Urinary Metabolites of PAH Derivatives as Exposure Biomarkers of Air Pollution Sources

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UCLA

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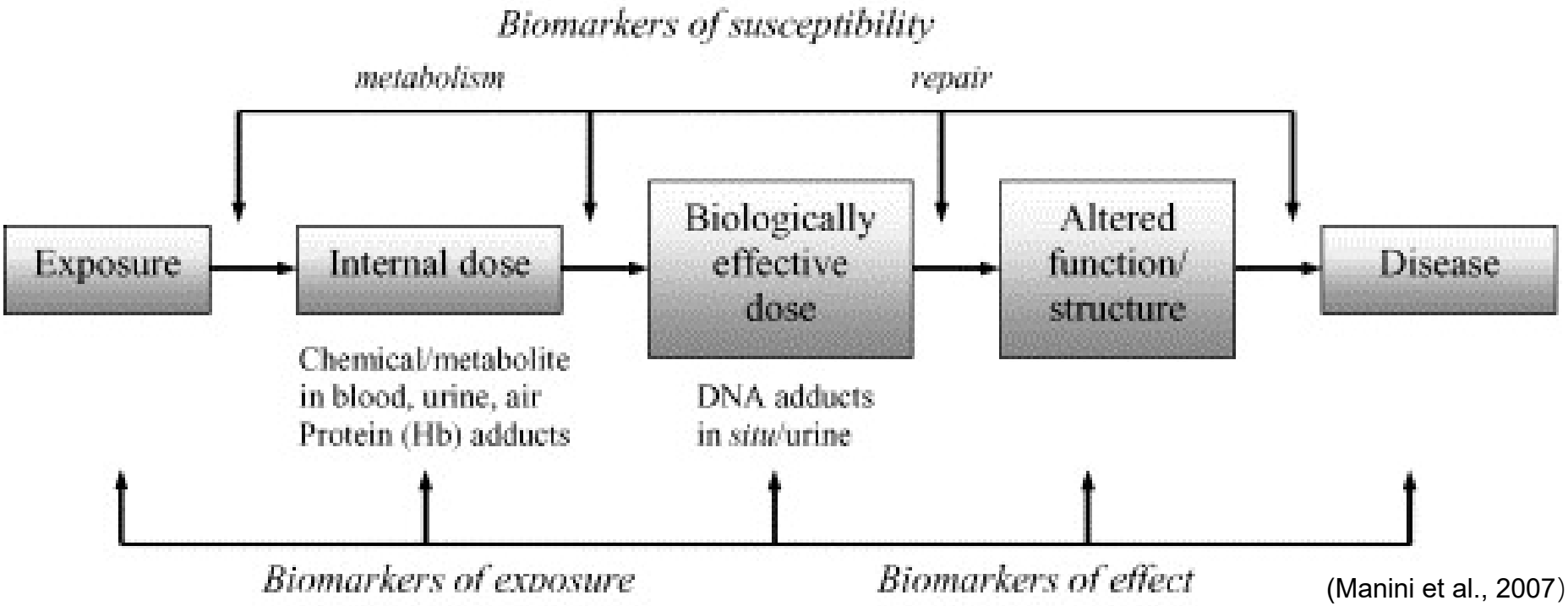
Disclosure

I declare no conflict of interest associated with this presentation.

Exposure Biomarker



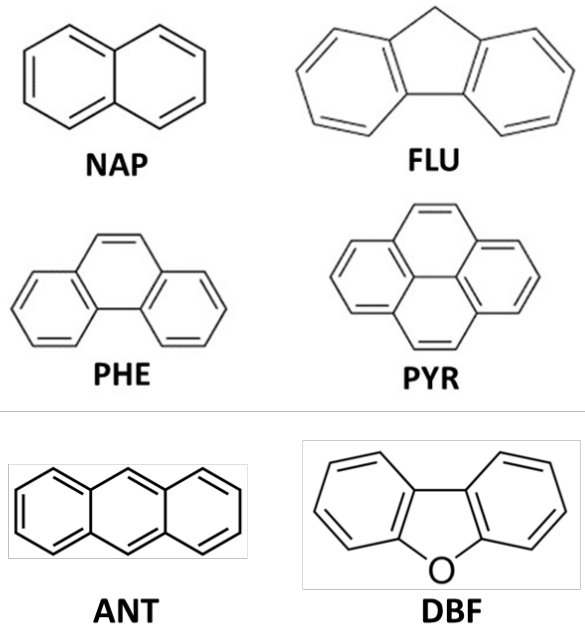
(Manini et al., 2007)

- **Exposure Biomarker:** A xenobiotic substance OR its metabolites OR the adducts between xenobiotic agent and biological molecules in biological systems and samples.

- **Air Pollution**: A chemical **MIXTURE!**

PAHs and Air Pollution

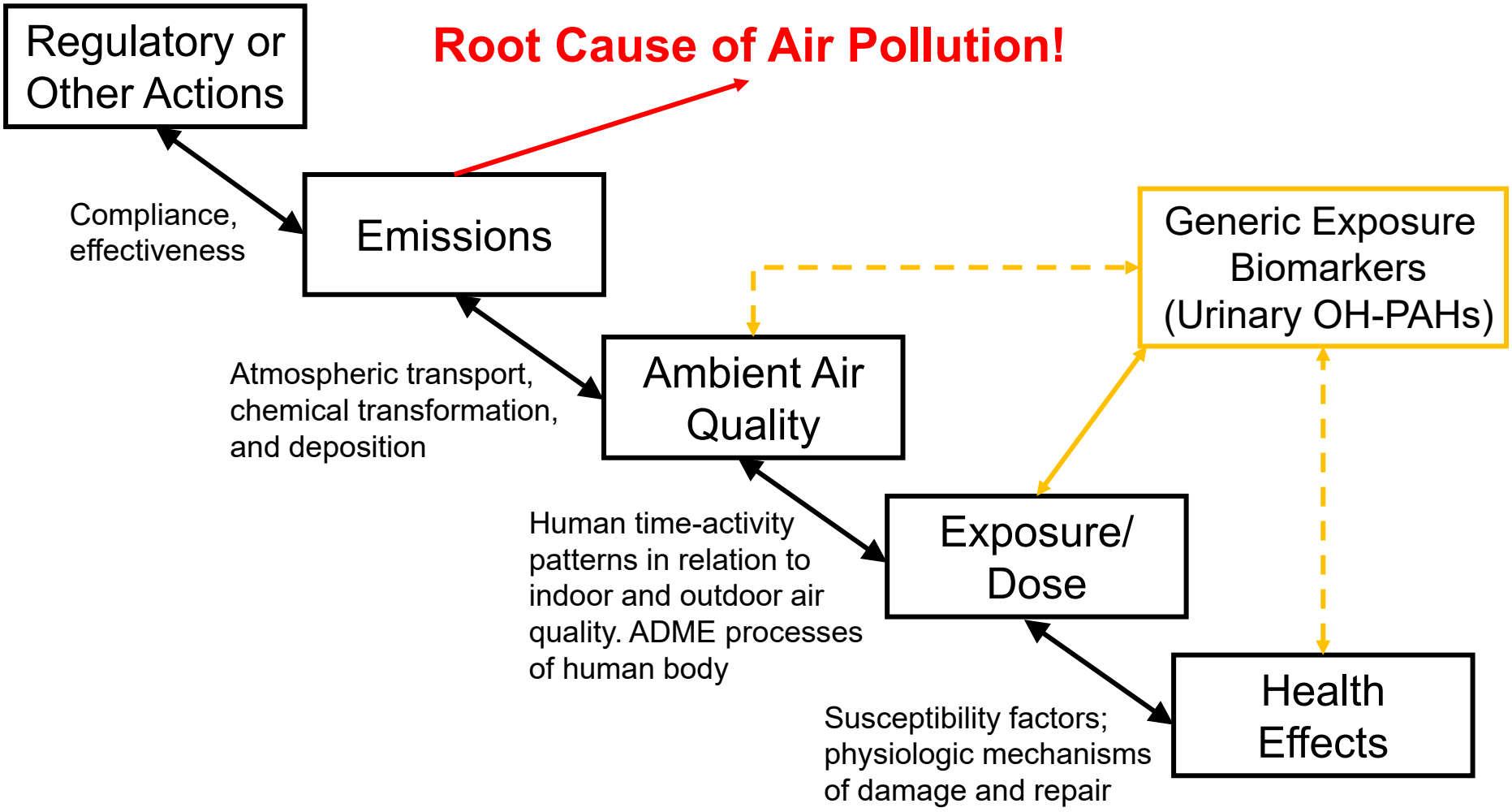
Polycyclic Aromatic Hydrocarbons (PAHs)



- ✓ **Source**: all combustion processes (e.g., vehicle emission)
- ✓ **Exposure routes**: inhalation and ingestion
- ✓ **Biomarkers:** Urinary metabolites, DNA-adduct, hemoglobin-adduct, albumin adducts.

