What Goes Around Comes Around: Chasing Polycyclic Aromatic Hydrocarbons from the Beijing Olympics to the U.S. West Coast

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Oregon State University

Superfund Research Program

National Science Foundation
WHERE DISCOVERIES BEGIN

Oregon State University

NIEHS Superfund Research Program

a hazardous waste research and training program

www.niehs.nih.gov/research/supported/srp/index.cfm

Superfund Research Program

Research

- Interdisciplinary
- Collaborative
- Solution-Oriented
- e.g. molecular tox, biomarker development, ecology, remediation

Training

- graduate and post doctoral
- interdisciplinary

Network of:

- 19 university-based research centers
- 11 individual research grants
- 5 SBIRs/STTRs

Products

- Over 6,000 publications
- 55 patents
- Enrichment materials, e.g., fact sheets, videos

Communication Tools

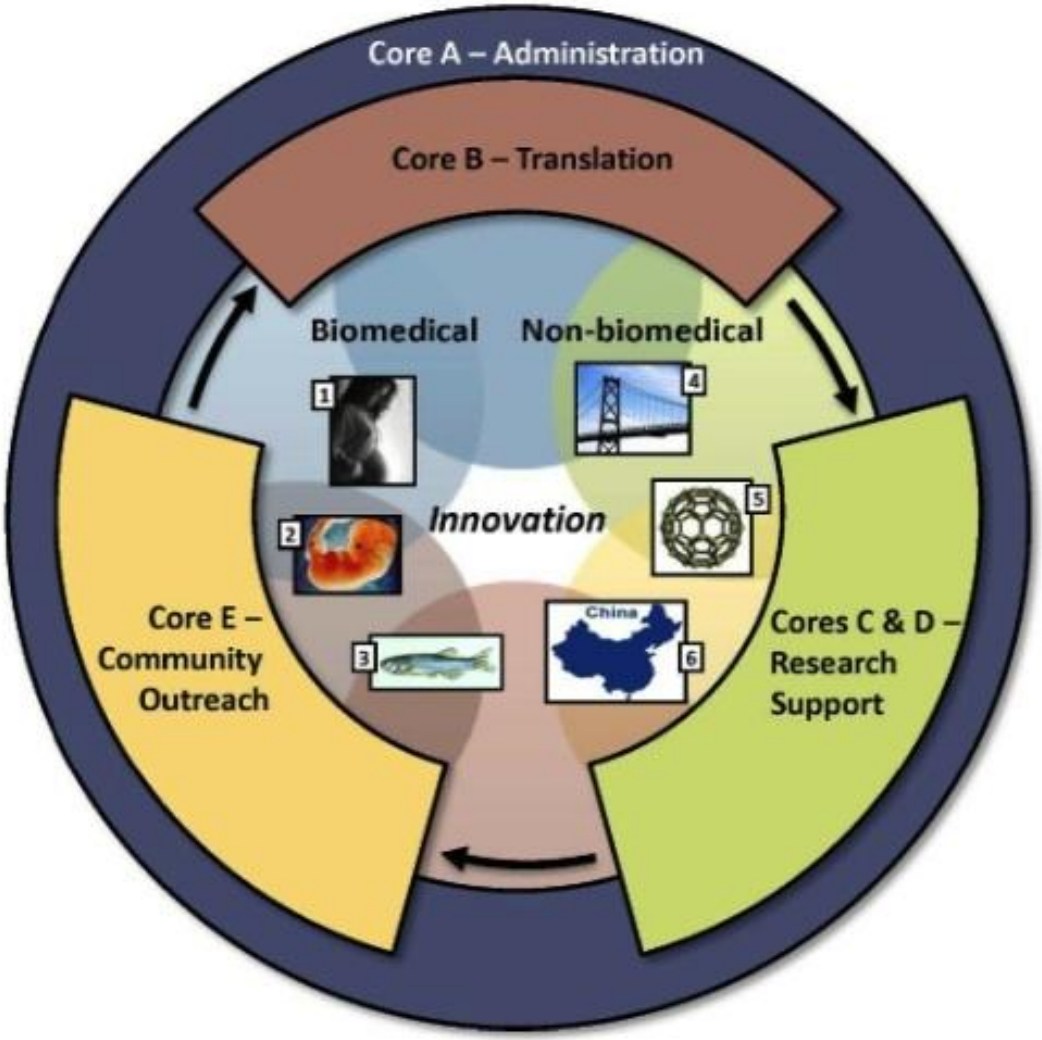
- Research Briefs
- Risk-e-Learning
- Workshops
- Conferences

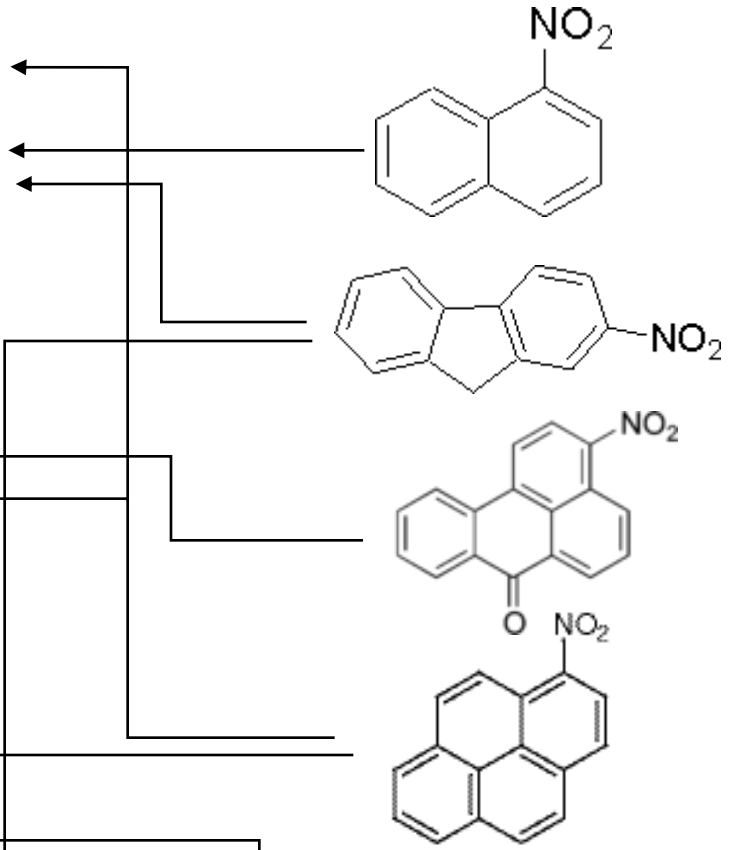
For more information, contact: SRPinfo@niehs.nih.gov

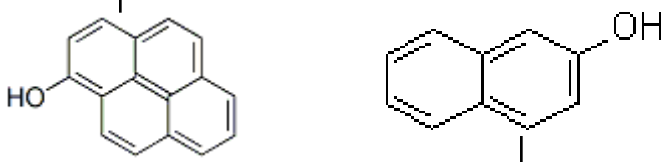
NIEHS
National Institute of Environmental Health Sciences

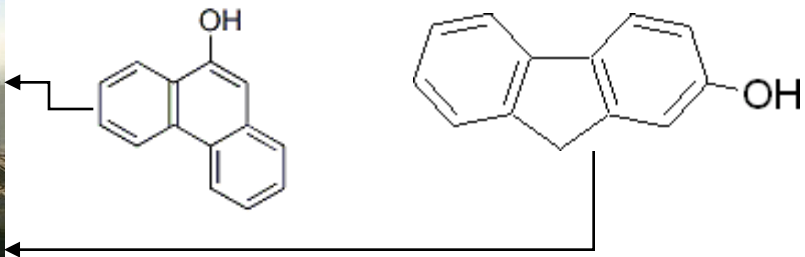
OSU Superfund Research Program (SRP)

Polycyclic Aromatic Hydrocarbons: New Technologies and Emerging Health Risks

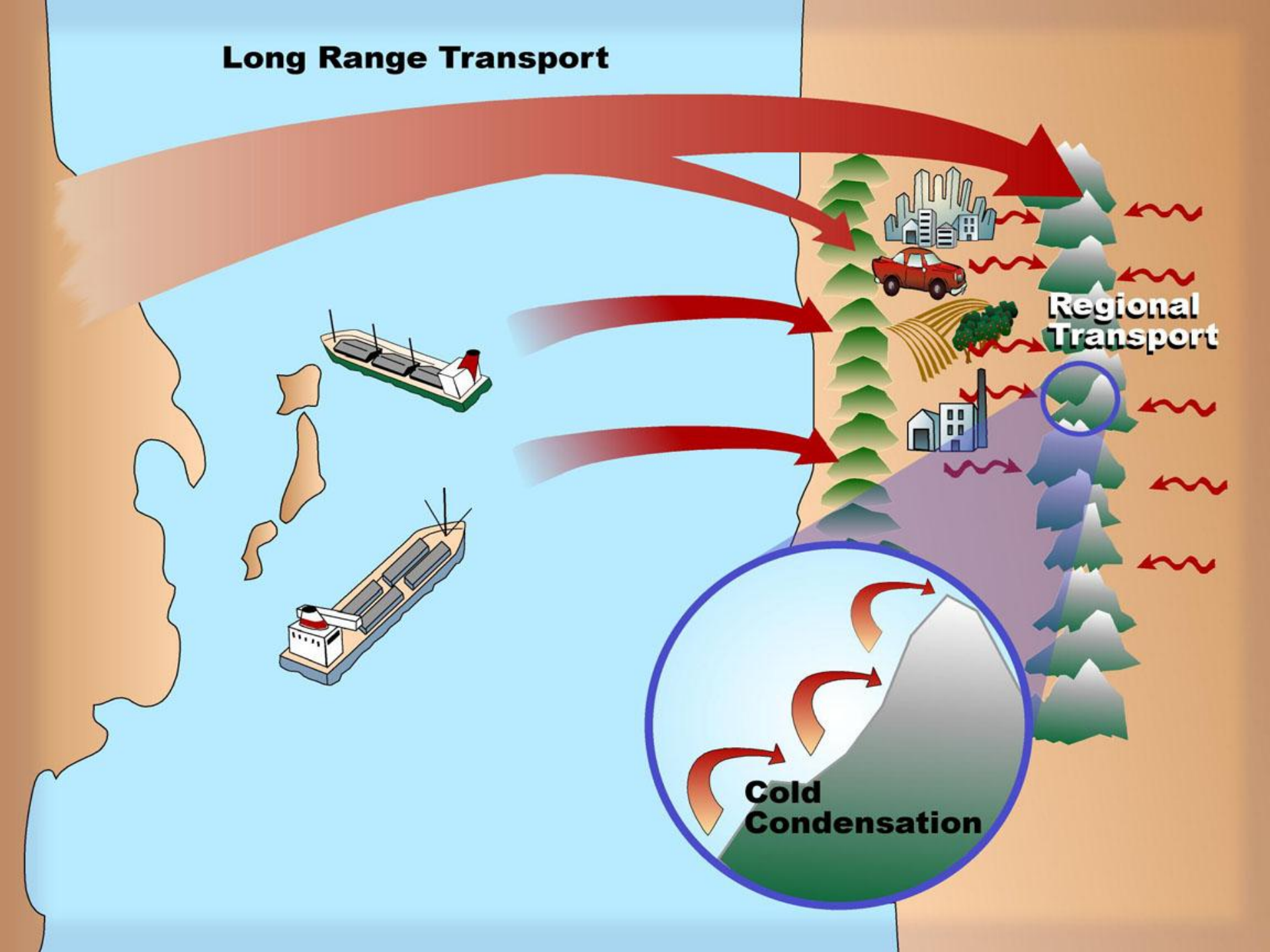



NO2
NO2
NO2
O
NO2

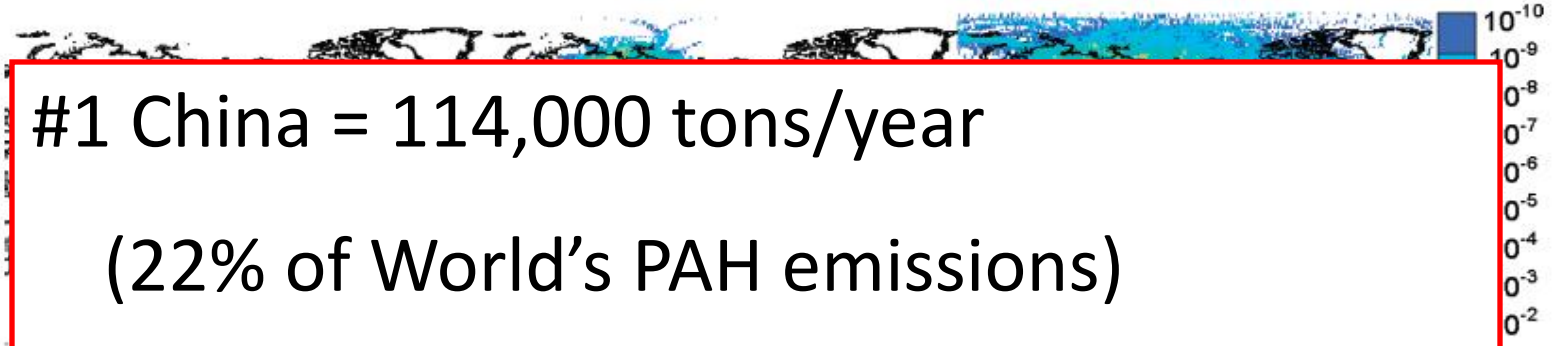

HO
OH


OH
OH

NO2
NO2
NO2
O
NO2
HO
OH
OH
OH


Long Range Transport
Regional Transport
Cold Condensation

PAH Emissions and Outflow from China



#1 China = 114,000 tons/year

(22% of World's PAH emissions)

