COMPOSITION OF EXTRACTABLE ORAGANIC MATTER OF AIR PARTICLES IN URBAN ATMOSPHERES OF ALGERIA

The atmospheric particulate have a very complex composition including inorganic species, elemental carbon as well as thousands of carbon containing compounds. These latter are comprised under the formula "particulate organic matter" (POM)

POM composition is very variable and depends upon three main factors:

1. The nature and relative intensity of emission sources insisting into a given site;
2. The chain processes of formation, decomposition and sink of pollutants which take place in the atmosphere due to presence of light and oxidants;
3. Dilution and transport of air masses by winds and boundary layer evolution.

ORGANICS POLLUTANTS SOURCES

1)/Anthropic:

Combustion (biomass burning)

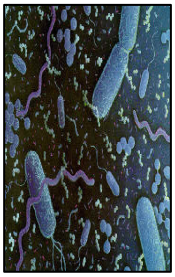
Traffic

Food cooking

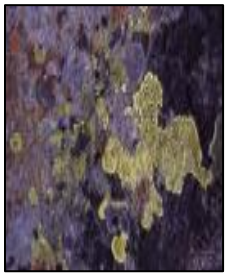
2/Natural:

Plants

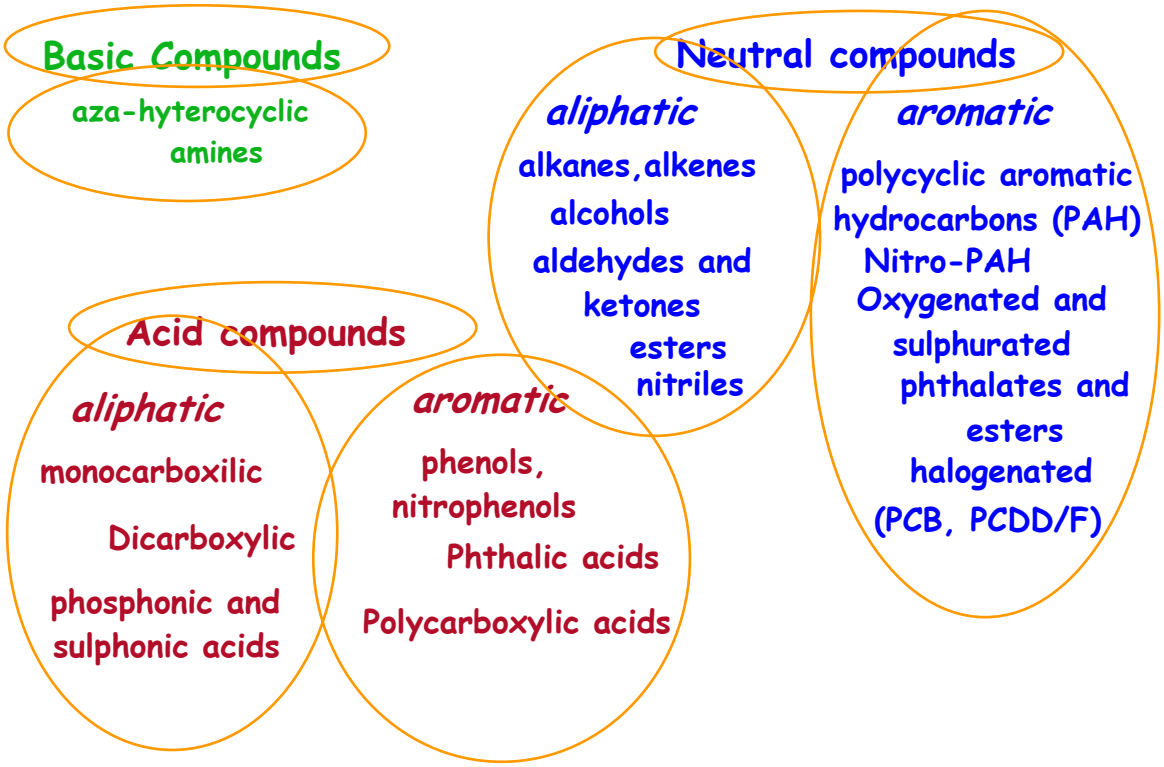
Bacteria



Fungi

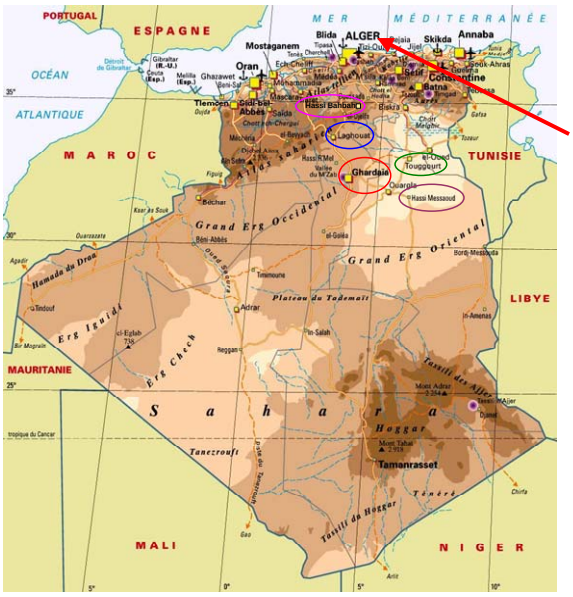


PARTICULATE ORGANIC MATTER COMPOSITION



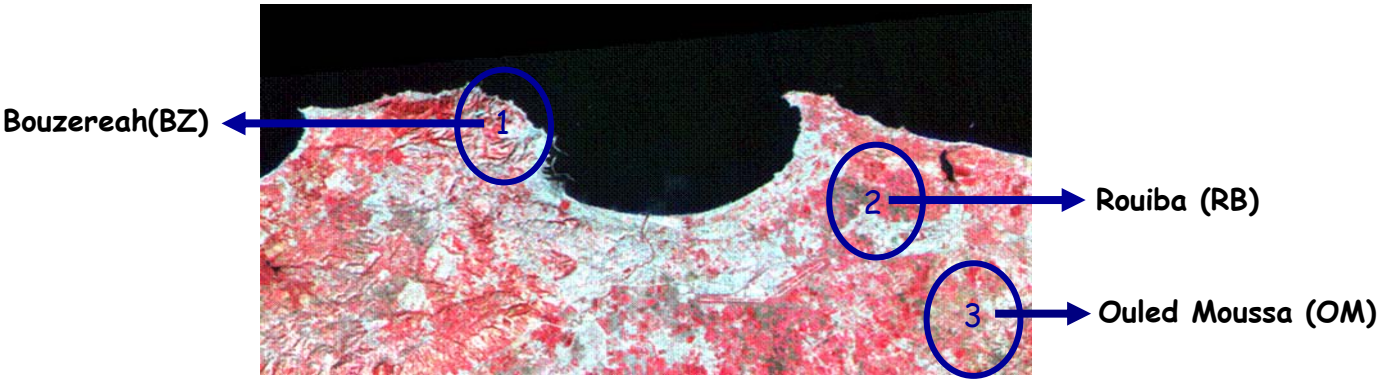
SAMPLING AND ANALYSIS

Sites sampling



Algiers

Map of Algeria

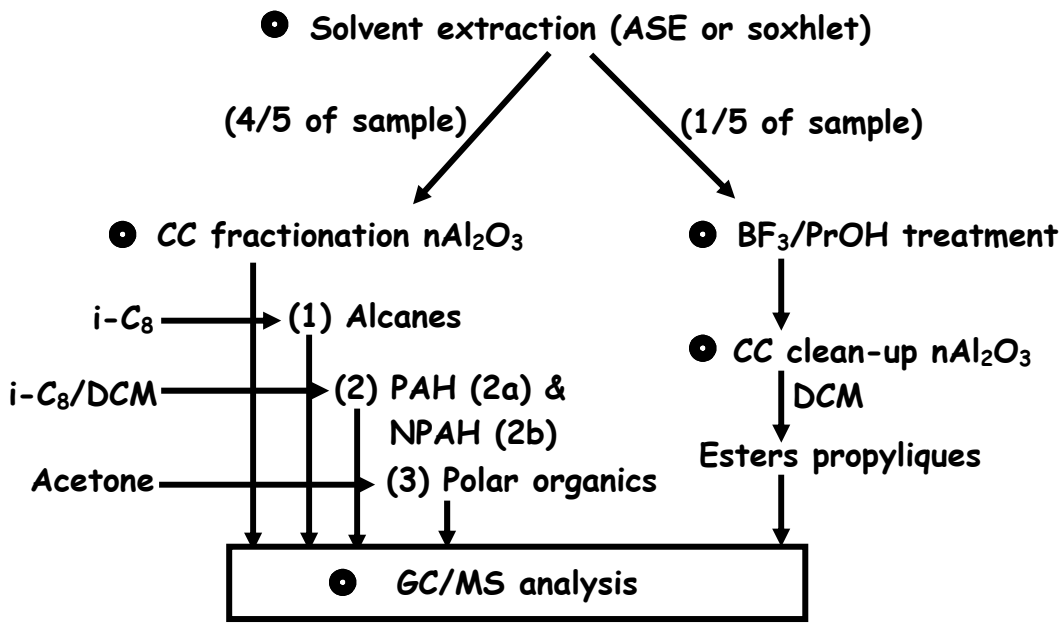


Distribution of vegetation and at locations sampling

Analysis

Sample Extraction, Clean-up

- Size-ruled sample collection
- Sample weighting and pooling (when required)
