

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

Y. Moussaoui, R. Ladj, N. Yassaa, C. Balducci A. Cecinato and B. Y. Meklati

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THE ATMOSPHERIC PARTICULATE

The atmospheric particulate have a very complex composition including inorganic species, elemental carbon as well as thousands of carbon containing compounds.

These latter are defined as “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 the presence of light and oxidants;
3. Dilution and transport of air masses by winds and boundary layer evolution.

Organics Pollutants Sources

Anthropic

Food Cooking



Traffic



Combustion



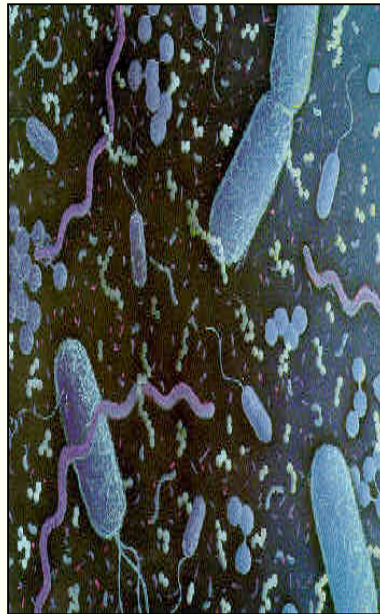
Organics Pollutants Sources

Natural

Plants



Bacteria



Fungi



Particulate Organic Matter composition

Basic Compounds

aza-heterocyclic
amines

Neutral compounds

aliphatic

alkanes, alkenes
alcohols
aldehydes and
ketones
esters
nitriles

aromatic

polycyclic aromatic
hydrocarbons (PAH)
Nitro-PAH
Oxygenated and
sulphurated
phthalates and
esters
halogenated
(PCB, PCDD/F)

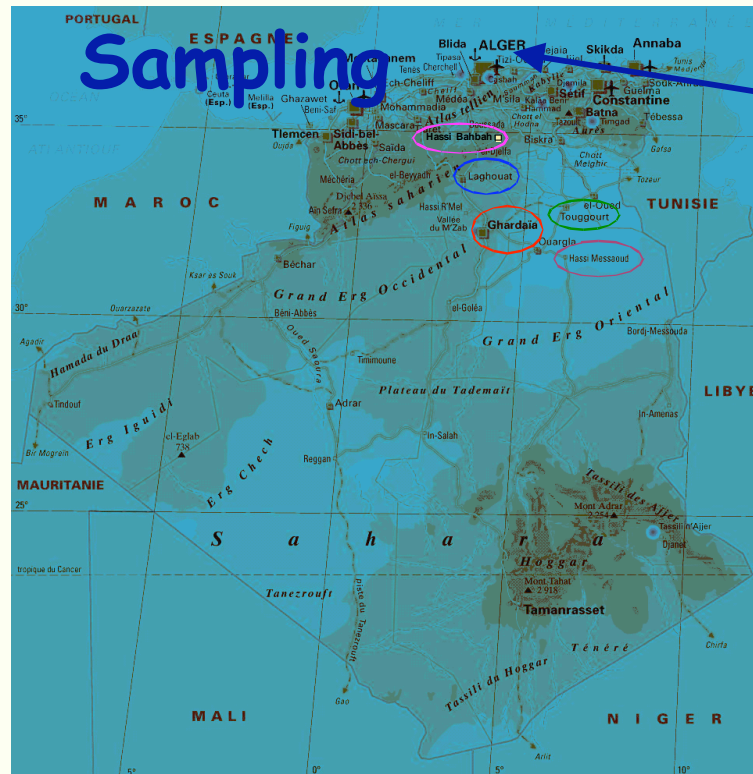
Acid compounds

aliphatic

monocarboxylic
Dicarboxylic
phosphonic and
sulphonic acids

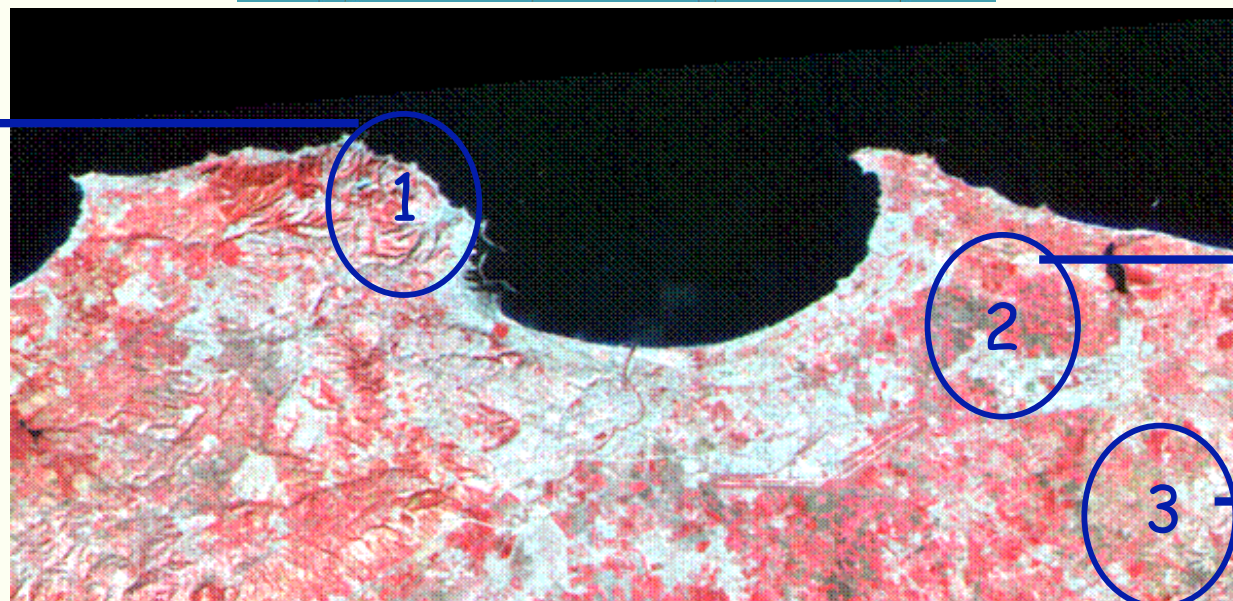
aromatic

phenols,
nitrophenols
Phthalic acids
Polycarboxylic acids



Algiers

Bouzerah
(BZ)



Rouiba
(RB)

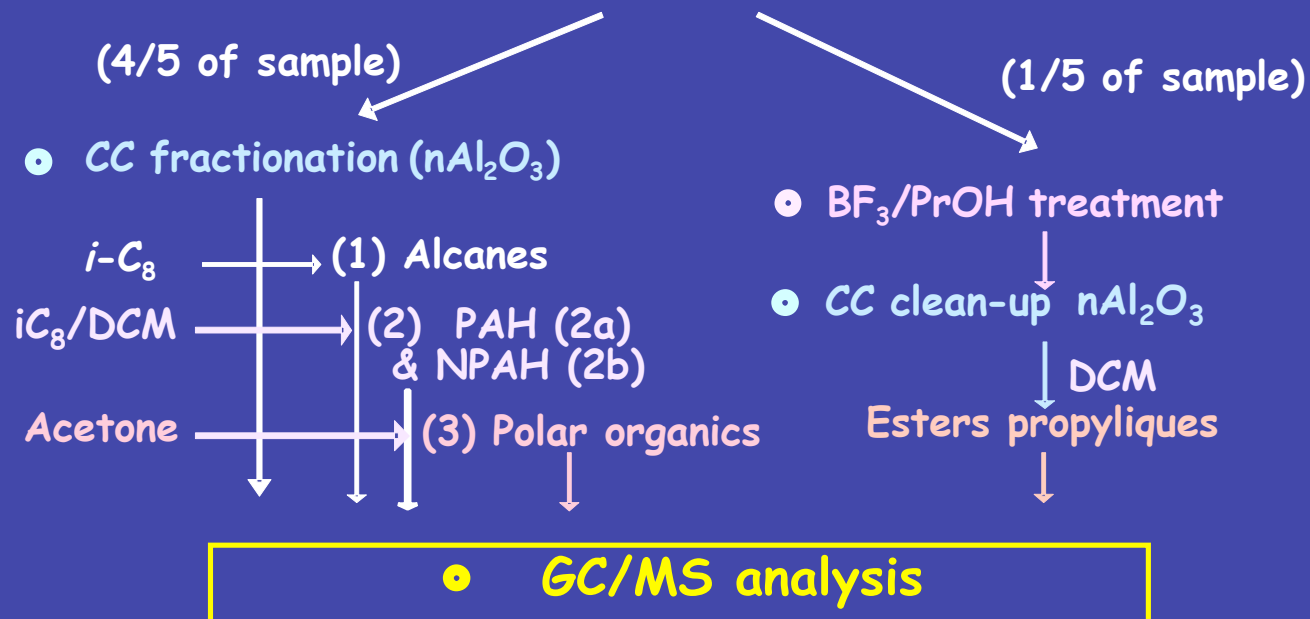
Ouled Moussa
(OM)

Airborne Aerosols Sampling

The sampling was carried in July-August period 2006, samples of particulate were collected by enriching 24 m³ of air onto Glass fiber filter inert membrane (47 mm o.d., 1 μm pore size). A medium volume aspirating pump (1 m³/h) was used for this purpose. It was equipped with a size selective inlet, and a volume counter for measuring the air passed through the filter. The particle-loaded filters were directly kept in dichloromethane solution to prevent any degradation and then stored at low temperature until chemical characterization.

Sample Extraction, Clean-up and Analysis

- Size-ruled sample collection
- Sample weighting and pooling (when required)
- Internal standard spiking (isotopically labelled cpds)
- Solvent extraction (ASE or soxhlet)



Sample Extraction, Clean-up and Analysis

n-Alkanes, n-alkanoic 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.

