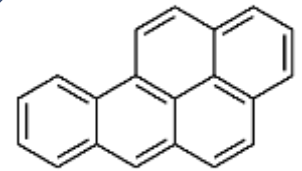


**Concentrations and gas-particle
partition of polycyclic aromatic
hydrocarbons (PAHs) in ambient air of
a medium-sized andean city**



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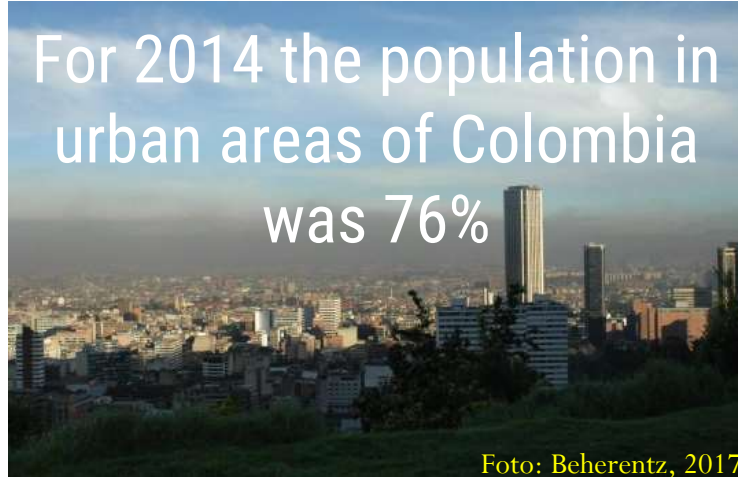


UNIVERSIDAD
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DE COLOMBIA



Small urban centers:
Rapid growth in
urbanization levels

For 2014 the population in
urban areas of Colombia
was 76%



9 out of 10 people
in the world
breathe polluted air

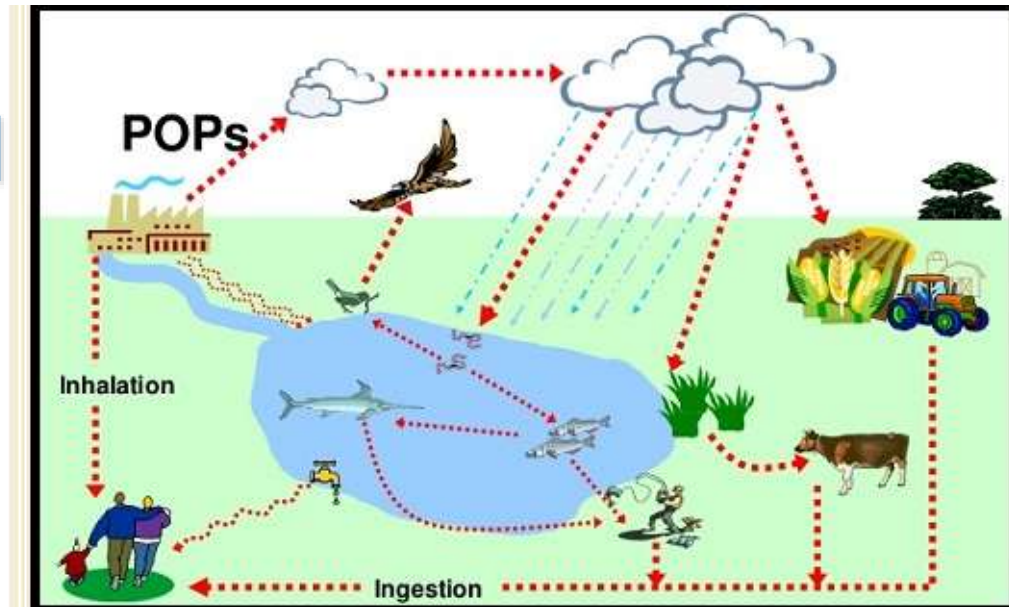
IMPORTANCE OF AIR QUALITY MONITORING

Fuente: OMS (2018)

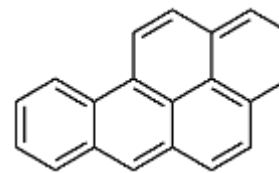
Hazardous pollutants – carcinogenic and mutagenic