- Internal standard spiking (isotopically laballed cpds)



GC/MS Analysis

n-Alkanes, n-alkanoic and dicarboxylic acids, PAHs, NPAHs and Polar compounds were determined by using gas chromatograph coupled with mass spectrometric operating in

SCAN mode, except for PAHs where SIM mode was used. Separations of analytes were obtained through a 25m long capillary column coated with a HP-5-type methylphenyl silicone stationary phase (i.d. = 0.2mm, film thickness = 0.33 µm). The column temperature was maintained at 80 °C for 2min, then programmed to 170 °C at 20 °C.min^{-1} rate and held constant for 2 min; a second ramp (4 °C.min^{-1} rate) heated column up to 280 °C and elution was completed isothermally within 15 min.The mass spectrometer system was operated in electron impact mode (ion source energy = 70 eV). Compounds identification was based upon comparison of eluted peaks with authentic analyte standards, GC retention times, literature mass spectra and interpretation of mass spectrometric fragmentation patterns. Quantification of the compounds was conducted by comparing GC peak areas with those of known coinjected standards.

RESULTS

1/ n-alkanes results (Fig 1a-1c)

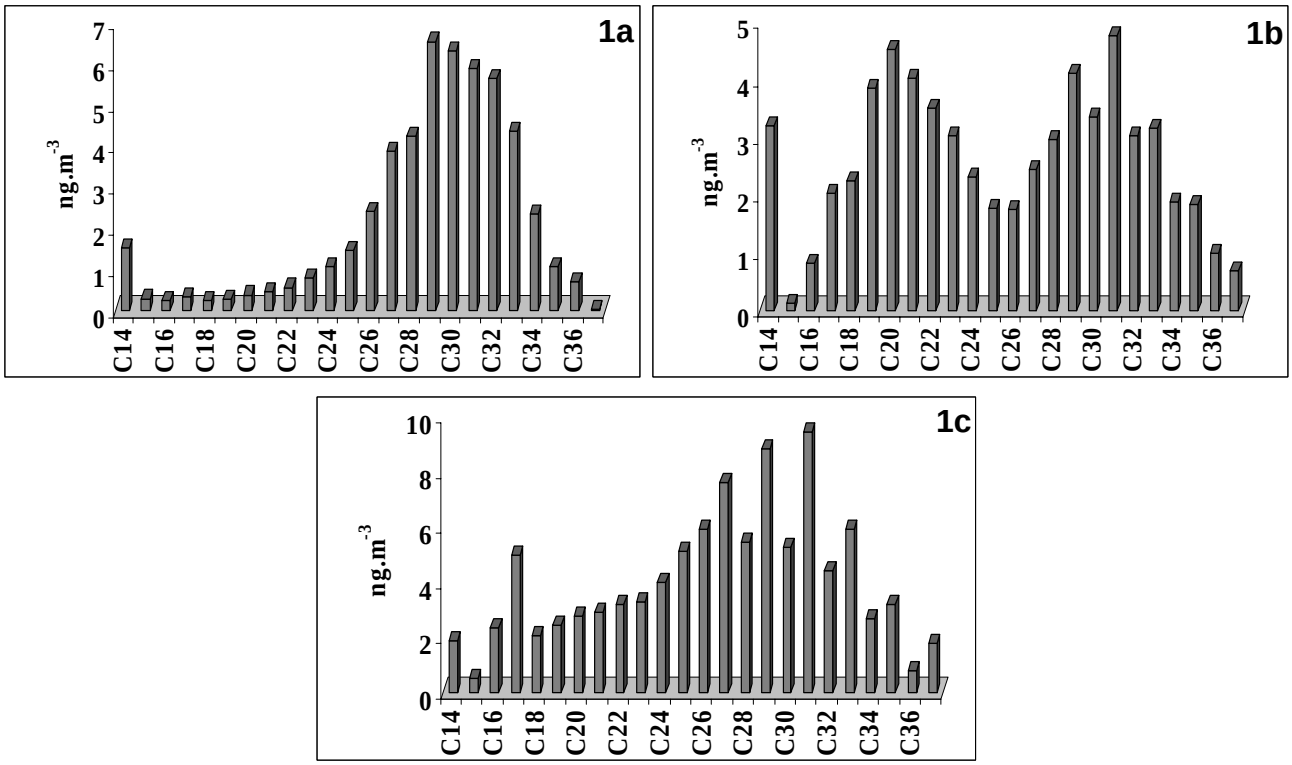


Fig.1. Distribution profiles of n-alkanes concentrations recorded in; 1a: Bouzereah, 1b: Rouiba, 1c: Ouled Moussa