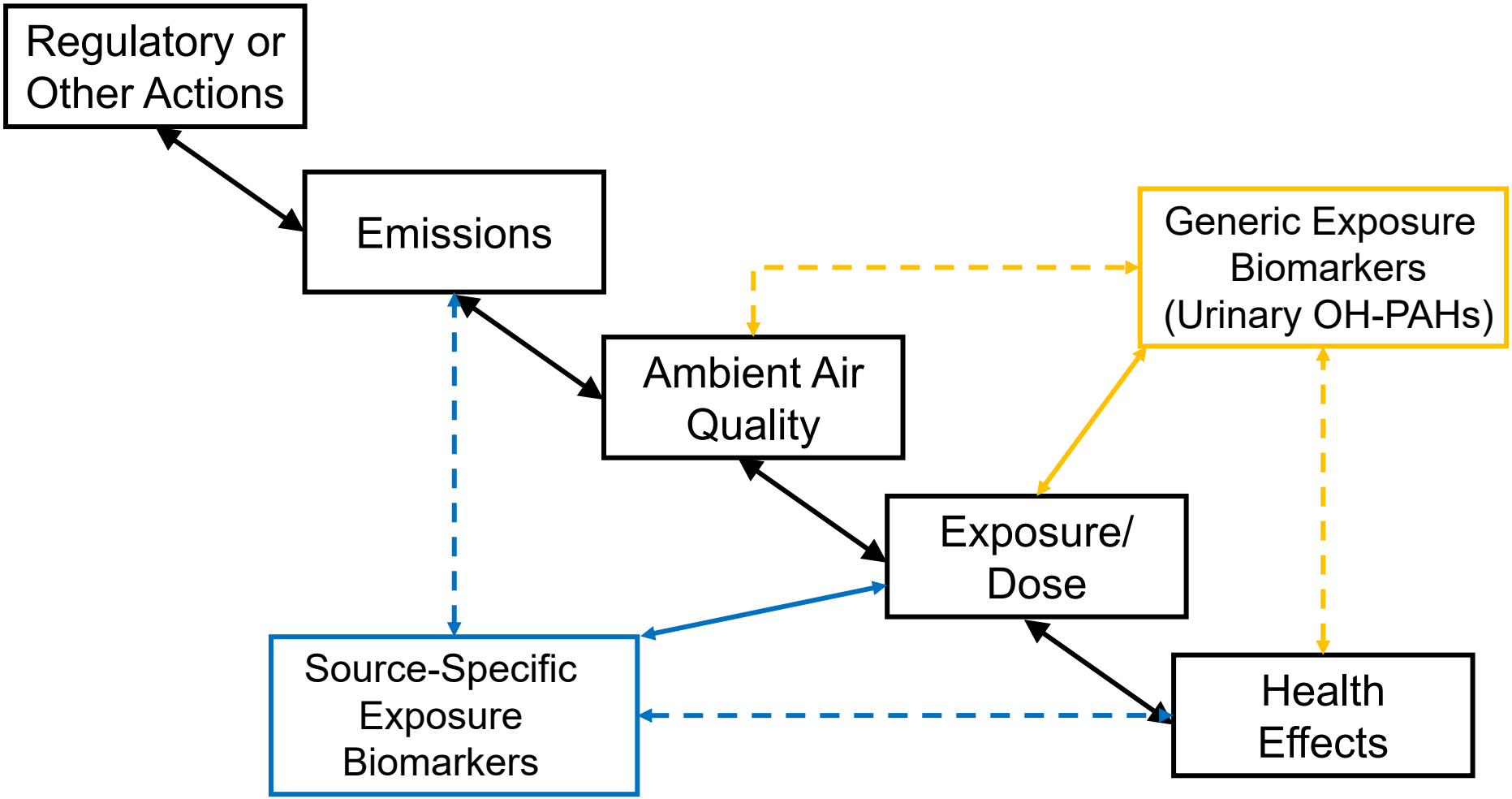
- ➢ PAHs are originated from major air pollution sources (e.g., vehicle emission, coal and biomass burning).
- ➢ PAHs are semi-volatile chemicals that exist in both gaseous and particulate phases.
- ➢ PAHs are considered as major toxic components of air pollution mixture.

Chains of Accountability – Air Pollution



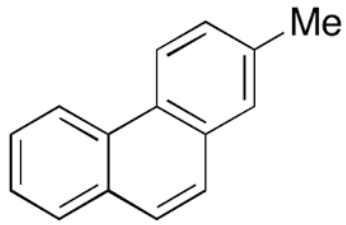
（Samet et al, 2003）

Generic vs. Source-specific Biomarkers

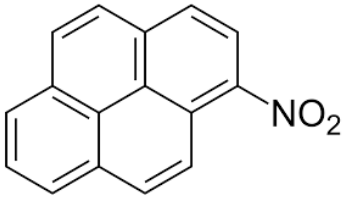


PAH Derivatives and Source Tracers

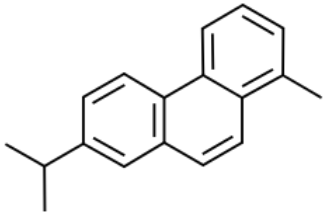
Some PAH derivatives are good tracers for sources.



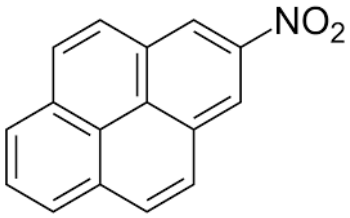
Petrogenic sources



Diesel exhaust



Wood smoke



Atmospheric reaction

Journal of Geophysical Research: Atmospheres

RESEARCH ARTICLE
10.1002/2015JD023628

Key Points:
- Level of $PM_{2.5}$-bound PAHs and derivatives was high in heating season in Beijing

Sources, transformation, and health implications of PAHs and their nitrated, hydroxylated, and oxygenated derivatives in $PM_{2.5}$ in Beijing

Yan Lin[1,2], Yiqiu Ma[1,3], Xinghua Qiu[1], Ran Li[1], Yanhua Fang[1], Junxia Wang[1], Yifang Zhu[2], and Di Hu[3,4]

ELSEVIER

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Concentrations and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs) in the atmosphere of North China, and the transformation from PAHs to NPAHs

Yan Lin [a], Xinghua Qiu [a, *], Yiqiu Ma [a], Jin Ma [b], Mei Zheng [a], Min Shao [a]

ELSEVIER

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

A novel approach for apportionment between primary and secondary sources of airborne nitrated polycyclic aromatic hydrocarbons (NPAHs)

Yan Lin [a, b], Xinghua Qiu [a, **], Yiqiu Ma [a], Junxia Wang [a], Yusheng Wu [a], Limin Zeng [a], Min Hu [a], Tong Zhu [a], Yifang Zhu [b, *]