#2 India = 90,000 tons/year

#3 U.S. = 32,000 tons/year

Lung cancer is 4th and 5th leading cause of death in Chinese men and women

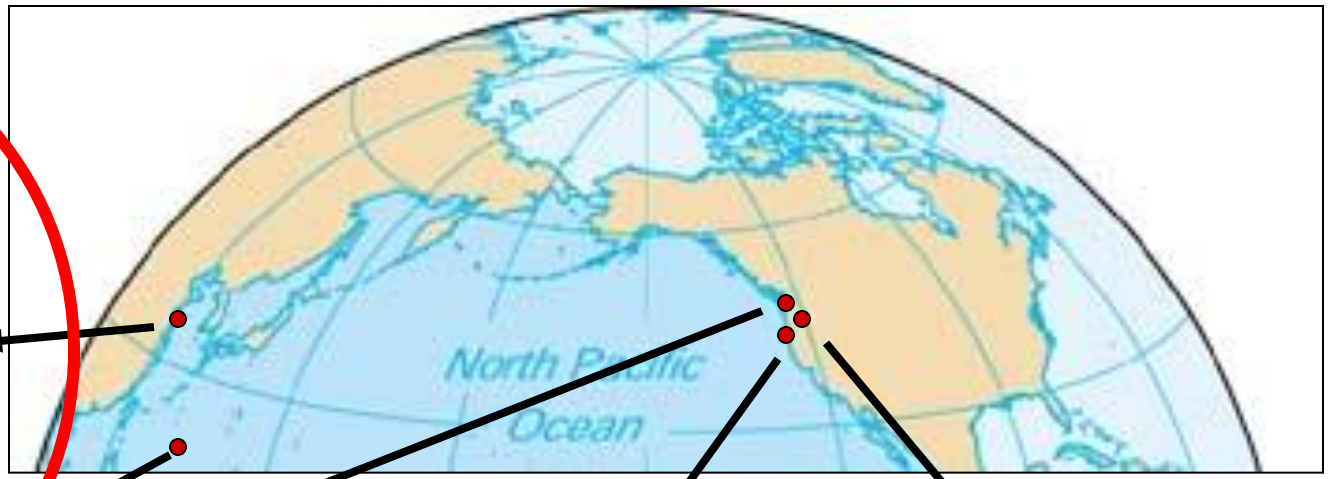
PAH emissions are increasing in developing countries

Lang, Tao, and Simonich et al, *Environ. Sci. Technol.* **2008**, 5196-5201

A New Look at ‘Old’ PAHs……

20	Parent PAH
10	Methyl-PAH
22	High Molecular Weight PAH (MW≥302)
27	Nitro-PAH
19	Oxy-PAH
34	Hydroxy-PAH
15	Chlorinated PAH
11	Brominated PAH

Simonich Lab Air Monitoring Sites

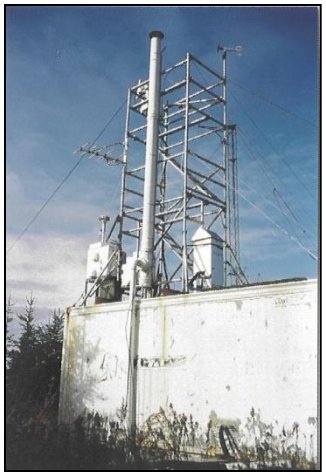


Beijing, China
45 m

Summer 2008

Okinawa, Japan
60 m

Cheeka Peak Observatory
Tip of Olympic Peninsula
500 m



Marys Peak
Oregon Coast Range
1250 m

Mt. Bachelor
Oregon Cascade Range
2700 m

2008 Beijing Olympic Games

http://hyun0124.wordpress.com/

- Beijing Olympic Games: Aug 8-24
- Source Control Period: Jul 20 – Sept 20

Traffic restricted on alternate days under an even-odd license plate system

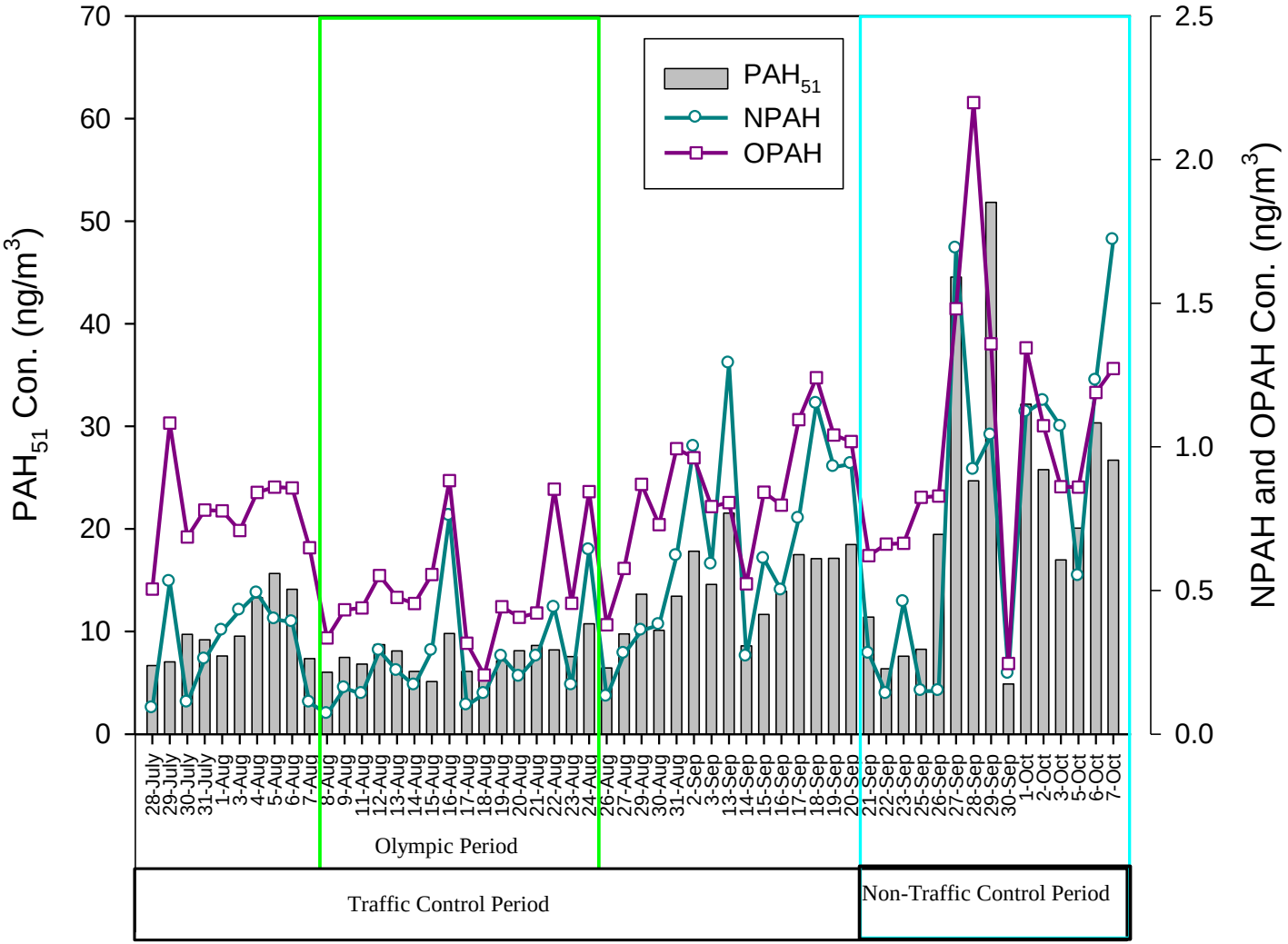
Construction sites closed

Operation of coal fired power plants strictly limited

Additional restrictions on coal-combustion

Source control measures less strictly implemented

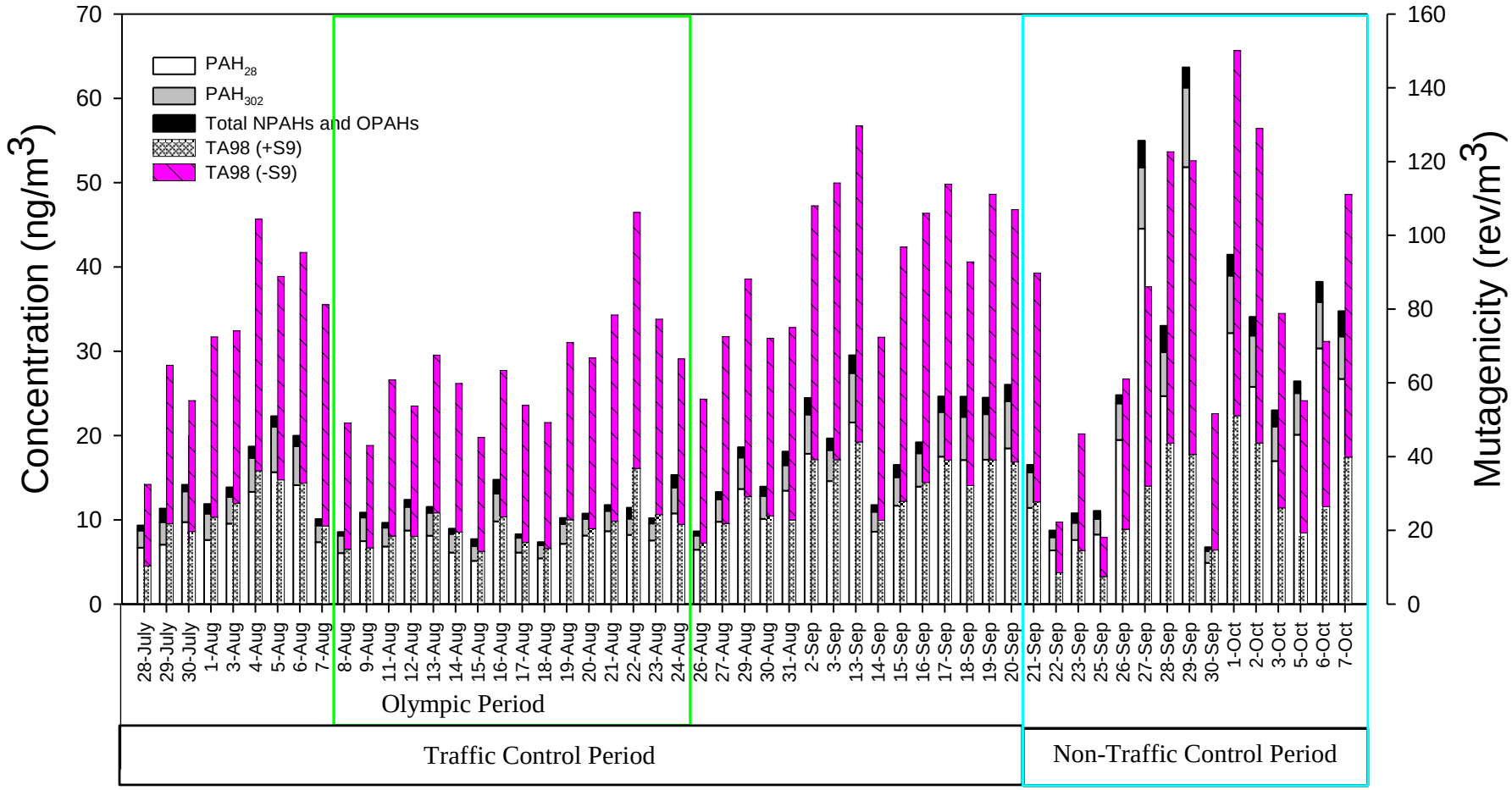
PAH Concentrations



Significant reductions in MW< 300 PAH (26% - 73%), MW 302 PAH (22% - 77%), NPAH (15% - 68%), OPAH (25% - 53%) measured during the source control and Olympic periods.

