Measurements of organic compounds in particulate matter and gaseous phase collected in the neighbourhood of an industrial complex in São Paulo (Brazil)

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São Paulo State

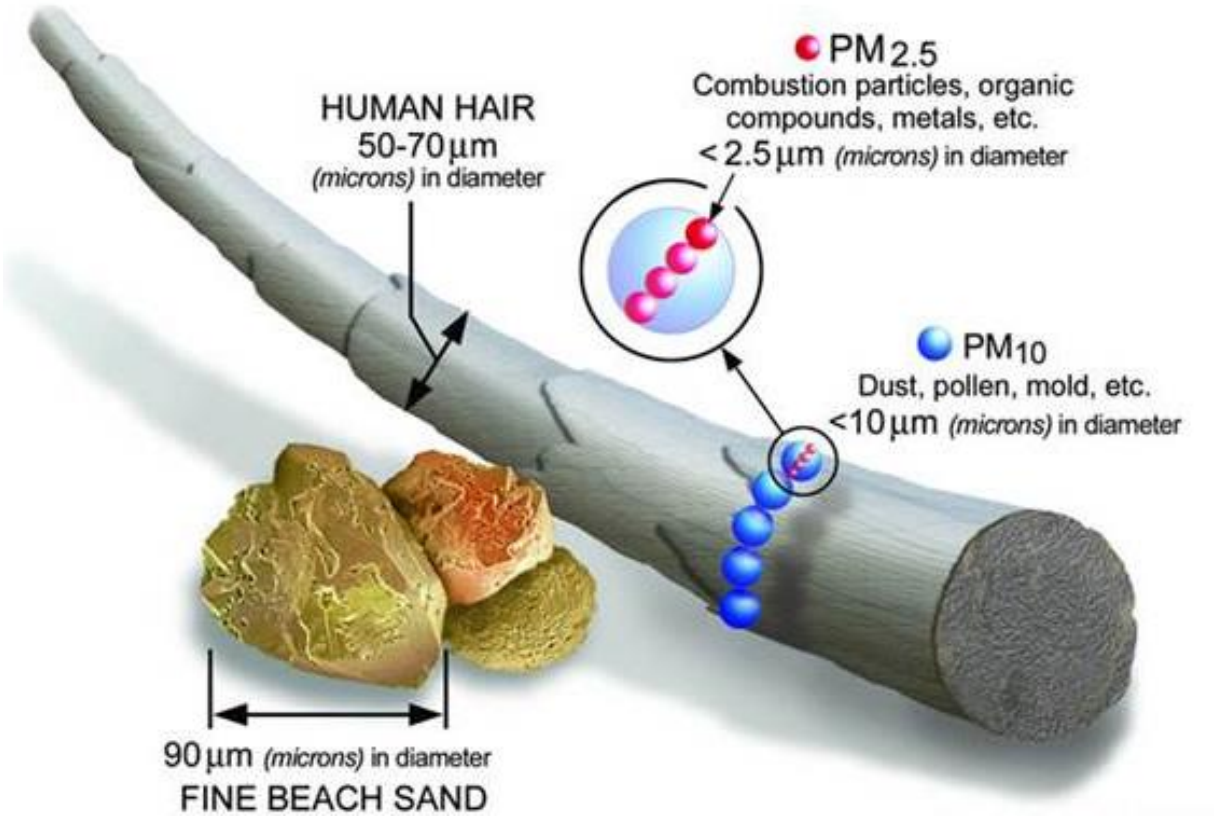
- 45 million inhabitants,
- 7,012 industries,
- 90% of new cars are flex fuel vehicles.

Petrochemical complex

- Responsible for production of 30% of the fossil fuels consumed in SPMA;
- Production capacity: 53 Thousand barrels of oil/day
- Area: 125 ha
- 14 industries
- Health problems

From: PETROBRAS and Polo ABC.

Particles distribution



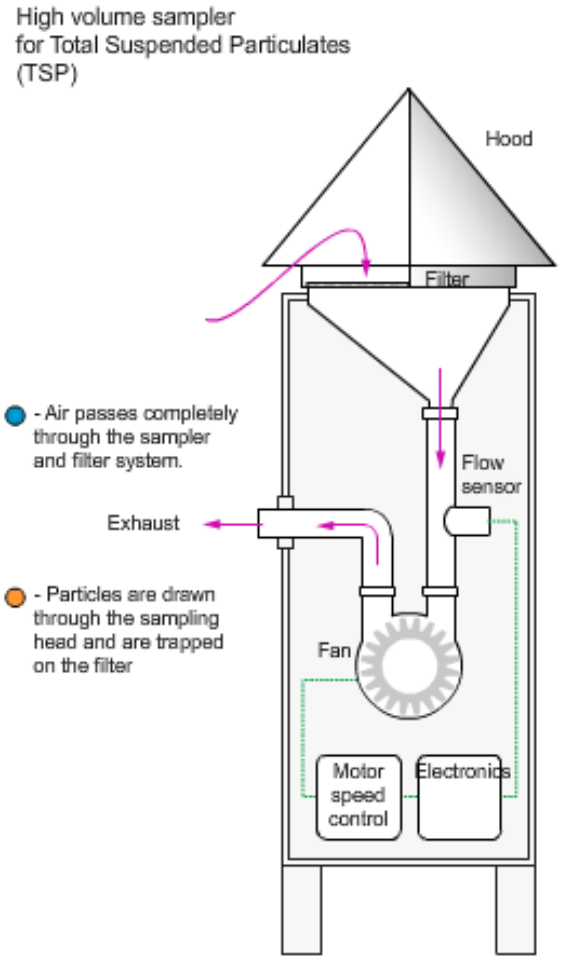
- TSP: ≤ 50µm
- PM_{10} : ≤ 10µm
- $PM_{2.5}$: ≤ 2.5µm

