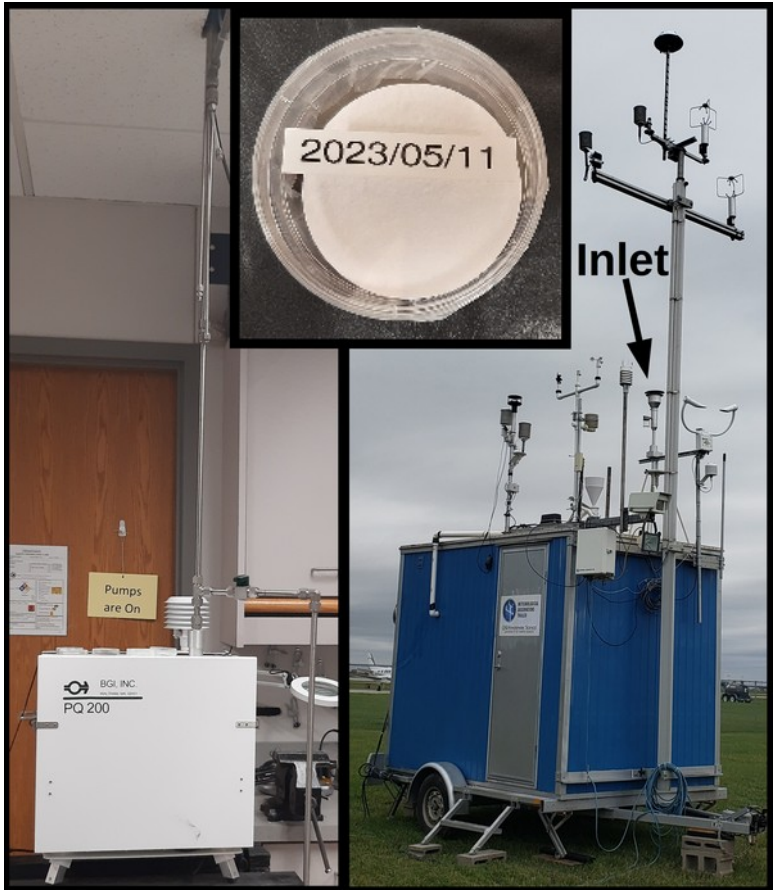


Image showing filter sampler (left), the MetTrailer (right), and a filter sample (top).

Lead Measurements and Monitoring

- **Sampling Methods**
  - High-volume Air Samplers
  - Size-selective Inlets
    - TSP, PM_{10}, $PM_{2.5}$
  - Teflon or Quartz Filters
  - 24-hour Integrated Samples
- **US Monitoring Network**
  - ~130 Monitors Strategically Located near Known Sources

Analytical Methods

- **X-ray fluorescence (XRF)**
  - Routine Monitoring
- **Inductively Coupled Plasma Mass Spectrometry (ICP-MS)**
  - Ultra-low Detection Limits (ppb or ppt)
- **Atomic Absorption Spectrometry (AAS)**
- **Isotopic Analysis**
  - Source Apportionment

X-ray Fluorescence (XRF)

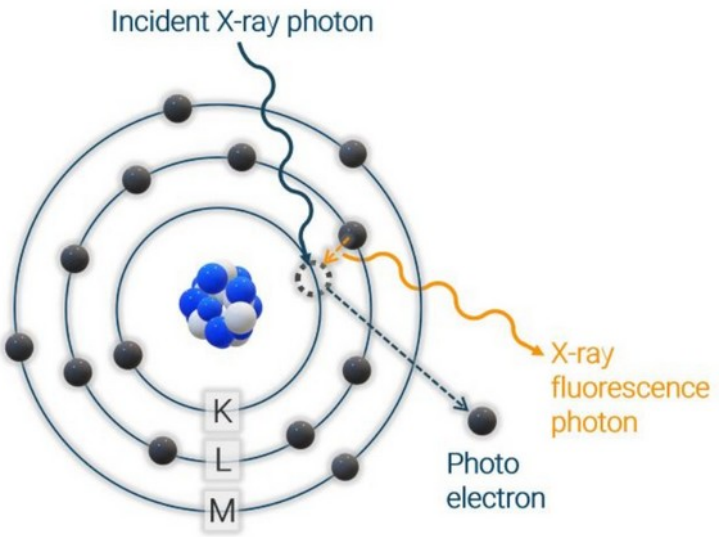


Image from Bruker.com

- X-ray Fluorescence (XRF) is an elemental analysis technique based on the photoelectric effect and characteristic X-ray emission.
  - What is the photoelectric Effect?
- High-energy X-rays have enough energy to eject inner-shell (K or L) electrons from atoms.
- An Electron from a higher energy outer shell drops down to fill the vacancy which releases energy as a Fluorescent X-ray photon.
- The emitted X-ray has an energy characteristic of the specific element.
- Measuring the energies of the emitted X-rays identifies the element.
- Measuring the intensities quantifies the concentrations.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