Wang and Simonich et al, *Environ. Sci. Technol.*, **2011**

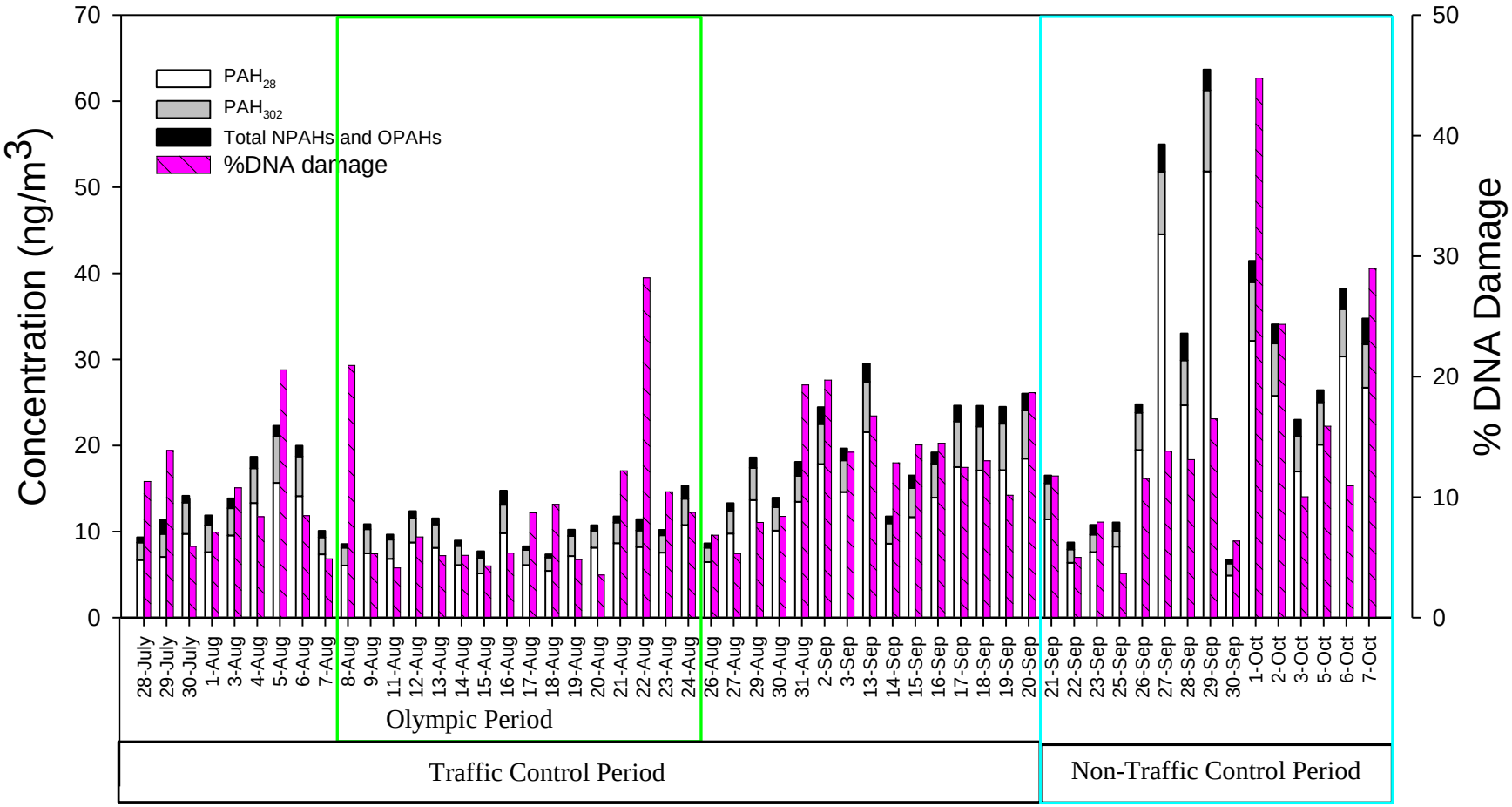
Toxicity Study - Ames Assay



ΣNPAH and ΣOPAH concentrations were 8% of the parent PAH concentrations, while the direct-acting mutagenicity was 200% higher than the indirect-acting mutagenicity.

Wang and Simonich et al, *Environ. Sci. Technol.,* **2011**

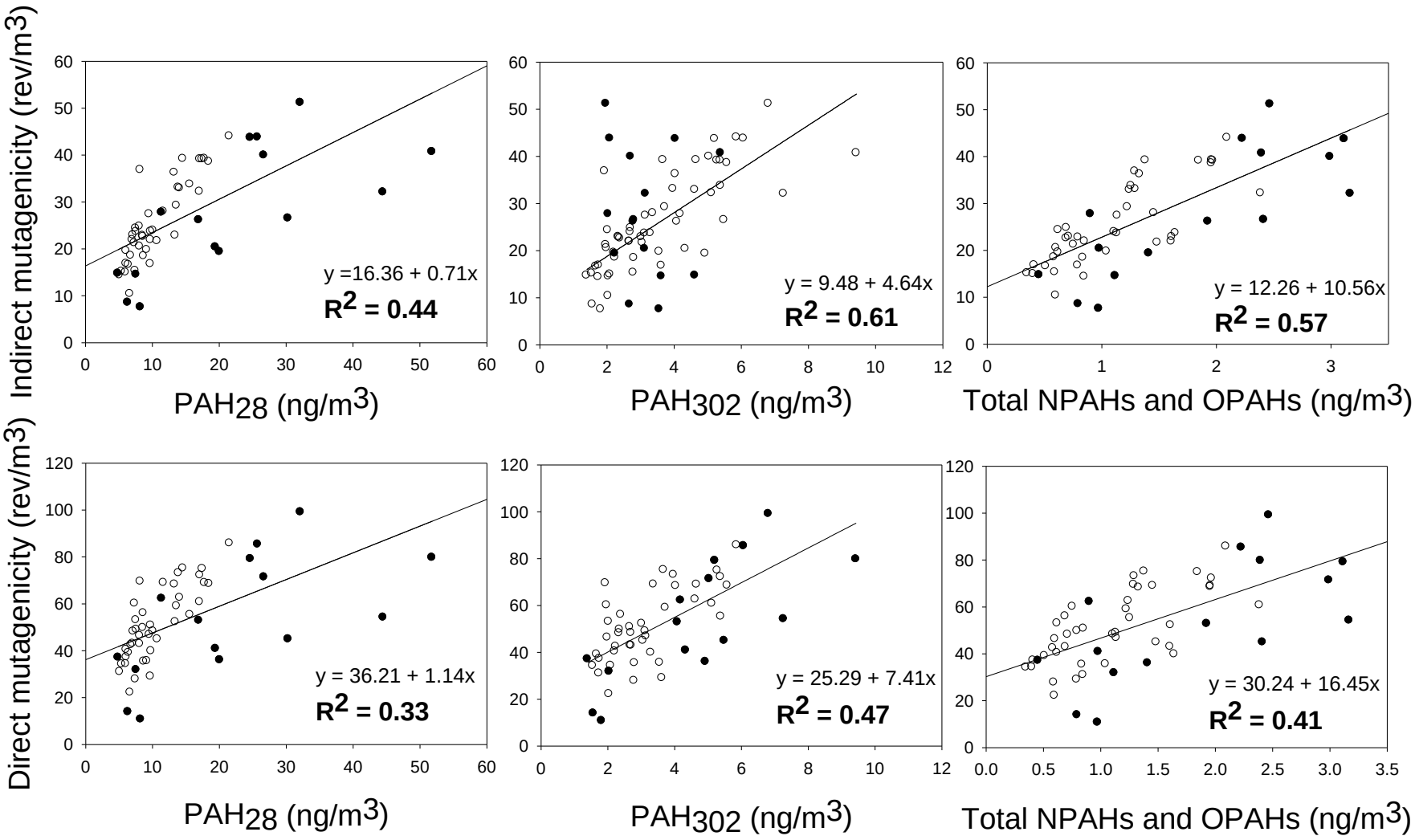
Toxicity Study - Comet Assay



The toxicity of PM and percent DNA damage were not statistically different between the source control and non-source control periods.

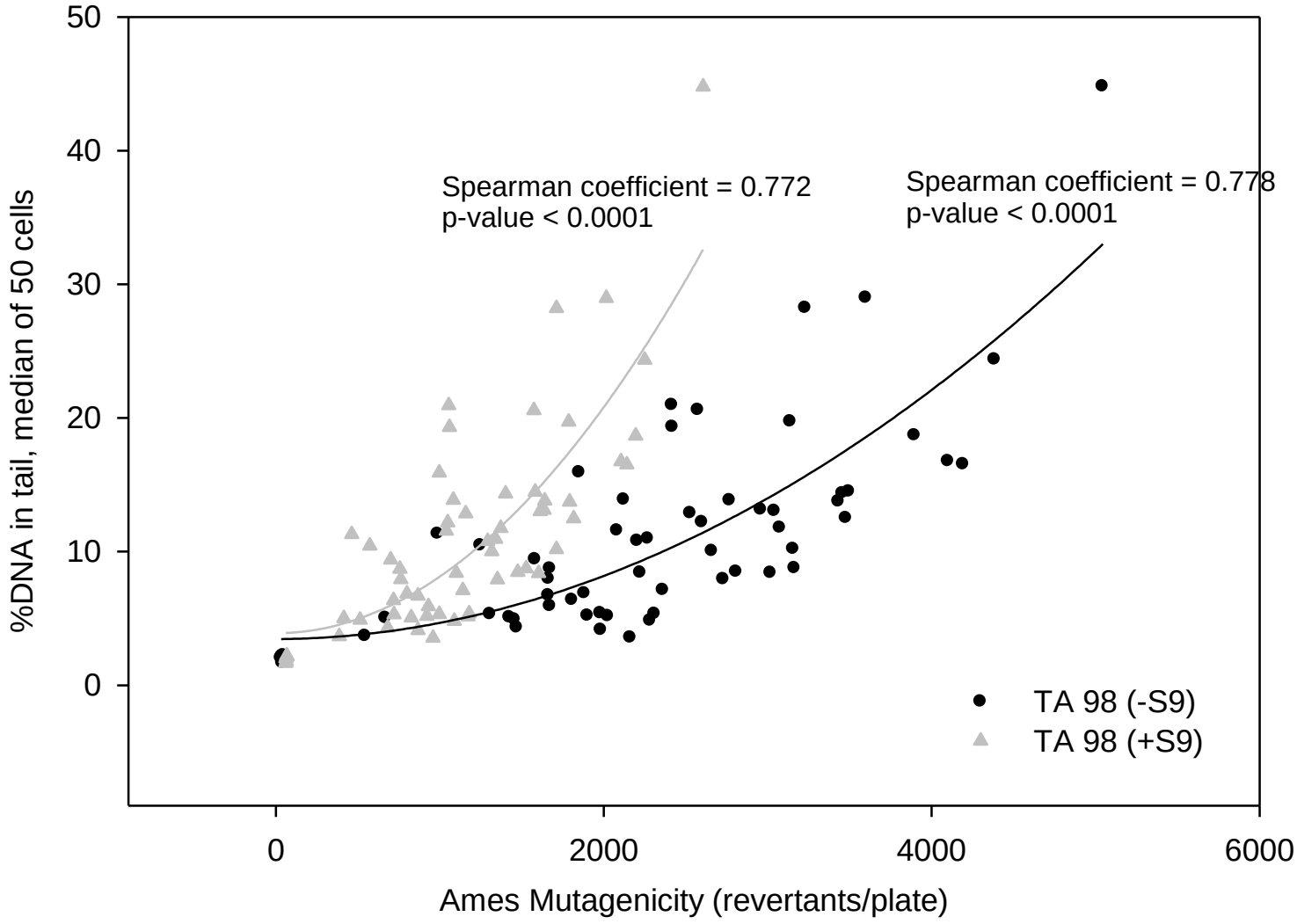
Wang and Simonich et al, *Environ. Sci. Technol.,* **2011**

Direct and Indirect Mutagenicity



Wang and Simonich et al, *Environ. Sci. Technol.,* **2011**

Comparison of Ames and Comet Assays



Wang and Simonich et al, *Environ. Sci. Technol.,* **2011**

PAH Risk Assessment – RPF Approach

- Relative Potency Factor (RPF) – ratio of the compound potency relative to the potency of an index PAH, i.e. benzo[a]pyrene (BaP);

$$CancerRisk = \sum_{i=1}^{n} \left(C_{PAH_i} \times RPF_i \right) \times UR_{BaP}$$

$BaP_{eq\text{-}i}$

- UR_{BaP} – Inhalation unit risk of BaP

  - *"the calculated, theoretical upper limit possibility of contracting cancer when exposed to BaP at a concentrations of one microgram per cubic meter of air for a 70 year lifetime" (OEHHA 1993, 2005)*