Monitored in urban air, water, food and soils

Persistent Organic Pollutants



PAH compound	Abbreviation	N° of rings	Vapor pressure (Pa, 25°C)	TEF ^b
Naphthalene	Nap	2	11.14	0.001
Acenaphylene	Acy	3	3.87	0.001
Acenafteno	Ace	3	3.07	0.001
Fluorene	Flu	3	1.66	0.001
Phenanthrene	Phe	3	1.06E-01	0.001
Anthracene	Ant	3	8.60E-04	0.01
Fluorantrene	Flt	4	8.61E-04	0.001
Pyrene	Pyr	4	5.00E-05	0.001
Benzene(a)anthracene	BaA	4	5.43E-04	0.1
Chrysane	Chr	4	4.00E-06	0.01
benzo(b)fluorantene	BbF	5	5.00E-07	0.1
Benzo(k)fluorantene	BkF	5	5.20E-08	0.1
Benzo(a)pyrene	BaP	5	6.00E-08	1
Dibenzo(a,h)anthracene	DBahA	5	1.33E-08	1
Indene(1,2,3-cd)pyrene	IcdP	6	1.27E-07	0.01
Benzo(g,h,i)perylene	BghiP	6	1.38E-08	0.1

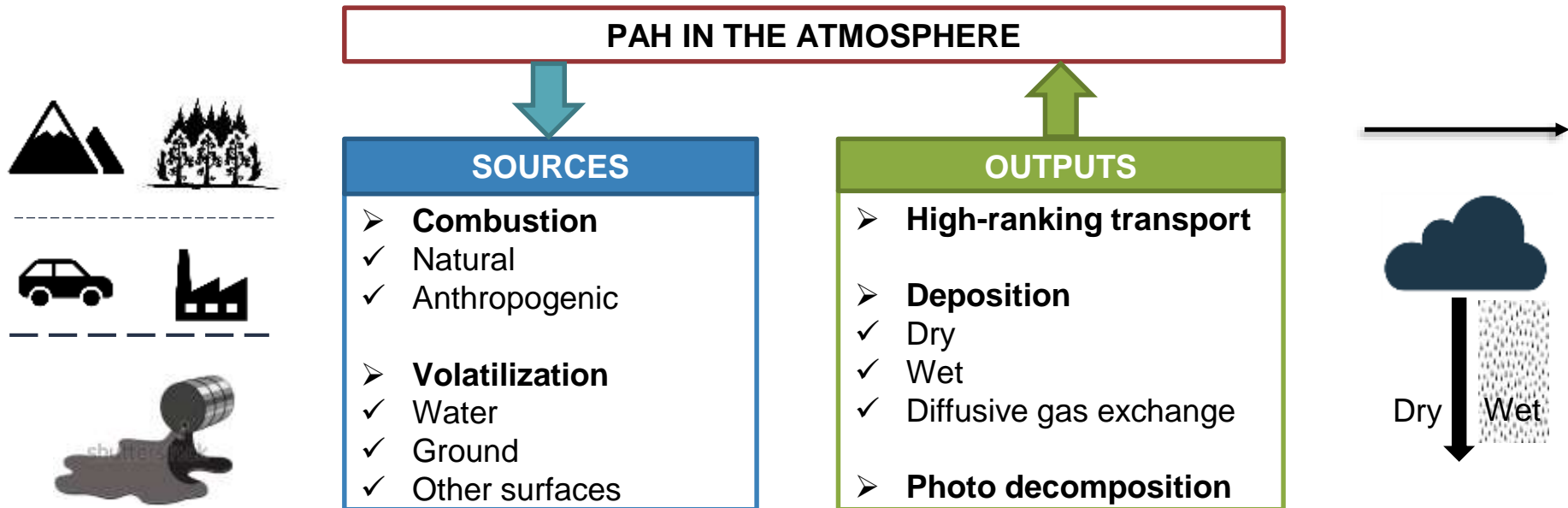


BaP



Country	Permissible limit of PAH in ambient air
European Union	1 ng BaP-ET-m ³
China	1 ng BaP-ET-m ³
India	1 ng BaP-ET-m ³
Colombia	1 ng BaP-ET-m³