1-1/ n-alkanes diagnostic ratios (Table 1)

Table 1: Diagnostic ratios of alkanes detected in airborne of: BZ, RB and OM

Sampling sites	BZ	RB	OM
[a] CPI1	0.99	1.38	1.04
[b] CPI2	0.85	1.19	0.89
[c]CPI3	1.02	1.47	1.15
Cmax	C29	C29	C29
Pr/Ph	0.3	1.71	0.29
[d] %wax Cn	10.8	22.2	15.5
Total	51.89	99.71	64.38

CPI: Carbon Preference Index
[a]Whole range for n-alkanes: CPI1 = ∑ (C15 – C37) / (C14 – C36)
[b]Petrogenic n-alkanes: CPI2 = ∑ (C15 – C25) / (C14 – C24)
[c]Biogenic n-alkanes: CPI3 = ∑ (C25 – C37) / (C24 – C36)
Cmax: Carbon number with the highest peak in the chromatogram
Pr: Pristane, Ph: Phytane
[d] %wax Cn = ∑ (Cn – 0.5(Cn-1 + Cn+1)) / ∑ Cn x 100%.

1-2/ Sources reconciliation (Fig.2.)

An odd carbon number predominance was found at both locations, wherein odd carbon number alkanes represent a major contribution of vascular plants waxes The isoprenoid hydrocarbons derived from petroleum (pristane and phytane) were also detected.

CPI ≈1 indicates petroleum contamination

it is possible to subtract this contribution to determine the residual plant wax alkanes. The concentrations of the wax *n*-alkanes are calculated by subtraction of the average of the next higher and lower even carbon numbered homologues, taking as zero the negative values of C_n.

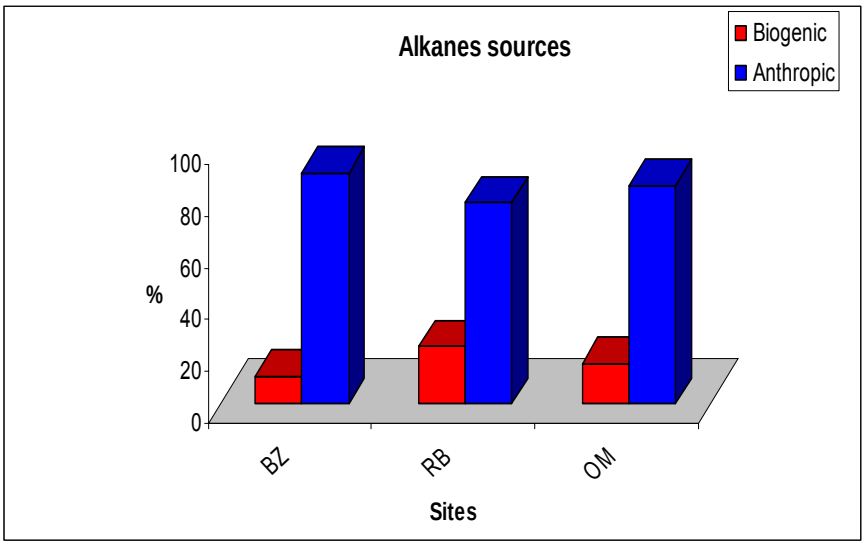
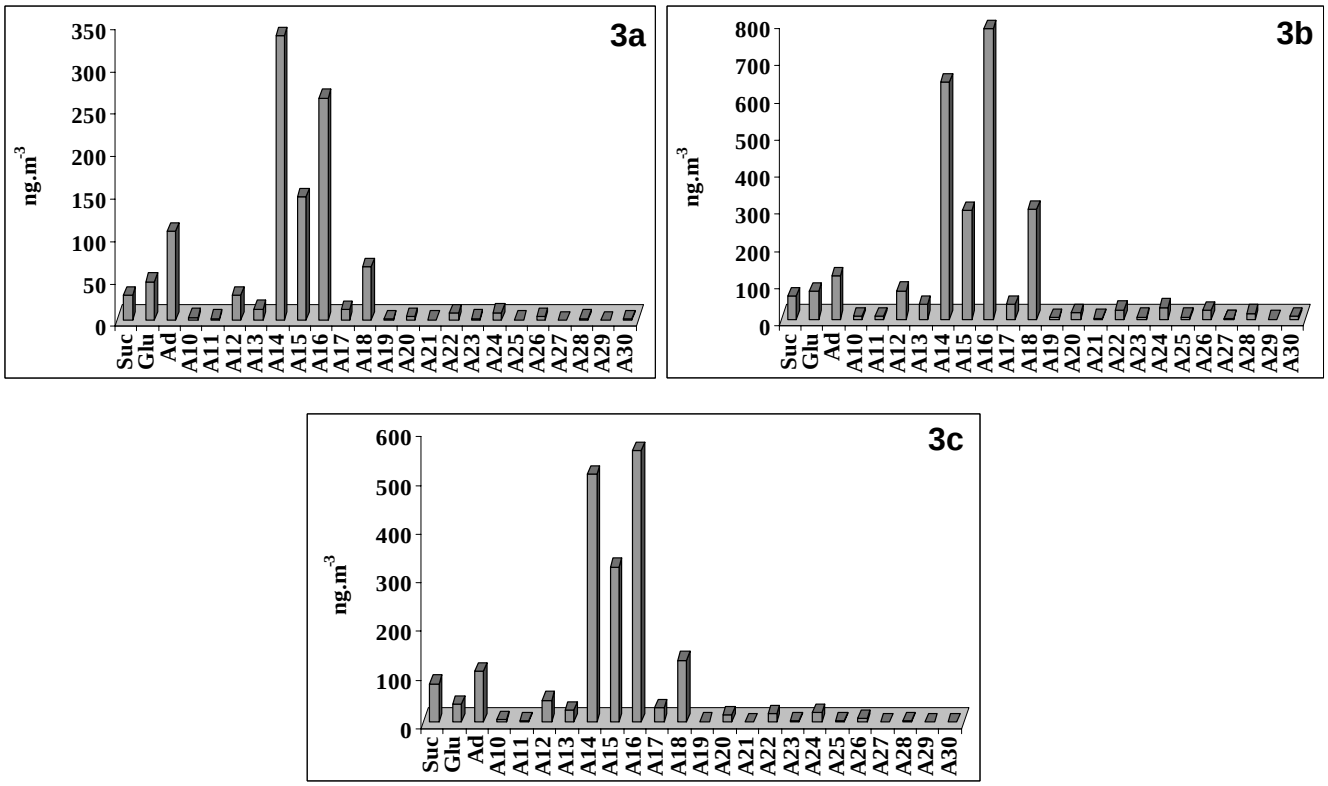


Fig.2. Distribution n-alkanes sources

2/ n-Alkanoic and dicarboxylic acids results (Fig.3a-3c)



2-1/ n-Alkanoic and dicarboxylic acids sources :