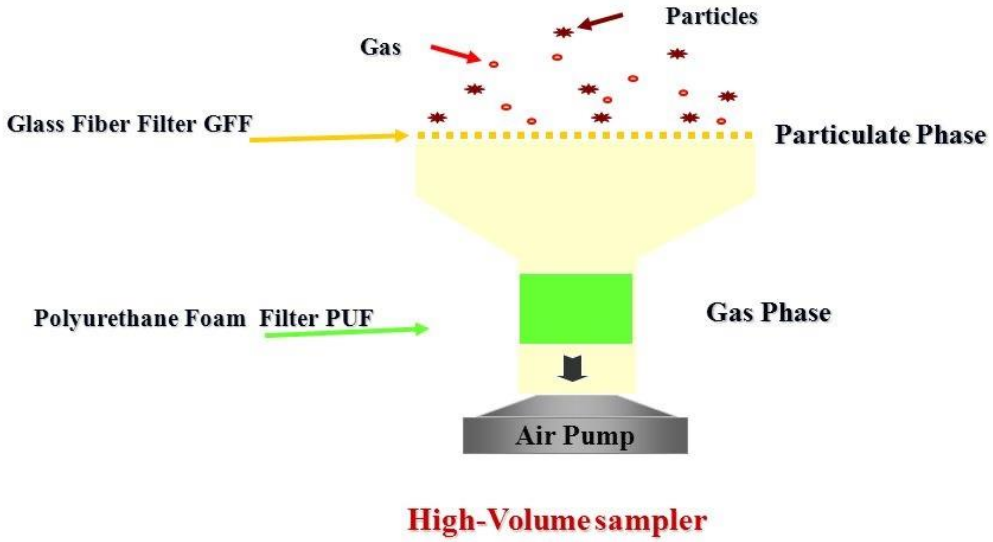
Fonte: https://www3.epa.gov/pm/

Sampling site

From: Google Earth.

TSP + PUF

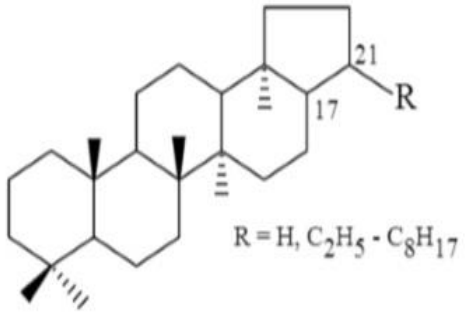

High volume sampler
for Total Suspended Particulates
(TSP)
Hood
Filter
- Air passes completely through the sampler and filter system.
Flow sensor
Exhaust
- Particles are drawn through the sampling head and are trapped on the filter
Fan
Motor speed control
Electronics

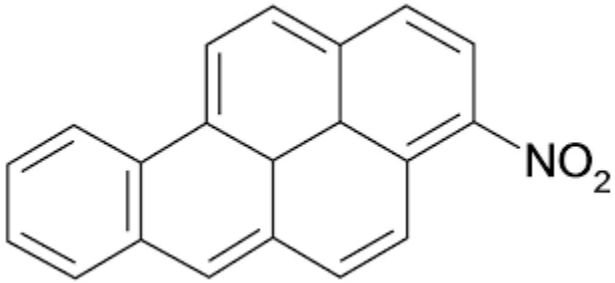

Particles
Gas
Glass Fiber Filter GFF
Particulate Phase
Polyurethane Foam Filter PUF
Gas Phase
Air Pump
High-Volume sampler

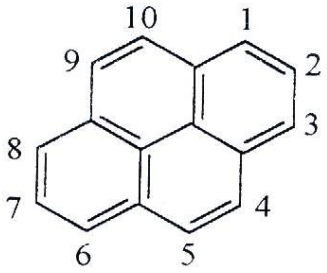
Sampling

Methodology

- Sampling: from October 16th to November 20th, 2015
- N=30 samples
- TSP + PUF
- EC and OC
- 14 hopanes
- *n*-alkanes: C_{11} – C_{35}
- 15 PAH
- 16 Nitro-PAH
- 4 Oxy-PAH







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- **OC and EC**

Thermal-optical analysis

Pio et al., 2011.

Hopanes, Alkenes

Universidade de São Paulo
Instituto de Química

universidade
de aveiro

From: Alves et al., 2016; Krumal, 2013; Wei et al, 2012.