- A liquid sample is pumped through a nebulizer to generate aerosol that passes through a spray chamber to filter out larger (>10 μm) droplets.
- The droplets enter an argon plasma torch (6,000-10,000 K) where desolvation removes the liquid, vaporization converts particles to gas, atomization breaks molecular bonds, and ionization strips electrons from atoms.
  - Creates predominantly singly-charged positive ions (M^+).
- Ions are extracted from the atmospheric-pressure plasma into a high-vacuum Mass Spectrometer where neutral species and photons are removed.
- Commonly a quadrupole mass analyzer is used; however, higher resolution, and time-of-flight analyzers are possible.
- Ions striking the detector generate a measurable signal proportional to concentration using calibration standards.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

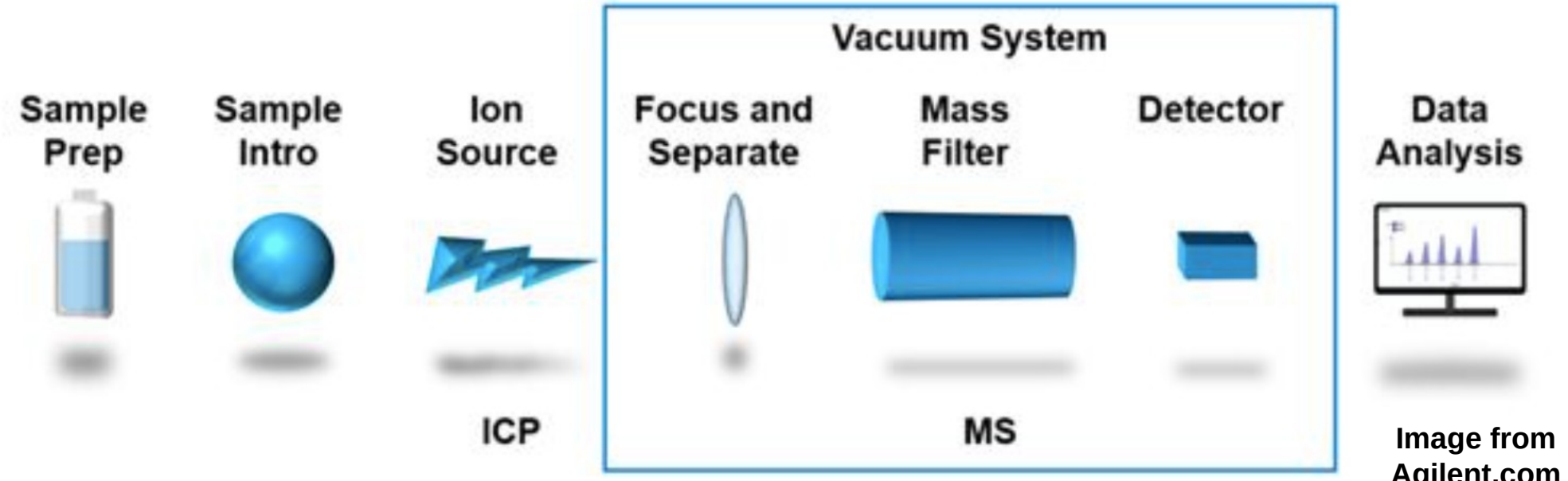
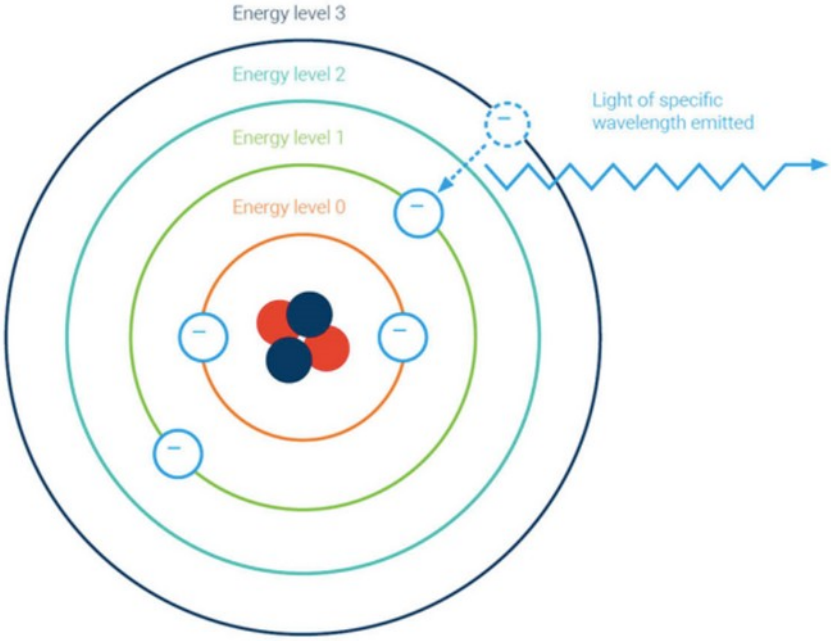


Image from Agilent.com

- ICP-MS is particularly well-suited for heavy metals like Lead (Pb) because it offers exceptional sensitivity (1 ppt), wide dynamic range (ppt to ppm), and isotope ratio measurements.
- Sample preparation typically involves acid digestion to get solid samples into solution so some of the filter sample is destroyed.