b: Toxic Equivalence Factor



The Gas-Particle Partitioning

Partition coefficient

$$Kp = \frac{C_p/TSP}{C_g} \text{ (}\mu\text{g/m}^3\text{)}$$

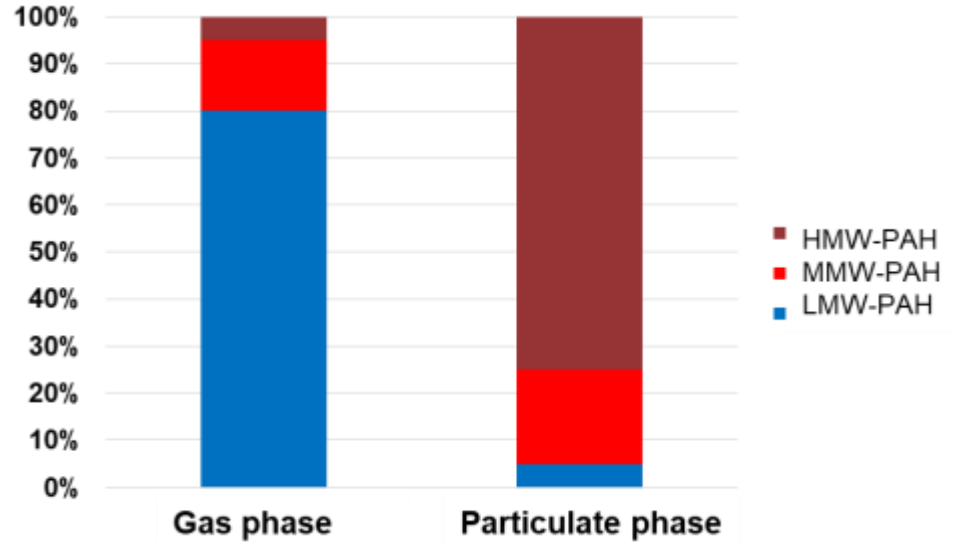
sub-cooled vapor pressure ratio

$$\text{Log } Kp = m_r \text{Log } P_L^0 + b_r$$

octanol-air partitioning coefficient ratio

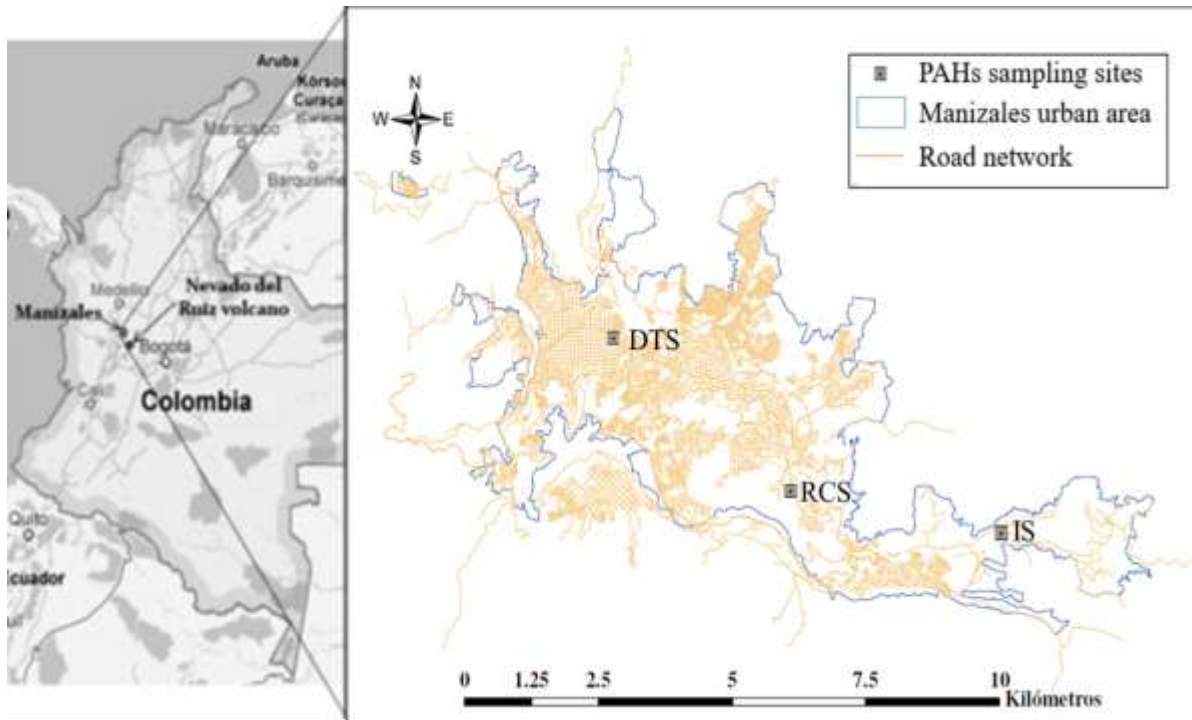
$$\text{Log } Kp = a \text{Log } Koa + b$$