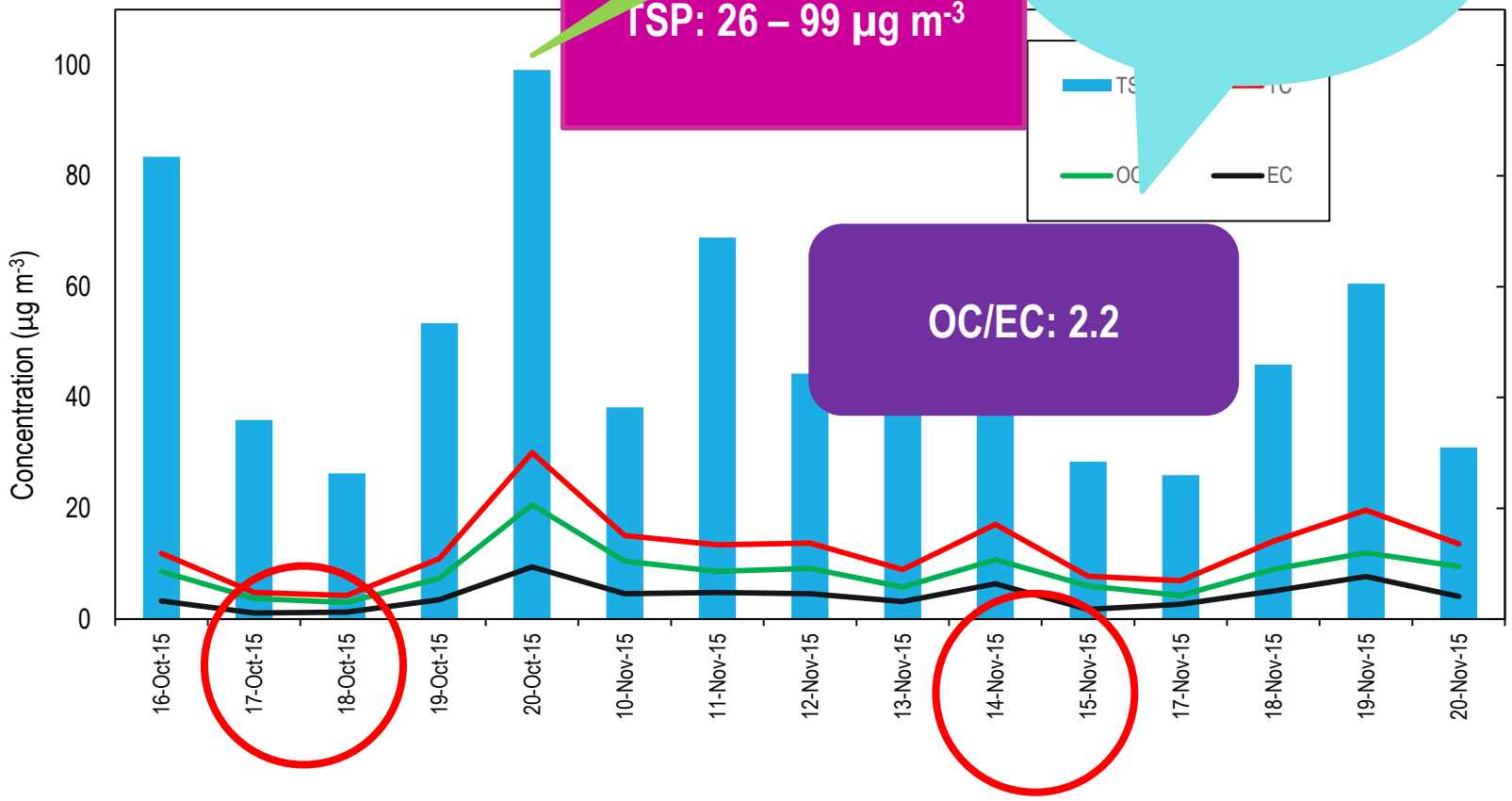
RESULTS
TSP, OC a

20-Oct-1
↑ TSP,

TSP: 26 – 99 µg m^{-3}

Vehicular emissions

OC/EC: 2.2



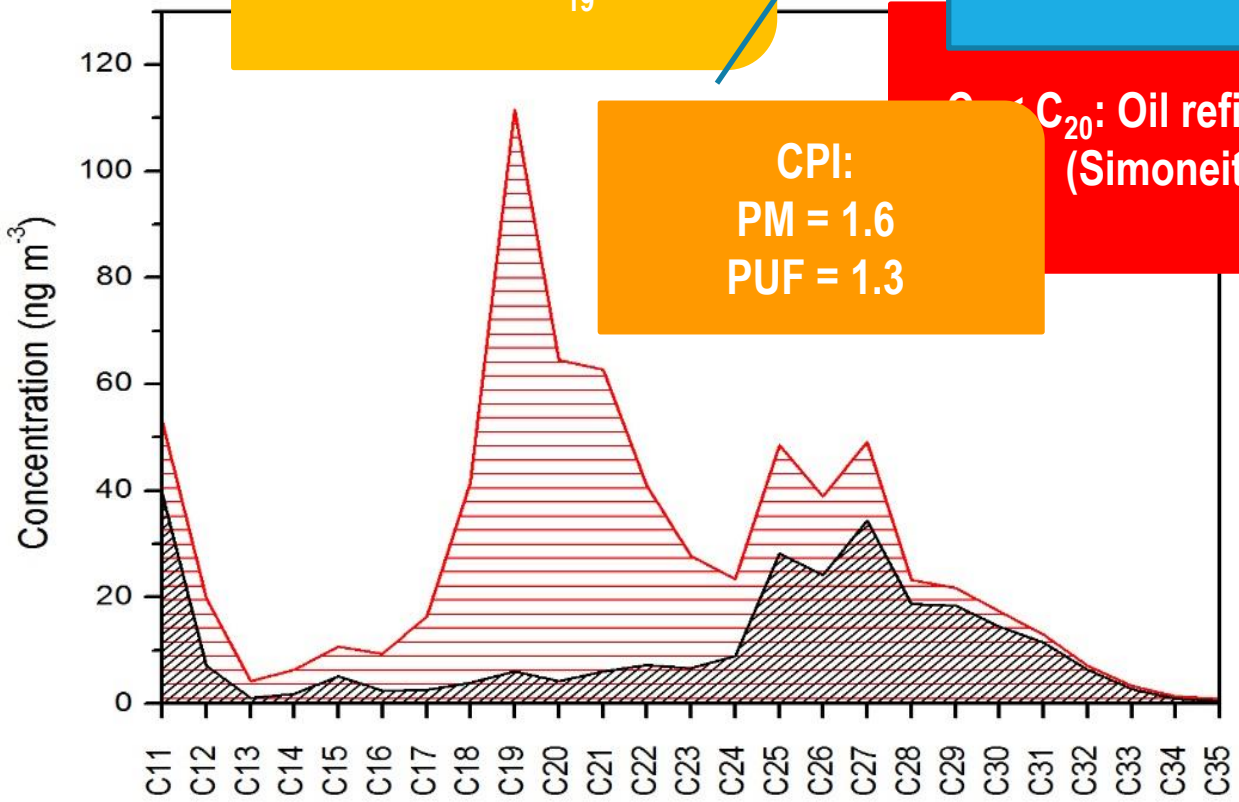
n-Alkanes
Biogenic and antropogenic emissions