Sample Extraction, Clean-up and Analysis

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

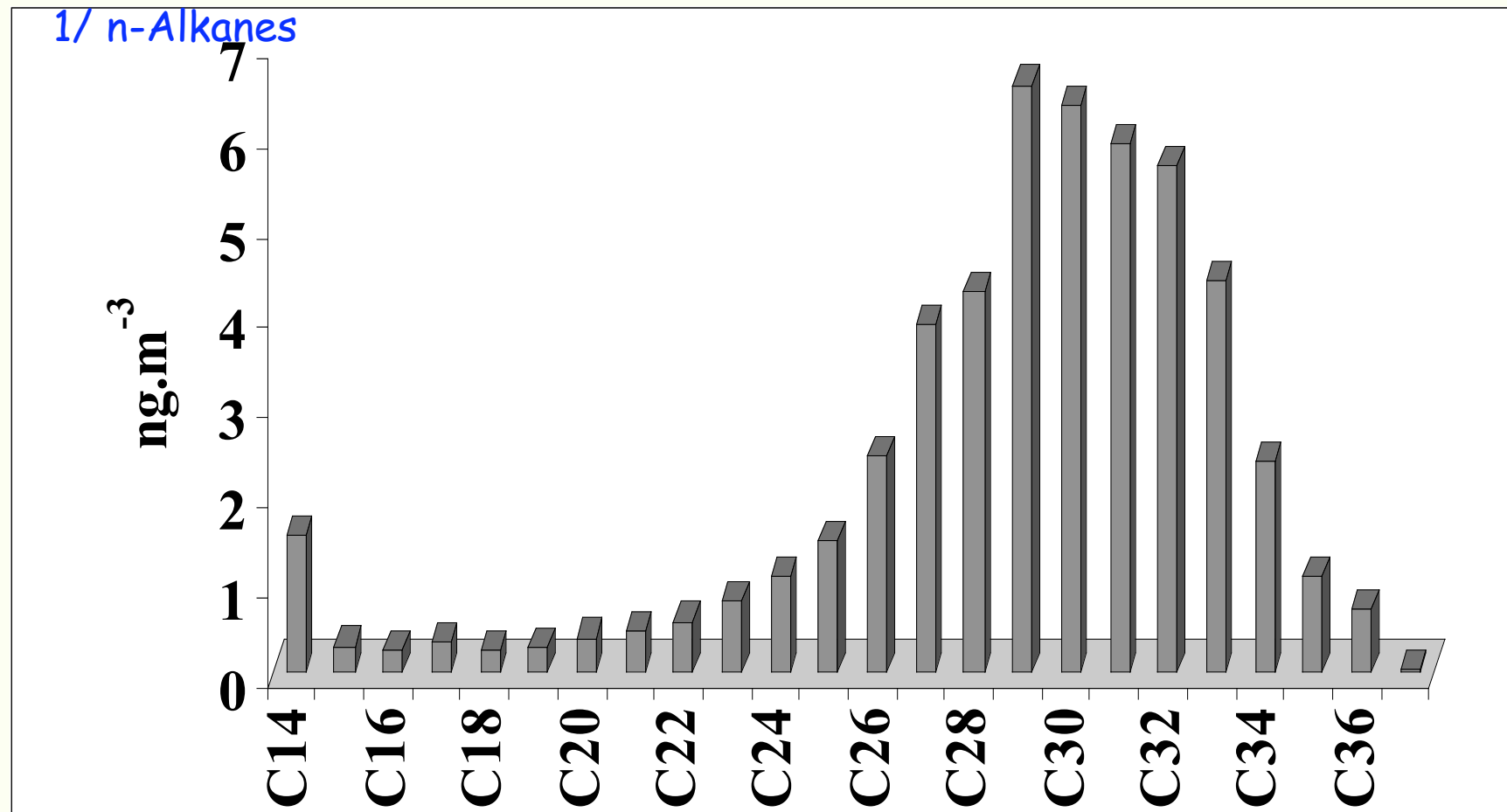


Fig. 1a. Distribution profiles of n-alkane concentrations recorded in Bouzereah

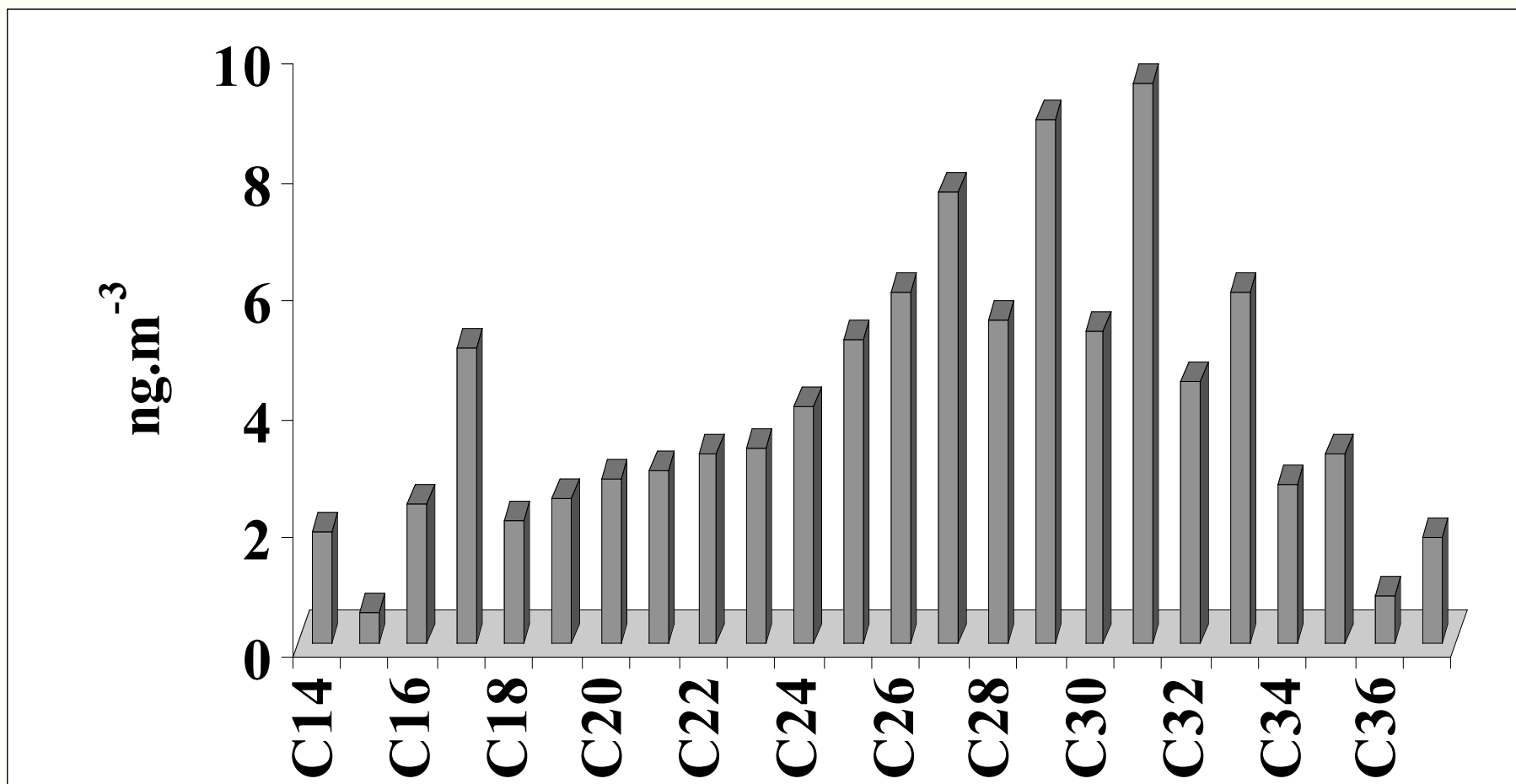


Fig.1b. Distribution profiles of n-alkane concentrations recorded in Rouiba

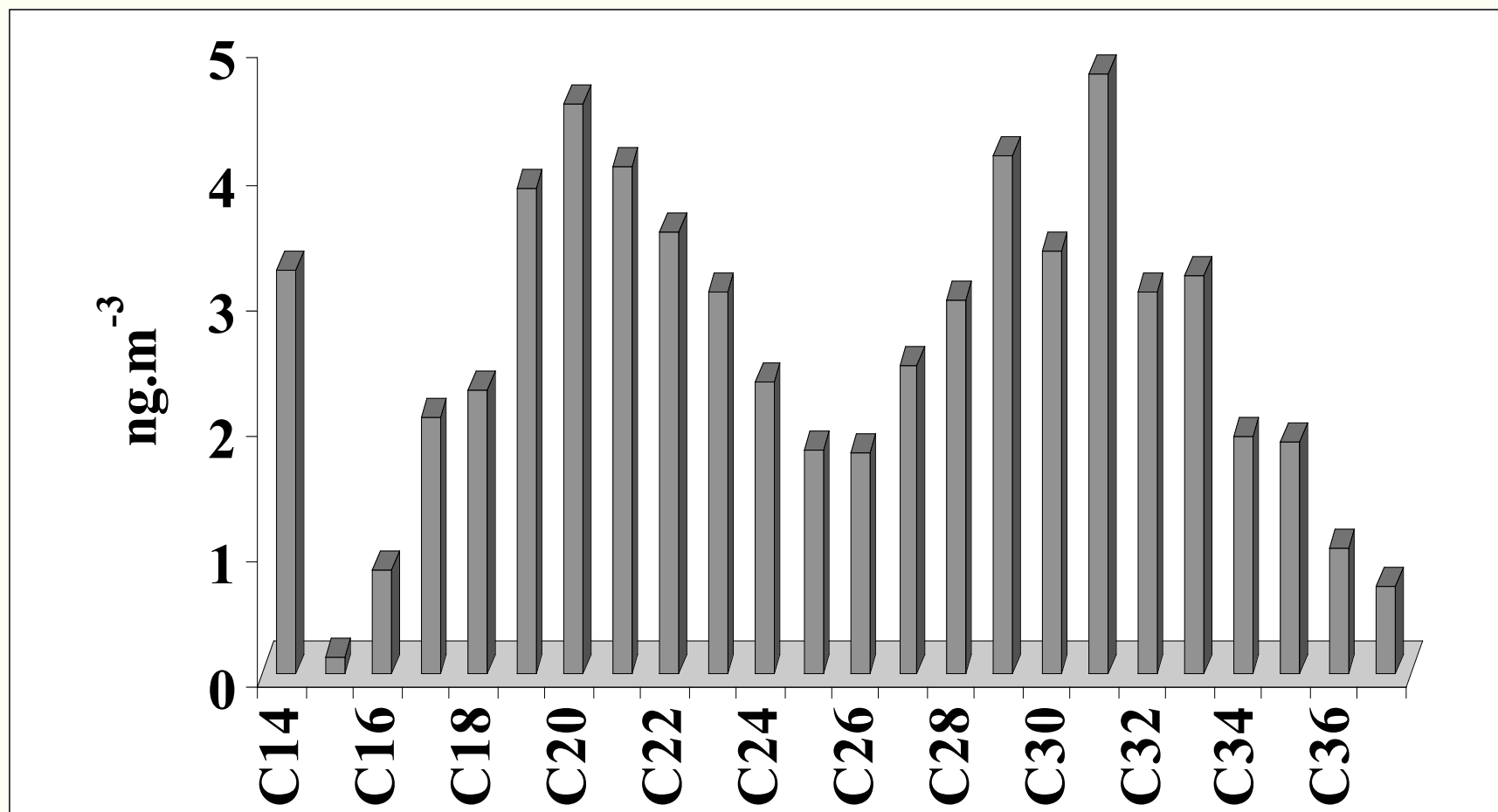


Fig 1c. Distribution profiles of n-alkanes concentrations recorded in Ouled Moussa

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

Sampling sites	BZ	RB	OM
^a CPI ₁	0.99	1.38	1.04
^b CPI ₂	0.85	1.19	0.89
^c CPI ₃	1.02	1.47	1.15
Cmax	C ₂₉	C ₂₉	C ₂₉
Pr/Ph	0.3	1.71	0.29
^d %wax C _n	10.8	22.2	15.5
Total	51.89	99.71	64.38

CPI: Carbon Preference Index

^a Whole range for n-alkanes: $CPI_1 = \sum (C_{15} - C_{37}) / (C_{14} - C_{36})$

^b Petrogenic n-alkanes: $CPI_2 = \sum (C_{15} - C_{25}) / (C_{14} - C_{24})$

^c Biogenic n-alkanes: $CPI_3 = \sum (C_{25} - C_{37}) / (C_{24} - C_{36})$

Cmax: Carbon number with the highest peak in the chromatogram

Pr: Pristane, Ph: Phytane

^d %wax C_n = $\sum (C_n - 0.5(C_{n-1} + C_{n+1})) / \sum C_n \times 100\%$.