- $<C_6 \sim C_{18}$: food cooking
- C_9, C_{11} : partly photochemically originated
- $C_{16} \sim C_{18}$: mixed anthropic sources (e.g. vehicles)
- $> C_{18}$: overall coming out from natural sources :
  - $C_{20} \sim C_{26}$: bacteria, micro-organisms
  - $C_{26} \sim C_{32}$: high plants

2-2/ n-Alkanoic and dicarboxylic acids diagnostic ratios (Table 2 & 3)

Table 2: Fatty acid indexes typical of various sources

Sampling sites	*Petrol*	*Bacteria, Algae*	*High plants*	*Antrhro. emissions*
Cmax	16 + 18	20, 22, 24	28, 30, 32	<20 (16)
I_{30}	<<1	<1	>>1	<<1

$$I_{30} = A_{30}/A_{24}$$

Table 3: Fatty acid indexes in sites sampling

Sampling sites	BZ	RB	OM
Cmax	16 + 18	16 + 18	16 + 18
I_{30}	<< 1	<< 1	<< 1

By looking the Table 2 and 3, we attribute the petrol source (e.g. vehicular emissions) as origin of n-alkanoic acids. As regards dicarboxylic acids, their emission sources is mainly photochemistry.

3/ PAHs results (Fig.4a-4c)

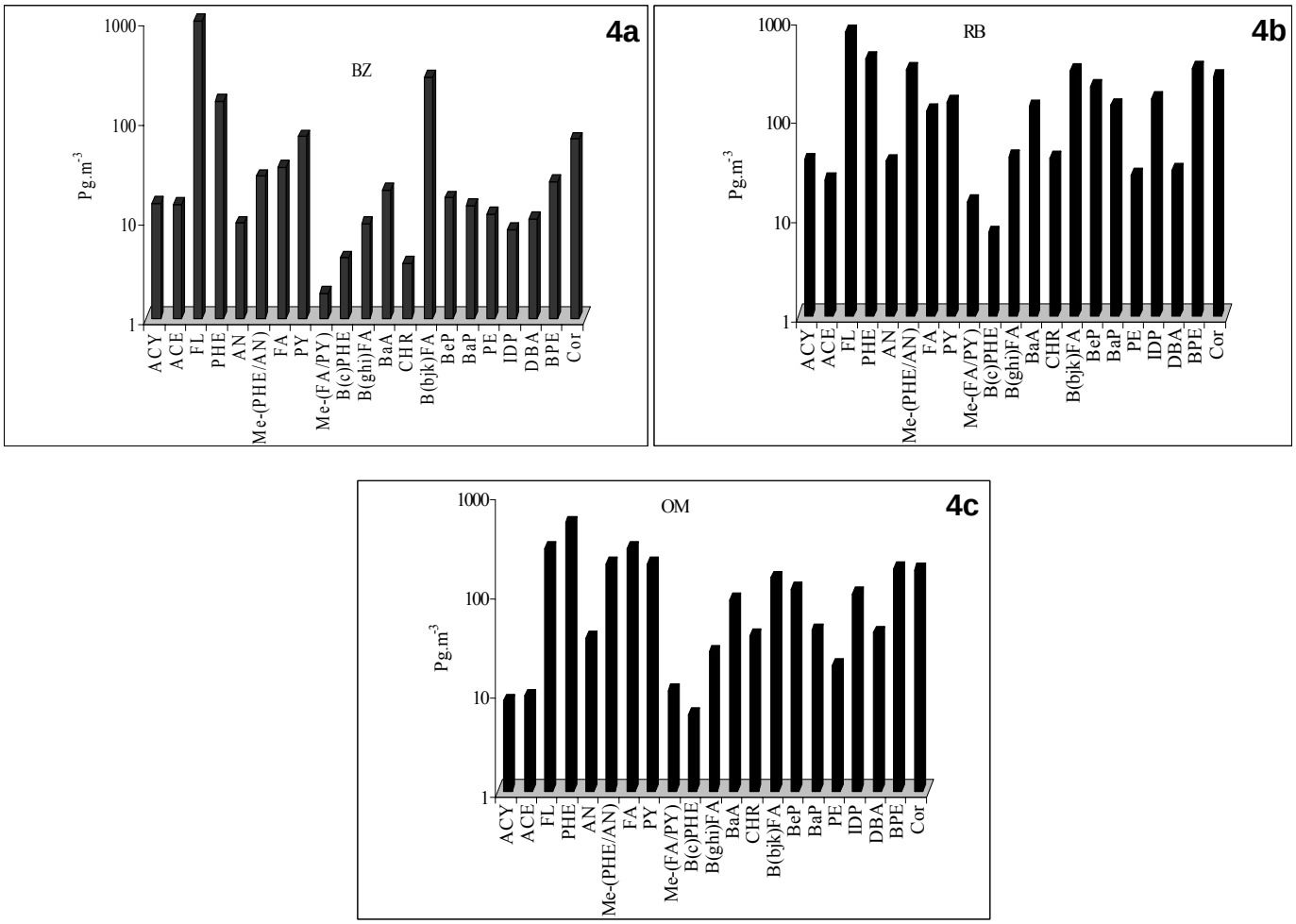


Fig.4. Distribution profiles of PAHs concentrations recorded in; 4a: Bouzeraeh, 4b: Rouiba, 4c: Ouled Moussa

3-1/ PAHs chemical structures : (Fig.5a-5c)