Adsorption and absorption processes are presented



Studied area and PAHs sampling sites

Manizales
 400,436 inhab.
 Urban area 54 km²
 44.1 Veh/100 inhab
 Altitude 2150 m.a.s.l



Downtown Site (DTS)

Residential Commercial (RCS)

Industrial Site (IS)

Air Sampling



High volume air sampler

Sampling time 24 h
Volume sampled 851–1164 m³



Polyurethane Foam Sampler (PUF).

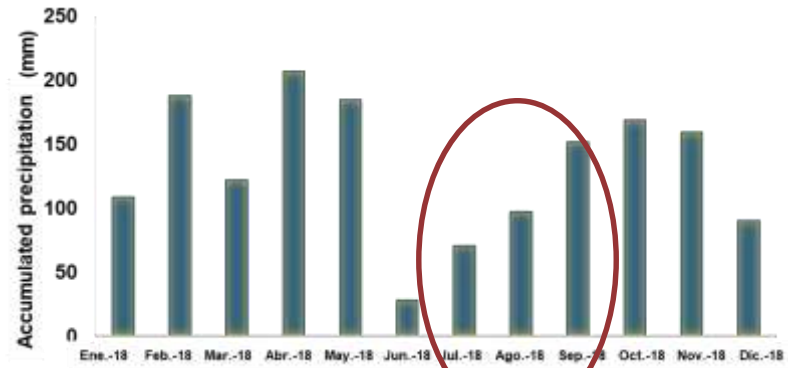
10 samples per site



Quartz microfiber filter (QFF)

10 samples per site

20 samples per site



Monitoring period

Qualitative and Quantitative Analysis

Internal standard method

Pretreatment

- ✓ QFF at 450 °C for 4 h
- ✓ PUF acetone extraction in ultrasonic bath



Extraction

- ✓ QFF for 10 min in ultrasonic bath acetonitrile /dichloromethane
- ✓ PUF for 1 hour in contact with acetone/hexane



filtration and concentration

- ✓ Filtered and concentrated on a centrifugal concentrator (60 °C and 1300 rpm).
- ✓ Final volume 1 mL



Addition of standards

Surrogate standard
(p-terphenyl-d₁₄)

Analysis performed at UFPR - Brazil

Qualitative and Quantitative Analyses

Clean up

- ✓ Florisil/silica gel columns

- ✓ Transferred to vials for further volume reduction
- ✓ Solvent was exchanged to hexane and the final volume adjusted to 1 ml

Addition of standards

Internal patterns standard
naphthalene-d₈,
acenaphthene-d₁₀,
phenanthrene-d₁₀,
chrysene-d₁₂ and
perylene-d₁₂

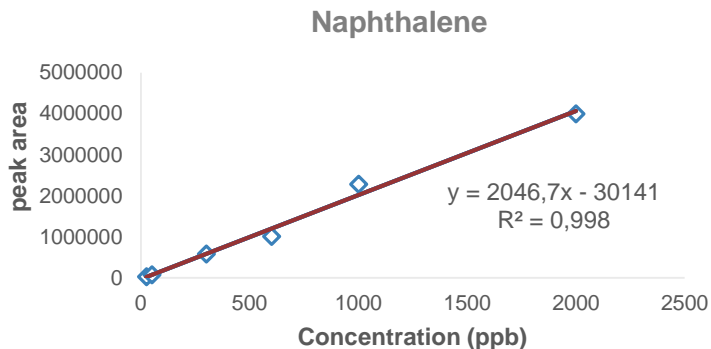
Chromatographic analysis

- ✓ Samples analyzed with a GC-MS TQ8040 triple quadrupole mass spectrometer (Shimadzu Corporation). SIM mode