Atomic Absorption Spectrometry (AAS)

- Measures how much light ground-state atoms absorb at characteristic wavelengths.
  - Each element has a unique absorption spectrum.
- Radiation at a target specific wavelength is generated that pass through a cloud of free atoms generated the sample.
- Ground-state atoms absorb photons that match transitions to excited electronic states, which reduces light intensity.
- The amount of absorption is proportional atom concentration.



An electron is excited from the ground state to higher energy level by absorbing energy at a specific wavelength. The wavelength of absorbed light is determined by the type of element and the energy levels the electrons are moving to. How much light is absorbed is determined by the concentration. Image from Agilent.com

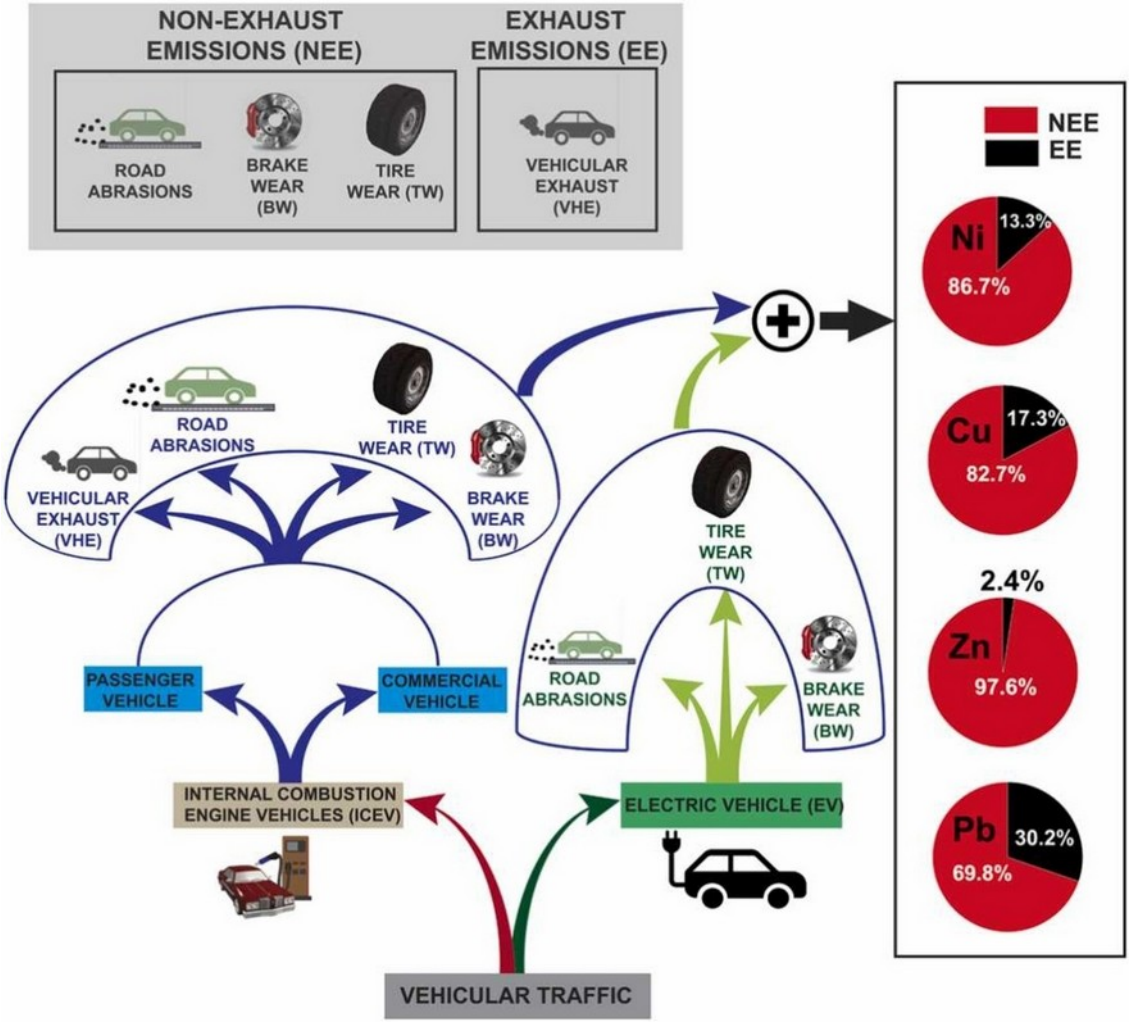
Lead Source Apportionment Methods

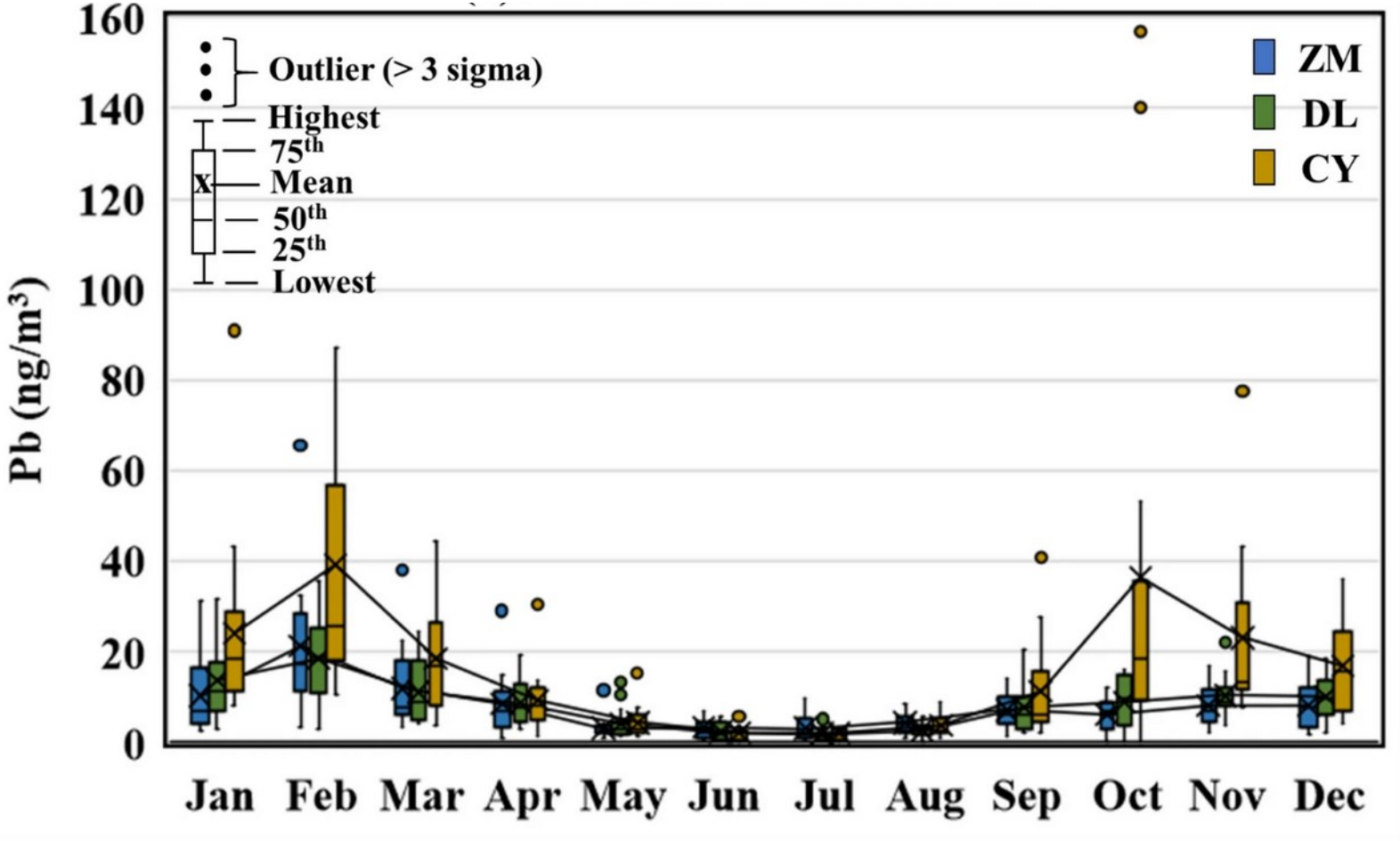
- **Isotopic Analysis**
  - 4 Stable Pb Isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb
  - Ratios Vary by Ore Source
  - Enables Quantitative Source Attribution
  - Measured by TIMS or ICP-MS
- **Chemical Mass Balance**
  - Uses Multiple Chemical Species
  - Requires Source Profiles
  - Linear Combination Approach
- **Positive Matrix Factorization**
  - Multivariate Statistics
  - No Pre-specified Profiles Needed
  - Incorporates Uncertainty