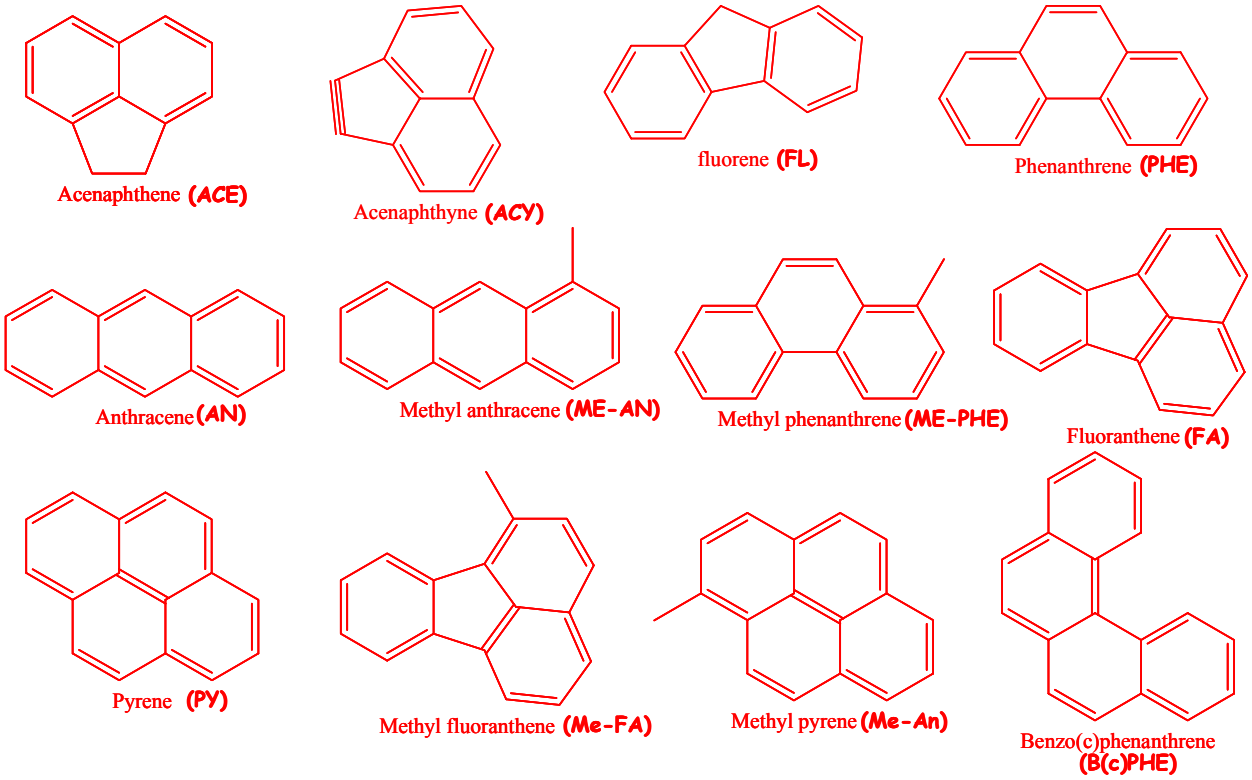


Fig.5a. PAHs chemical structure comprise three and four rings

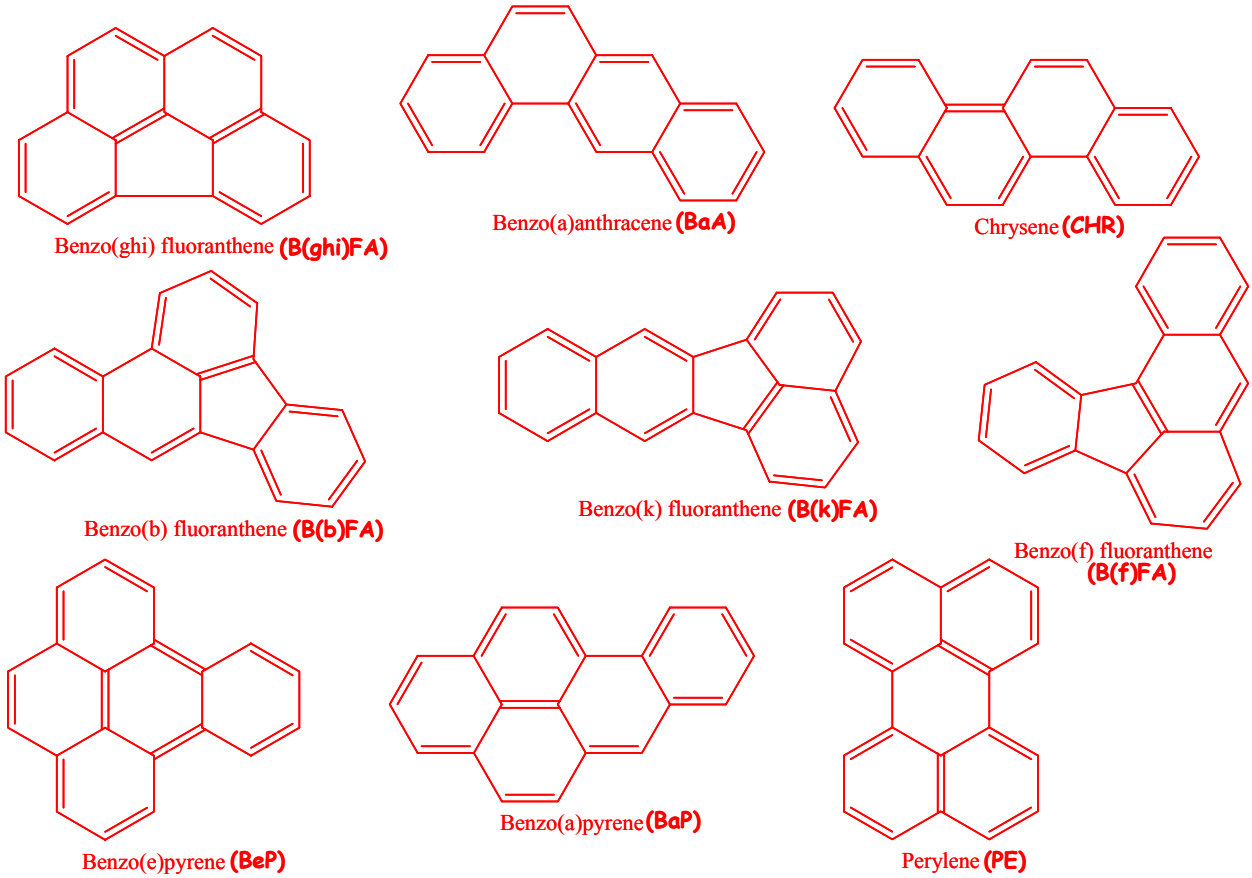


Fig.5b. PAHs chemical structure comprise four and five rings

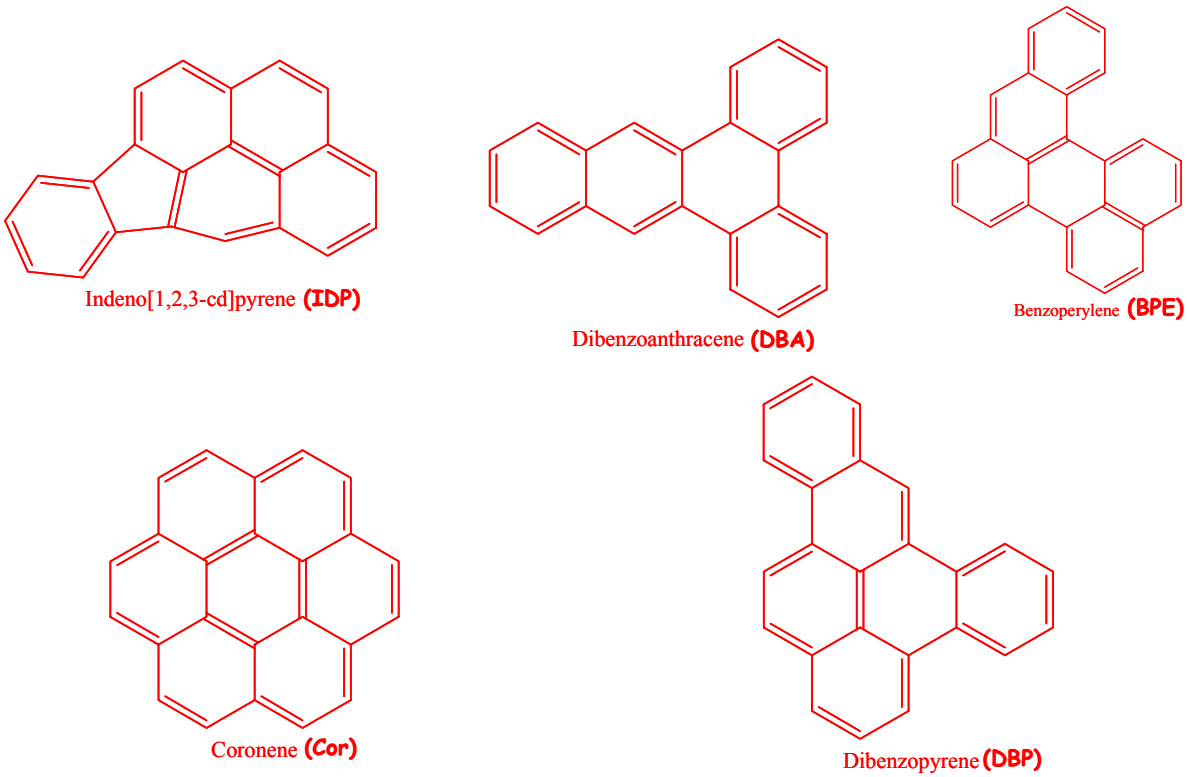


Fig.5c. PAHs chemical structure comprise five, six and seven rings

<u>3-2/ PAHs diagnostic ratios</u>: Table 4

Table 4: Concentrations ratios between PAH

	Typical ratios	Ratios for aerosols sites				Interpretation
		BZ	RB	OM	CH	
IPY/IPY+BPE	0.18-040 (vehicular emissions) 0.56 (coal soot) 0.62 (wood burning)	0.25	0.33	0.36	0.36	Indicates vehicular emission sources
BePY/BePY+ BaPY	≥ 0.47	0.55	0.61	0.72	0.69	Reflects pyrolytic emissions; characteristic of a faster decay of BaP, indicating an origin from distant source
FA/FA+PY	≥ 0.4	0.33	0.5	0.59	0.60	Approaches the ratios reported for vehicular emissions
0.41≤CPAH/TPAH	≤ 0.49	0.25	0.45	0.47	0.32	Indicates PAH with urban origin, especially emitted from catalytic automobiles