ELSEVIER

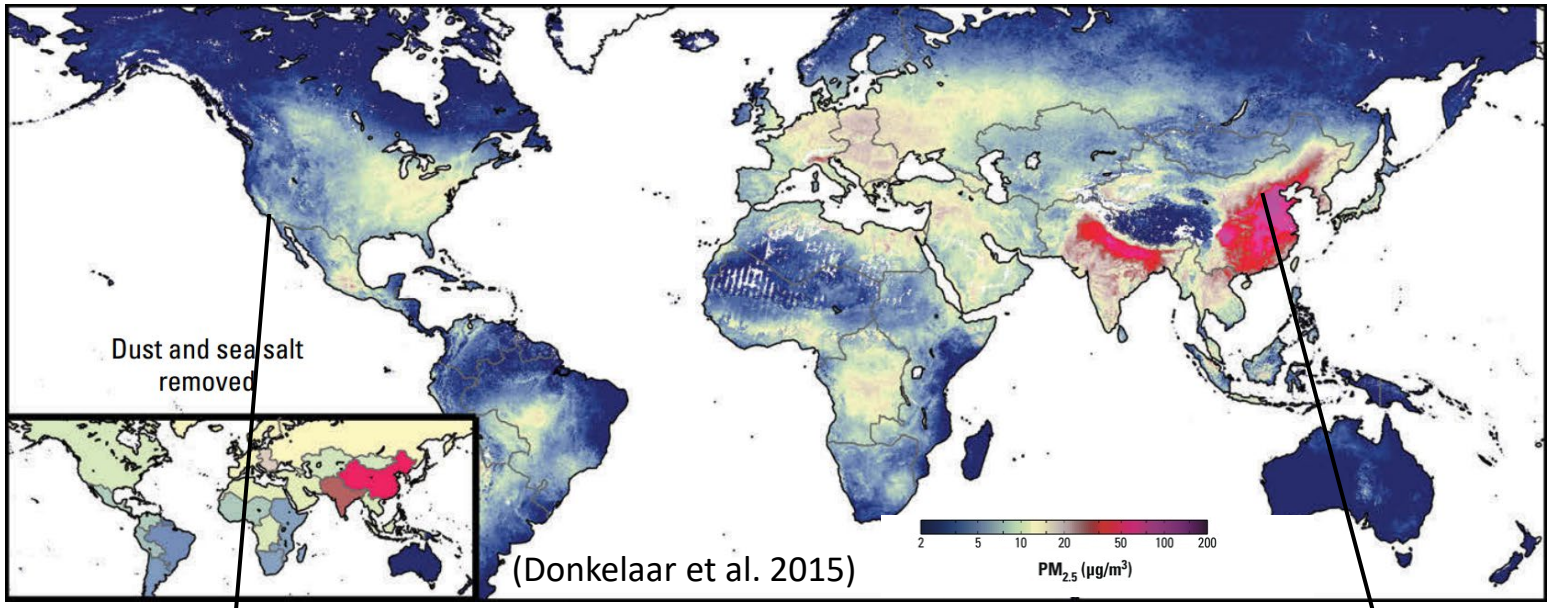
Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Atmospheric PAHs in North China: Spatial distribution and sources

Yanjun Zhang [a], Yan Lin [a,b], Jing Cai [a], Yue Liu [a], Linan Hong [a], Momei Qin [a], Yifan Zhao [a], Jin Ma [a,c], Xuesong Wang [a], Tong Zhu [a], Xinghua Qiu [a], Mei Zheng [a,*]

Air Pollution in Global Mega-Cities



(Donkelaar et al. 2015)

Los Angeles

$PM_{2.5}$ levels: ~16.2 µg/m^3

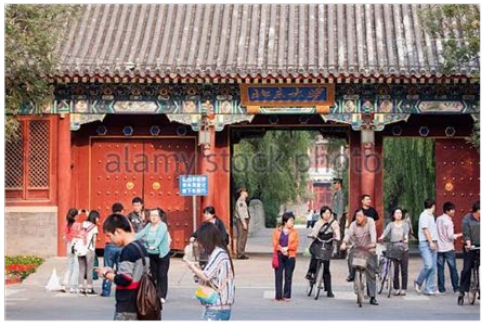
Source: Pyrogenic + Petrogenic

Beijing

$PM_{2.5}$ levels: ~87.0 µg/m^3

Source: Pyrogenic

Air Pollution and Cross-boundary Travels



Subjects

UCLA (LA-before) — Sample collection

PKU (Beijing) — Sample collection

UCLA (LA-after) — Sample collection

2014 → 2015 → 2016 → 2017

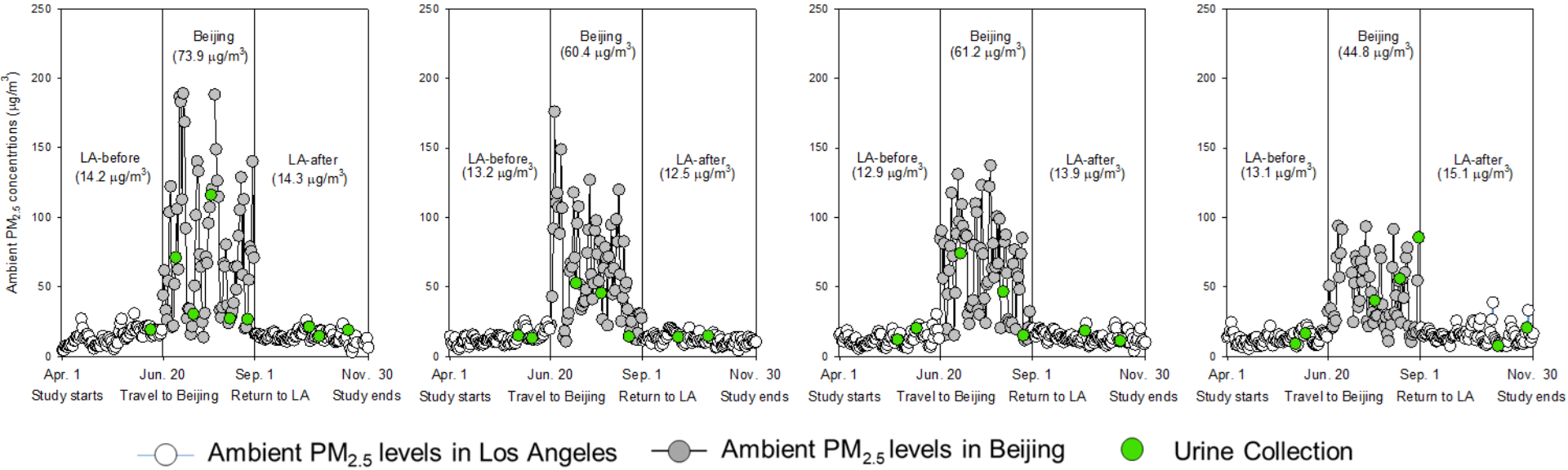
Air Pollution Levels During the Travel

Panel 2014
14 students
5 men and 9 women
Average age=23.3 years

Panel 2015
13 students
3 men and 10 women
Average age=27.8 years

Panel 2016
8 students
3 men and 5 women
Average age=22.6 years

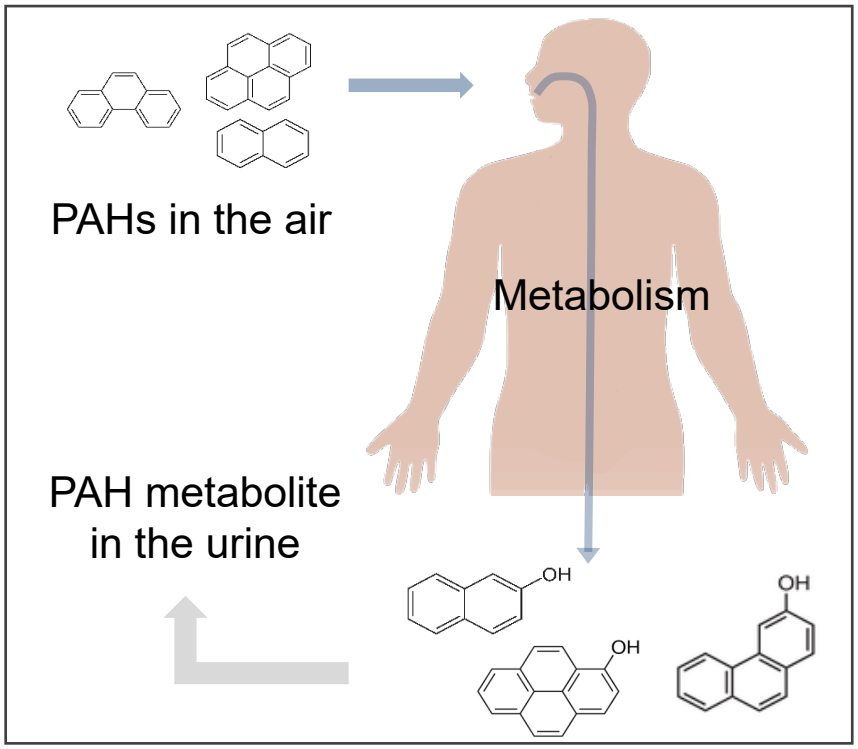
Panel 2017
10 students
8 men and 2 women
Average age=22.0 years



- Air pollution level is constantly higher in Beijing than Los Angeles;
- Air quality has been improved in Beijing from 2014 to 2017.