An odd carbon number predominance was found at all 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.

$CPI \approx 1$ indicates vehicular exhaust emissions

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

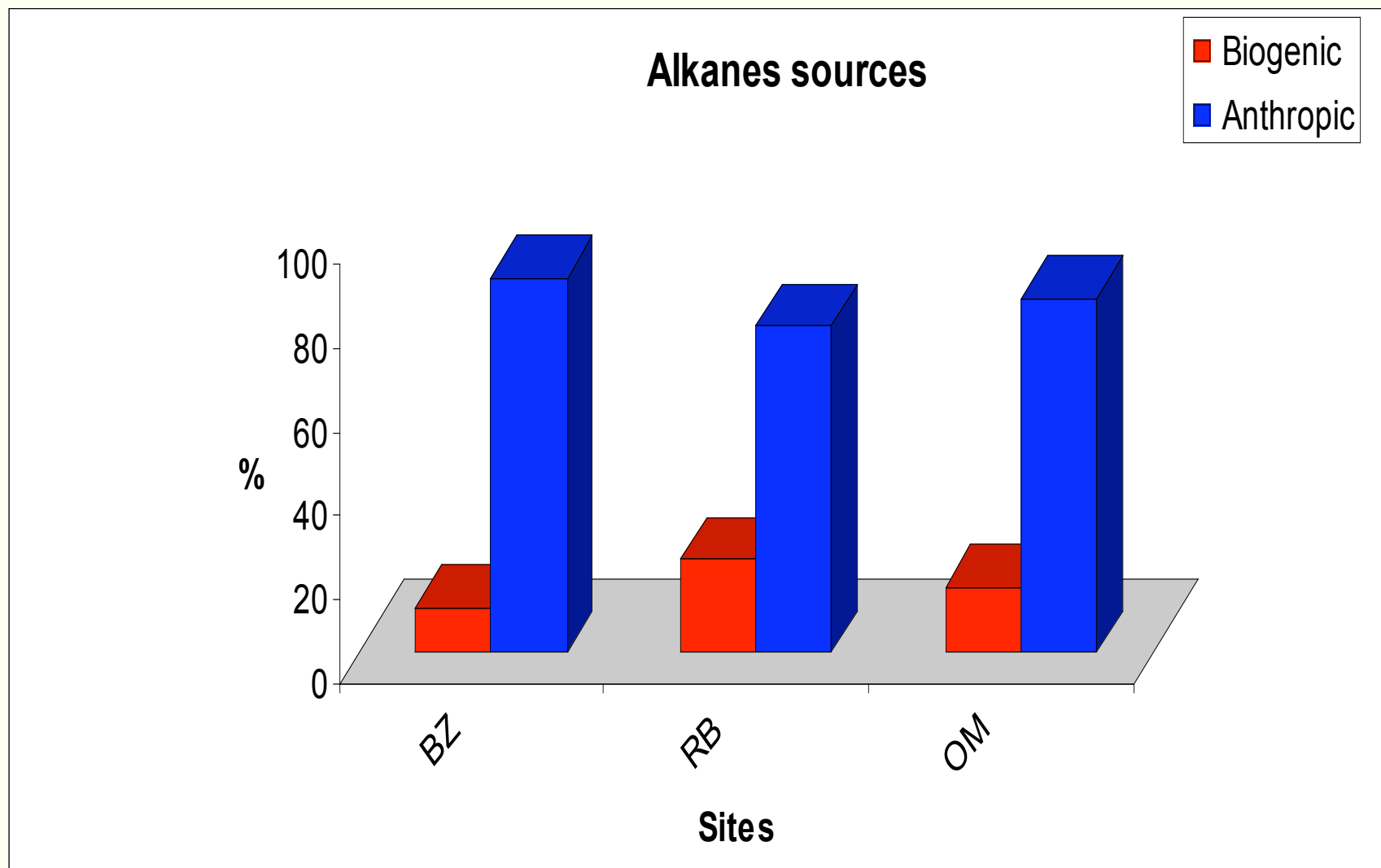


Fig 1d: Contribution of natural and anthropic sources from n-alkane emissions for all sites investigated

2/n-Alkanoic and dicarboxylic acids

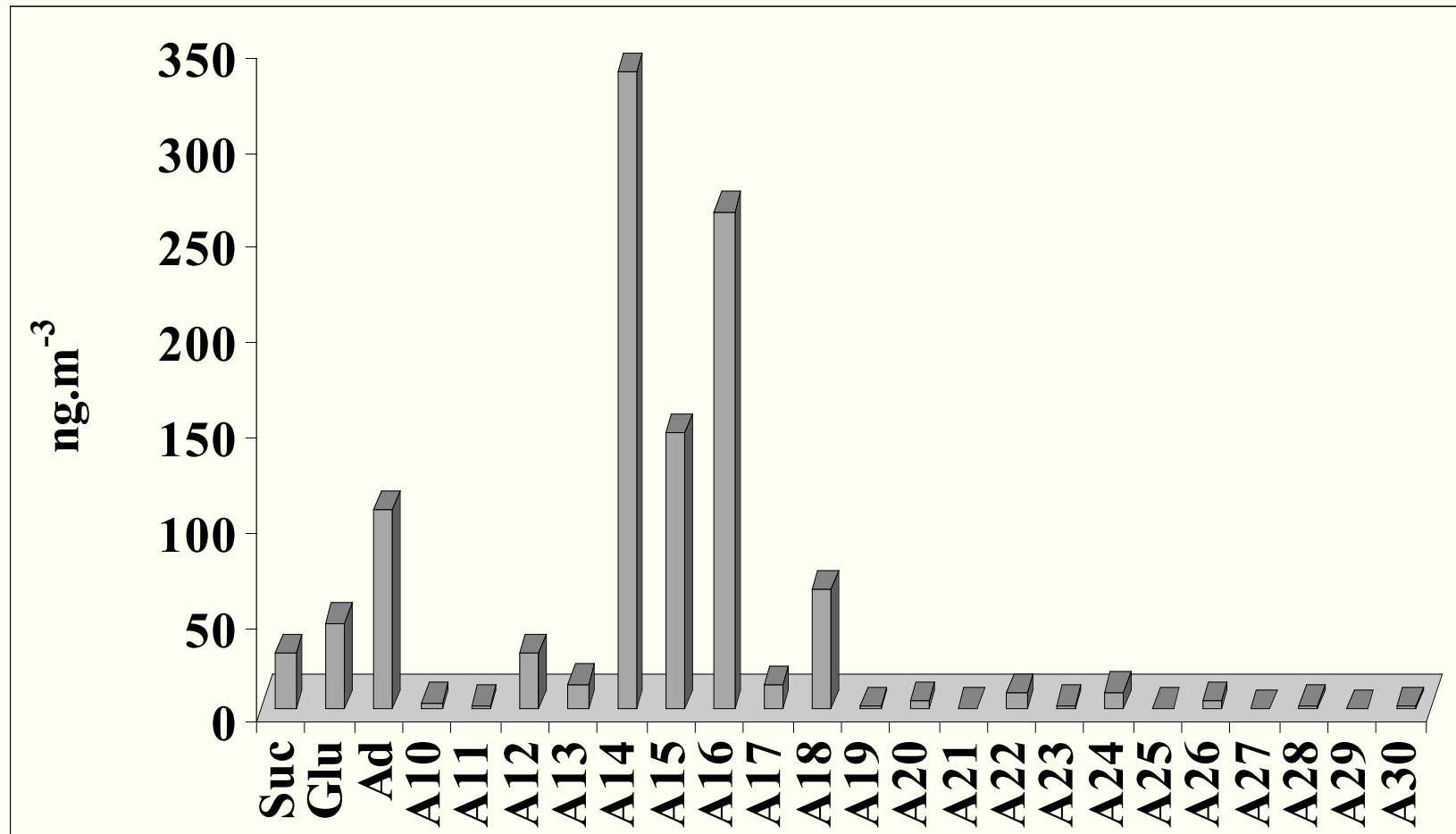


Fig.2a. Distribution profiles of n-alkanoic and dicarboxylic acids concentrations recorded in Bouzereah