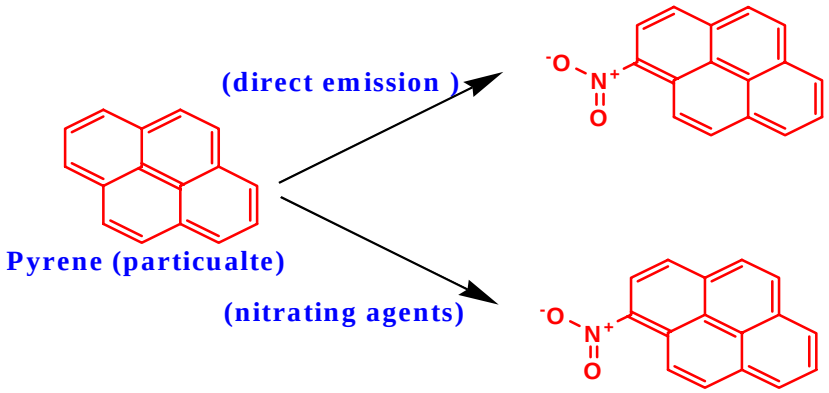
The diagnostic ratio of PAHs indicates, mixed emissions sources: vehicular emissions and pyrolytics.

4/ NPAHs results : (Table 5)

Table 5: Average NPAHs concentration (pg.m^{-3}) recorded in: BZ, RB, OM

Sampling sites	BZ	RB	OM	CH
1-NNAP	67.7	1.68	n.d	1.3
2-NNAP	131	<1	1.19	0.64
2-NFL	13	2.23	n.d	2.48
9-NANT	6.1	22.42	5.73	0.33
9-NPHE	2.2	2.04	2.46	0.74
1-NPHE	14.5	6.48	1.93	0.76
3-NPHE	n.d	2.07	3.46	0.69
2-NPHE	1.5	n.d	1.08	0.45
1-NFA	n.d	3.51	4.01	1.35
7-NFA	5.4	1.03	n.d	n.d
2-NFA	17.2	4,54	n.d	2.06
3-NFA	2.5	3.31	<1	1.18
4-NPY	10,9	1,64	1,71	1.27
8-NFA	2,3	2,29	8,82	1,36
1-NPY	6,2	25.97	11.99	2.73
2-NPY	n.d	22.27	125.19	2.18
TOTAL	281	101	169	20

4-1/ Primary and secondary sources of NPAHs: Fig.6a-6b



6a

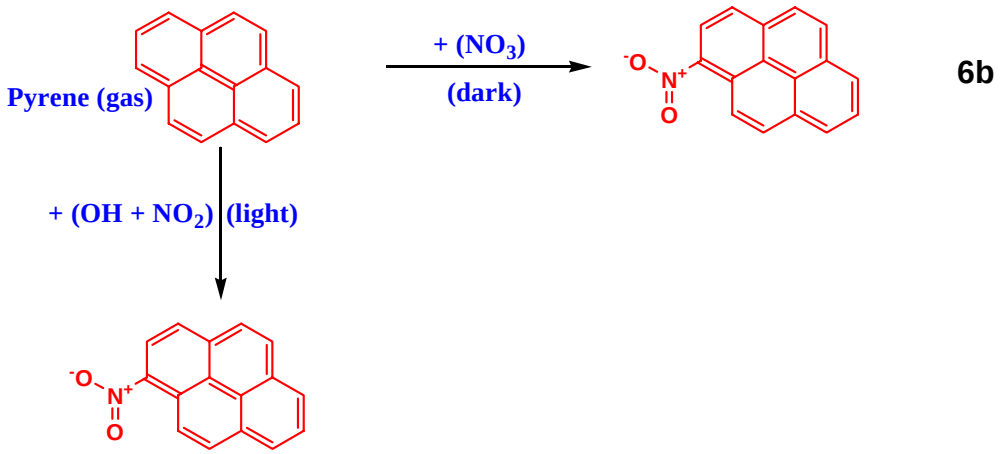


Fig.6. formation of nitropyrene ; 6a Primary source, 6b: secondary source

4-2/ NPAHs chemical structures: (Fig.7)