  - Based on a rodent study: 1.1×10^{-6} $(ng/m^3)^{-1}$ *(OEHHA, 2005)*

    Based on an epidemiology study: 8.7×10^{-5} $(ng/m^3)^{-1}$ *(WHO, 2000)*

Jia and Simonich et al, *Environmental Health Perspectives,* **2011**

PAH Risk Assessment – RPF Approach

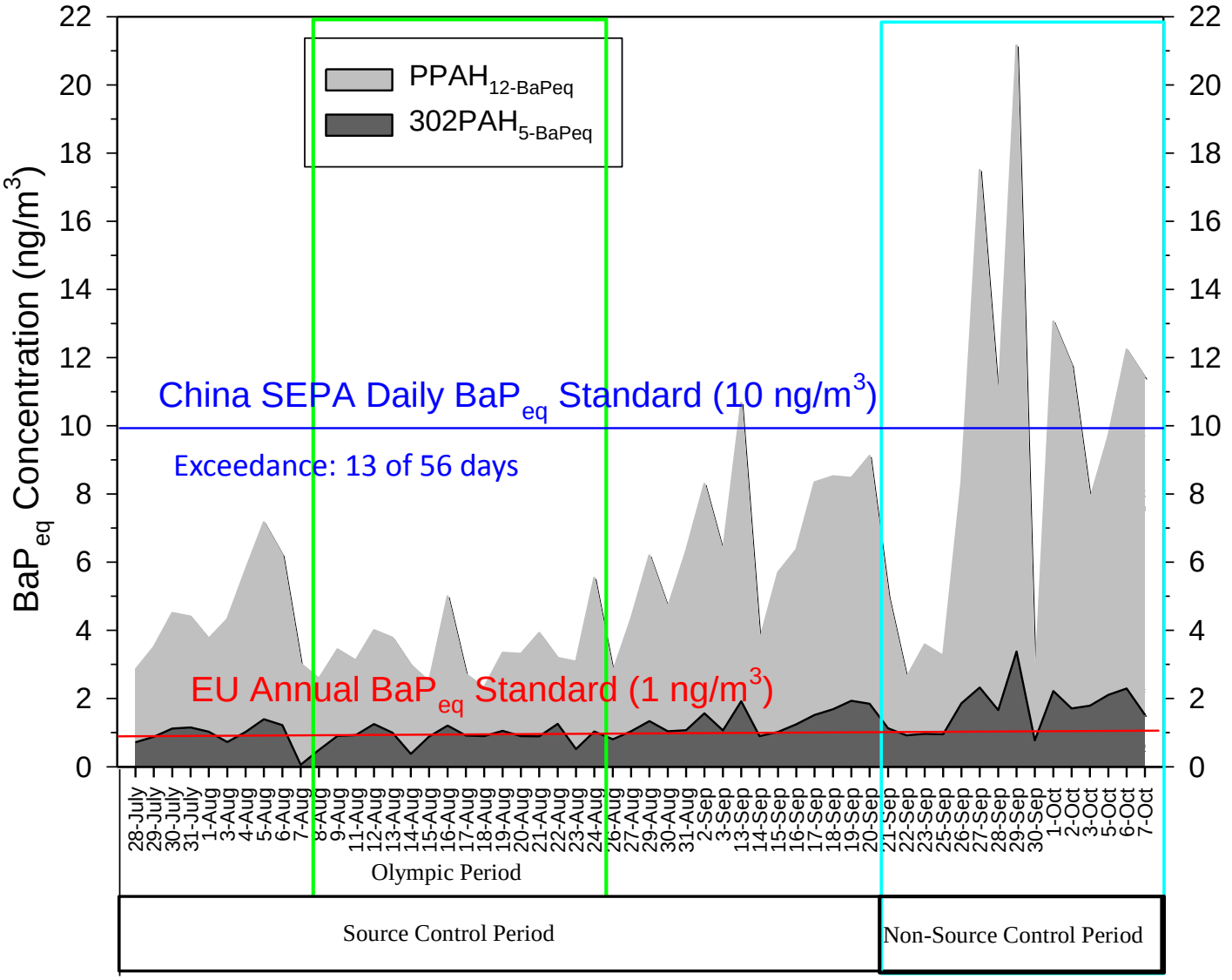
- RPFs from an EPA draft under review by the Integrated Risk Information System (IRIS) Program *(USEPA 2010)*

12 priority pollutant PAHs

5 MW 302 PAHs

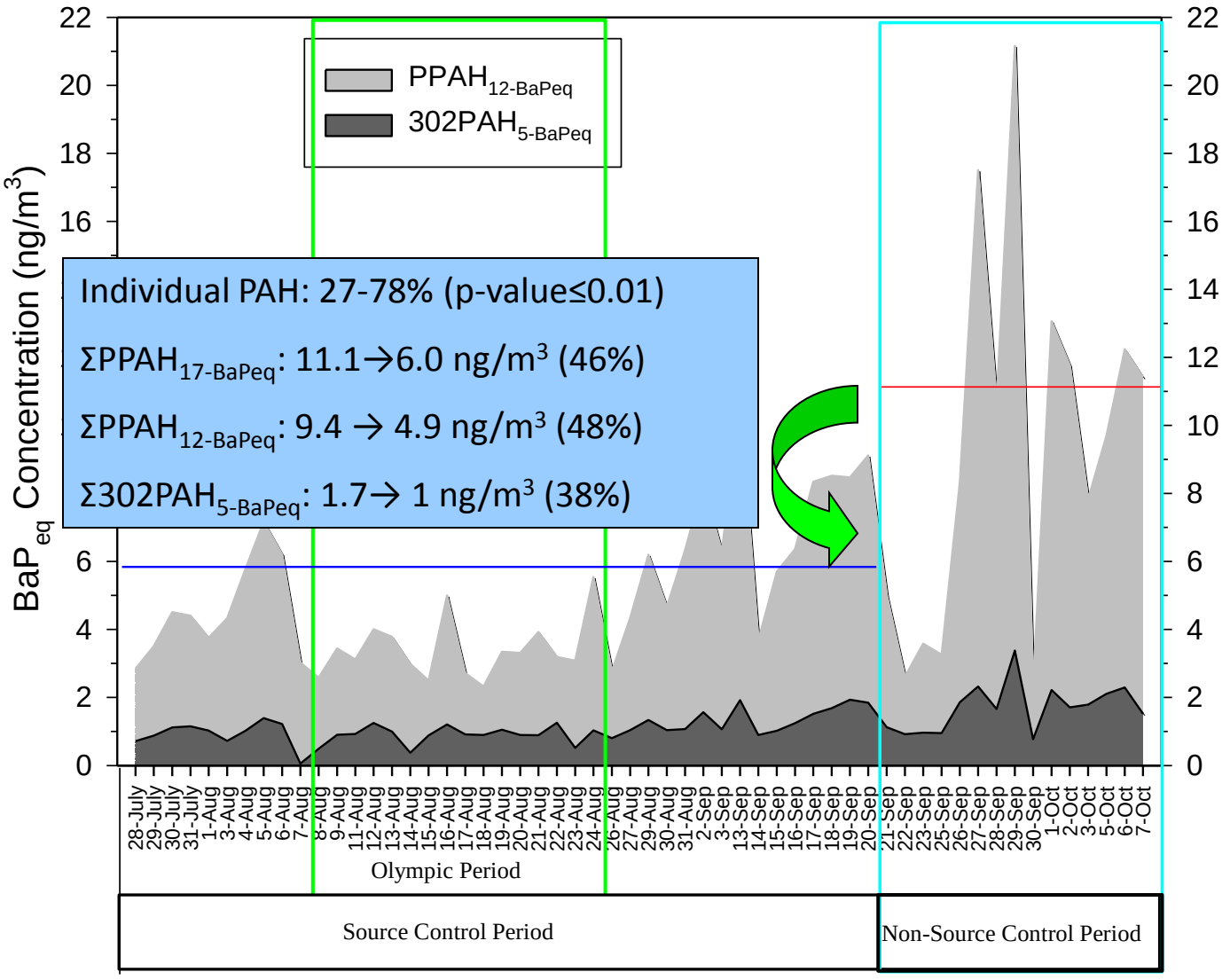
PAH	Abbreviation	RPF
Anthracene	ANT	0
Benz[a]anthracene	BaA	0.2
Benzo[b]fluoranthene	BbF	0.8
Benzo[g,h,i]perylene	BghiP	0.009
Benzo[k]fluoranthene	BkF	0.03
Chrysene	CHR	0.1
Dibenz[a,h]anthracene	DahA	10
Fluoranthene	FLA	0.08
Indeno[1,2,3-cd]pryene	IcdP	0.07
Phenanthrene	PHE	0
Pyrene	PYR	0
Benzo[a]pyrene	BaP	1
Dibenzo[a,l]pyrene	DBalP	30
Naphtho[2,3-e]pyrene	N23eP	0.3
Dibenzo[a,e]pyrene	DBaeP	0.4
Dibenzo[a,i]pyrene	DBaiP	0.6
Dibenzo[a,h]pyrene	DBahP	0.9

BaP_{eq} Concentration During the Olympics



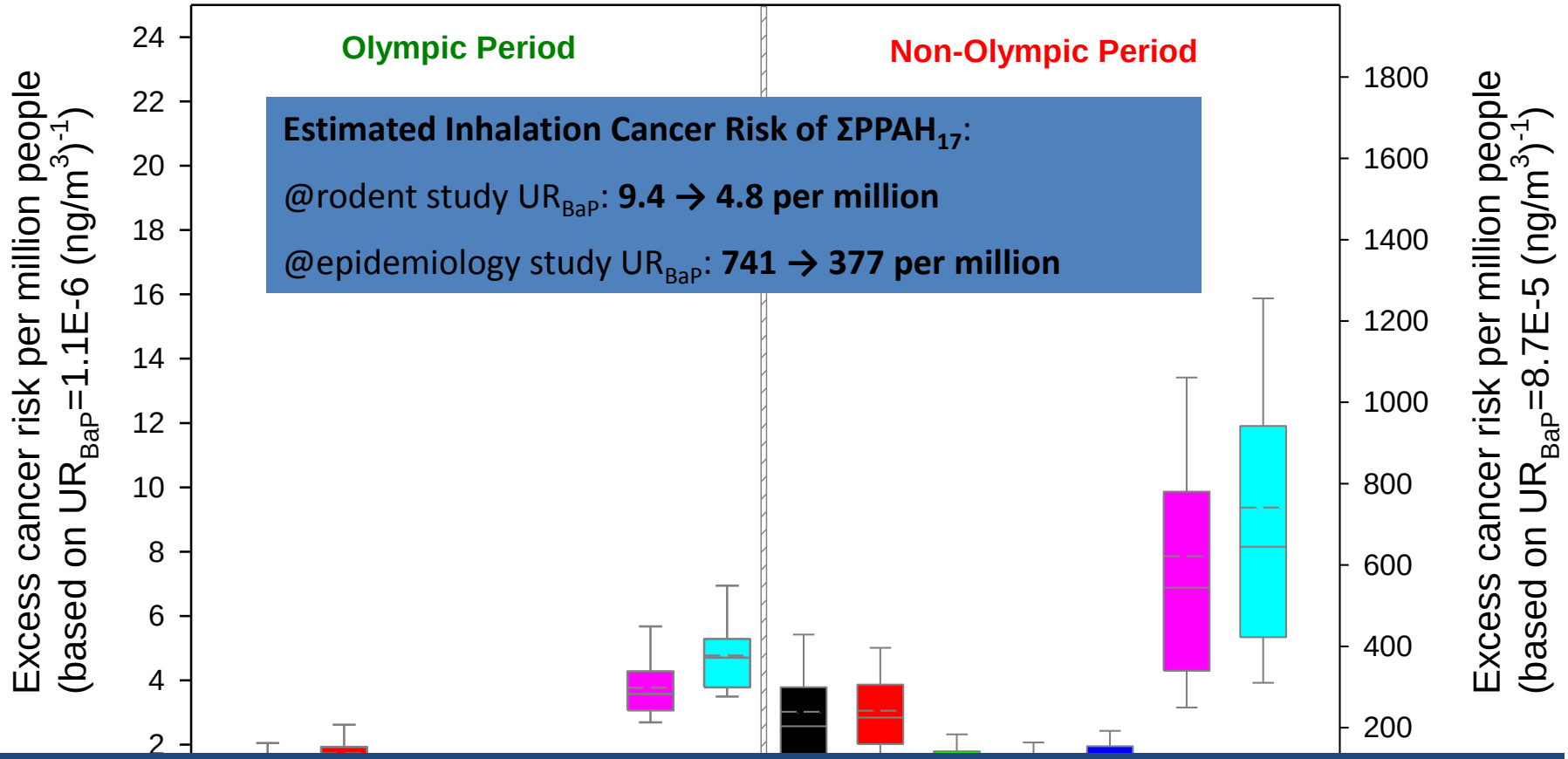
Jia and Simonich et al, *Environmental Health Perspectives,* **2011**