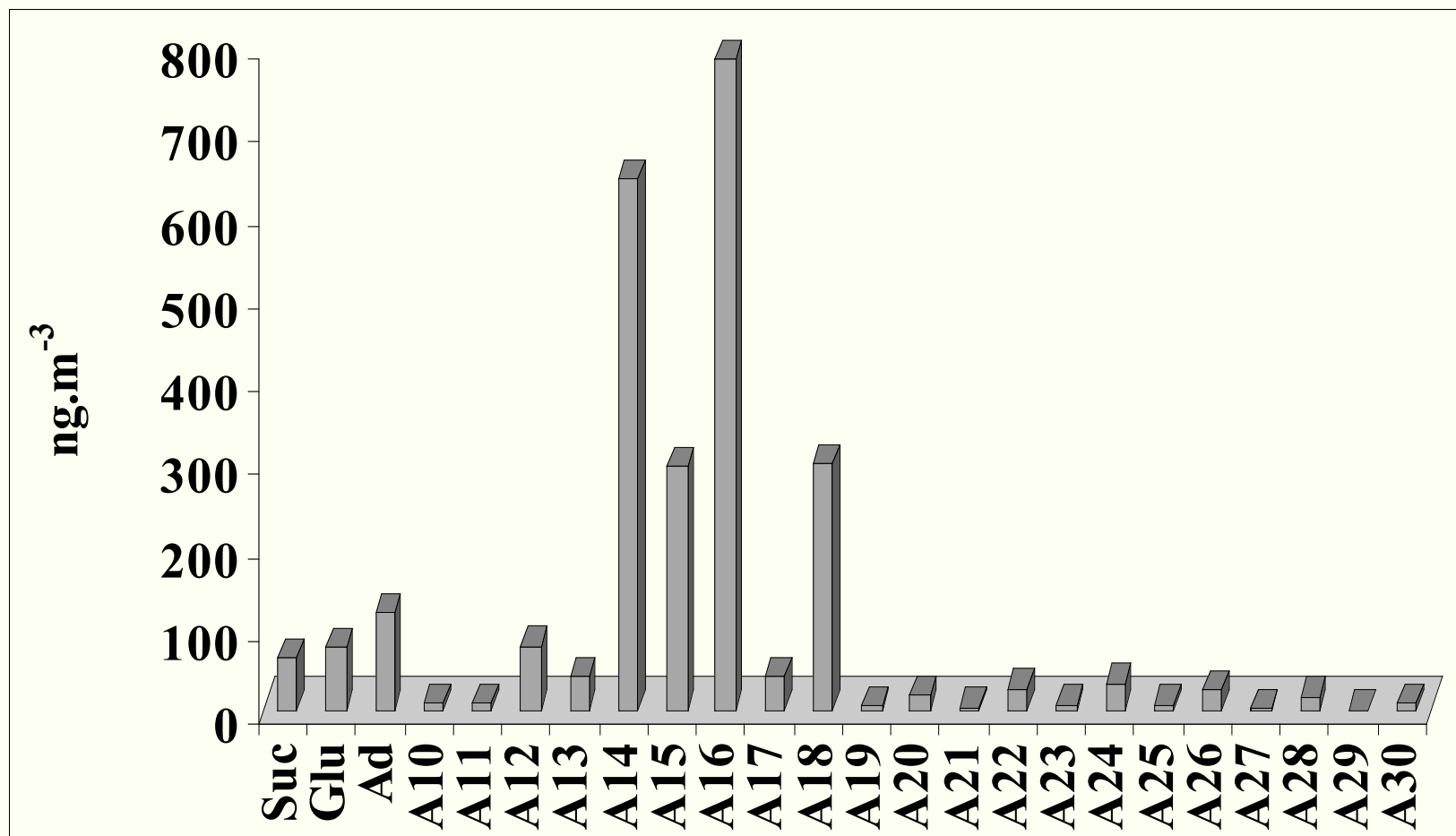


Fig.2b. Distribution profiles of n-alkanoic and dicarboxylic acids concentrations recorded in Rouiba

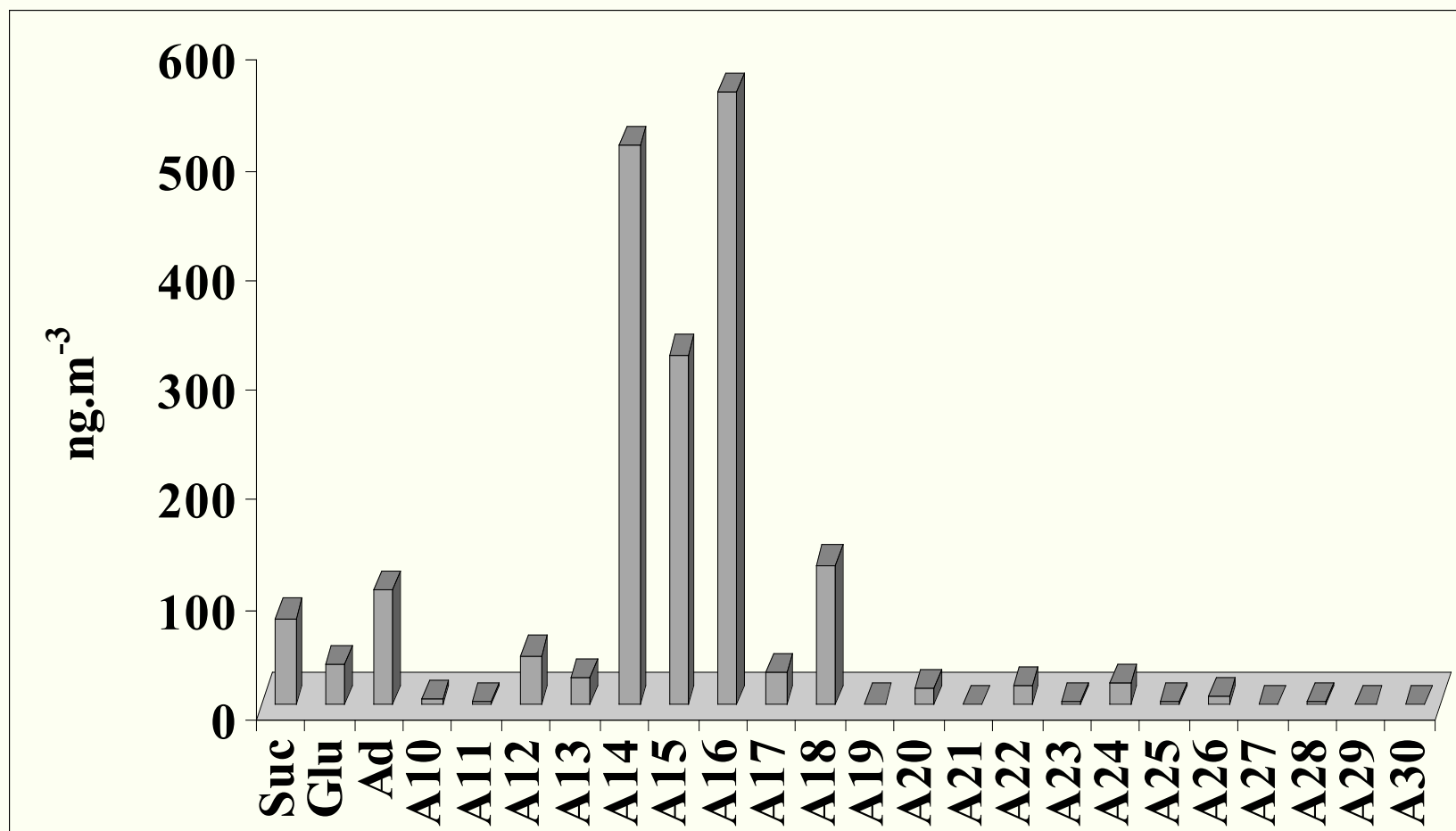


Fig.2c. Distribution profiles of n-alkanoic and dicarboxylic acids concentrations recorded in Ouled Moussa

Fatty acids sources

(*n*-alkyl, mono/dicarboxylic, saturated & unsaturated)

✱ $<C_6 \sim C_{18}$: 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

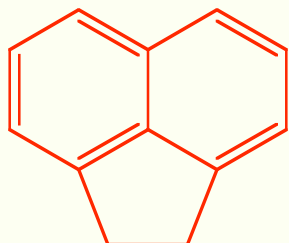
Fatty acid indexes typical of various sources

	<i>Petrol</i>	<i>Bacteria, algae</i>	<i>High plants</i>	<i>Anthrro. emissions</i>
C_{max}	16 + 18	20, 22, <u>24</u>	28, <u>30</u> , 32	<20 (16)
I_{30}	<<1	<1	>>1	<<1

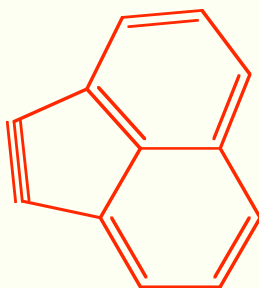
$$I_{30} = A_{30} / A_{24}$$

<i>Sampling sites</i>	<i>BZ</i>	<i>RB</i>	<i>OM</i>
C_{max}	16 + 18	16 + 18	16 + 18
I_{30}	<< 1	<< 1	<< 1

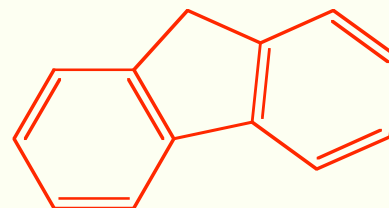
3/PAHs



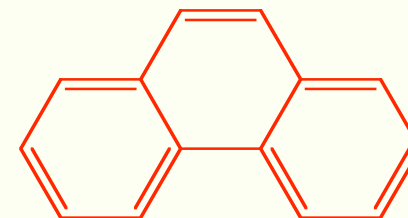
Acenaphthene (**ACE**)



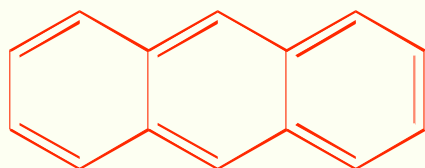
Acenaphthylene (**ACY**)



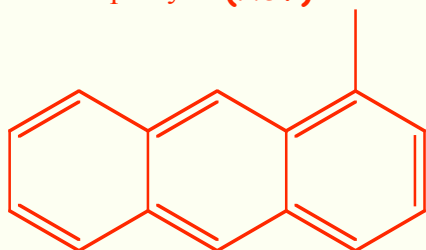
fluorene (**FL**)



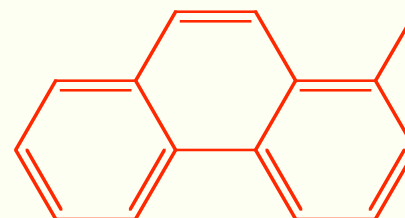
Phenanthrene (**PHE**)



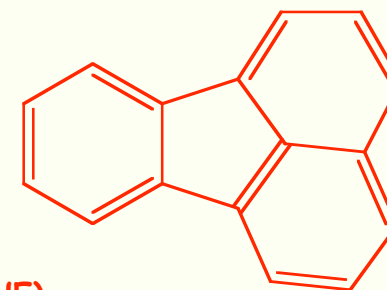
Anthracene (**AN**)



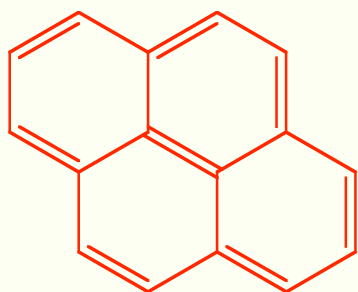
Methyl anthracene (**ME-AN**)



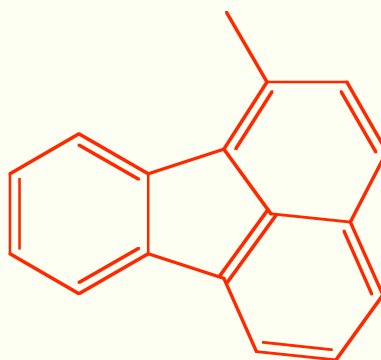
Methyl phenanthrene (**ME-PHE**)



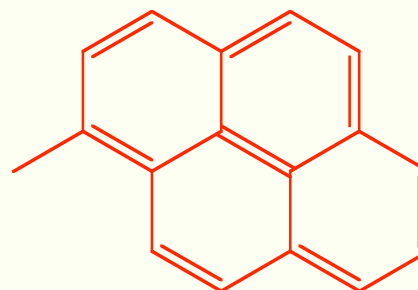
Fluoranthene (**FA**)