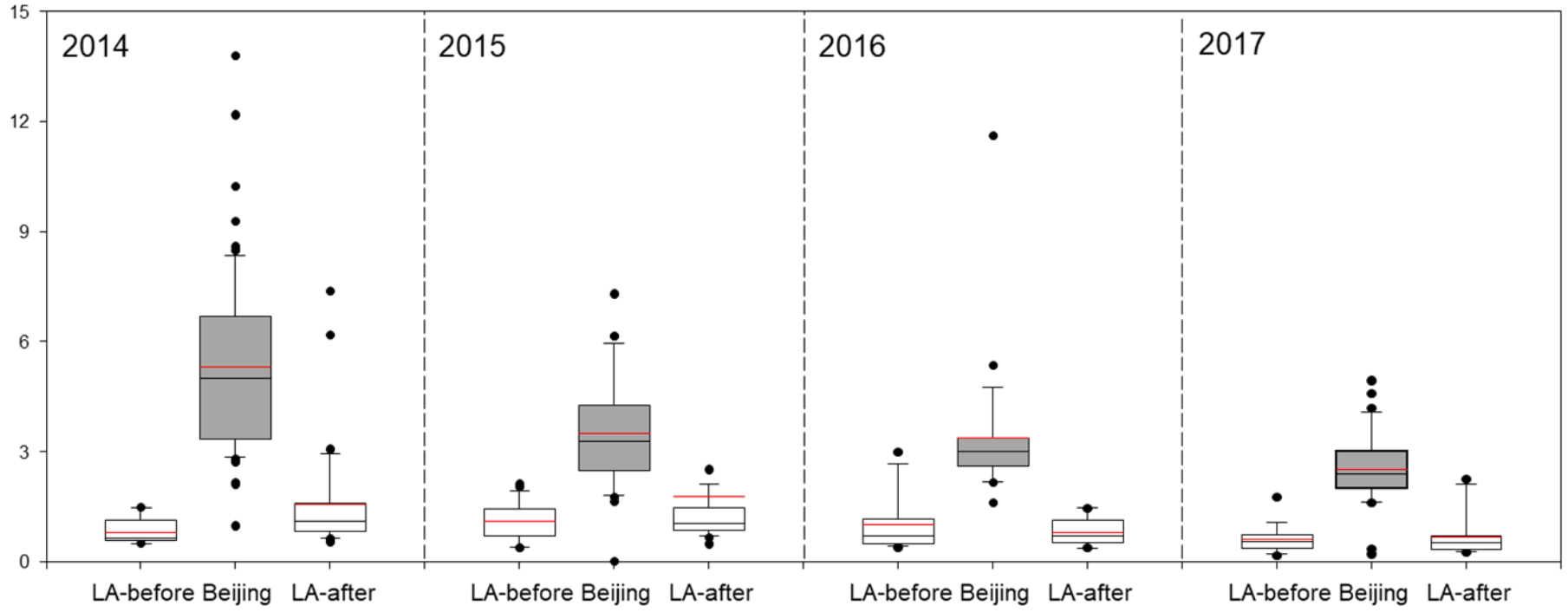
（Data source: national air quality monitors within 30 km of the UCLA (n=4) and Peking University (n=18）

Exposure Assessment



- **Smoking:** all non-smokers, secondhand smoke monitored by urinary cotinine.
- **Diet:** 8 hour fast prior to urine collection, barbeque intake surveyed by questionnaire.

Urinary PAH Metabolites



Levels of urinary PAH metabolites were

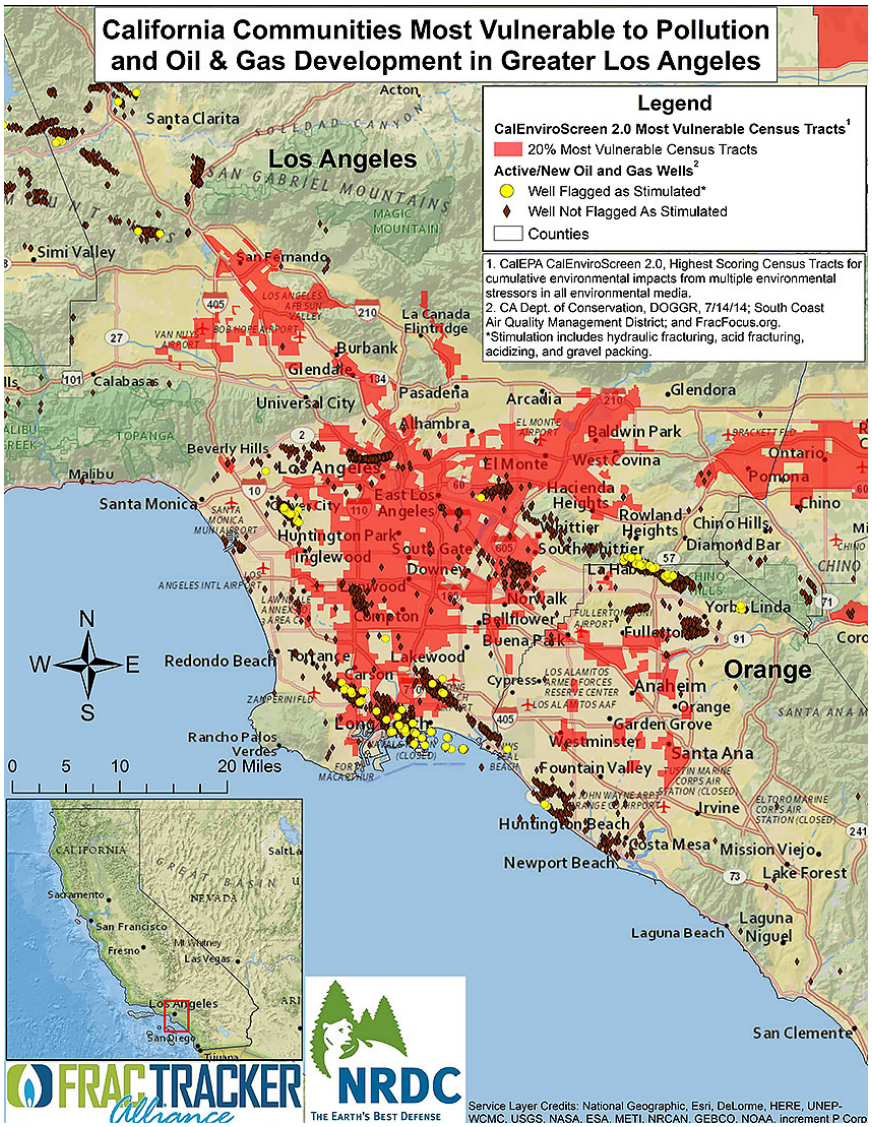
- Higher in Beijing
- Decreased from 2014 to 2017 in Beijing
- Associated with ambient NO_2 and $PM_{2.5}$ levels

Petrogenic Sources in Los Angeles

1 out of 3 People in Los Angeles Lives Within a Mile of an Oil Well

As the fight over fracking heats up, a new report shows that millions of Californians live uncomfortably close to oil and gas rigs.

- There are substantial pyrogenic emissions (i.e., vehicle exhaust) in both Los Angeles and Beijing.
- Los Angeles also has many petrogenic sources.

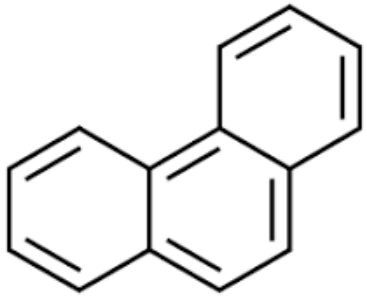


Pyrogenic vs. Petrogenic Sources

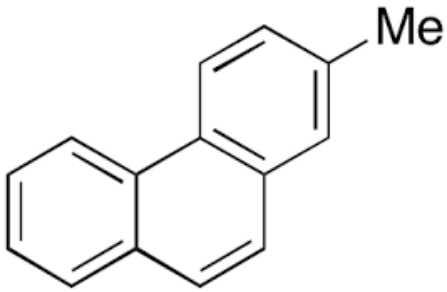
Pyrogenic sources
(combustion process, including vehicle exhaust, coal and biomass burning)

- ✓ **PAHs are more abundant in pyrogenic sources.**
- ✓ **Methylated-PAHs (e.g., 2-MePHE) are more abundant in petrogenic sources.**
- ✓ **Urinary OH-PAHs are metabolites of PAHs, providing a tool to assess exposure to pyrogenic pollutants.**

Petrogenic sources
(non-combustion process related to fossil fuel and refine oil products)