Main isotopes[1]			Decay	
	abun-dance	half-life ($t_{1/2}$)	mode	pro-duct
^{202}Pb	synth	5.25×10^4 y	ε	^{202}Tl
^{204}Pb	1.40%	stable		
^{205}Pb	synth	1.70×10^7 y	ε	^{205}Tl
^{206}Pb	24.1%	stable		
^{207}Pb	22.1%	stable		
^{208}Pb	52.4%	stable		
^{209}Pb	trace	3.235 h	β^-	^{209}Bi
^{210}Pb	trace	22.2 y	β^-	^{210}Bi
			α	^{206}Hg
^{211}Pb	trace	36.16 min	β^-	^{211}Bi
^{212}Pb	trace	10.627 h	β^-	^{212}Bi
^{214}Pb	trace	27.06 min	β^-	^{214}Bi

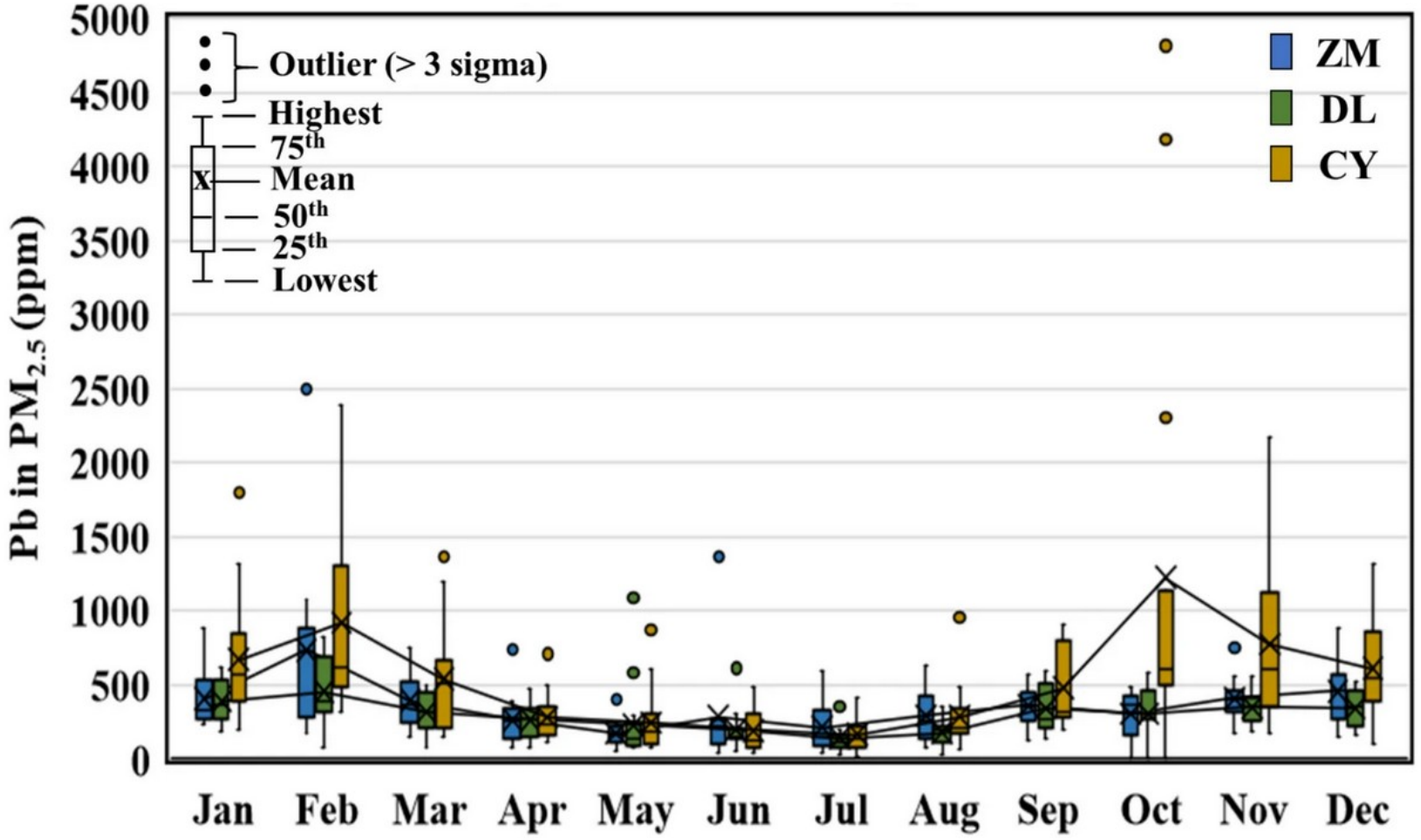
Source Apportionment and Emission Projections of Heavy Metals from Traffic Sources in India: Insights from Elemental and Pb Isotopic Compositions (Lahiri et al., 2024)

- Sources of metals in urban road dust identified using elemental concentration and Pb isotopes.
- Both exhaust and non-exhaust sources contribute significantly to metal-enriched urban road dust.
- Predicted metal emissions to rise by 163-184 % for Ni, Cu, Zn, Pb from 2022 to 2045.