Analysis performed at UFDP

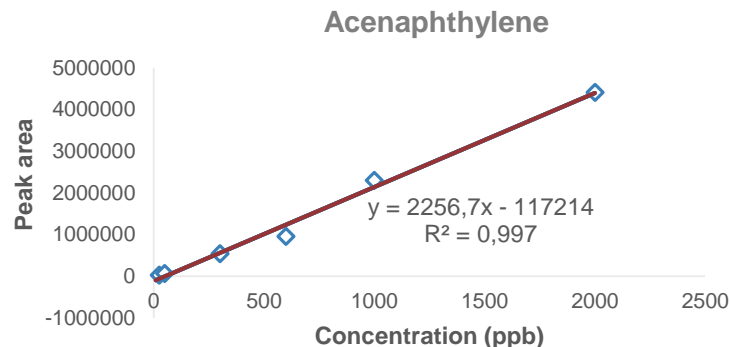
Quality Assurance/Quality Control (QA/QC)



The detected amounts in field blanks were negligible compared to the samples.

Recoveries of the PAHs were in the range of 75% and 129%.

6 points between 10 and 2000 ppb, 3 repetitions each
Average Relative Response Factors (RRFs),
Relative Standard Deviation (%RSD) and
Relative Retention Times (RRT) were validated.



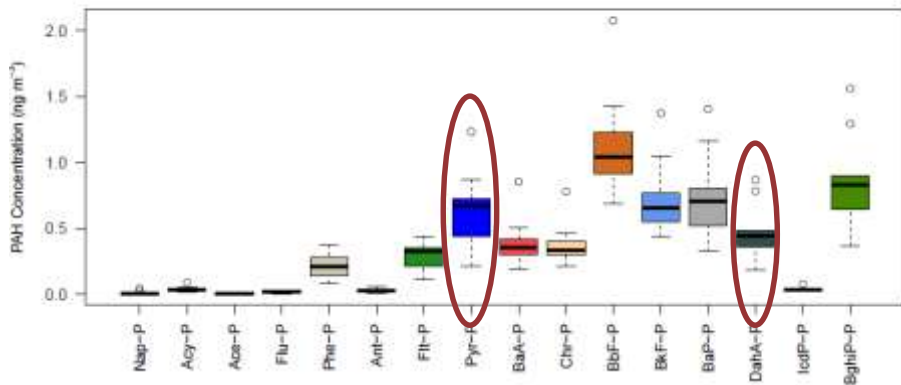
Average concentrations (ng/m³)

PAHs ng m ⁻³	Downtown		Residential Commercial		Industrial		
	DTS (n = 20)		RCS (n = 18)		IS (n = 20)		
	Part.	Gas	Part.	Gas	Part.	Gas	
Nap	0.013	1.171	0.006	1.846	0.004	0.654	2 rings
Acy	0.042	1.028	0.004	0.775	0.008	0.521	
Ace	0.003	0.118	<LQ	0.135	<LQ	0.150	3 rings
Flu	0.017	1.732	0.007	1.244	0.007	2.419	
Phe	0.213	3.661	0.076	4.597	0.132	8.864	
Ant	0.033	0.582	0.012	0.753	0.019	1.480	4 rings
Flt	0.291	1.987	0.105	2.444	0.334	5.839	
Pyr	0.632	3.227	0.205	1.549	0.581	1.954	
BaA	0.392	0.028	0.194	0.032	0.350	0.070	
Chr	0.377	0.055	0.254	0.090	0.327	0.152	5 rings
BbF	1.142	<LQ	0.819	0.026	1.567	0.115	
BkF	0.731	<LQ	0.492	0.027	1.071	0.096	
BaP	0.743	<LQ	0.616	0.015	1.551	0.099	6 rings
IcdP	0.474	0.210	0.593	0.007	1.424	0.002	
DBahA	0.044	<LQ	0.041	<LQ	0.085	<LQ	
BghiP	0.860	0.194	1.175	0.006	1.837	<LQ	
Σ16 PAHs	5.983	13.668	4.589	13.453	9.292	22.263	