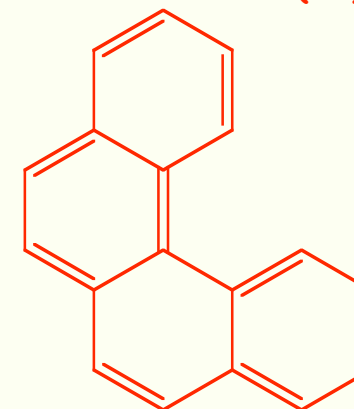
Pyrene (**PY**)



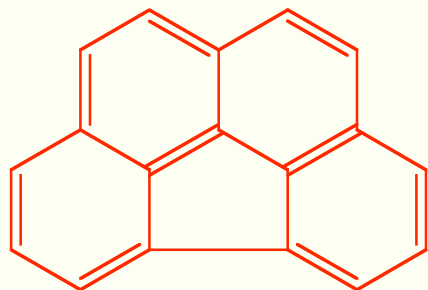
Methyl fluoranthene (**Me-FA**)



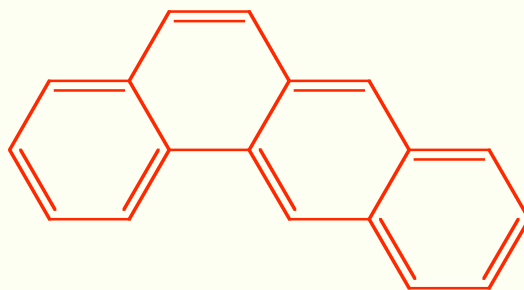
Methyl pyrene (**Me-An**)



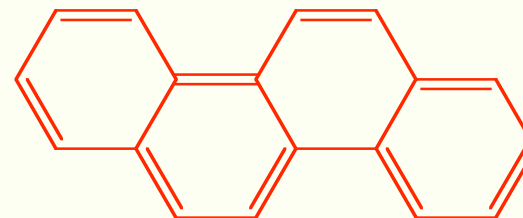
Benzo(c)phenanthrene
(**B(c)PHE**)



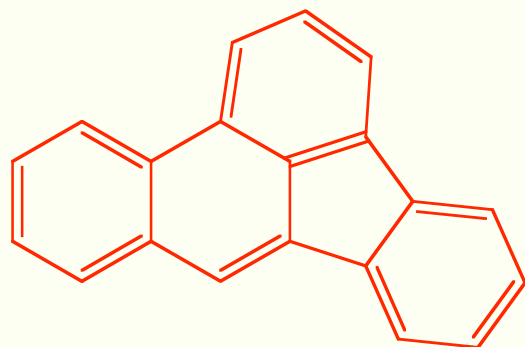
Benzo(ghi) fluoranthene (**B(ghi)FA**)



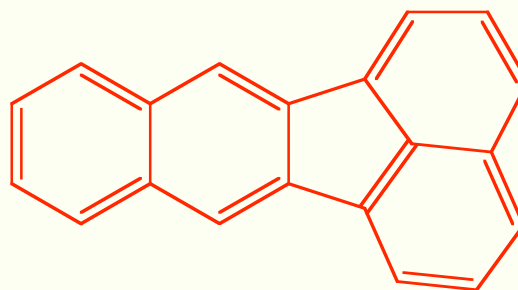
Benzo(a)anthracene (**BaA**)



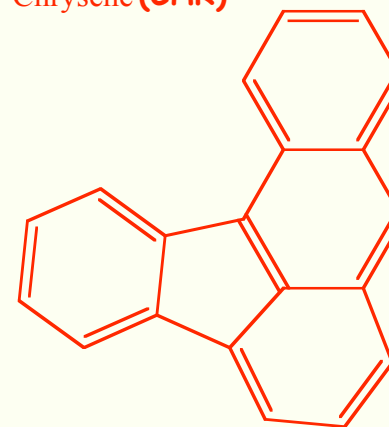
Chrysene (**CHR**)



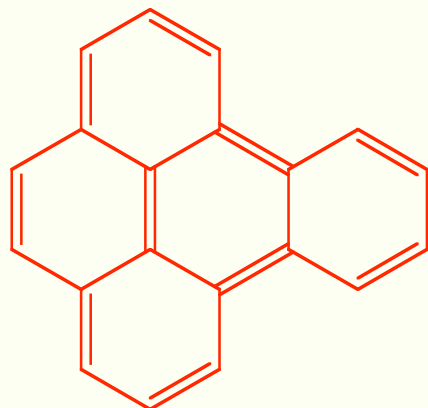
Benzo(b) fluoranthene (**B(b)FA**)



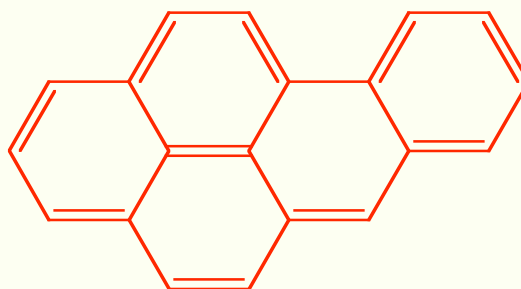
Benzo(k) fluoranthene (**B(k)FA**)



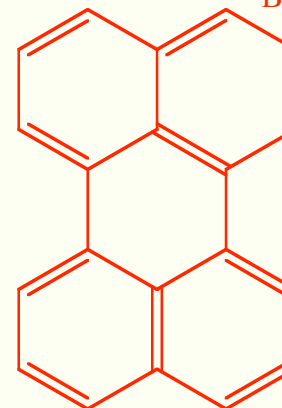
Benzo(f) fluoranthene (**B(f)FA**)



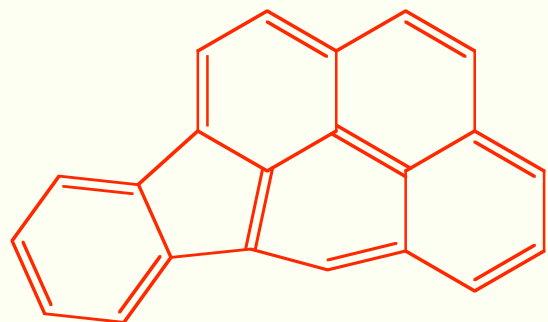
Benzo(e)pyrene (**BeP**)



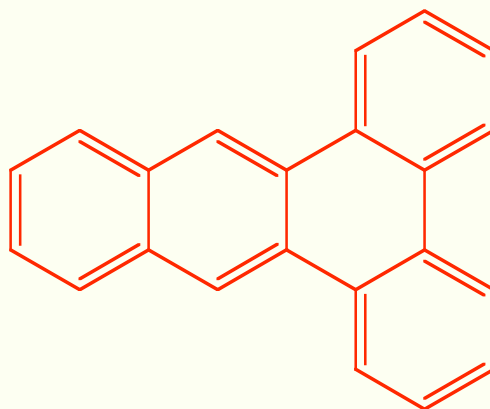
Benzo(a)pyrene (**BaP**)



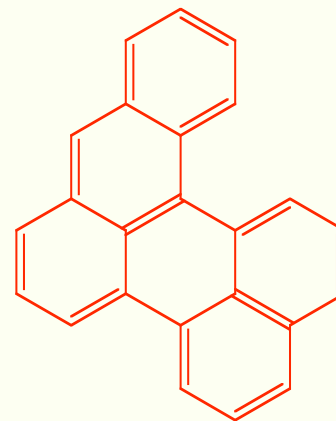
Perylene (**PE**)



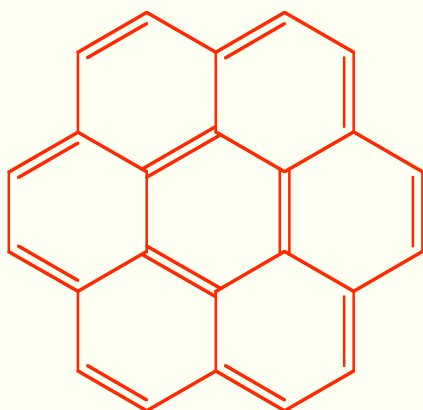
Indeno[1,2,3-cd]pyrene (**IDP**)



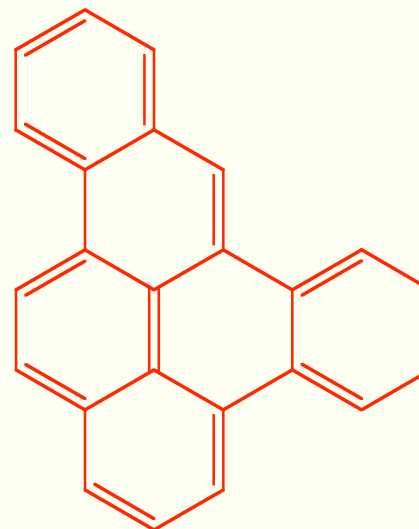
Dibenzoanthracene (**DBA**)



Benzoperylene (**BPE**)



Coronene (**Cor**)



Dibenzopyrene (**DBP**)