C_{max} :
PM = C_{11}, C_{25}, C_{27}
PUF = C_{19}

CPI ≈ 1: anthropogenic emissions

CPI:
PM = 1.6
PUF = 1.3

C_{20}: Oil refining process (Simoneit, 1984)



Alkenes

- *N*-alkenes are terminal olefins;
- Squalene: diesel soot, biomass burning emissions.

($ng.m^{-3}$)	PM		PUF	
	Mean	Min-Max	Mean	Min-Max
n-tetradec-1-ene	0.8	0.05 - 2.1	1.1	0.3 – 5.4
n-hexadec-1-ene	0.8	0.5 - 1.9	2.3	0.6 – 10.2
n-octadec-1-ene	2.0	0.6 - 3.8	22	11 – 59
n-eicos-1-ene	2.5	0.8 - 5.8	36	10 – 62
n-tricos-1-ene	4.2	2 - 7	12	3.1 – 23.5
Squalene	13	1.6 – 32	85	6.0 – 987

Hopanes
Petroleum and lubricating oil emissions

17α(H), 21β(H): mature petroleum

China = 15 ng m^{-3}

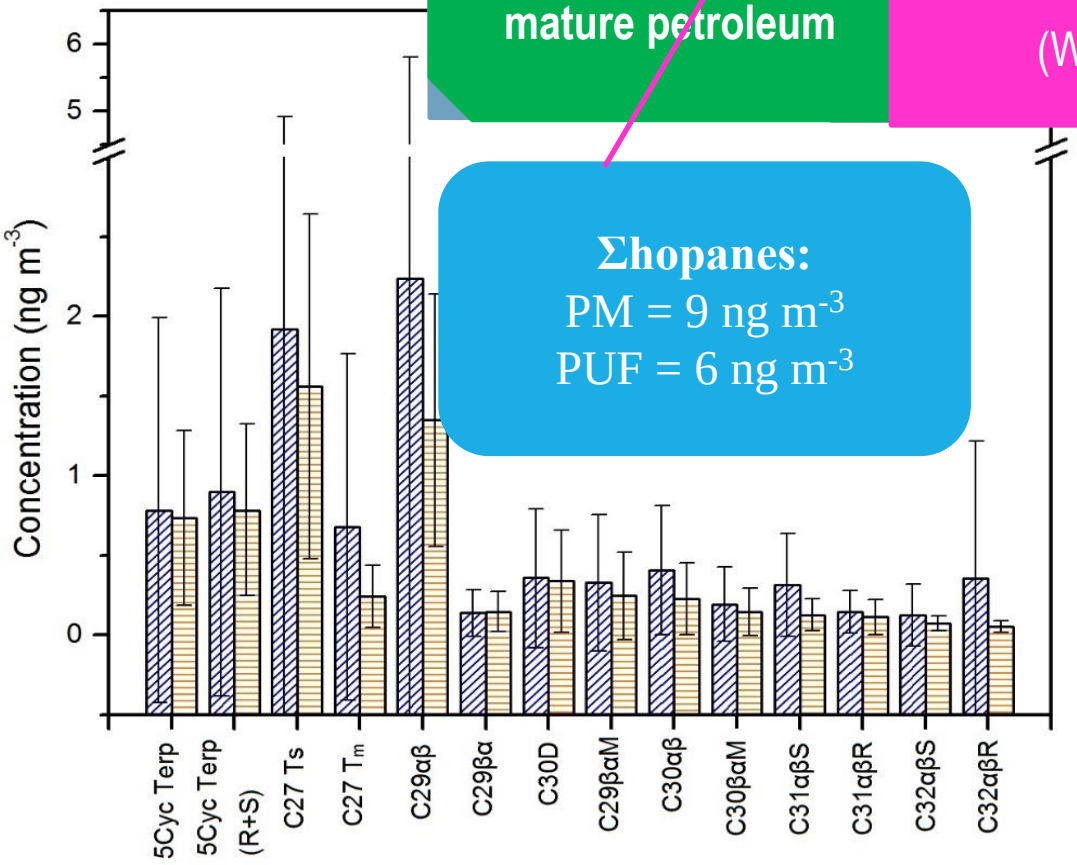
New Zeland = 6 ng m^{-3}

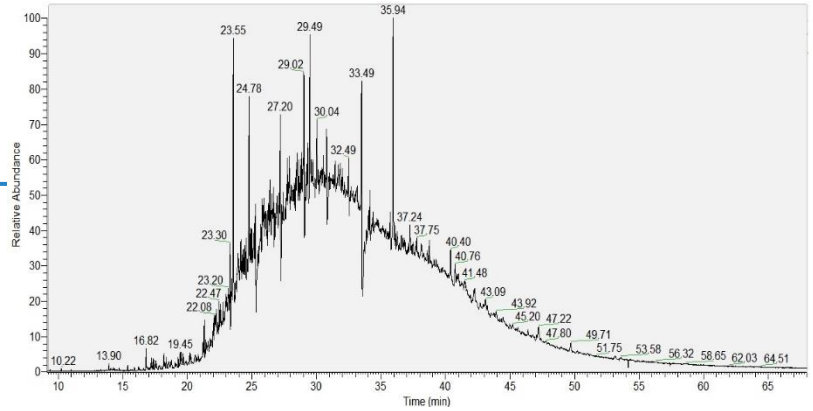
(Wang et al., 2006)

Σhopanes:

PM = 9 ng m^{-3}

PUF = 6 ng m^{-3}



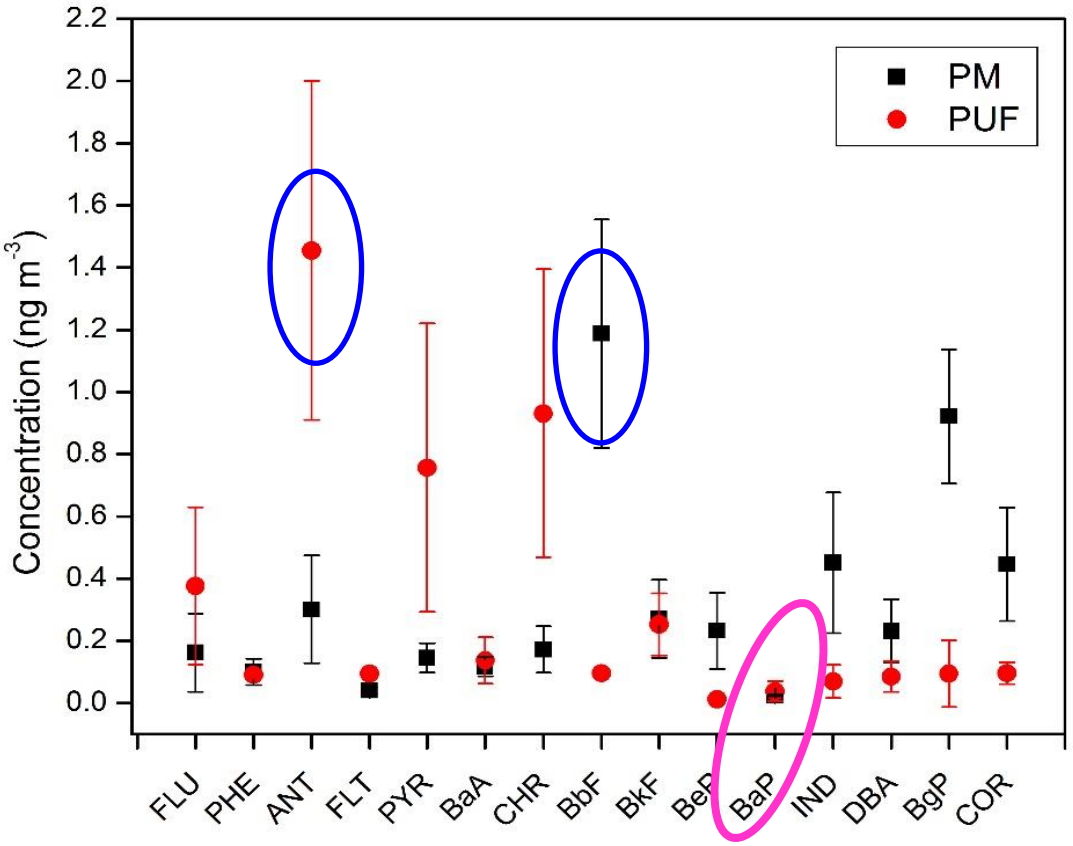


~1: petroleum products

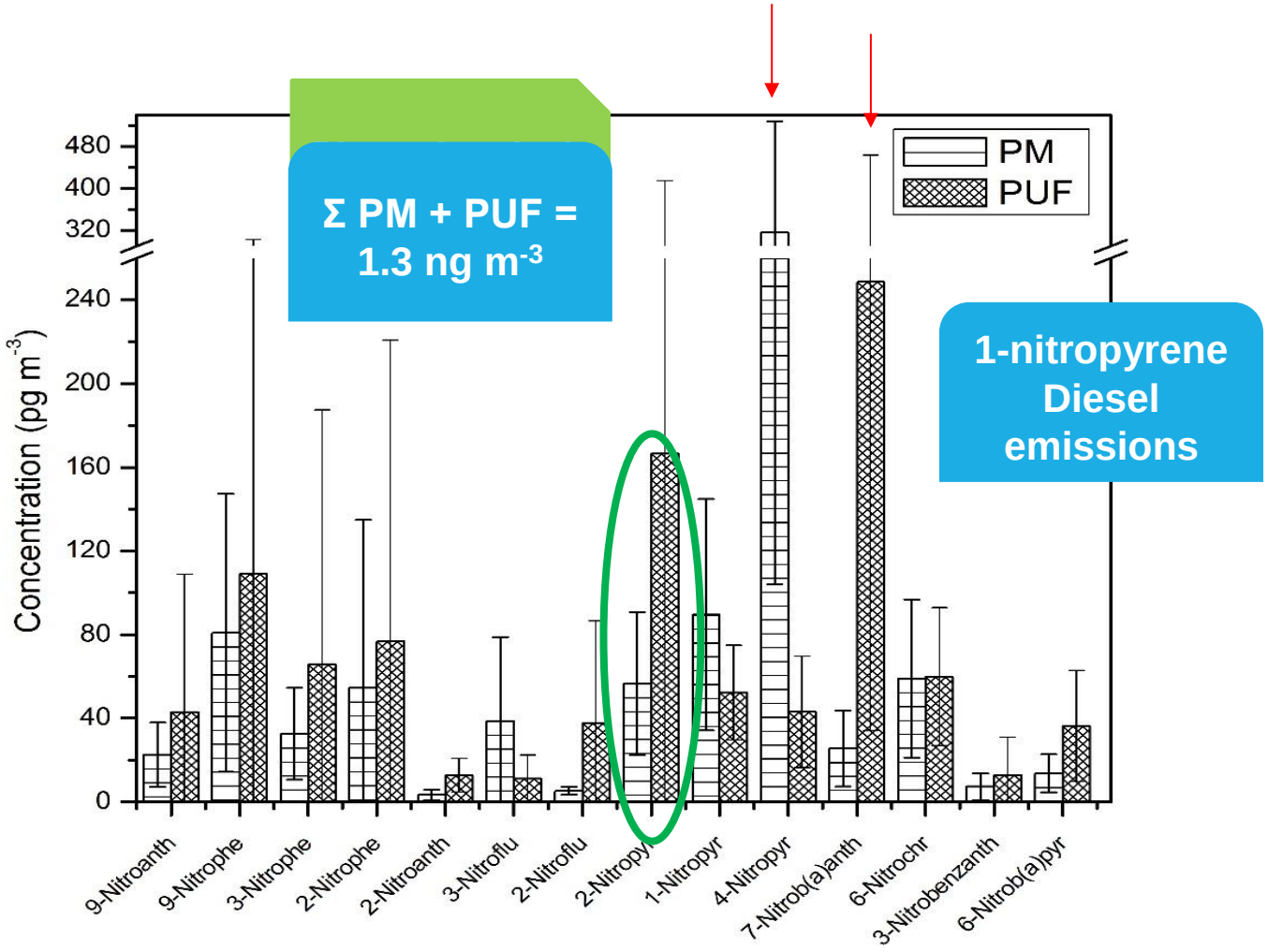
	PM		PUF	
	Mean	Min - Max	Mean	Min - Max
Σ *n*-alkanes (ng m^{-3})	263	168 – 397	453	246 – 850
CPI	1.6	-	1.3	-
C_{max}	C_{11}	-	C_{19}	-
%WNA	0.9	-	1.21	-
Σ Hopanes (ng m^{-3})	8.8	1.2 – 52.0	6.1	1.3 – 12.0
UCM/R	1.9	0.002 – 4.3	2.3	0.002 – 4.5