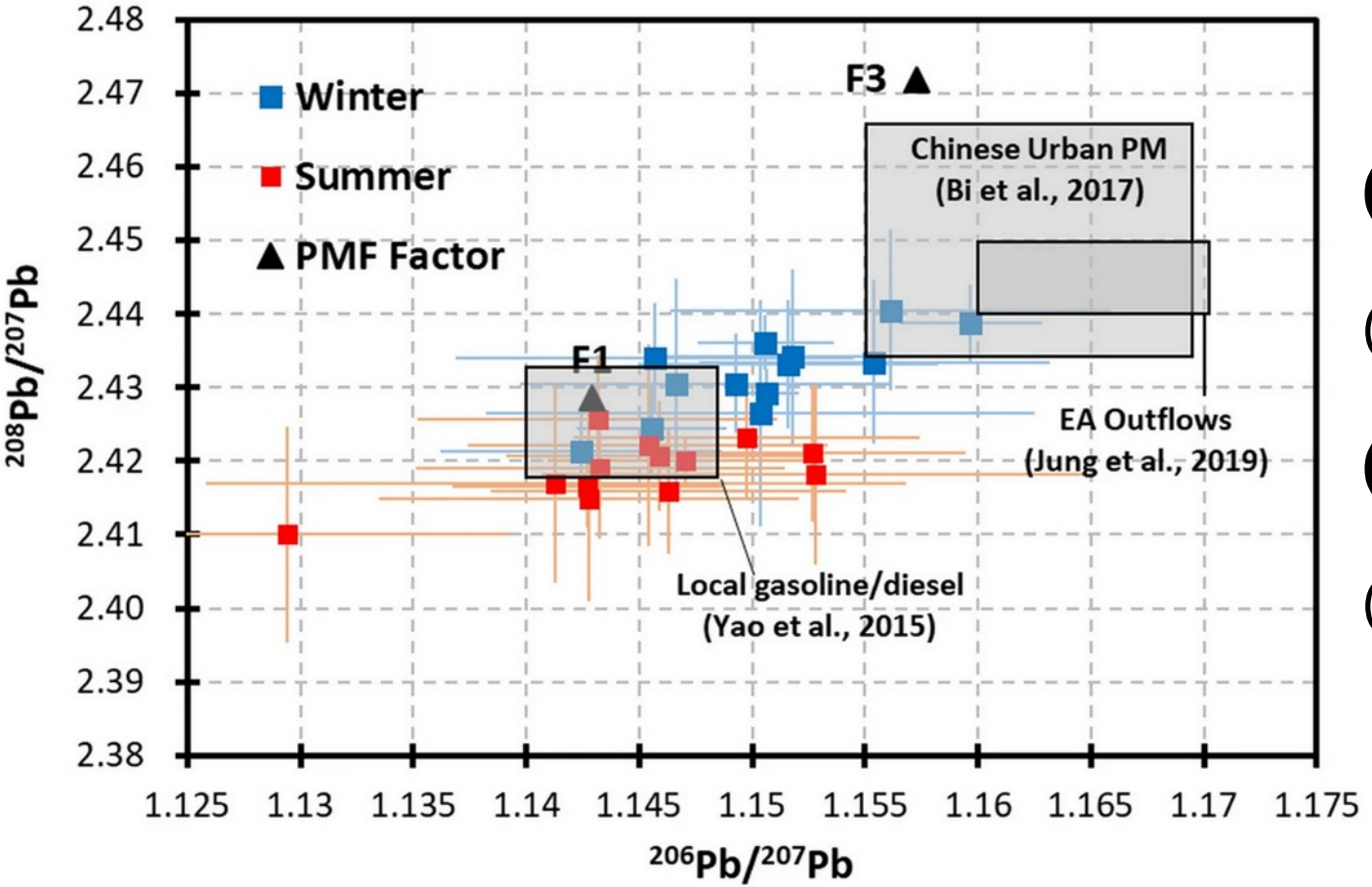




Seasonal variations in the ambient concentrations of Pb in $PM_{2.5}$ for samples are collected at the Zhongming (ZM), Douliu (DL), and Chiayi (CY) sites of the Taiwan EPA $PM_{2.5}$ speciation network from 2017–2019 (Jung et al, 2022).



Seasonal variations in the mass mixing ratios of Pb in $PM_{2.5}$ for samples are collected at the Zhongming (ZM), Douliu (DL), and Chiayi (CY) sites of the Taiwan EPA $PM_{2.5}$ speciation network from 2017–2019 (Jung et al, 2022).