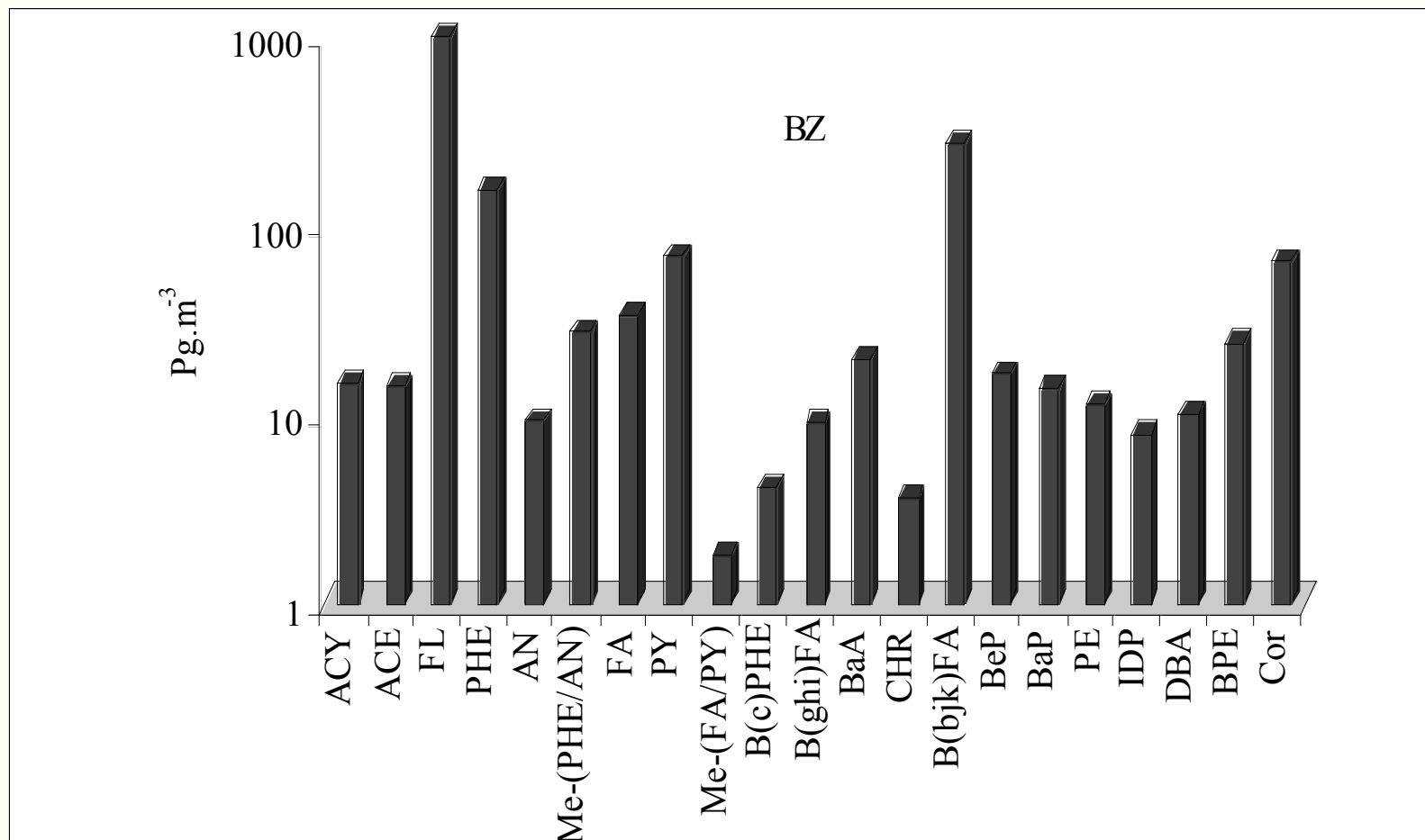


Fig.3a. Distribution profiles of PAHs concentrations recorded in Bouzereah

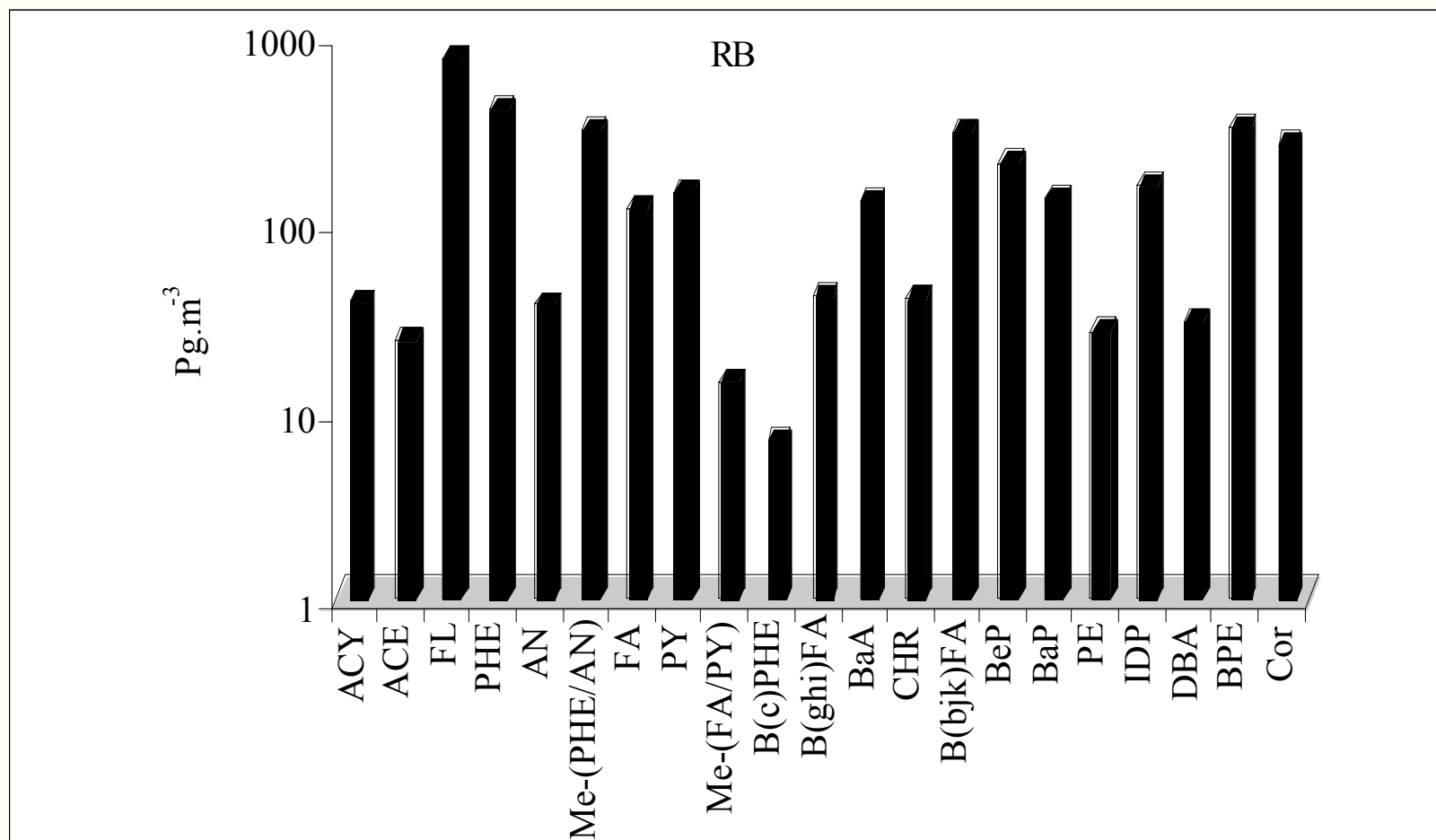


Fig.3b. Distribution profiles of PAHs concentrations recorded in Rouiba

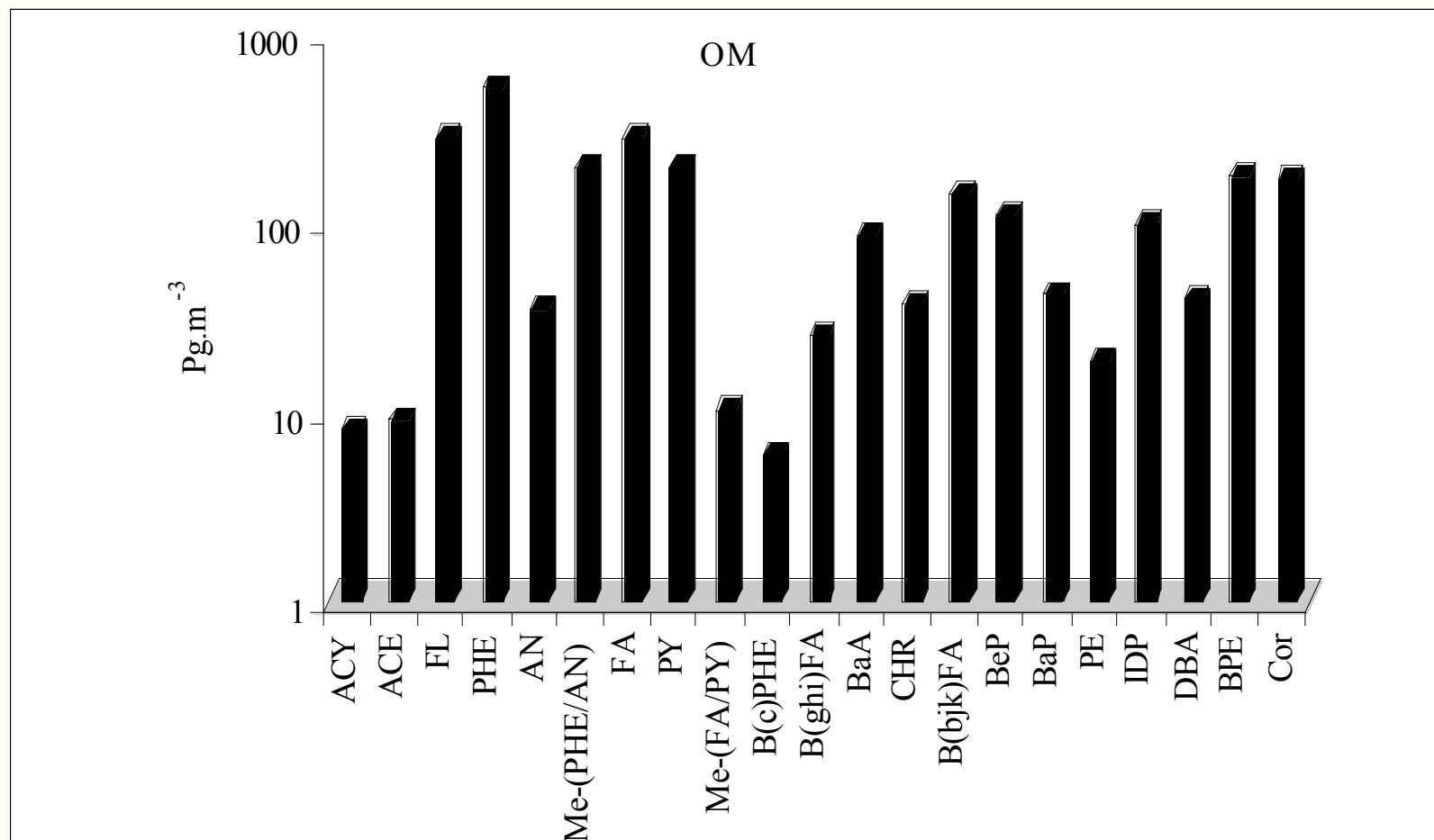


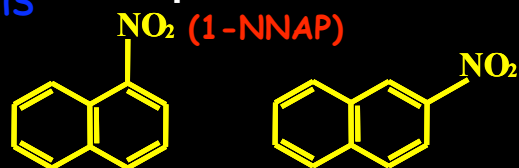
Fig.3c Distribution profiles of PAHs concentrations recorded in Ouled Moussa

Table 2 : Concentrations ratios between PAH

	Typical ratios	Ratios for aerosols sites			Interpretation
		BZ	RB	OM	
IPY/IPY+BPE	0.18-0.40 (vehicular emissions) 0.56 (coal soot) 0.62 (wood burning)	0.25	0.33	0.36	Indicates vehicular emission sources
BePY/BePY+ BaPY	≥ 0.47	0.55	0.61	0.72	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	Approaches the ratios reported for vehicular emissions
$0.41 \leq \text{CPAH/TPAH}$	≤ 0.49	0.25	0.45	0.47	Indicates PAH with urban origin, especially emitted from catalytic automobiles