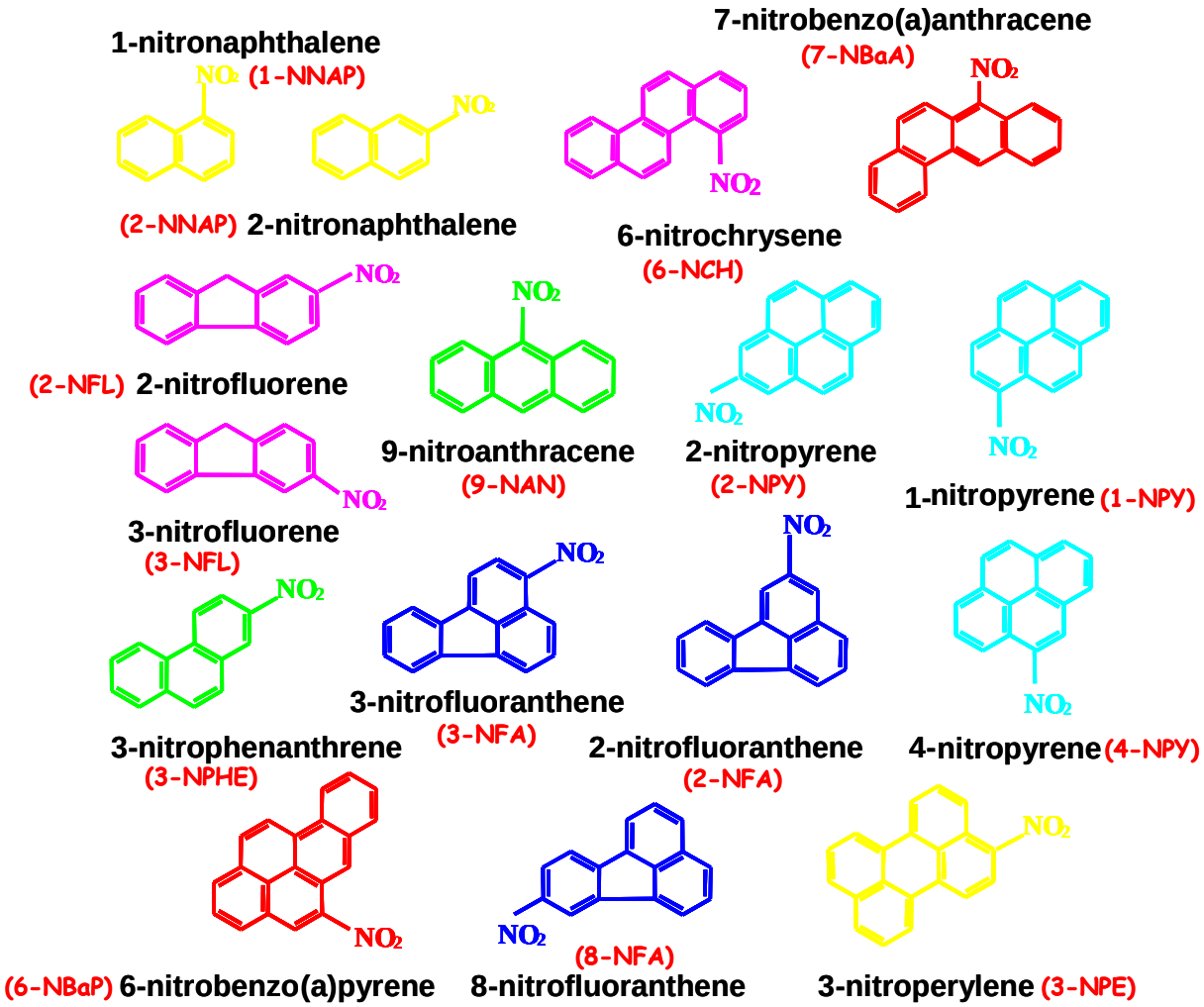


Fig.7. NPAHs chemical structures

4-3/ NPAHs diagnostic ratios: Table 6 &7

Table 6: Ratios of NPAHs of samples collected

Sampling sites	2-NFA	3-NFA	1-NPY	2-NPY	R_1	R_2	R_3
BZ	17.2	2.5	6.2	n.d	0.36	n.d	2.48
RB	4.54	3.33	25.97	22.27	5.72	4.90	7.8
OM	n.d	<1	11.99	125,19	n.d	n.d	>>1

R_1 = [1-NPY]/[2-NFA], R_2 = [2-NPY]/[2-NFA], R_3 = [1-NPY]/[3-NFA]

Table 7: Typical rates of Nitro-PAH ratios observed for emission and atmospheric particulates

N-PAH index	***diesel vehicles***	***gasoline cars***	***stationary sources***	***daytime chemistry***	***nighttime chemistry***
[1-NPY]/[2-NFA]	**>> 1**	***n.v.***	***n.v.***	***~ 0***	***~ 0***
[2-NPY]/[2-NFA]	***n.v.***	***n.v.***	***n.v.***	***~100***	***~10***
[1-NPY]/[3-NFA]	**>> 1**	***< 1***	***≥ 1***	***n.v.***	***n.v.***

NPAHs sources are attributed for:

BZ site :

R_1 : daytimes and nighttimes chemistry

R_3 : stationary sources

RB site :

R1 and R3 : diesel vehicles

R2 : nighttimes chemistry

OM site:

