HOW ELECTRON BEAM COULD AFFECT THE PAH FORMATION MECHANISM AT ENERGY GENERATION

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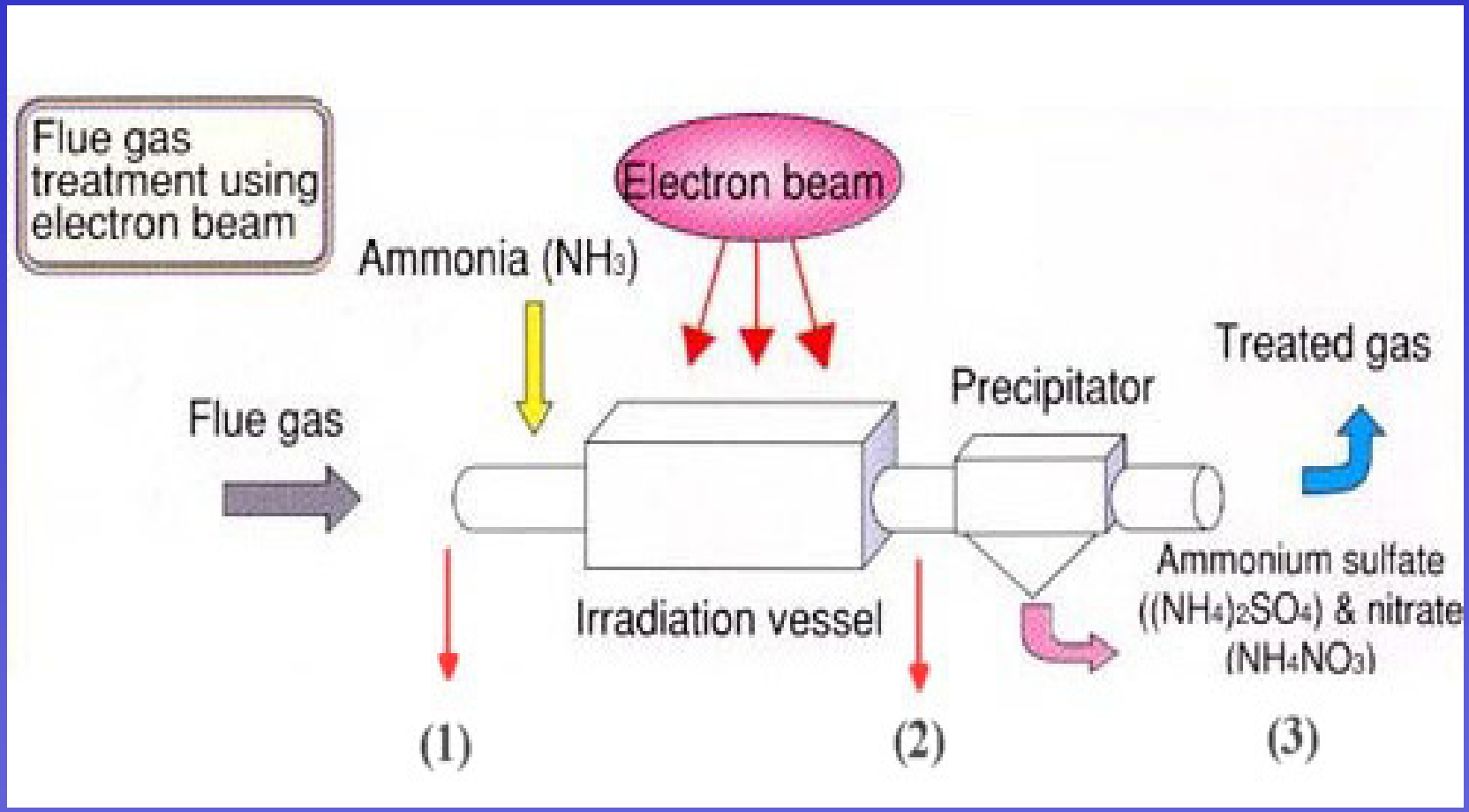