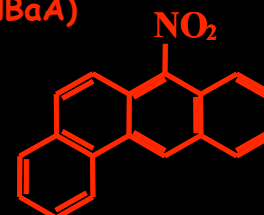
4/NPAHs

1-nitronaphthalene



7-nitrobenzo (a)anthracene

(7-NBaA)

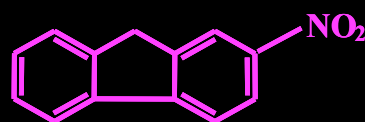


6-nitrochrysene

(6-NCH)

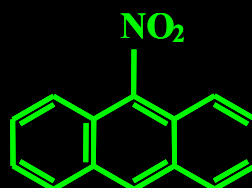


(2-NFL) 2-nitrofluorene



9-nitroanthracene

(9-NAN)

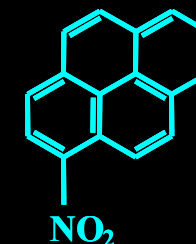


2-nitropyrene

(2-NPY)

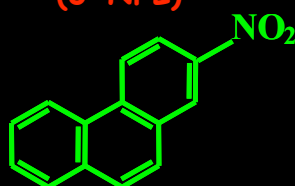


1-nitropyrene (1-NPY)



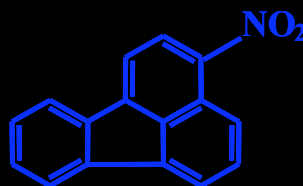
3-nitrofluorene

(3-NFL)



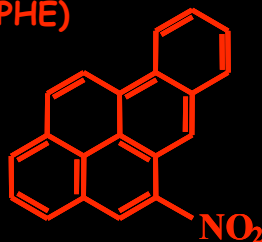
3-nitrofluoranthene

(3-NFA)



3-nitrophenanthrene

(3-NPHE)

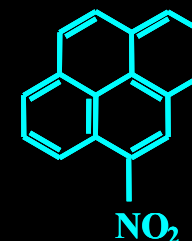


2-nitrofluoranthene

(2-NFA)



4-nitropyrene (4-NPY)



(6-NBaP) 6-nitrobenzo (a)pyrene

8-nitrofluoranthene

(8-NFA)

3-nitroperylene (3-NPE)

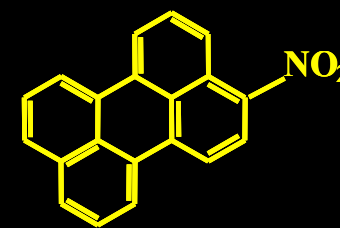


Table 3: Average NPAHs concentration (pg.m⁻³) recorded in: BZ, RB, OM

Sampling sites	BZ	RB	OM
1-NNAP	67.7	1.68	n.d
2-NNAP	131	<1	1.19
2-NFL	13	2.23	n.d
9-NANT	6.1	22.42	5.73
9-NPHE	2.2	2.04	2.46
1-NPHE	14.5	6.48	1.93
3-NPHE	n.d	2.07	3.46
2-NPHE	1.5	n.d	1.08
1-NFA	n.d	3.51	4.01
7-NFA	5.4	1.03	n.d
2-NFA	17.2	4,54	n.d
3-NFA	2.5	3.31	<1
4-NPY	10,9	1,64	1,71
8-NFA	2,3	2,29	8,82
1-NPY	6,2	25.97	11.99
2-NPY	n.d	22.27	125.19
TOTAL	281	101	169

Primary and secondary sources of nitropyrenes

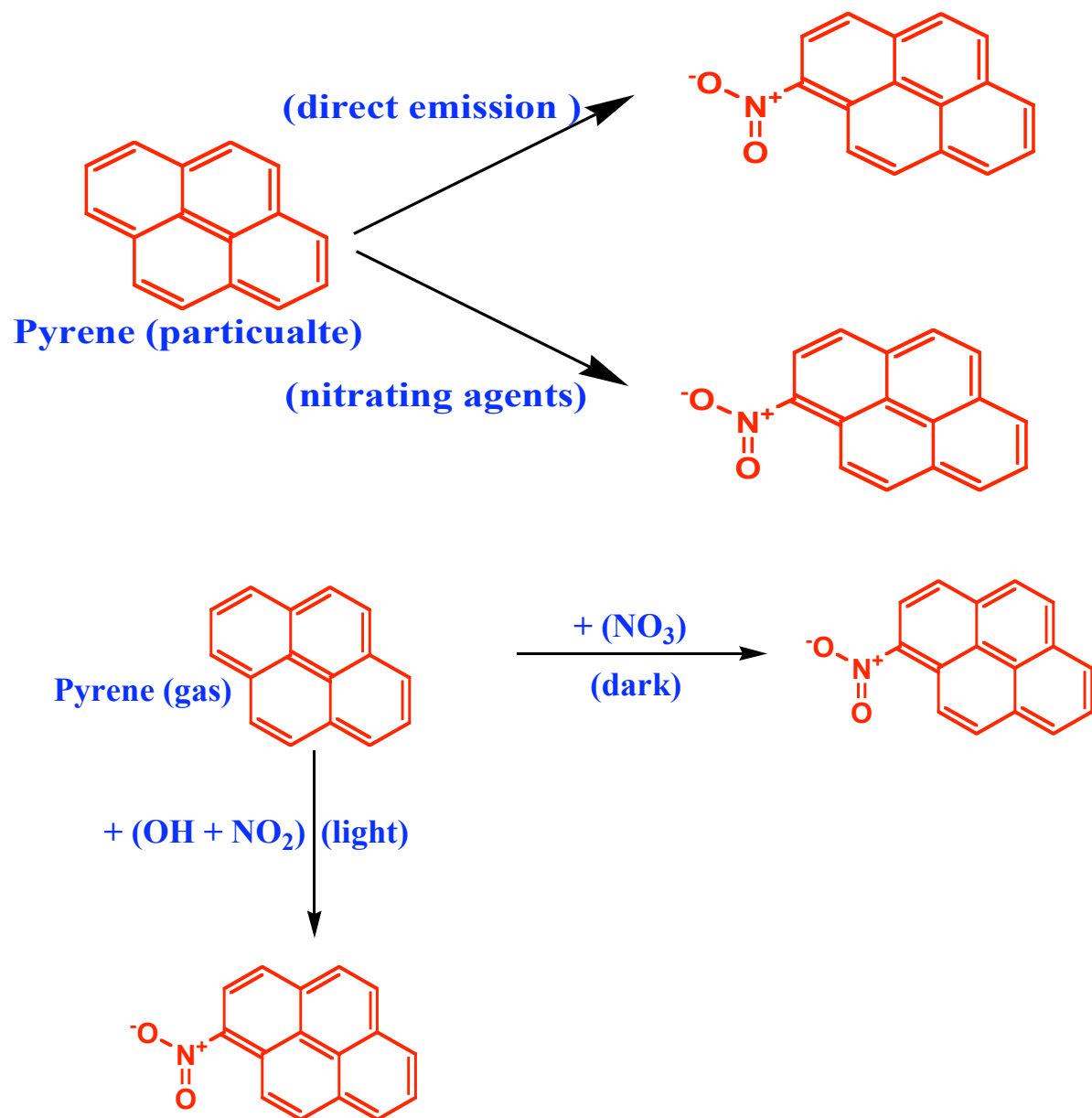


Table 4: Typical rates of Nitro-PAH ratios observed for emission and atmospheric particulates

<i>N-PAH index</i>	<i>diesel vehicles</i>	<i>gasoline cars</i>	<i>stationary sources</i>	<i>daytime chemistry</i>	<i>nighttime chemistry</i>
[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.

Table 5 : 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

BZ :

R_1 : daytimes and nighttimes chemistry

R_3 : stationary sources

RB :

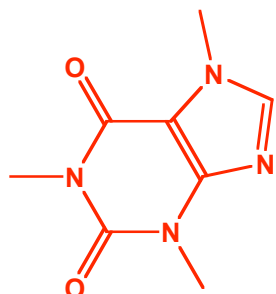
R_1 and R_3 : diesel vehicles

R_2 : nighttimes chemistry

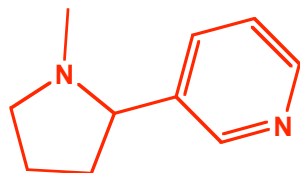
OM :