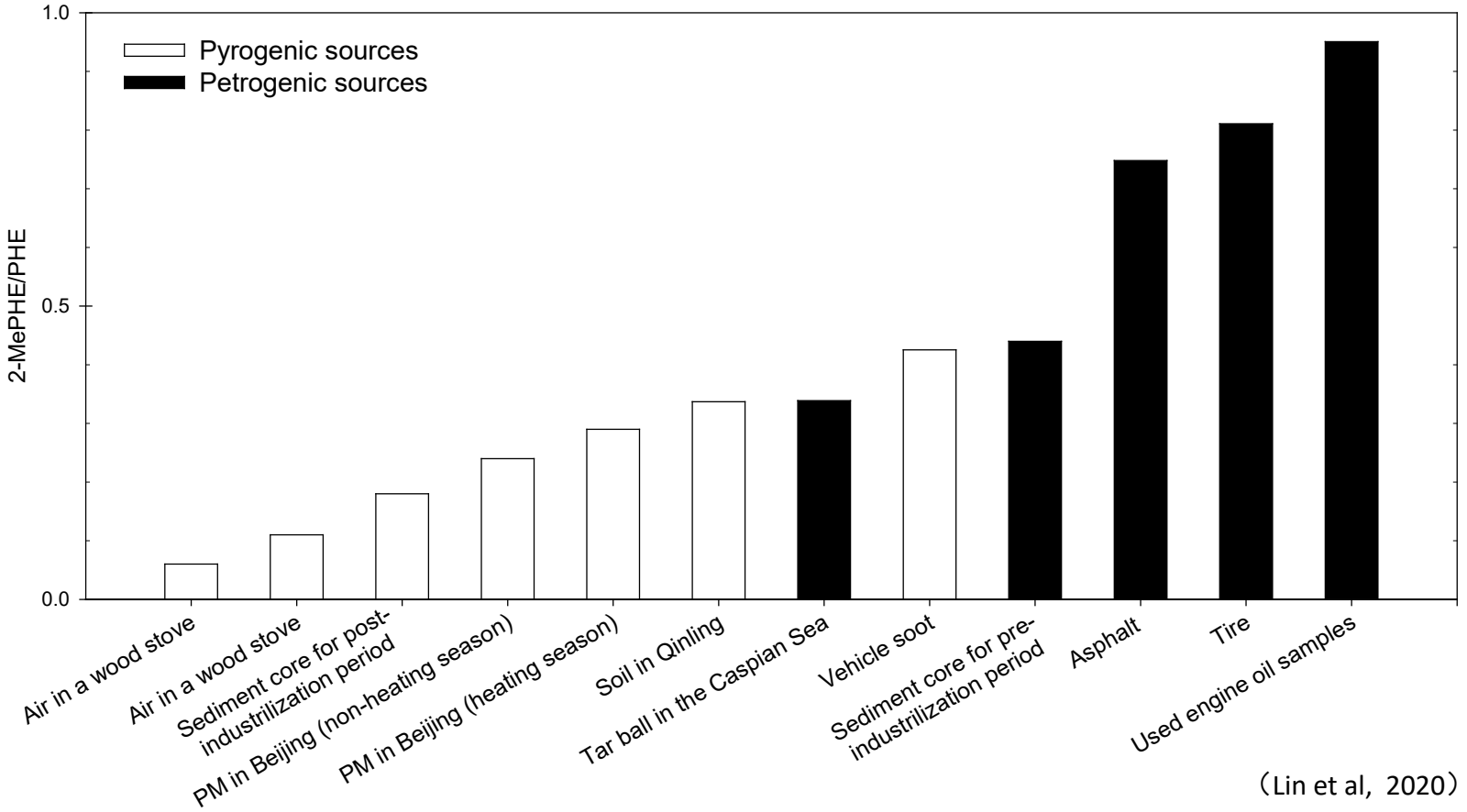


Phenanthrene
(PHE)



2-Methyl-Phenanthrene
(2-MePHE)

2-MePHE/PHE as a Source Diagnostic Ratio

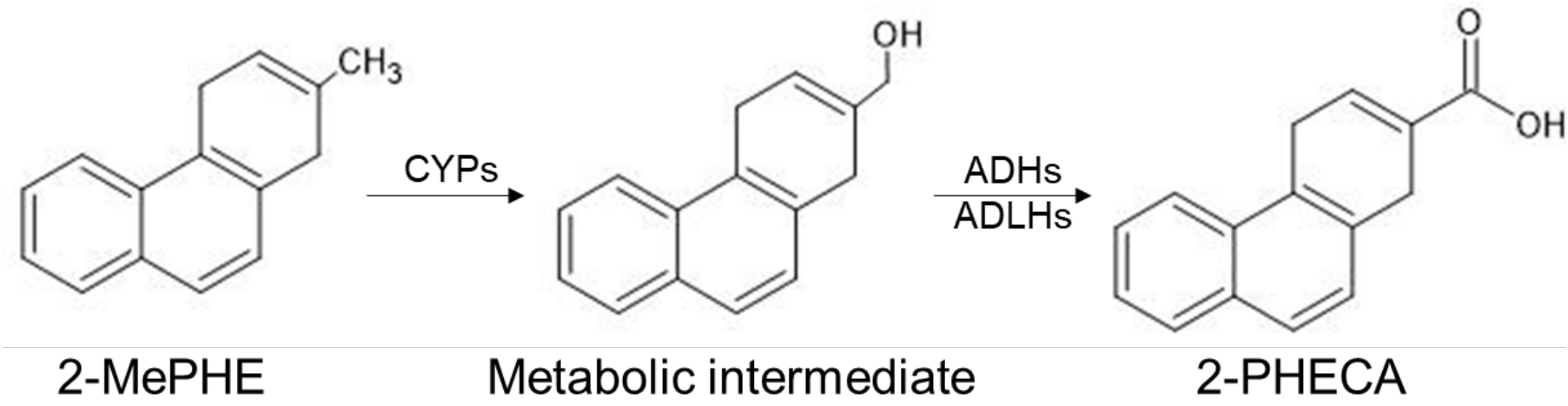


（Lin et al, 2020）

2-MePHE/PHE ratio in environmental samples linked to pyrogenic or petrogenic sources (Boonyatumanond et al., 2007; Hedberg et al., 2002; Lin et al., 2015; Liu et al., 2017; Nalin et al., 2016; Pereira et al., 1999)

No biomarker is available to assess exposure to Methylated-PAHs.

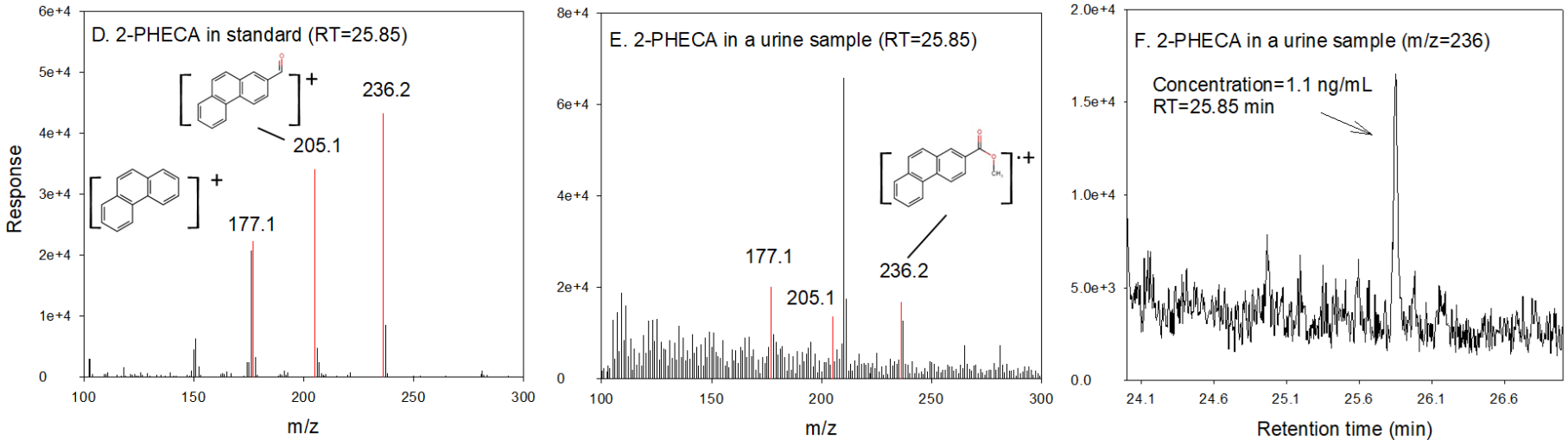
Carboxylic Acid Metabolite of Methylate-PAHs



(Huang et al, 2017)

- In-vitro studies based on human liver microsome found PAHs carboxylic acid as the major metabolites of methylated-PAHs.
- However, it is unknown whether 2-PHECA exists in human urine.