Major Sources (PMF)

(1) Traffic Emissions

12 ± 5 %

(2) Petrol Industry

11 ± 4 %

(3) Coal-fired Facilities

49 ± 12 %

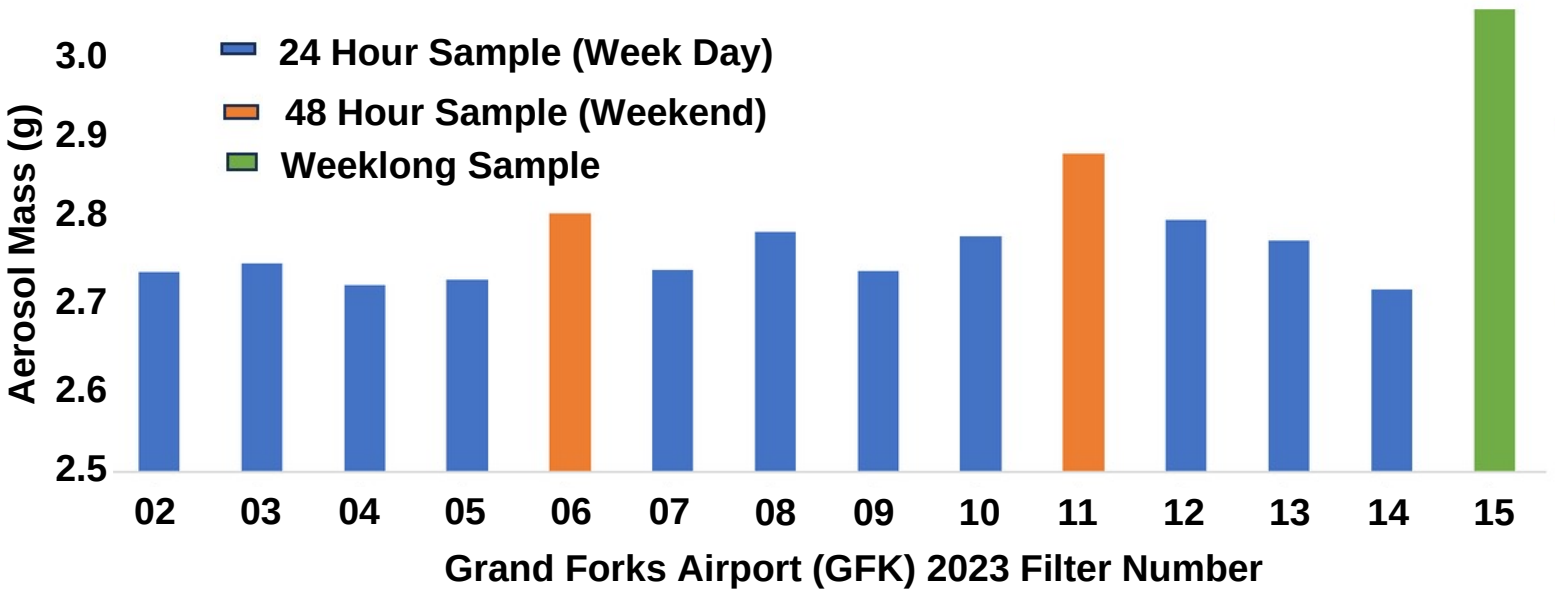
(4) Oil-fired Facilities

10 ± 5 %

Samples are collected at 13 sampling sites in central-western Taiwan during 5 field campaigns from 2016–2018. The site-specific averages are denoted by symbols with ranges of ± 1 standard deviation, as shown by the error bars. The isotopic ratios of 2 PMF factors (F1 and F3) are denoted by triangles. The ranges of the isotopic ratios for fuels supplied in Taiwan, Chinese urban particulate matter and $PM_{2.5}$ transported by outflows are indicated with gray squares, with relevant references noted (Jung et al, 2022)