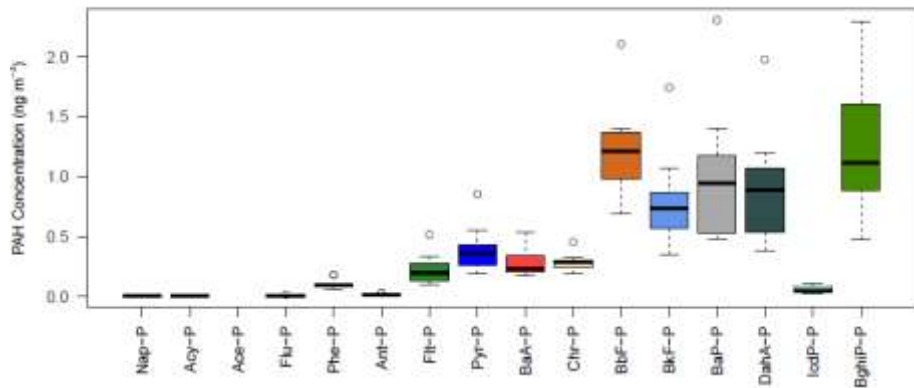
Gaseous fractions ranged from 43% to 90% of the total PAHs and were predominant in 90% of the samples.

Total concentration range
DTS: 11.5 ng/m³ to 35.2 ng/m³
RCS: 7.1 ng/m³ to 33.5 ng/m³
IS: 13.9 ng/m³ to 114.4 ng/m³

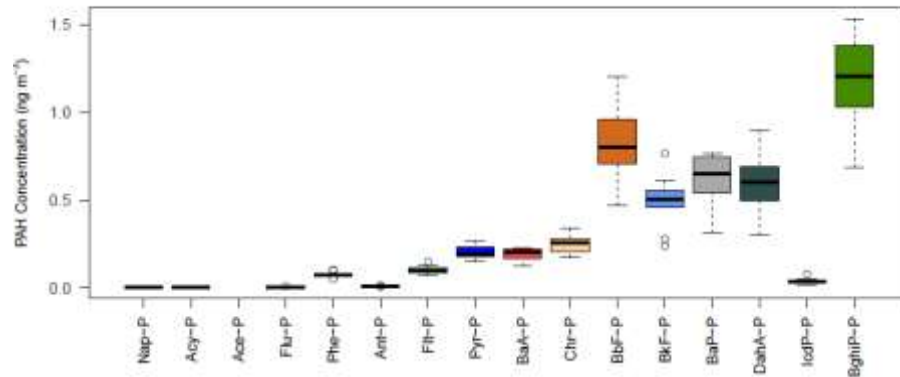
PAH Particle DTS

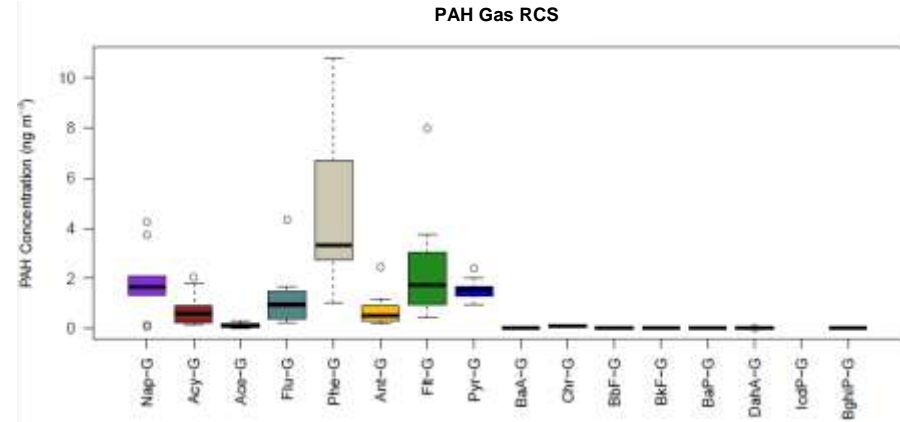
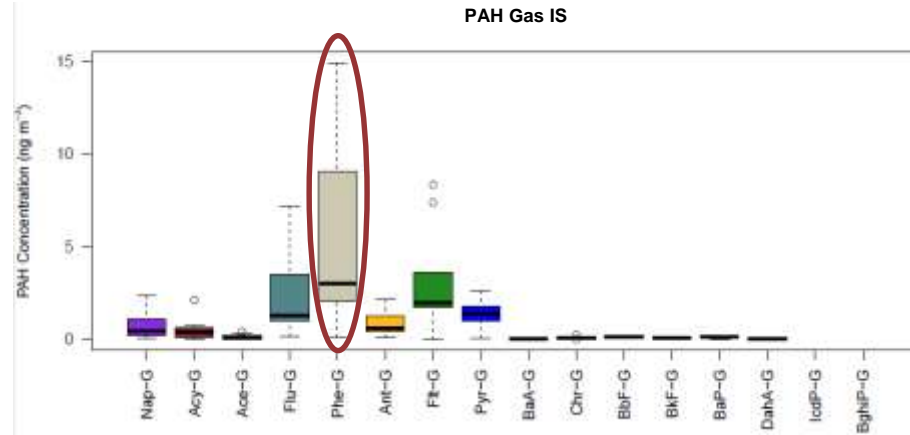
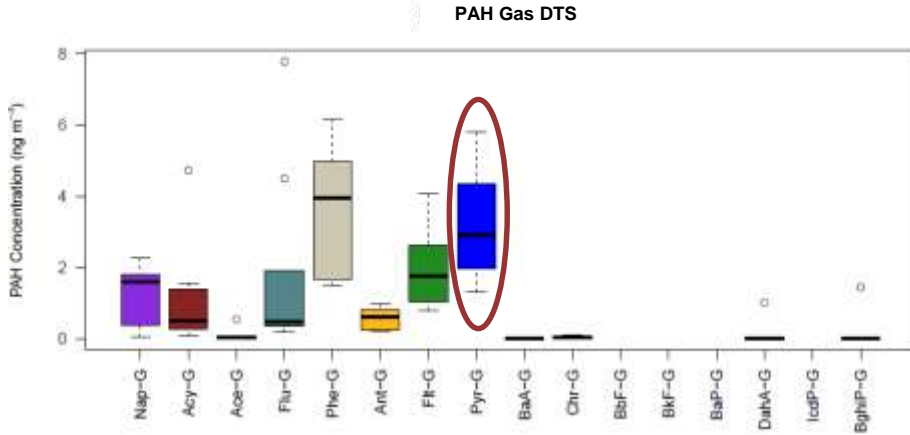