R_3 : diesel vehicles

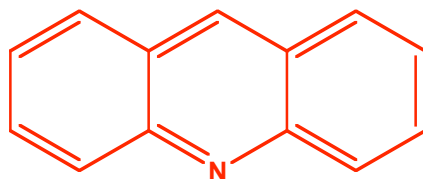
5/Polar Compounds



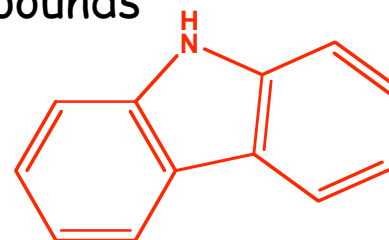
CAFFEINE



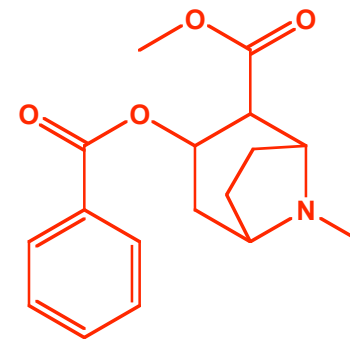
NICOTINE



ACRIDINE

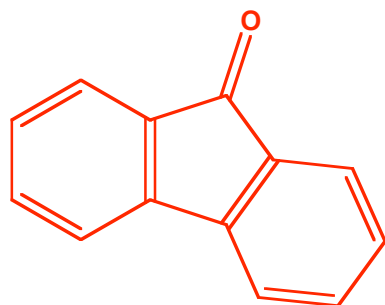


CARBAZOLE

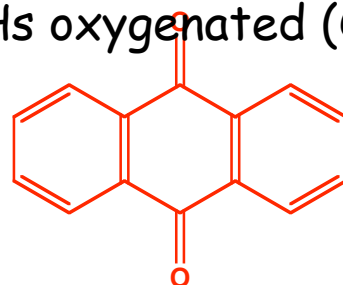


COCAINE

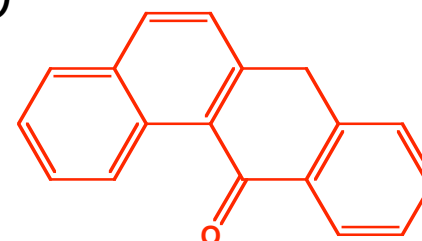
Heterocyclic compounds



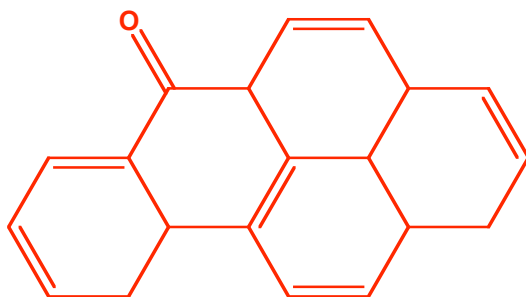
FLUORENONE



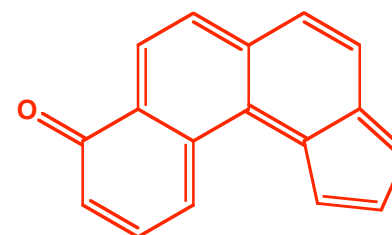
9,10-ANTHRAQUINONE



BENZANTHRONE



BENZOPYRENONE



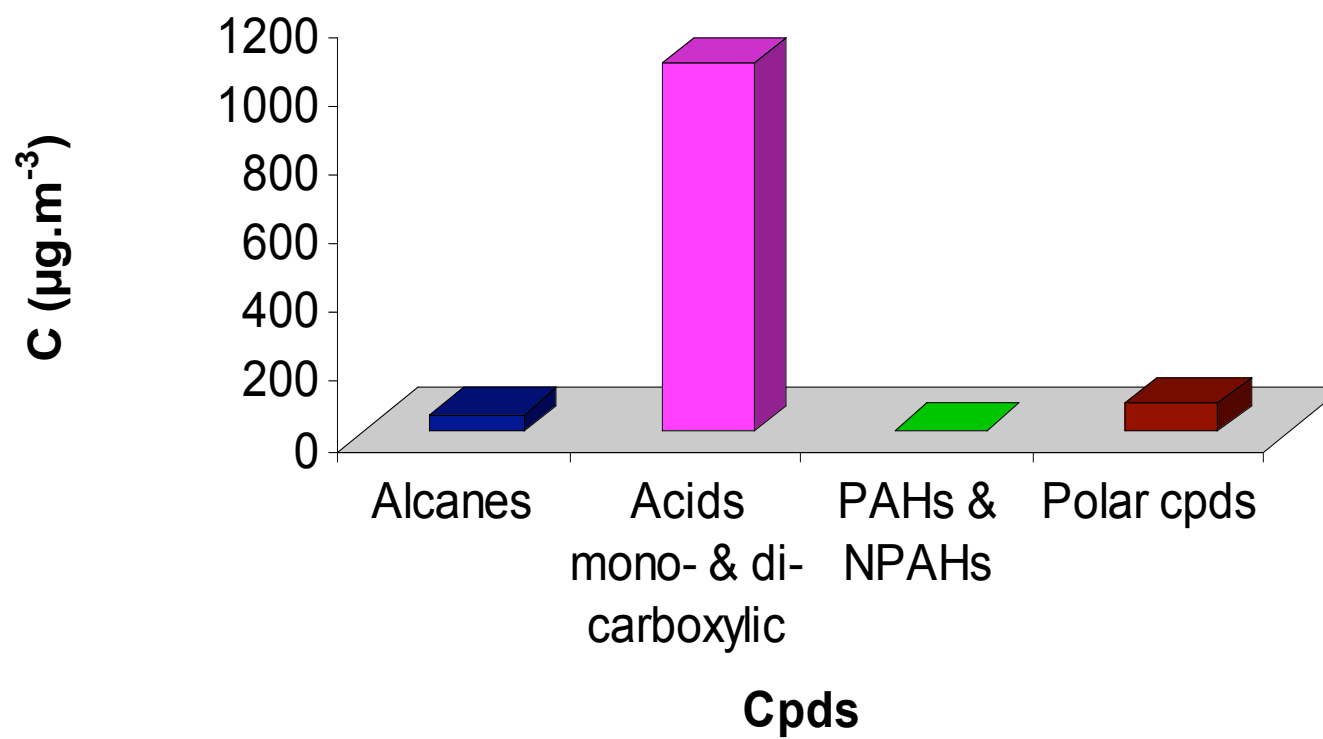
CYCLOPENTA[C]PHENANTHREN-8-ONE

PAHs oxygenated (Oxy-PAHs)

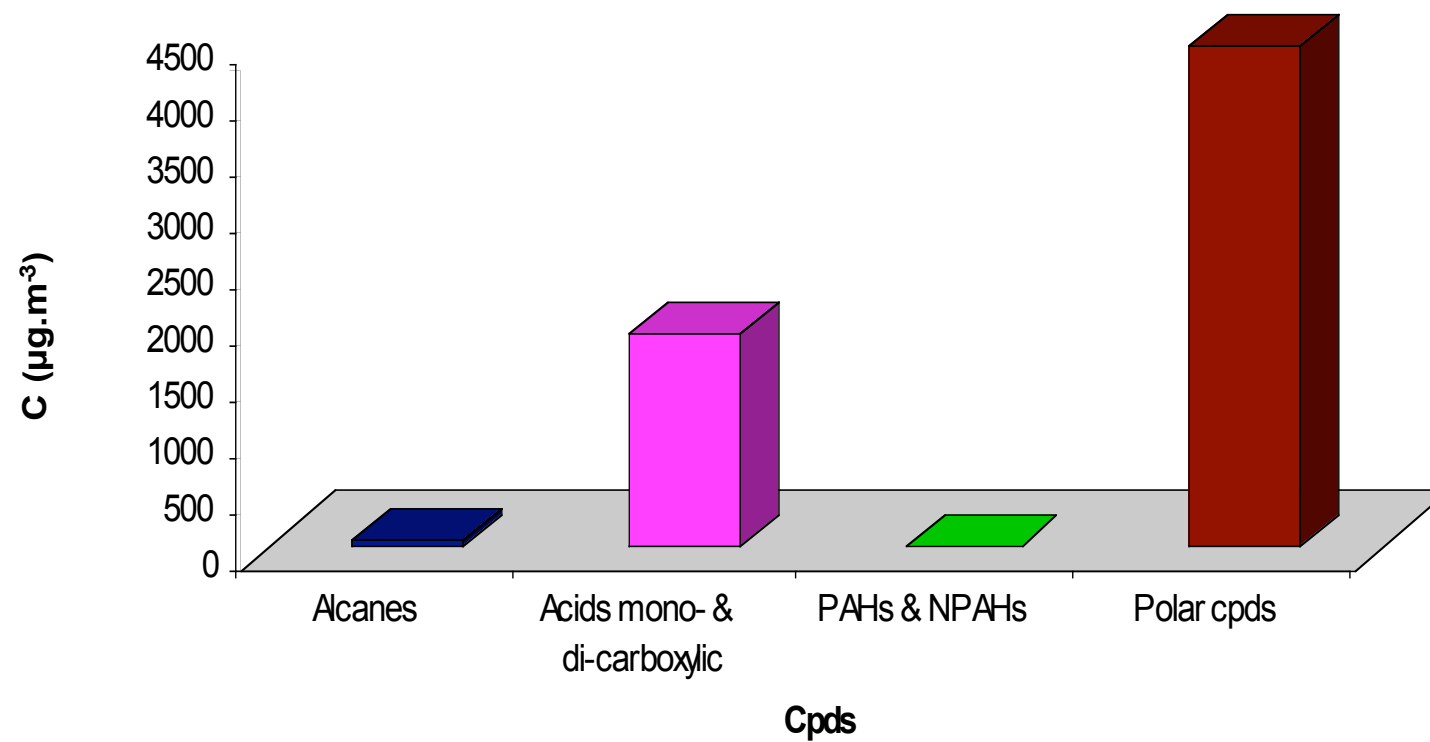
Table 6: Average High Polar concentration (ng.m⁻³) recorded in: BZ, RB and OM

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
Cyclopentaphenanthrenone	0.08	0.19	2.53
Cocaine	n.d	n.d	n.d
Benzanthrone	1.36	14.06	10.58
Benpyrenone	n.d	n.d	n.d

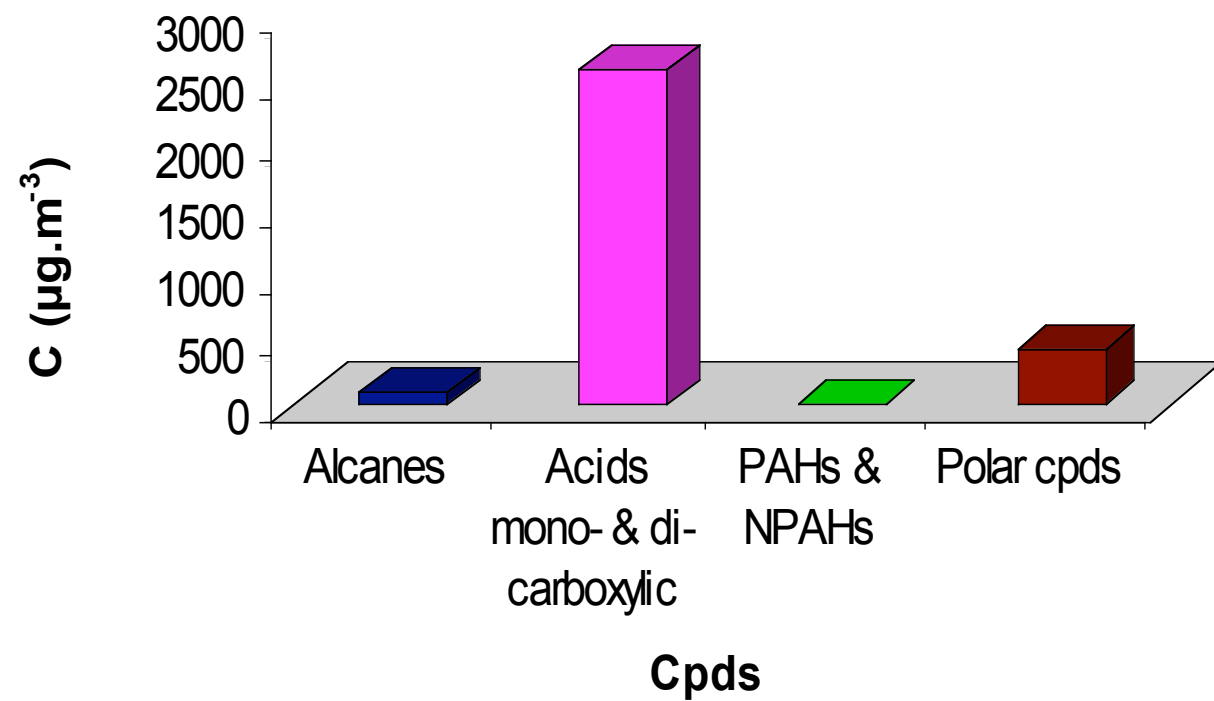
BZ



OM



RB



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.

Conclusion

Due to the small concentrations reached by PAHs and NPAHs 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} .

THANK YOU FOR YOUR ATTENTION