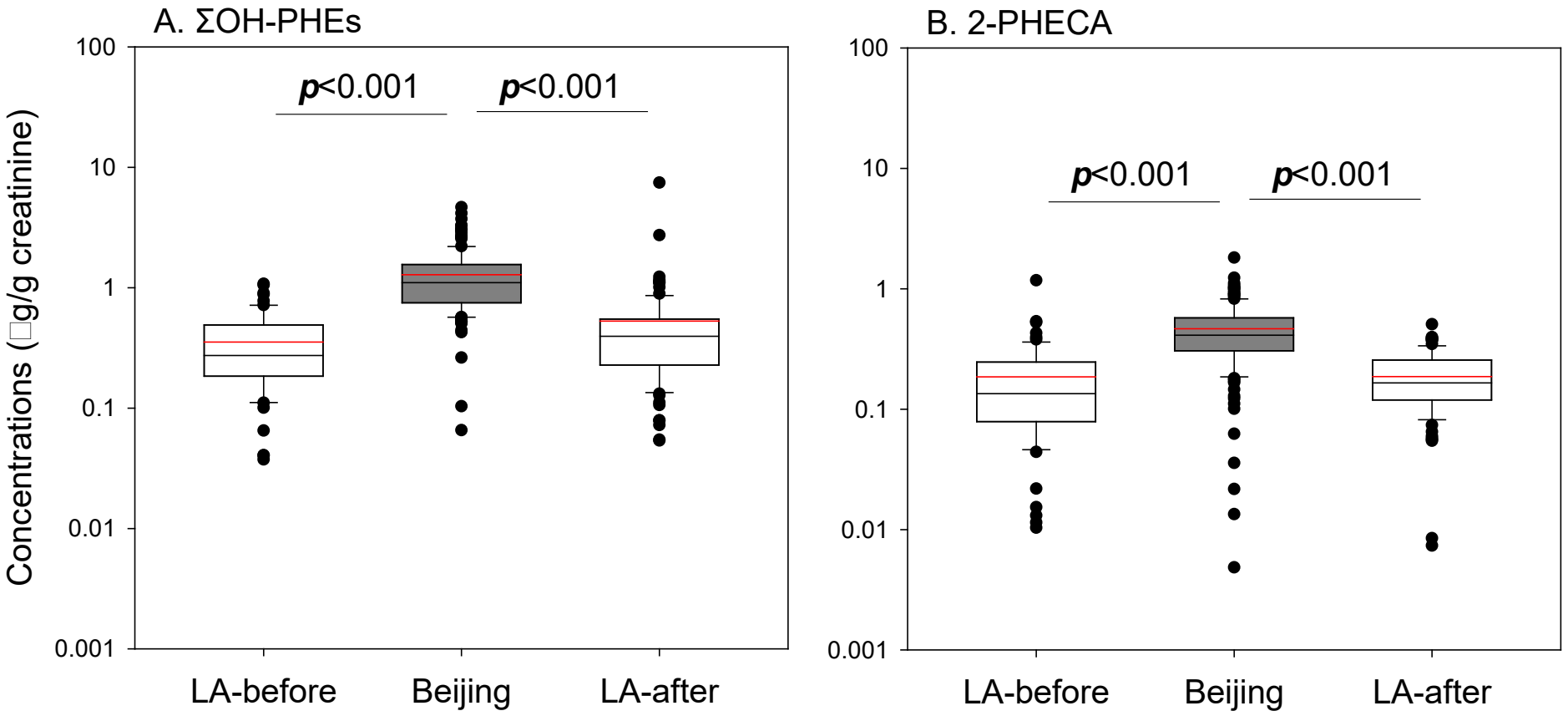
Analytical Method



（Lin et al, 2020）

- We developed a state-of-the-art analytical method for simultaneous detection of ΣOH-PHEs and 2-PHECA in human urine.

Field Study

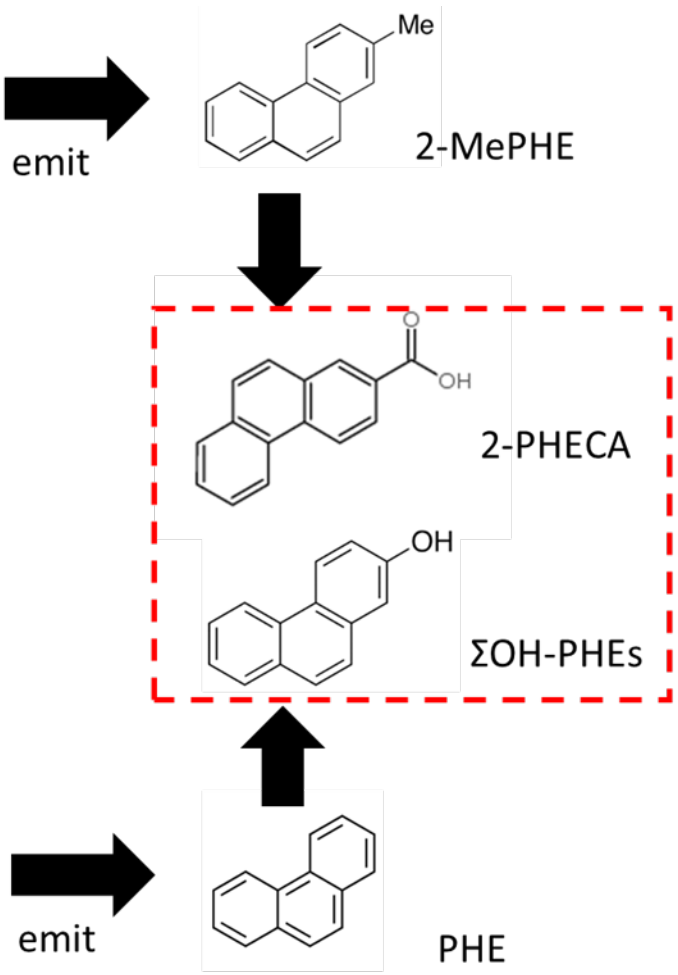


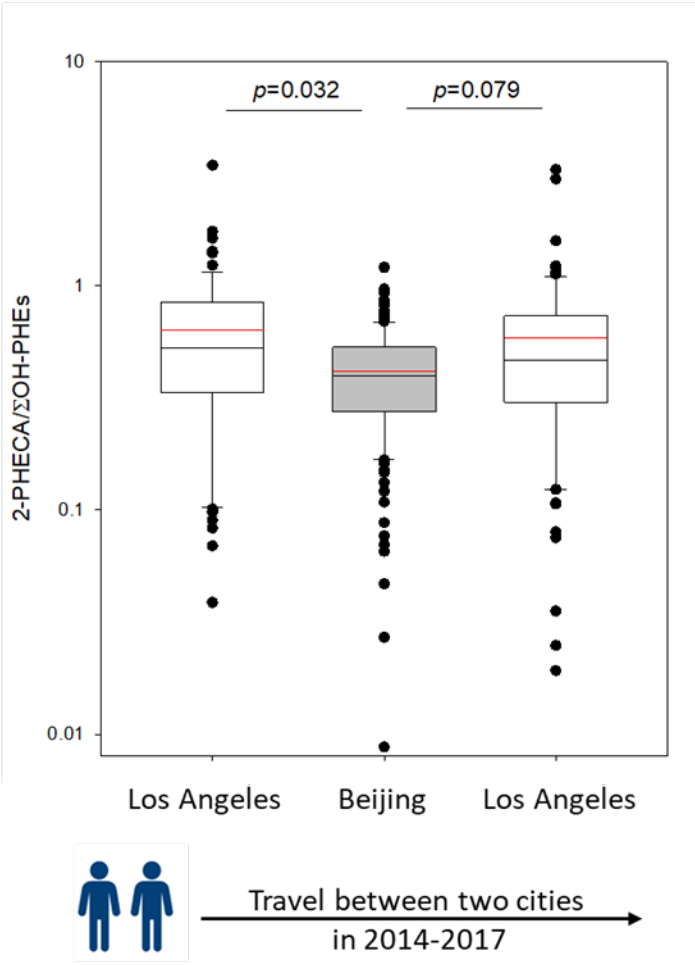
- Both 2-PHECA and ΣOH-PHEs levels were higher in Beijing than LA.