Strong contamination by petroleum emissions

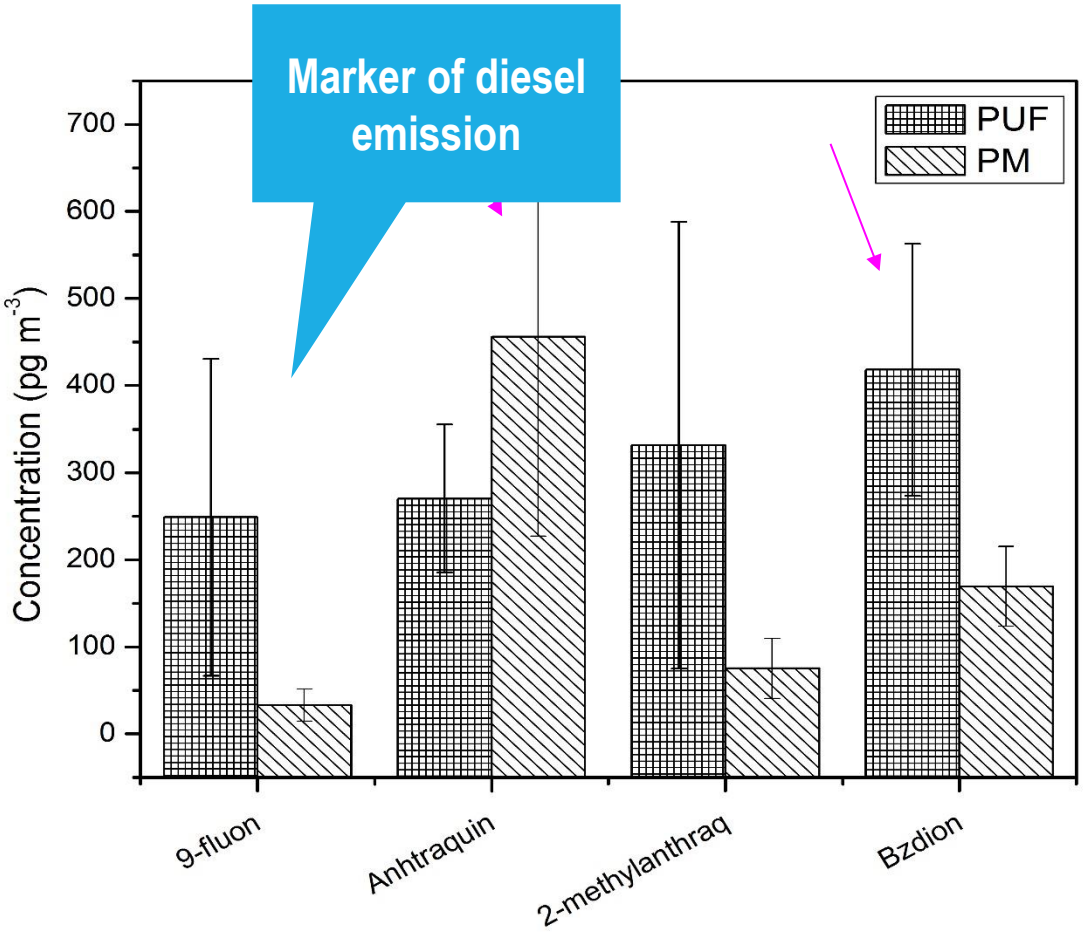
PAH


Concentration (ng m-3)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
PM
PUF
FLU
PHE
ANT
FLT
PYR
BaA
CHR
BbF
BkF
BeP
BaP
IND
DBA
BgP
COR

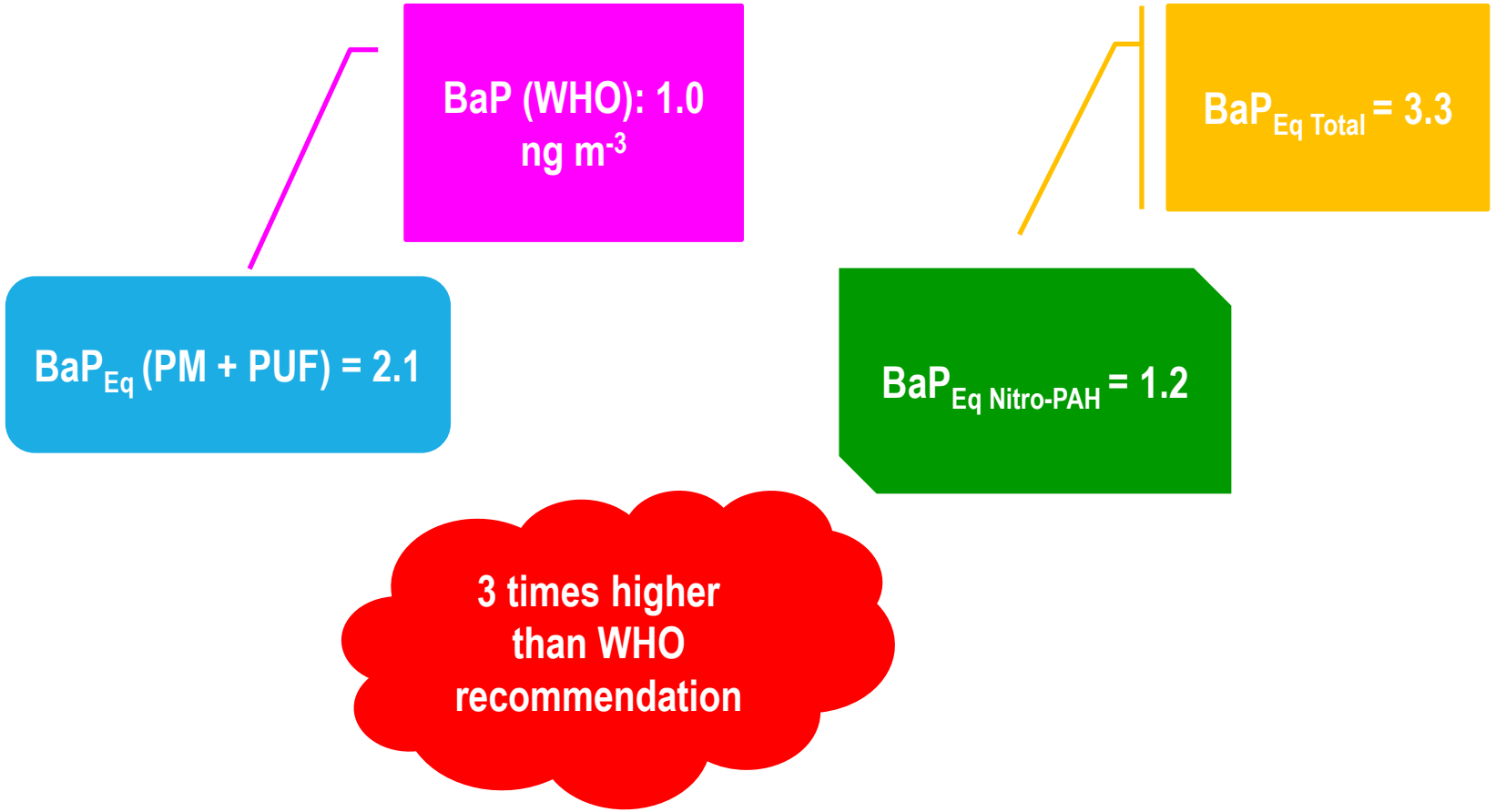
Nitro-PAH


Σ PM + PUF = 1.3 ng m-3
1-nitropyrene Diesel emissions
PM
PUF
Concentration (pg m-3)
480
400
320
240
200
160
120
80
40
0
9-Nitroanth
9-Nitrophe
3-Nitrophe
2-Nitrophe
2-Nitroanth
3-Nitroflu
2-Nitroflu
2-Nitropyr
1-Nitropyr
4-Nitropyr
7-Nitrob(a)anth
6-Nitrochr
3-Nitrobenzanth
6-Nitrob(a)pyr