BaP_{eq} Concentration Reduction



Jia and Simonich et al, *Environmental Health Perspectives,* **2011**

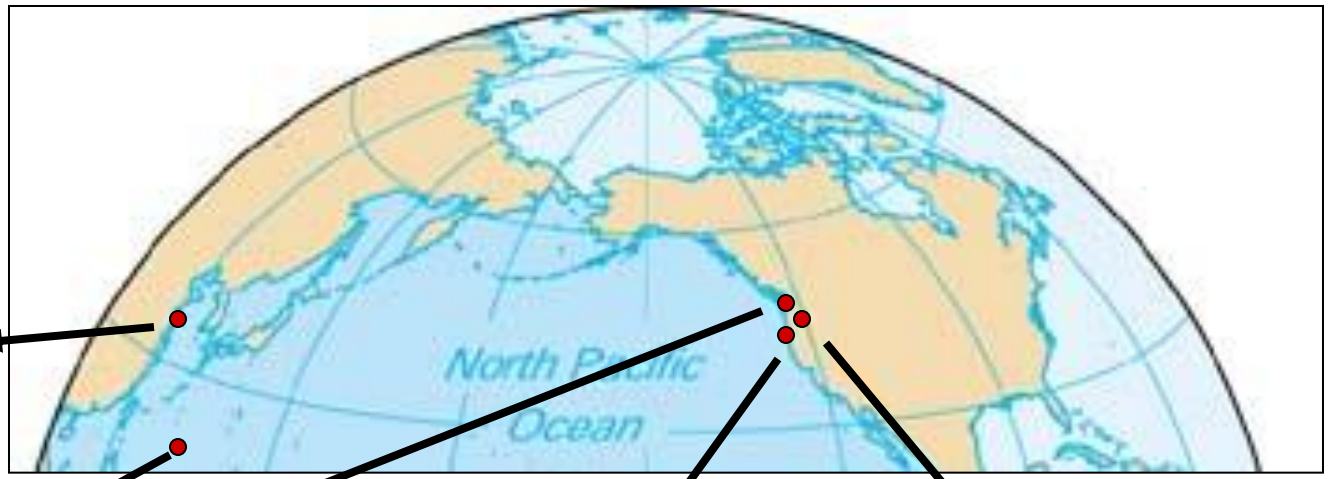
Cancer Risk Assessment



Estimated cancer risk is 46% lower due to source control measures if they were sustained over time.

The total excess cancer risk would be underestimated by 23% if the 5 MW 302 PAHs were not included in the estimate

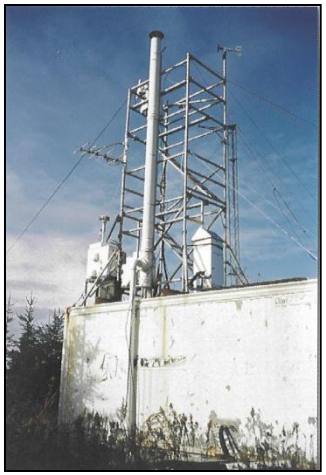
Simonich Lab Air Monitoring Sites



Beijing, China
45 m

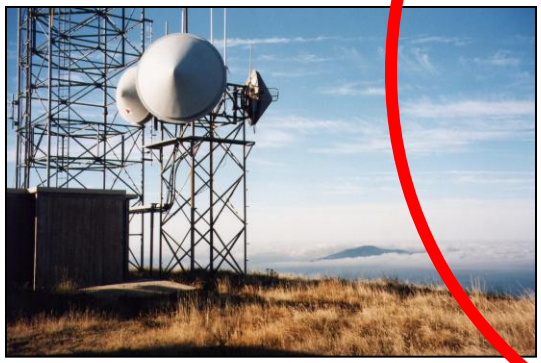
2004-2006

Cheeka Peak Observatory
Tip of Olympic Peninsula
500 m



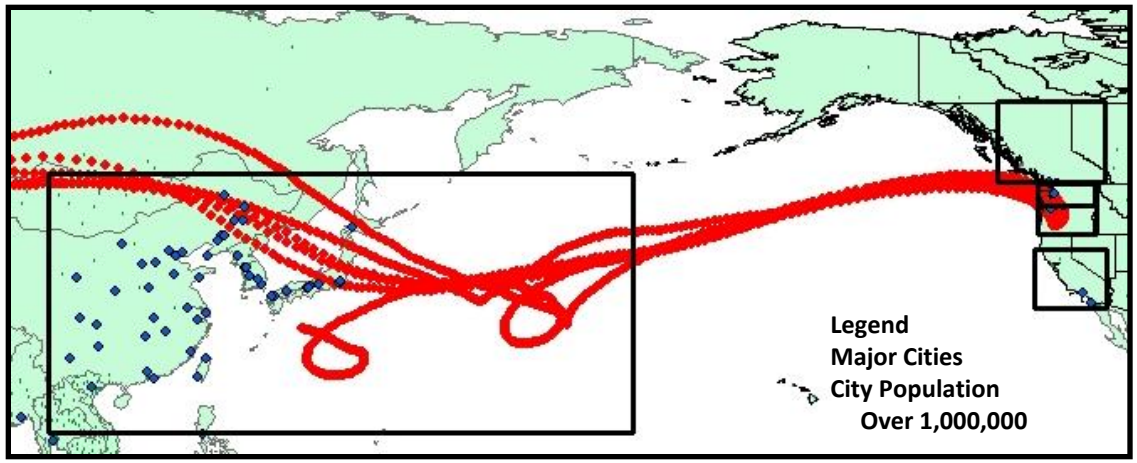
Okinawa, Japan
60 m

Marys Peak
Oregon Coast Range
1250 m

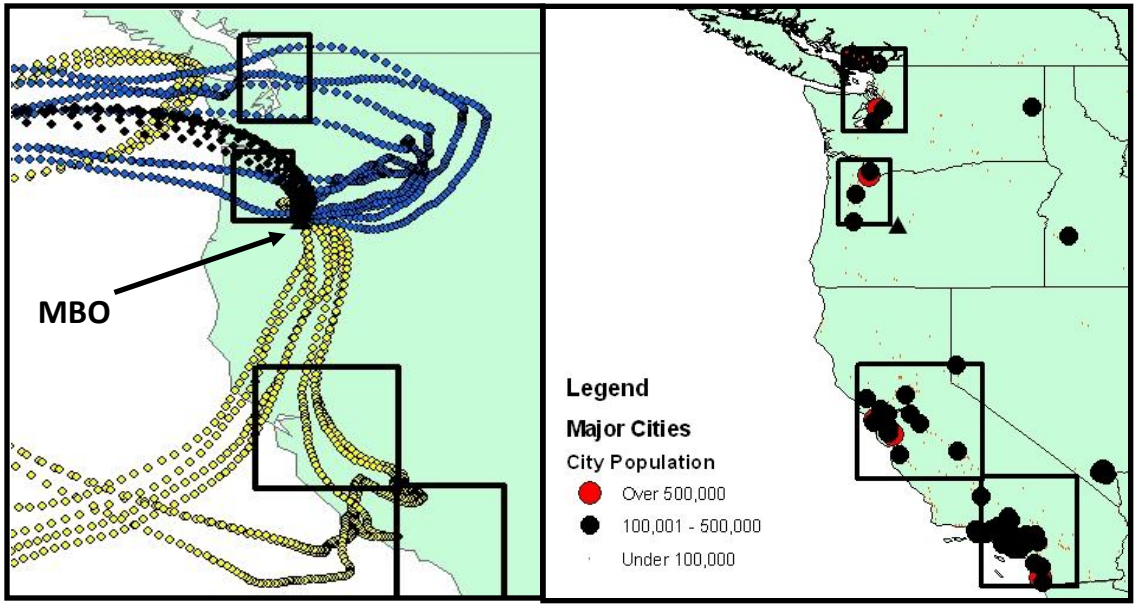


Mt. Bachelor
Oregon Cascade Range
2700 m

Mt. Bachelor Source Regions



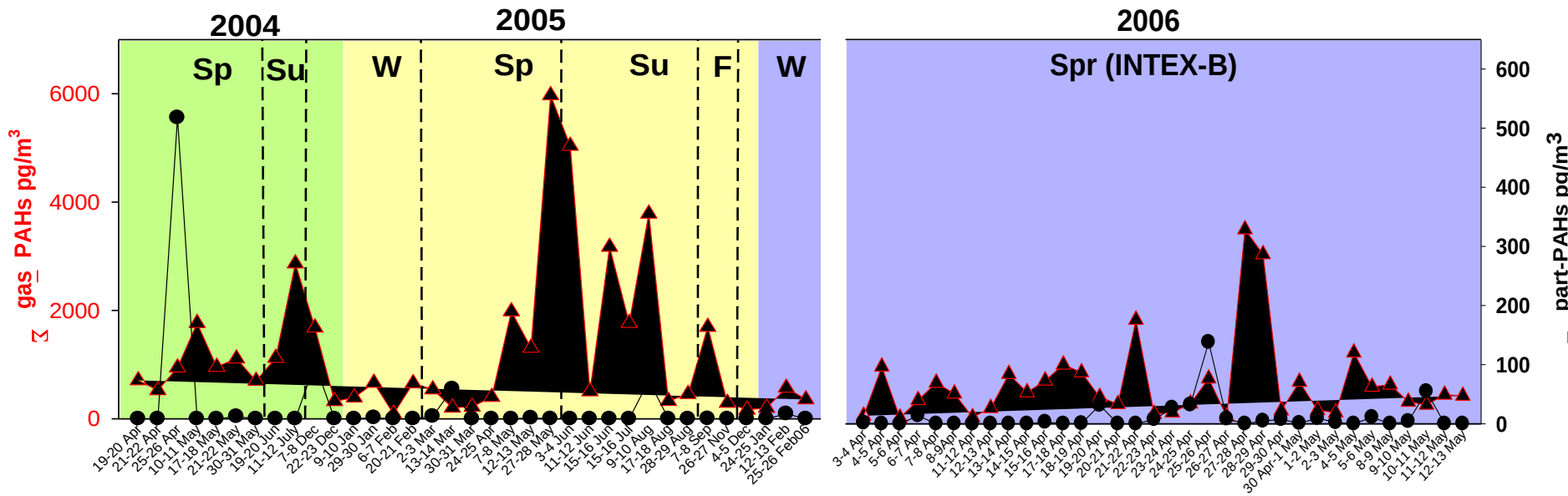
Asian and North American Source Regions



Western U.S. Urban Source Regions

Primbs and Simonich et al, *Environ. Sci. Technol.* **2008**, 6385-6391.