Field Study

Petrogenic sources
(in Los Angeles)

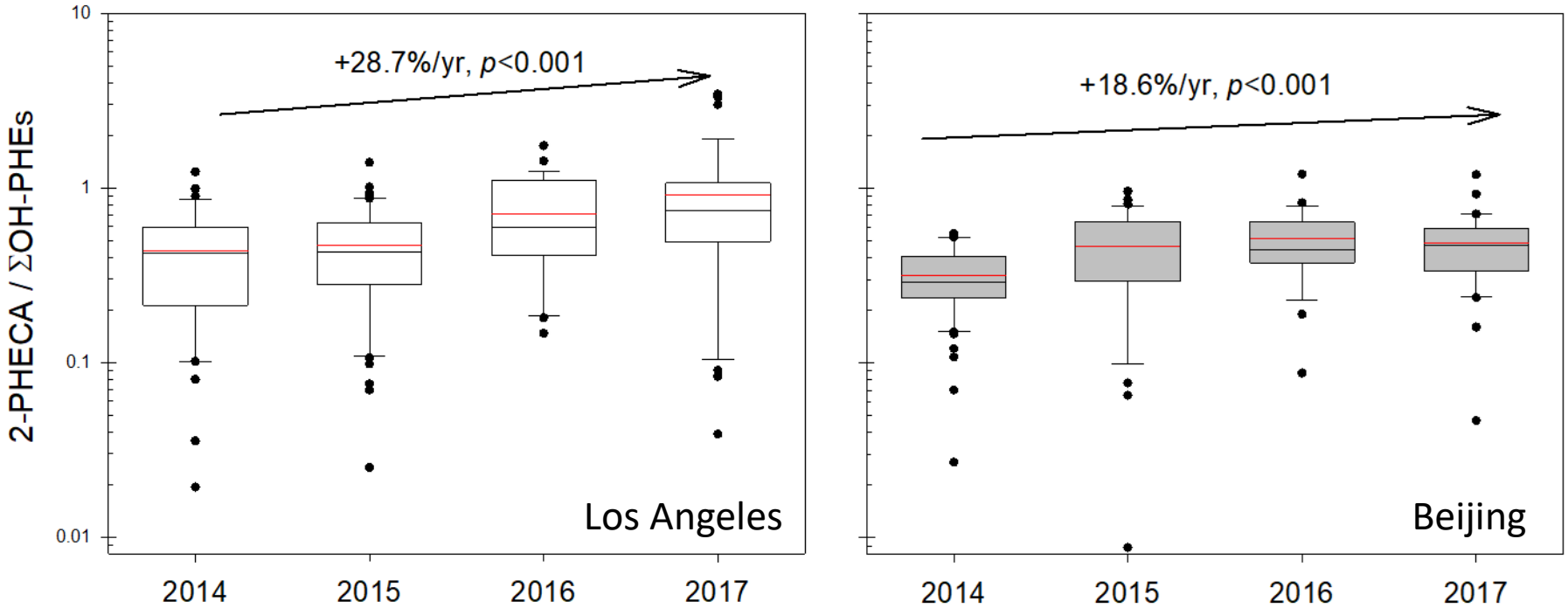
Pyrogenic sources
(in Beijing)





- We observed higher 2-PHECA/ΣOH-PHEs ratio in Los Angeles, suggesting greater contribution from petrogenic sources.

Field Study



- There are significant increases in 2-PHECA/ΣOH-PHEs ratio from 2014 to 2017 in both Los Angeles and Beijing.
- This may relate to both cities' efforts to reduce pyrogenic sources such as vehicle emission.

Cross-Validation Study

589 paired samples from 120 Beijing residents

Associations?

Personal air samples

2-MePHE

2-MePHE/PHE

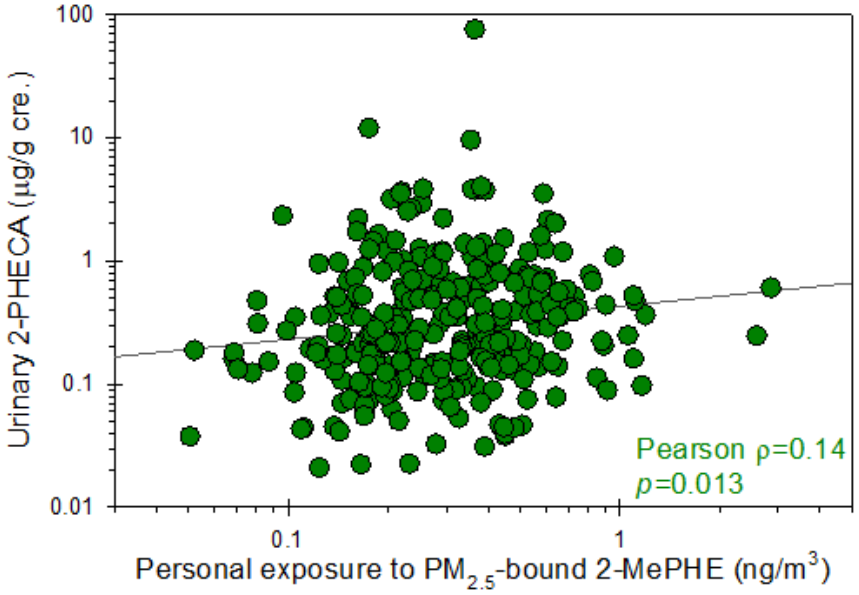
Morning urine samples

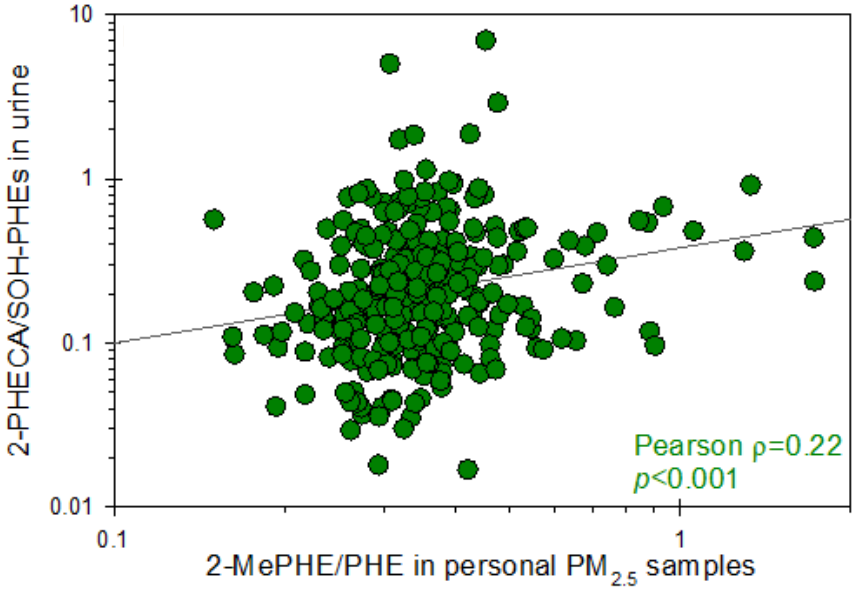
2-PHECA

2-PHECA/ΣOH-PHEs

- A cross-validation study was conducted among 120 residents of Beijing.
- 589 paired urine and personal $PM_{2.5}$ samples were collected in 2013-2015.
- Associations were examined between personal exposure to 2-MePHE and urinary levels of 2-PHECA, and between personal 2-MePHE/PHE ratio and urinary 2-PHECA/ΣOH-PHEs ratio.