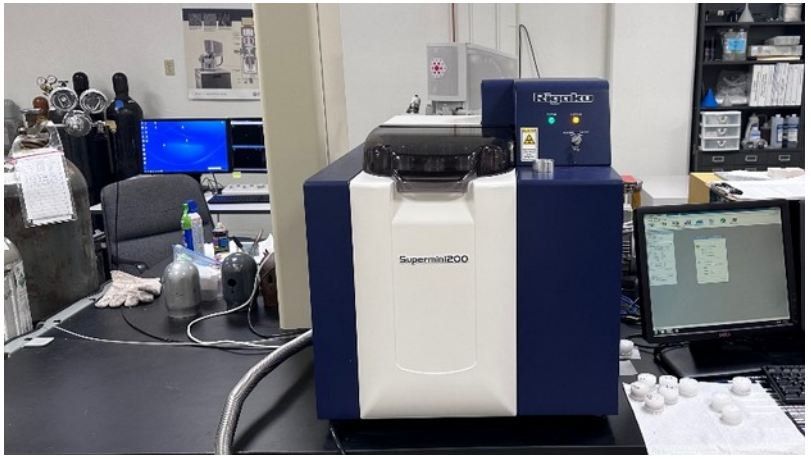
Lead Particle Filter Sampling

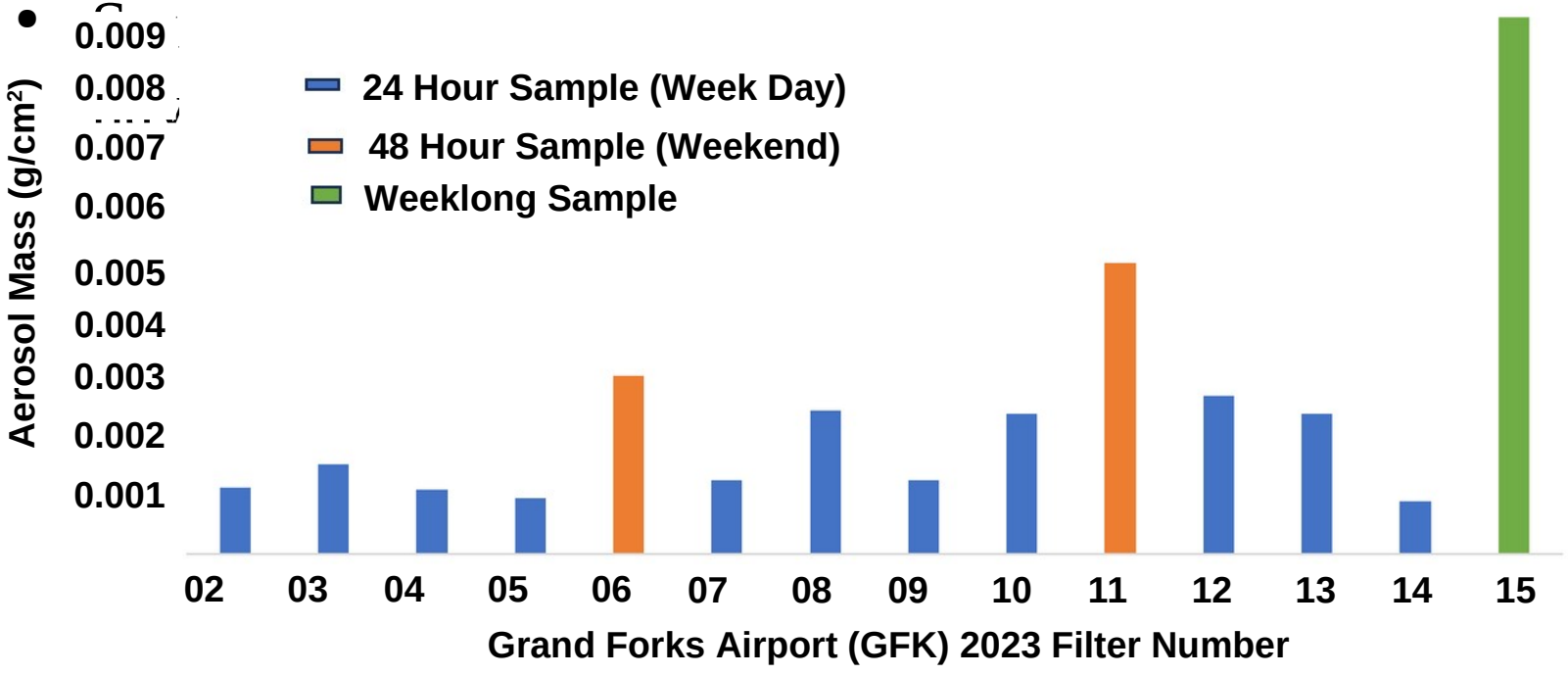
- Samples were collected on 8”x10” glass fiber filters.
- The Filters were pre and post weighed.
- Average aerosol mass for the daily samples was 2.78 grams.
- Elemental composition was analyzed using X-Ray Fluorescence.



Filter Analysis

- Elemental composition was analyzed using X-Ray Fluorescence (XRF).
- Filters were found to have too high of background (blank) lead amounts.
- [illegible]





Summary

- Lead pollution has severe health effects with no safe threshold in children.
- Leaded gasoline has been reduced.
  - US children blood lead changed from 15 to <1 μg/dL
  - Atmospheric lead reduced greater than 90 %
- Contemporary sources are industrial facilities, **aviation fuel**, and legacy contamination.
- Monitoring shifted from broad coverage to source-oriented approach.
- Regulatory frameworks combining standards, controls, and phase-outs proved effective.