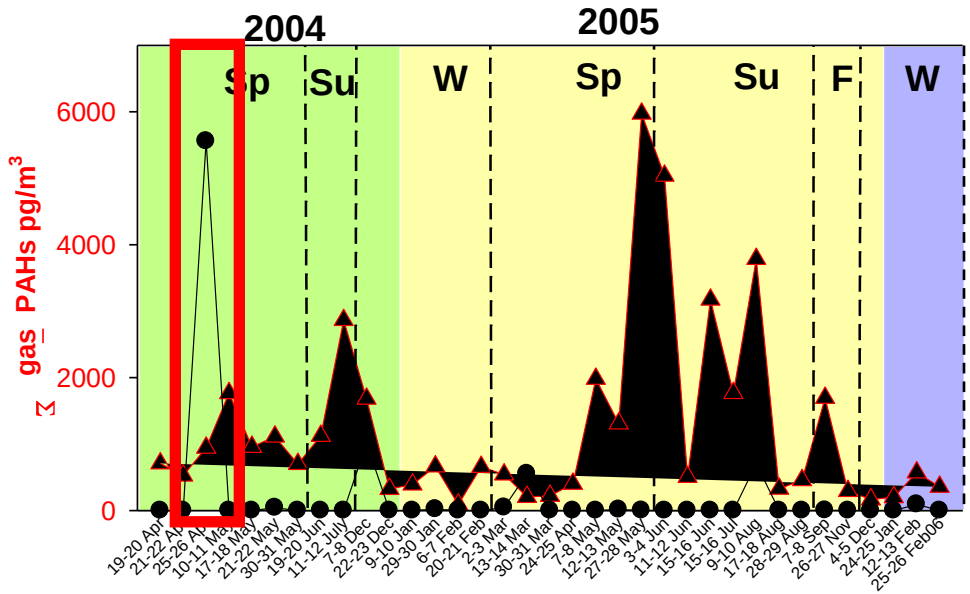
Gas and Particle Phase PAHs

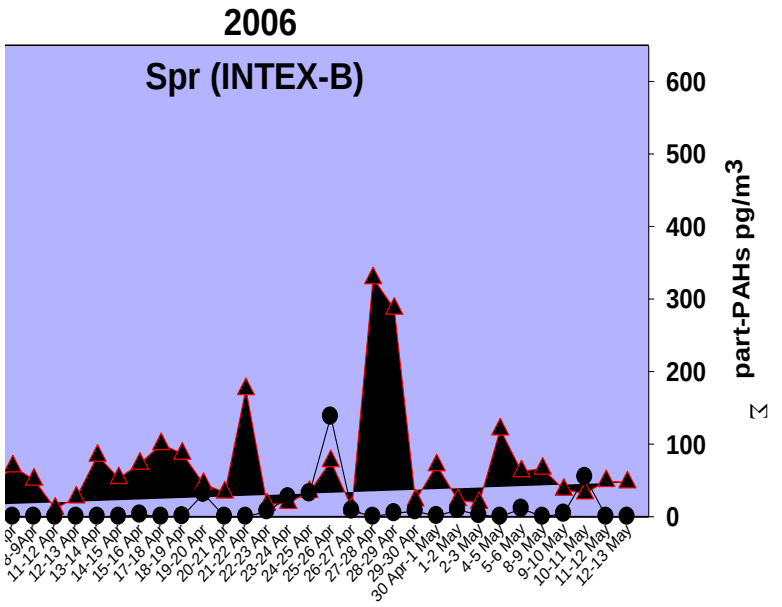


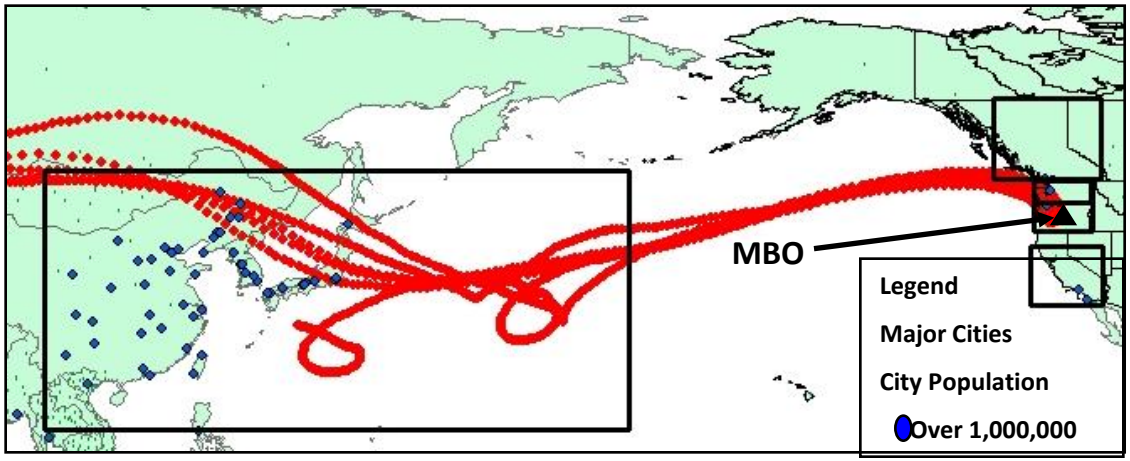
- Gas phase PAHs <u>not correlated</u> with particle phase PAH concentrations
- Gas phase PAHs <u>positively correlated</u> with Fluorotelomer Alcohol (FTOH), PCB, retene, and levoglucosan concentrations ($p<0.05$)
- Particle phase PAHs <u>not correlated</u> with FTOH, PCB, retene or levoglucosan concentrations ($p<0.05$)
- Anthracene <u>positively correlated</u> with other gas phase PAH and FTOH concentrations ($p<0.05$)

Primbs and Simonich et al, *Environ. Sci. Technol.* **2008**, 6385-6391.

Trans-Pacific Transport of Particulate Phase PAHs





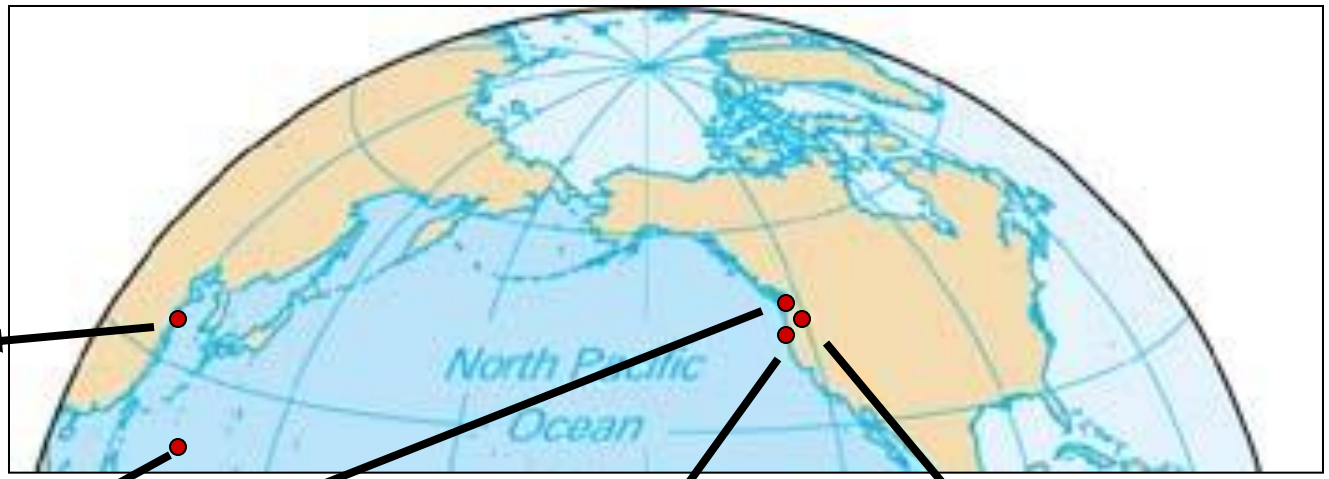


April 25-26, 2004

Primbs and Simonich et al, *Environ. Sci. Technol.* **2008**, 6385-6391.

Simonich Lab Air Monitoring Sites

Beijing, China
45 m



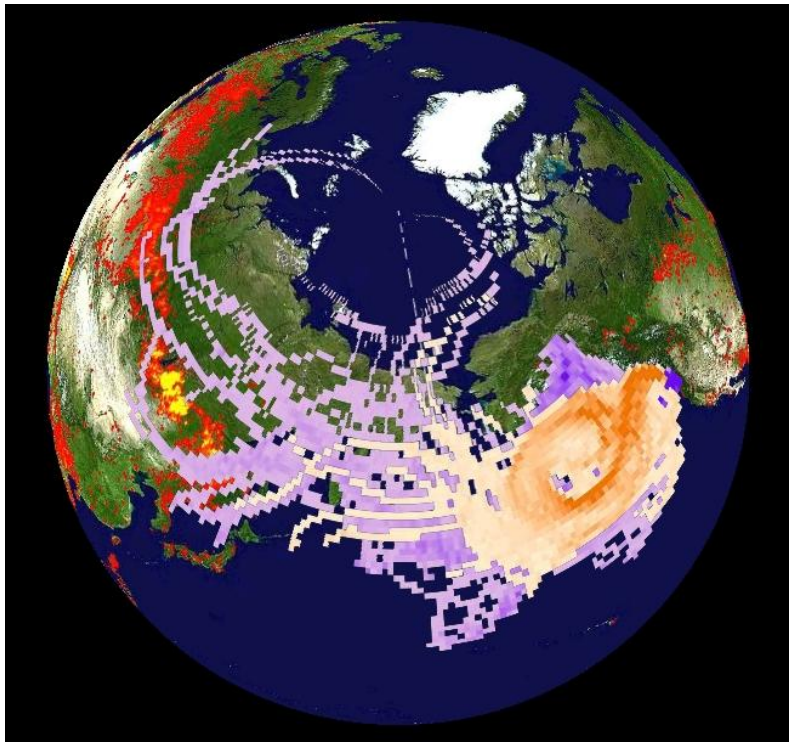
Cheeka Peak Observatory
Tip of Olympic Peninsula
500 m