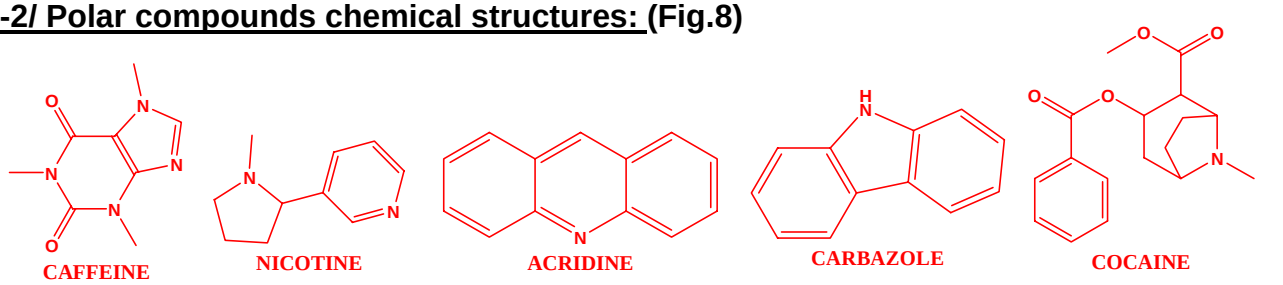
R3 : diesel vehicles

5/ Polar Compounds results : Table 8

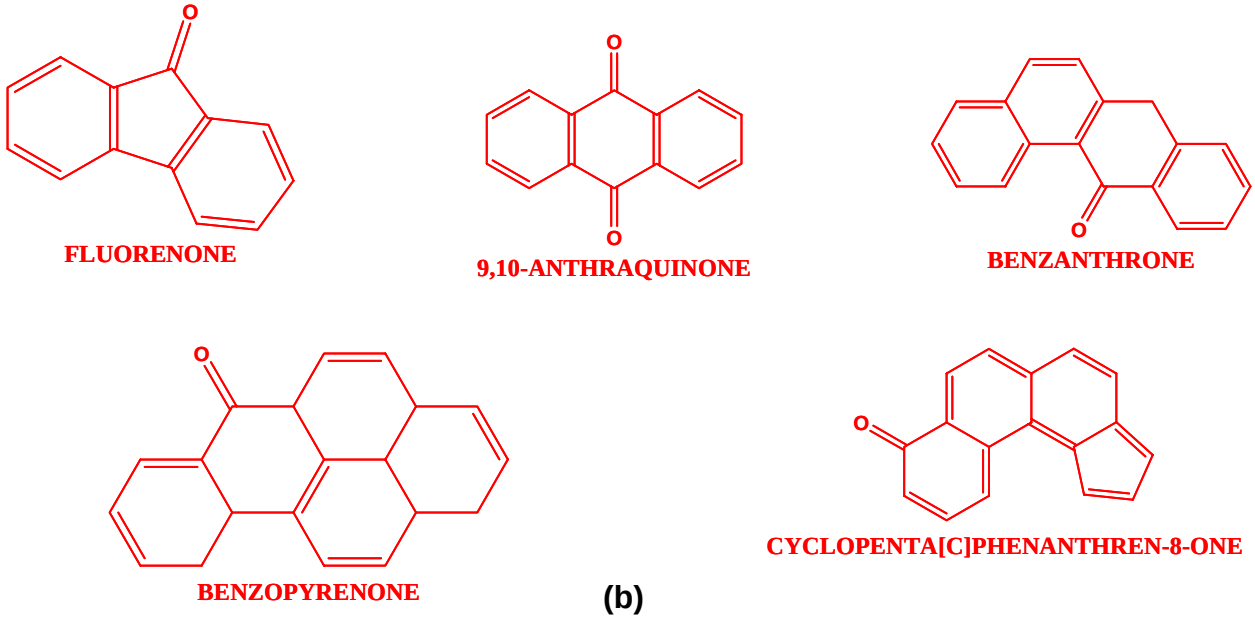
Table 8: Average High Polar concentration (ng.m^{-3}) recorded in: BZ, RB and OM

Sampling sites	BZ	RB	OM
nicotine	30.84	175.99	268.05
acridine	0.13	0.66	2.06
fluorenone	4.19	2.93	11.36
carbazole	0.31	1.19	4.22
caffeine	42.16	203.39	4149.06
9,10-anthraquinone	3.38	10.29	23.80
cyclopentaphenantrenone	0.08	0.19	2.53
cocaïne	n.d	n.d	n.d
benzanthrone	1.36	14.06	10.58
benpyrenone	n.d	n.d	n.d

4-2/ Polar compounds chemical structures: (Fig.8)



(a)



(b)

Fig.8. Polar compounds chemical structures; 8a: Heterocyclic compounds, 8b: PAHs oxygenated (Oxy-PAHs)

PARTICULATE MATTER COMPOSITION: Fig 9a-9c

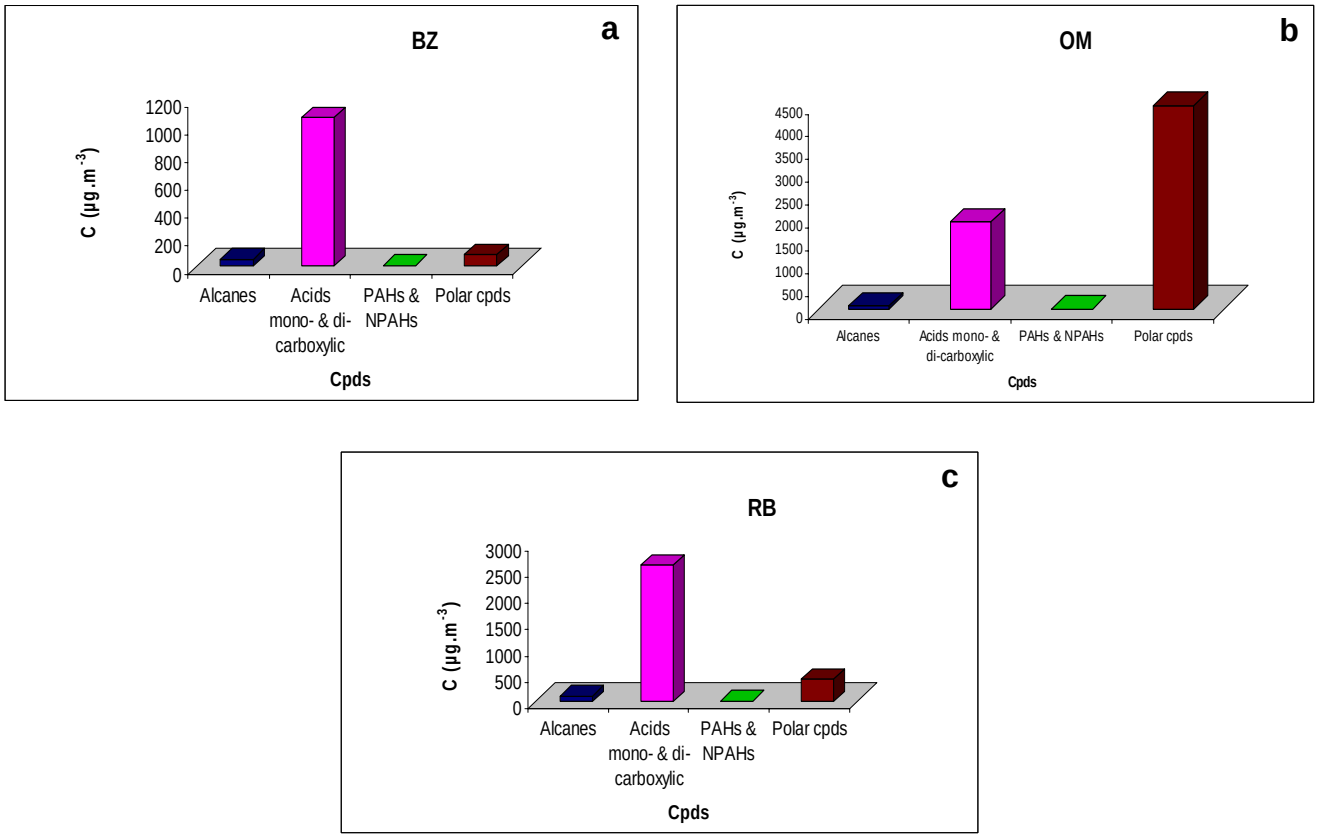


Fig.9. Composition of particulate matter; 9a: Bouzereah, 9b: Rouiba, 9c: ouled moussa

CONCLUSION

The exam of diagnostic ratios of alkanes showed that a predominance of anthropic sources in addition to minor contribution of biogenic sources in all investigated locations. n-Alkanoic and dicarboxylic acids were major class compounds of organic particles in Bouzereah and Rouiba, while the polar compounds were the important species of organic particles in Ouled Moussa.

PAHs and NPAHs were usually present at low concentrations in all locations. The reactive PAH, such as benzo[a]pyrene, seemed to be unable to be driven over long distances through the atmosphere, before being decomposed.

Due to the small concentrations reached by PAHs and NPHs they did not seem to contribute to the whole carcinogenicity/mutagenicity of organic aerosols in all locations.

Nicotine and caffeine can be used as tracers for tobacco smoke and cooking respectively.

The Benzopyrenone and Cocaine are not detected in all locations. In contrast Cecinato et al., have detected Cocaine in the air for the first time at the Italian sites Rome and Taranto, where its concentrations sometimes exceeded 100 pg m^{-3}.