PAH Particle IS

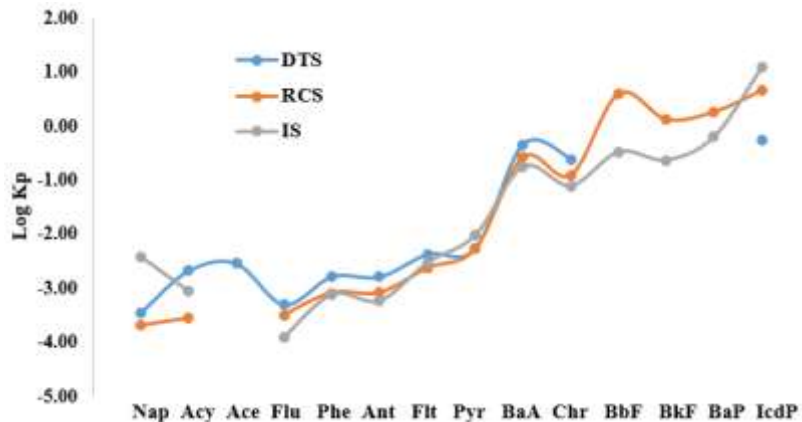


PAH Particle RCS





The Gas-Particle Partitioning Coefficient (K_p) and relationship with P_L^0 or K_{oa}



K_p values of PAHs increased with the increasing of the molecular weight.

There were good linear correlation between $\log K_p$ and $\log P_L^0$, the partitioning was absorption as well as for adsorption mechanism.

Linear correlation between $\log K_p$ and $\log K_{oa}$. Both adsorption and absorption mechanism are observed in the partitioning mechanisms

Site	T (°C)	P (mmHg)	$\log P_L^0$			$\log K_{oa}$		
			M_r	b_r	R^2	a	b	R^2
DTS	17.8	590	-0.49	-3.00	0.84	0.26	-3.78	0.76
RCS	18.2	596	-0.75	-3.78	0.93	0.72	-8.48	0.94
IS	16.3	576	-0.83	-3.80	0.96	0.80	-9.02	0.97

Both adsorption and desorption are observed in different magnitude for the three sites, this indicates differences in the sorbents, that is, differences in the composition of the particulate material.

These results will be related to the investigation of potential sources of PAHs calculated by diagnostic ratios for all three study sites.

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Thanks

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