Okinawa, Japan
60 m

Marys Peak
Oregon Coast Range
1250 m

Mt. Bachelor
Oregon Cascade Range
2700 m

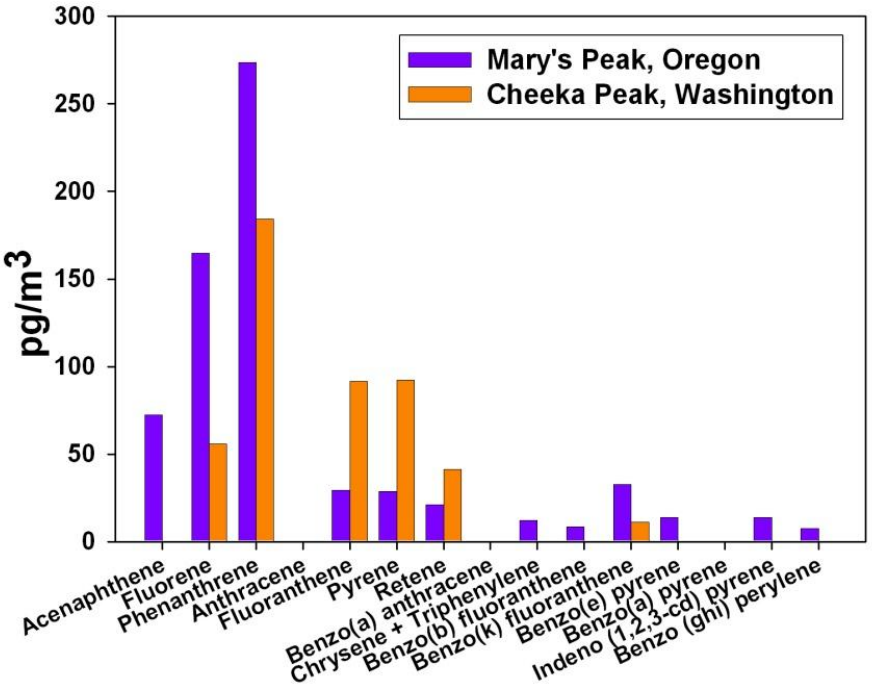
PAH Emissions from Siberian Fires



June 2, 2003

10-day Air Mass Back Trajectories

Marys Peak and Cheeka Peak

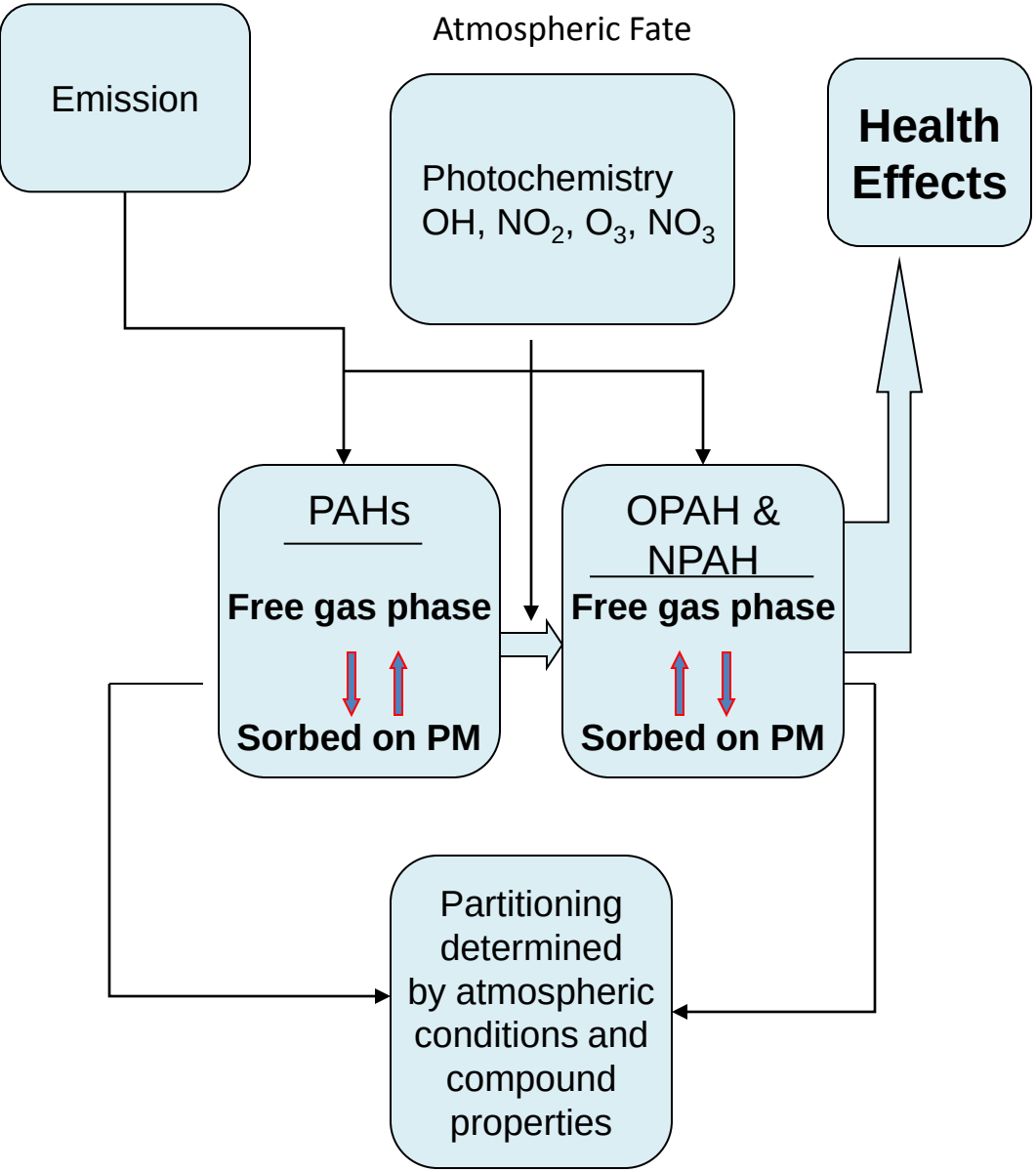


June 2, 2003

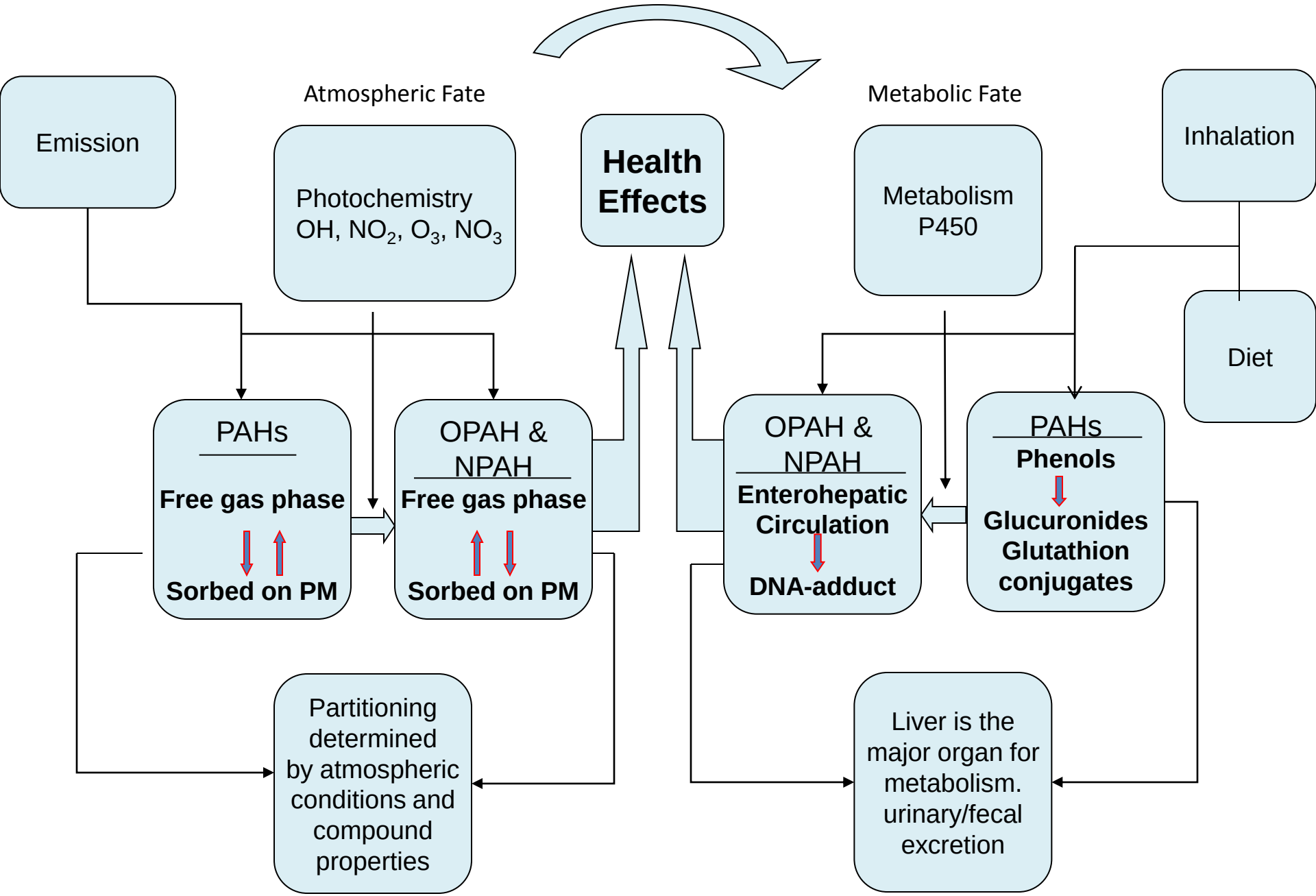
PAH Air Concentrations

Marys Peak and Cheeka Peak

Genualdi and Simonich et al, *Environ. Sci. Technol.* **2009**, 1061-1066

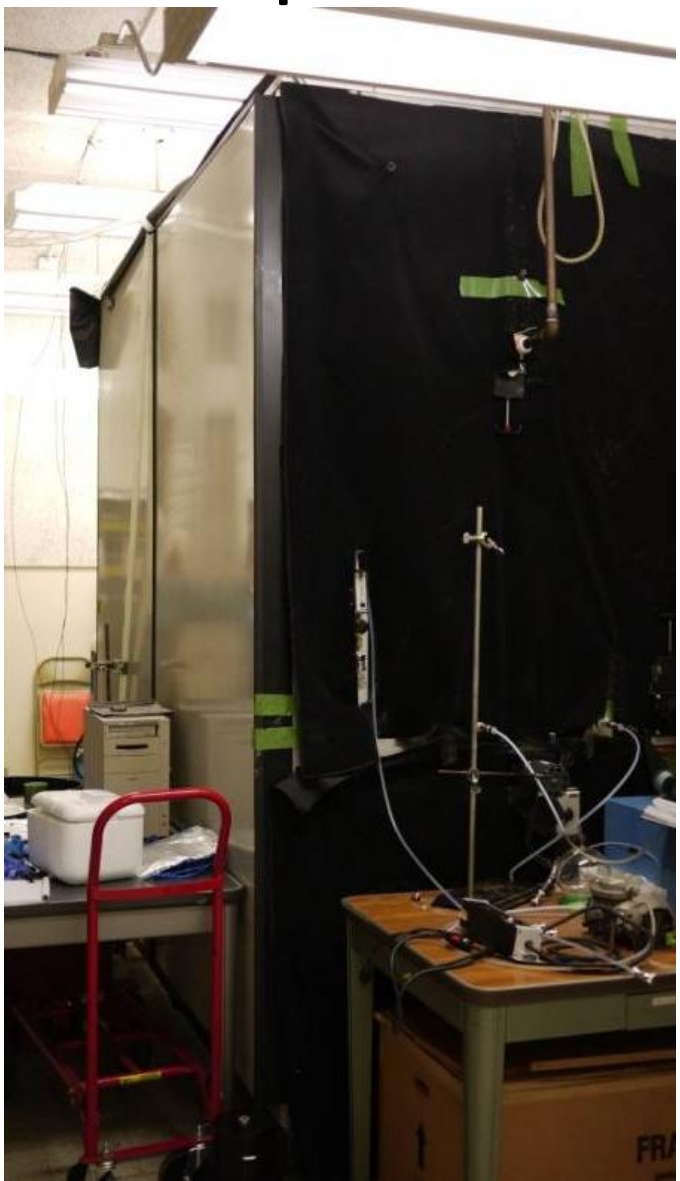


Simonich et al, *Chemico-Biological Interactions*, **2010**



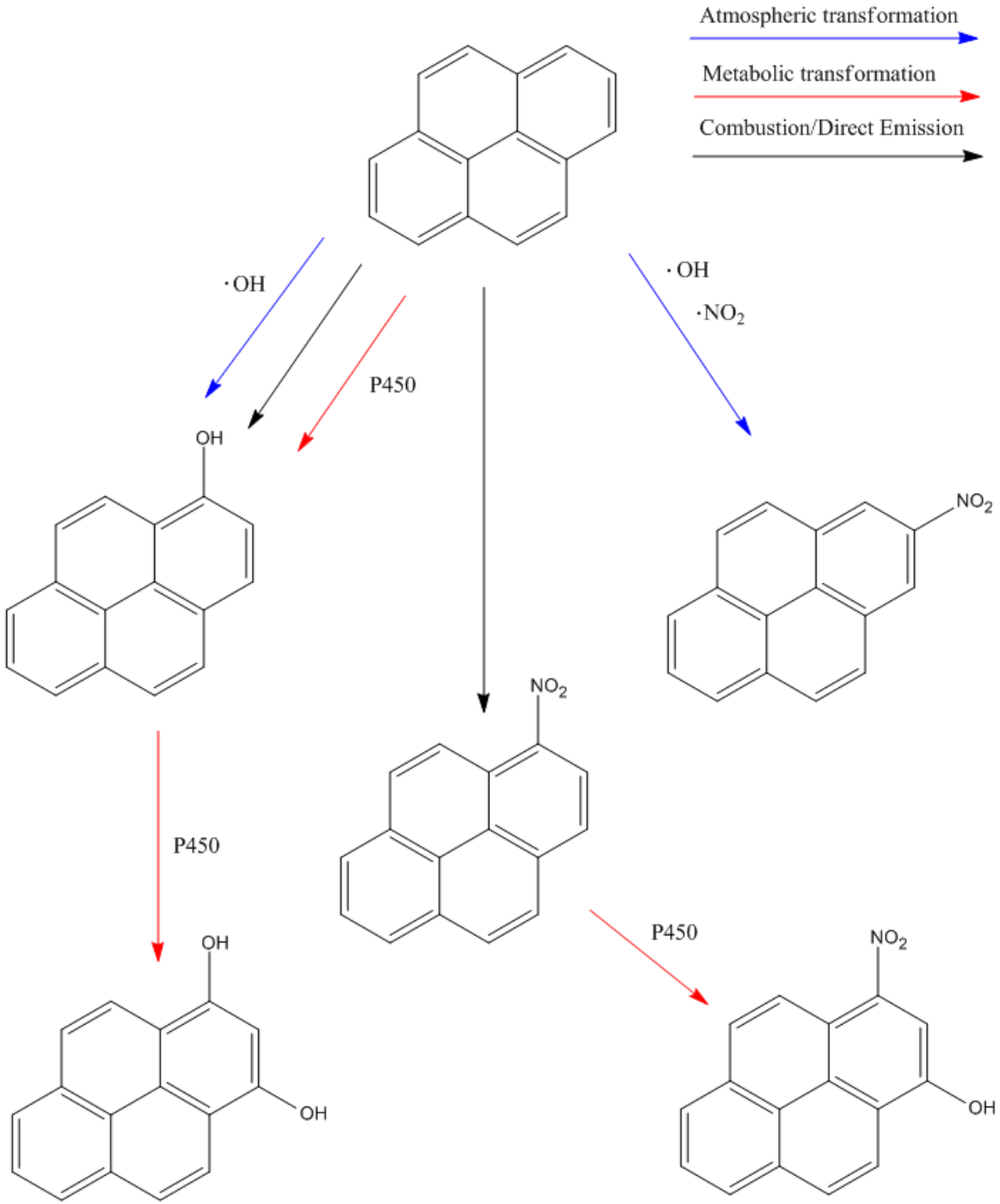
Simonich et al, *Chemico-Biological Interactions*, **2010**

Simulating Photochemical Transformation During Trans-Pacific Transport



Personal PAH Exposure - China

Personal PAH Exposure - CTUIR



Simonich et al, *Chemico-Biological Interactions*, **2010**

Sodium acetate buffer 5 mL

Spike Labeled Standards

Enzymatic hydrolysis of PAH urinary glucoronides

β-glucuronidase/ arylsulfatase

17-18 hr incubation, 37º C

SPE Plexa and/or C18

eluted w/different solvent

Split sample 50:50

Evaporate to dryness

60 µL Hexane

10 µL IS mixture

1-[^{2}D]hydroxynaphthalene	Fluorene-d10
2-[^{2}D]hydroxyfluorene	Phenanthrene-d10
3-[^{13}C]hydroxybenzo(c)phenanthrene	Pyrene-d10
1-[^{13}C]hydroxypyrene	Triphenylene-d12
1-[^{13}C]hydroxybenzo(a)anthracene	Benzo(a)pyrene-d12
3-[^{13}C]hydroxybenzo(a)fluoranthene	Benzo(ghi)perylene-d12
3-[^{13}C]hydroxyphenanthrene	
3-[^{13}C]hydroxychrysene	

BSA

30 µL for 1,2 OH-Nap determination

Derivatizing agents

75ºC overnight

Evaporate to ~20µL

40 µL

Concentrated, reconstituted to 300 µl of ethyl acetate

100 µL ACN
20 µL Toluene
10 µL IS mixture

Evaporate to ~20µL

MTBSTFA
30 µL for
33 OH-PAH
determination

65ºC, 25 min

GC/MS

Eluted w/DCM 100mL

Silica

ASE Solvents

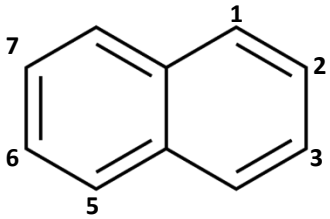
Spike Labeled Standards

Atmospheric Particulate matter

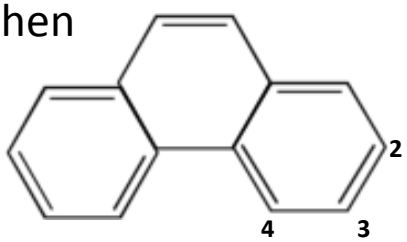
1. Journal of Chromatography B. 835: 47-54.
2. Talanta (2008), doi:10.1016/j.talanta.2008.09.043