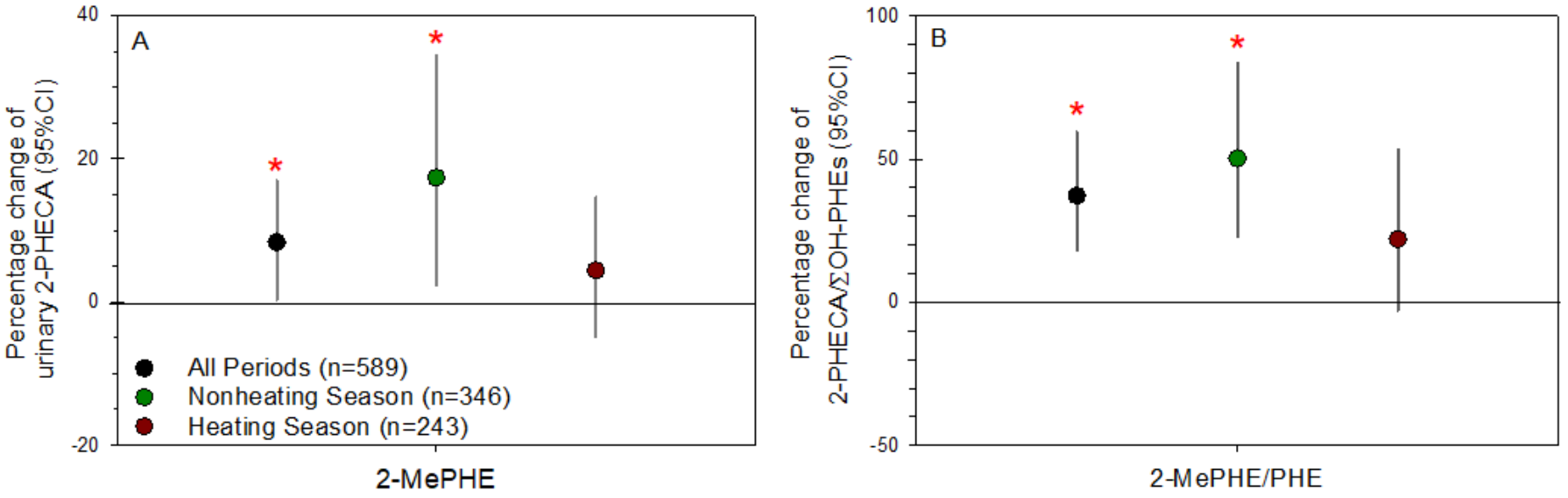
Cross-Validation Study





- Personal exposure to 2-MePHE was positively associated with urinary levels of 2-PHECA.
- Personal 2-MePHE/PHE ratio was positively associated with urinary 2-PHECA/ΣOH-PHEs ratio.

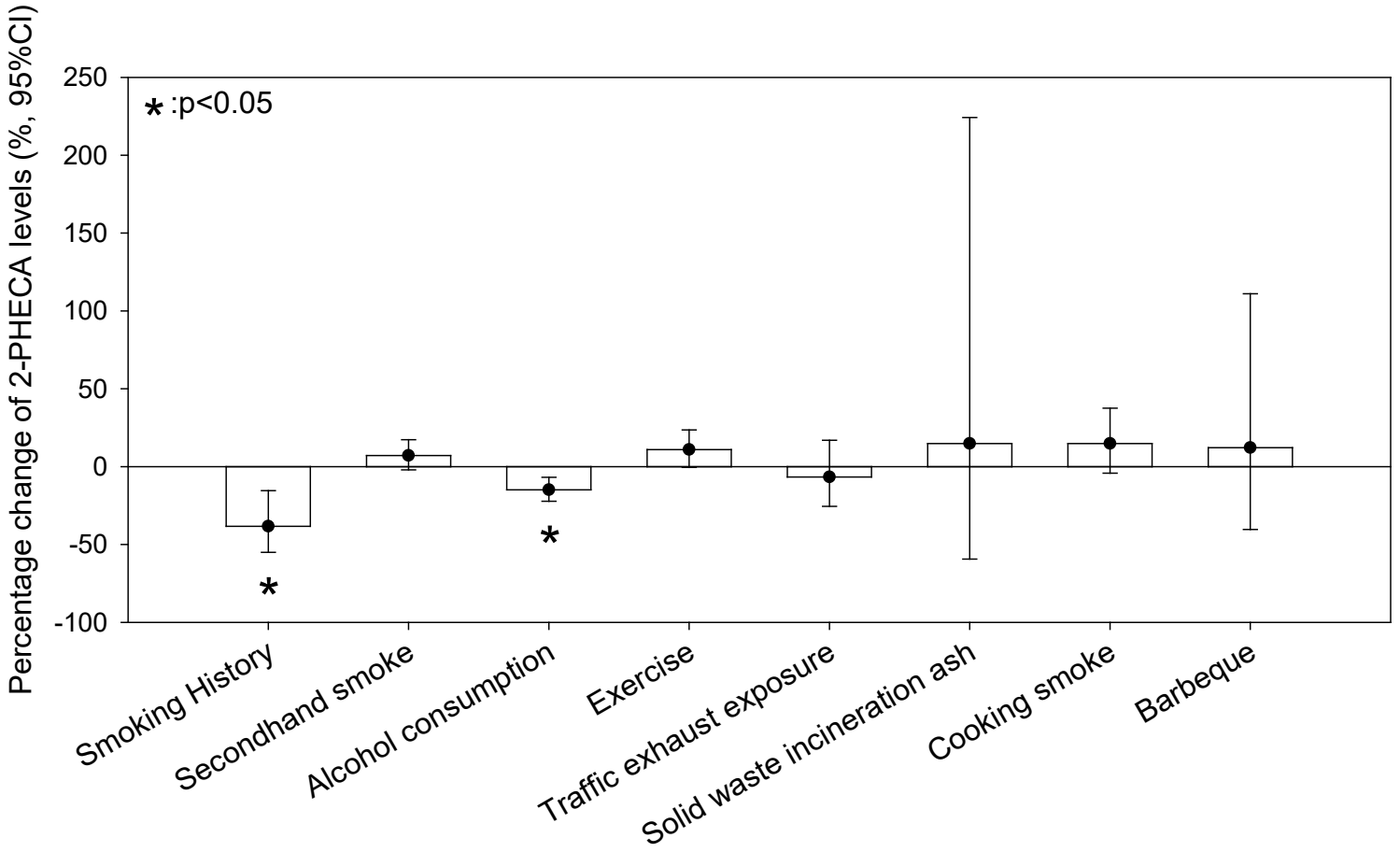
Cross-Validation Study

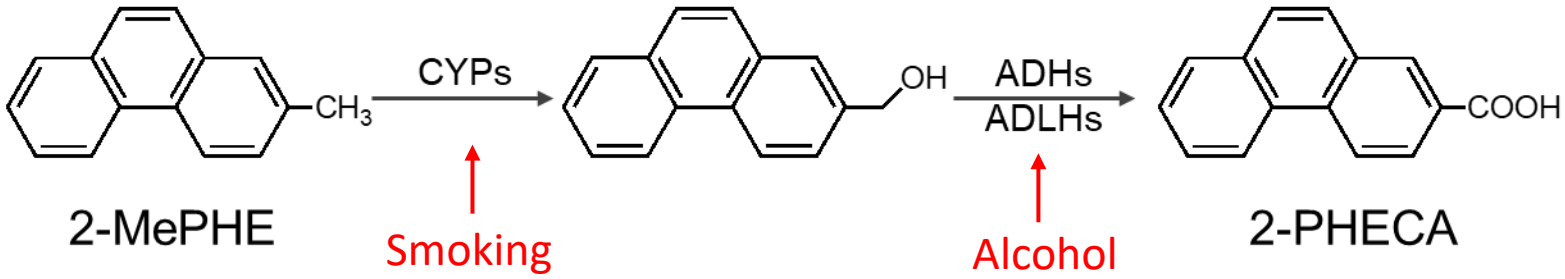


- There are drastic differences in air pollution levels and sources, as well as resident's time-activity pattern between heating and non-heating seasons.

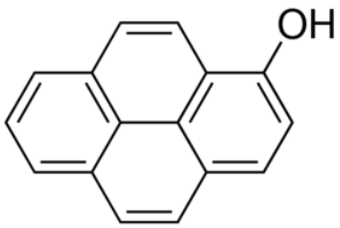
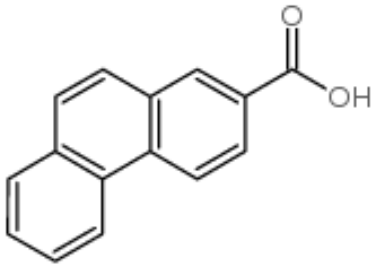
- We found the association was modified by season, suggesting another factor that might influence the relationship between external exposure and biomarker levels.

Cross-Validation Study





Summary

Biomarker	 OH-PAHs	 PAH carboxylic acid
Environmental Precursors	PAHs	Methylated-PAHs
Air Pollution Sources	Generic Combustion	Petrogenic > Pyrogenic
Non-Air Pollution Factors	Tobacco smoke, diet	Tobacco smoke, alcohol

Acknowledgement

PKU

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Tong Zhu
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Jing Shang
Yiqun Han
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Duke

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Thank
you!!