Oxy-PAH


Marker of diesel emission
PUF
PM
Concentration (pg m-3)
700
600
500
400
300
200
100
0
9-fluon
Anhtraquin
2-methylanthraq
Bzdion

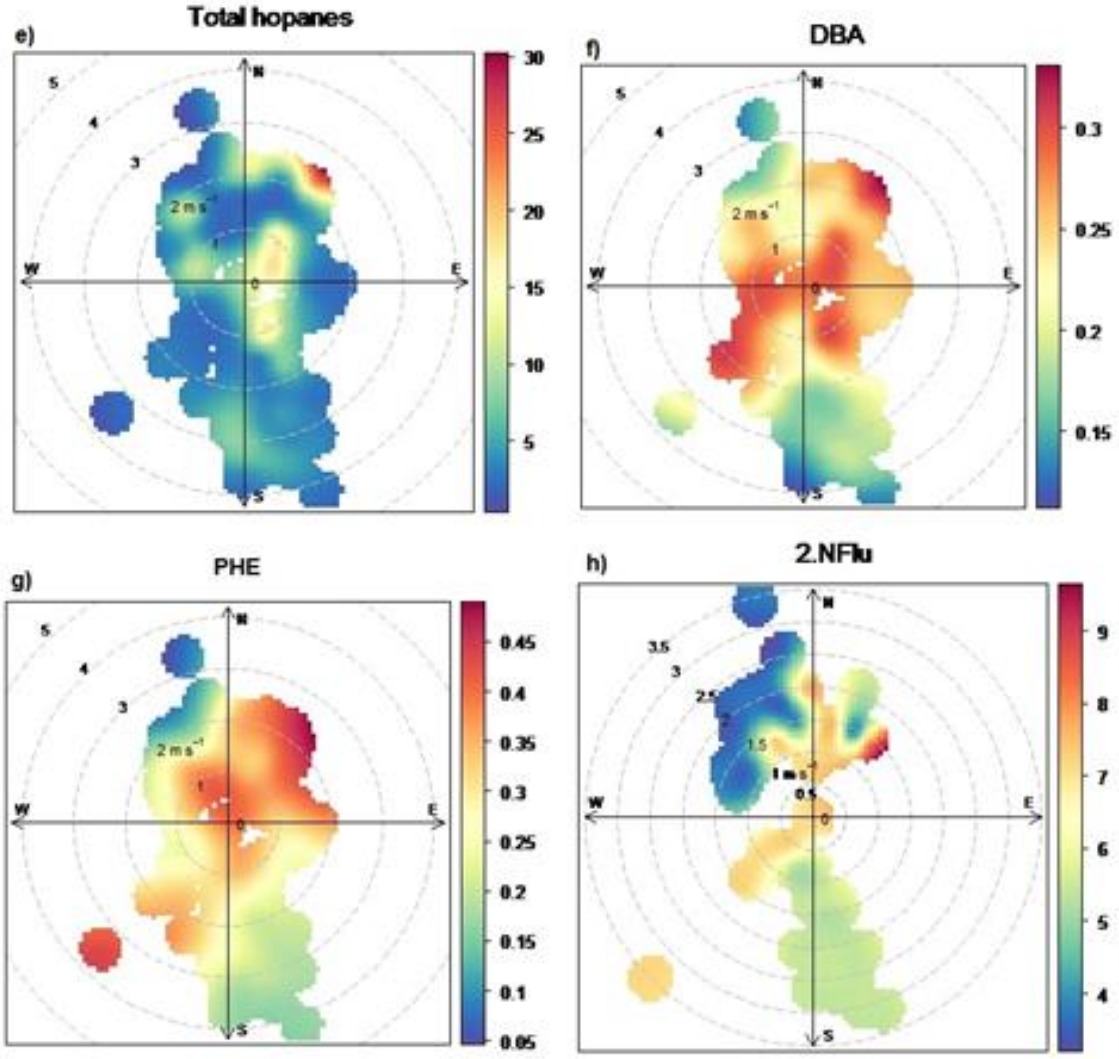
Cancer risk
BaP_{Eq}



$BaP_{Eq\ Nitro\text{-}PAH}$ = [1-nitropyr] x 0.10 + [4-nitropyr] x 0.10 + [6-nitrochr] x 10.00 + [2-nitroflu] x 0.01

(BaP_{Eq}) = [BaA] x 0.1 + [CHR] x 0.01 + [BbF] x 0.1 + [BkF] x 0.1 + [BaP] x 1 + [IND] x 0.1 + [DBA] x 5 + [BgP] x 0.01

Polar plots



Conclusions

- [OC] > [EC] for all samples;
- ↑ *N*-alkanes from anthropogenic sources;
- Hopanes: emissions from completely mature petroleum;
- BaP_{Eq}: higher than recommended by WHO;
- The polar plots: emissions from the petrochemical complex.

Thank you

Agradecimentos

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