OH-PAHs Measured

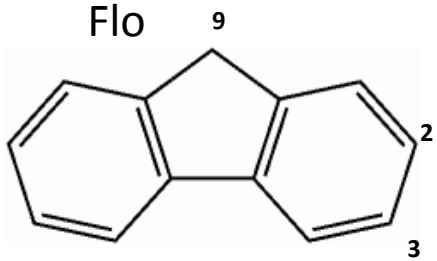
Nap



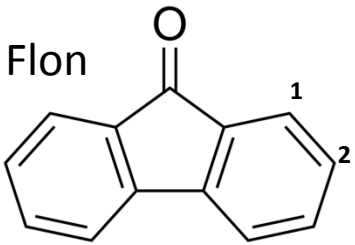
Phen

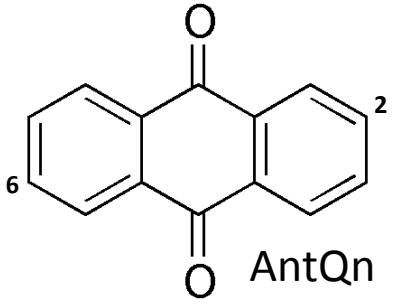


Flo

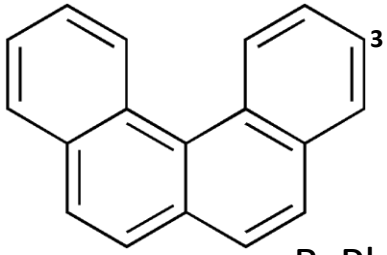


Flon



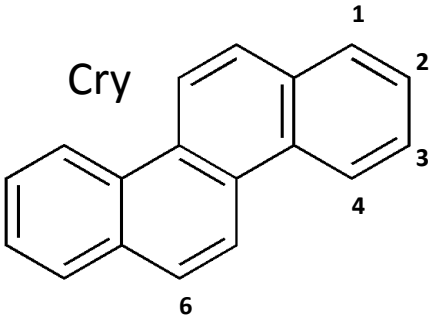


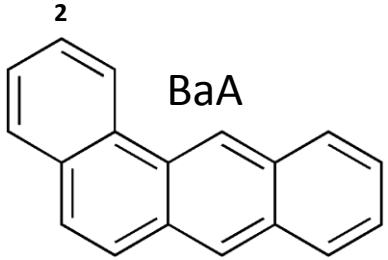
AntQn



BcPhen

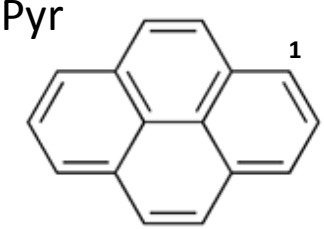
Cry



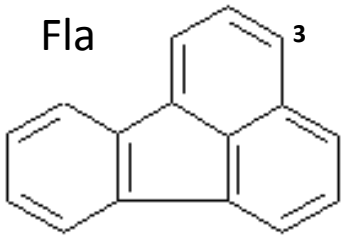


BaA

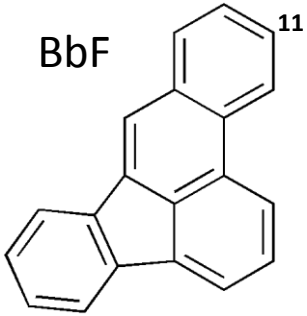
Pyr



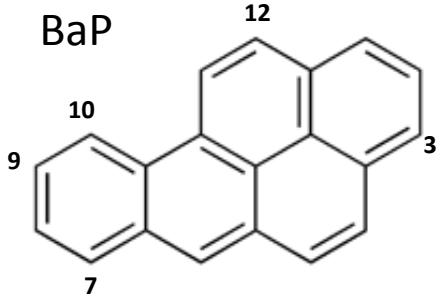
Fla



BbF

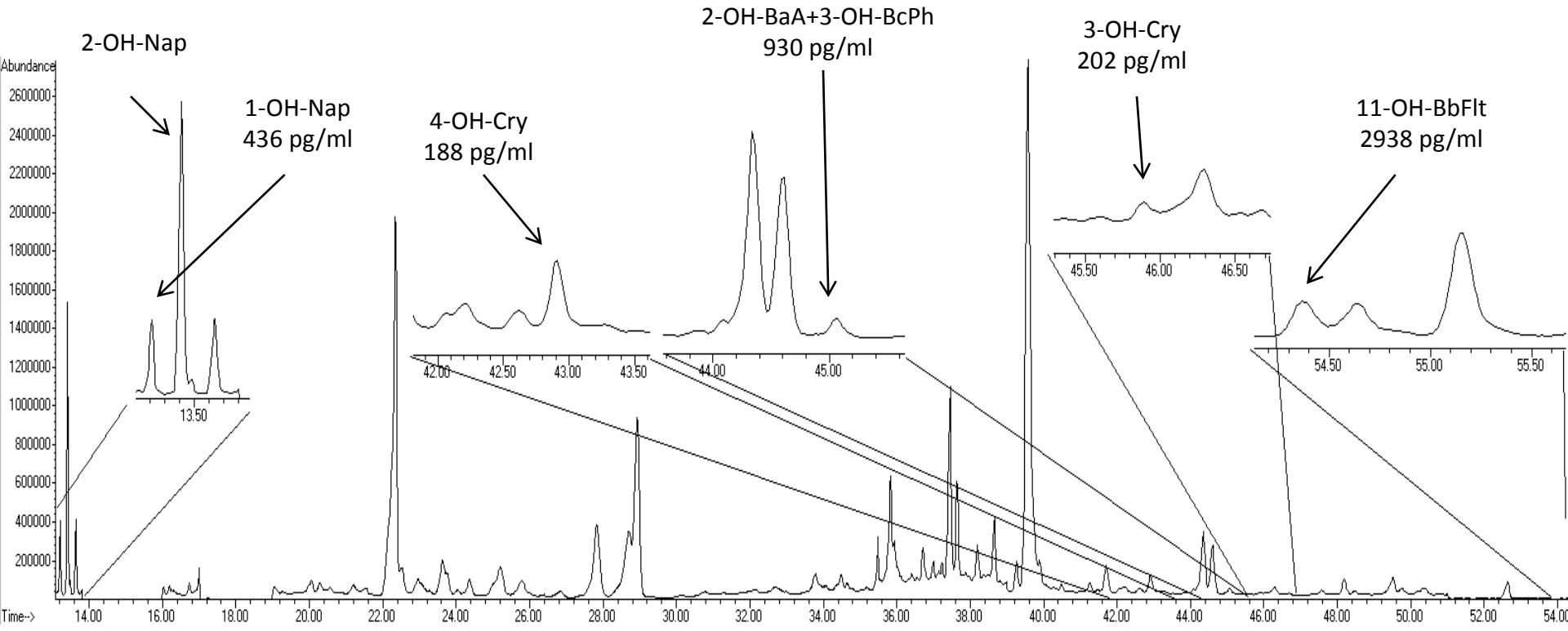


BaP



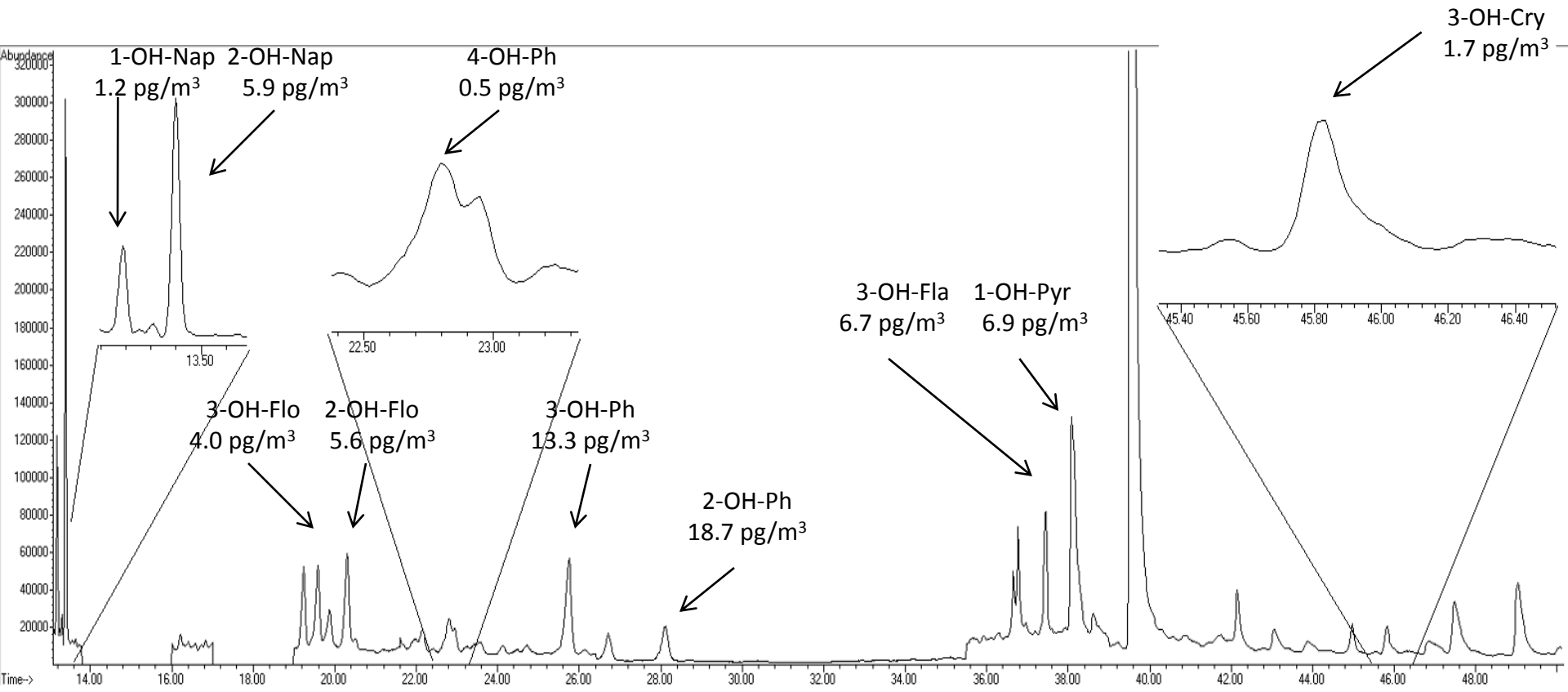
1-OH-Nap	3-OH-Fla
2-OH-Nap	2-OH-AntQn
1,3-OH-Nap	2,6-OH-AntQn
1,5-OH-Nap	1-OH-Cry
1,6-OH-Nap	2-OH-Cry
1,7-OH-Nap	3-OH-Cry
2,6-OH-Nap	4-OH-Cry
2,7-OH-Nap	6-OH-Cry
2-OH-Flo	3-OH-BcPhen
3-OH-Flo	2-OH-BaA
9-OH-Flo	3-OH-BaP
2-OH-Phen	7-OH-BaP
3-OH-Phen	9-OH-BaP
4-OH-Phen	10-OH-BaP
1-OH-Flon	12-OH-BaP
2-OH-Flon	11-OH-BbF
1-OH-Pyr	

OH-PAHs in Human Urine



15 of 33 OH-PAHs detected in urine sample

OH-PAHs in Beijing Particulate Matter



14 of 33 OH-PAHs detected in particulate matter sample

1- and 2-OH-Nap, 2-OH-Flo, 3-OH-Phen, 3-OH-Fla, 1-OH-Pyr, 3-OH-Cry, 2-OH-BaA, 3-OH-BcPhen were detected both in urine and PM samples

Conclusions

- Significant reduction in PAH concentration and inhalation cancer risk during Beijing Olympic source control measures
- NPAH and OPAH made up a significant portion of overall mutagenicity of $PM_{2.5}$ in Beijing
- MW 302 PAH concentrations significantly contributed to the overall inhalation cancer risk
- PAHs undergo episodic trans-Pacific atmospheric transport to the U.S. West Coast
- Experiments underway to simulate the photochemical transformation of PAHs during trans-Pacific atmospheric transport
- Personal exposure studies underway in China and Confederated Tribes of the Umatilla Indian Reservation

OSU SRP Renewal: Non-biomedical Project

"Formation of novel PAH Intermediates in Complex Environmental Mixtures and Evaluation of Human Exposure"

Predict, identify and quantify novel PAH intermediates at Superfund sites pre- and post-remediation, using computational methods, as well as laboratory and field experiments, in order to determine the importance of human exposure to these intermediates.

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