OBJETIVE

- To know how the EBT could affect organic emissions when applied for SO_2 and NOx gas cleaning at energy generation from coal combustion

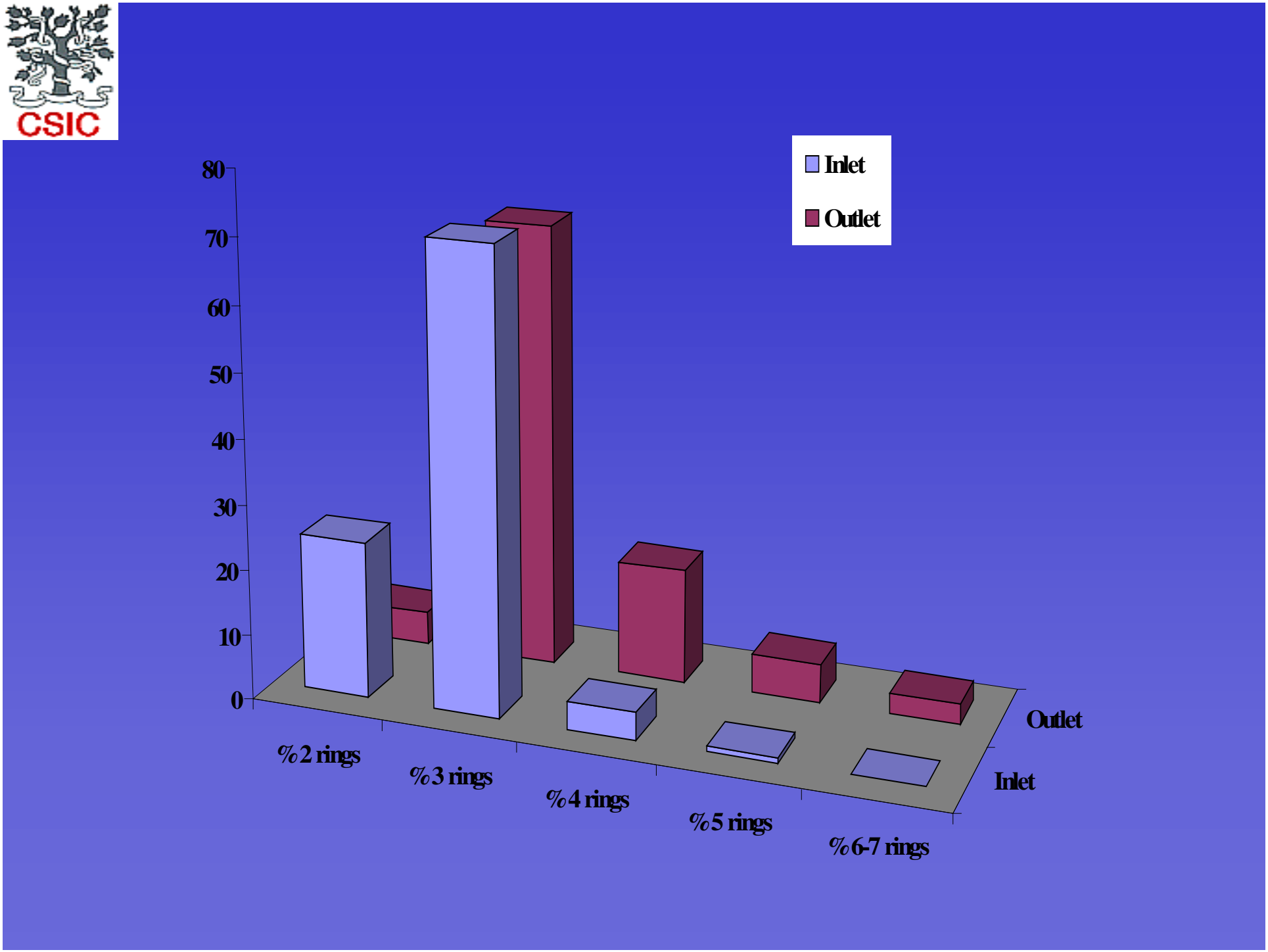


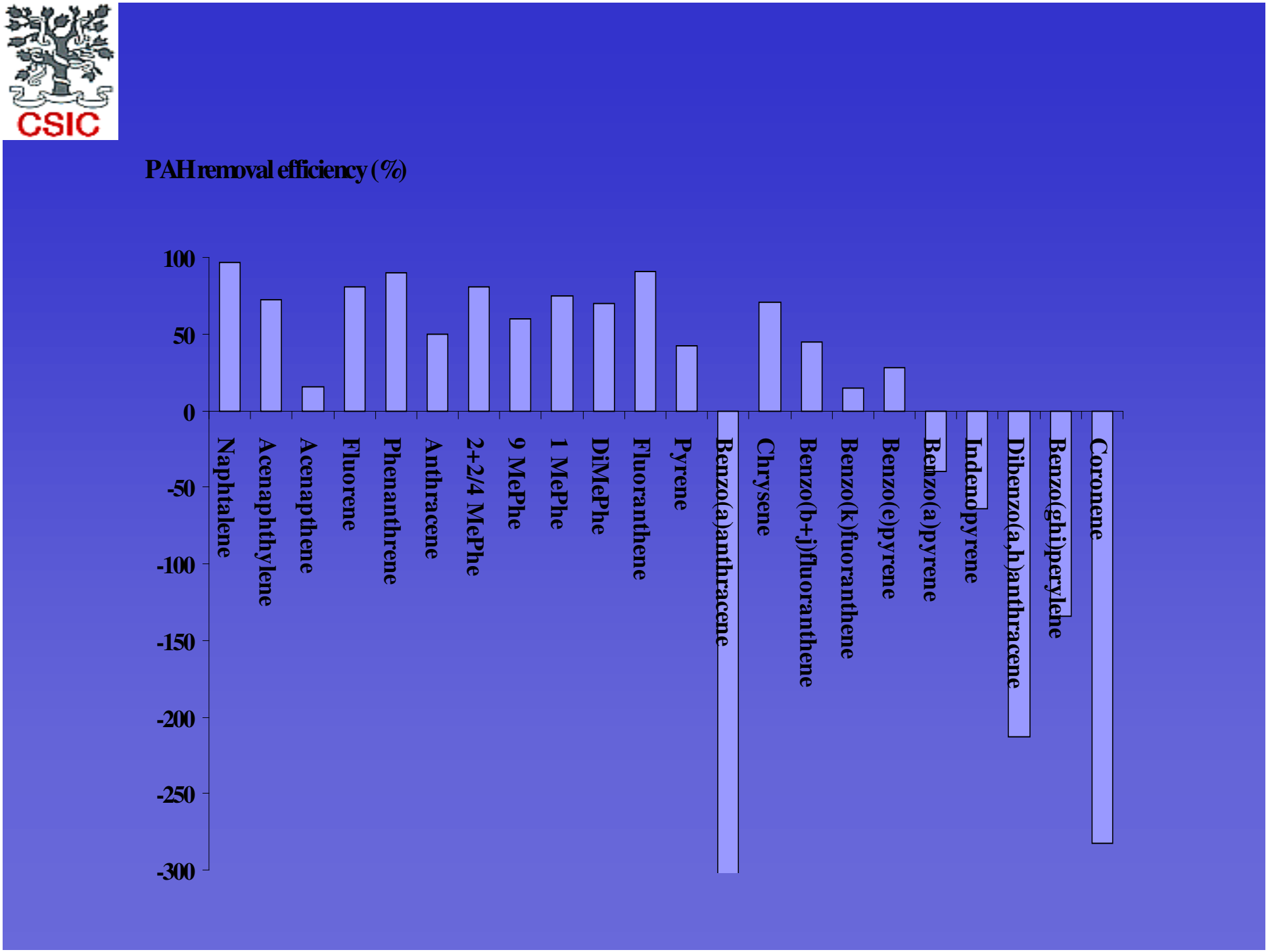
(1) Inlet sampling point; (2) Outlet sampling point; (3) Solids sampling point

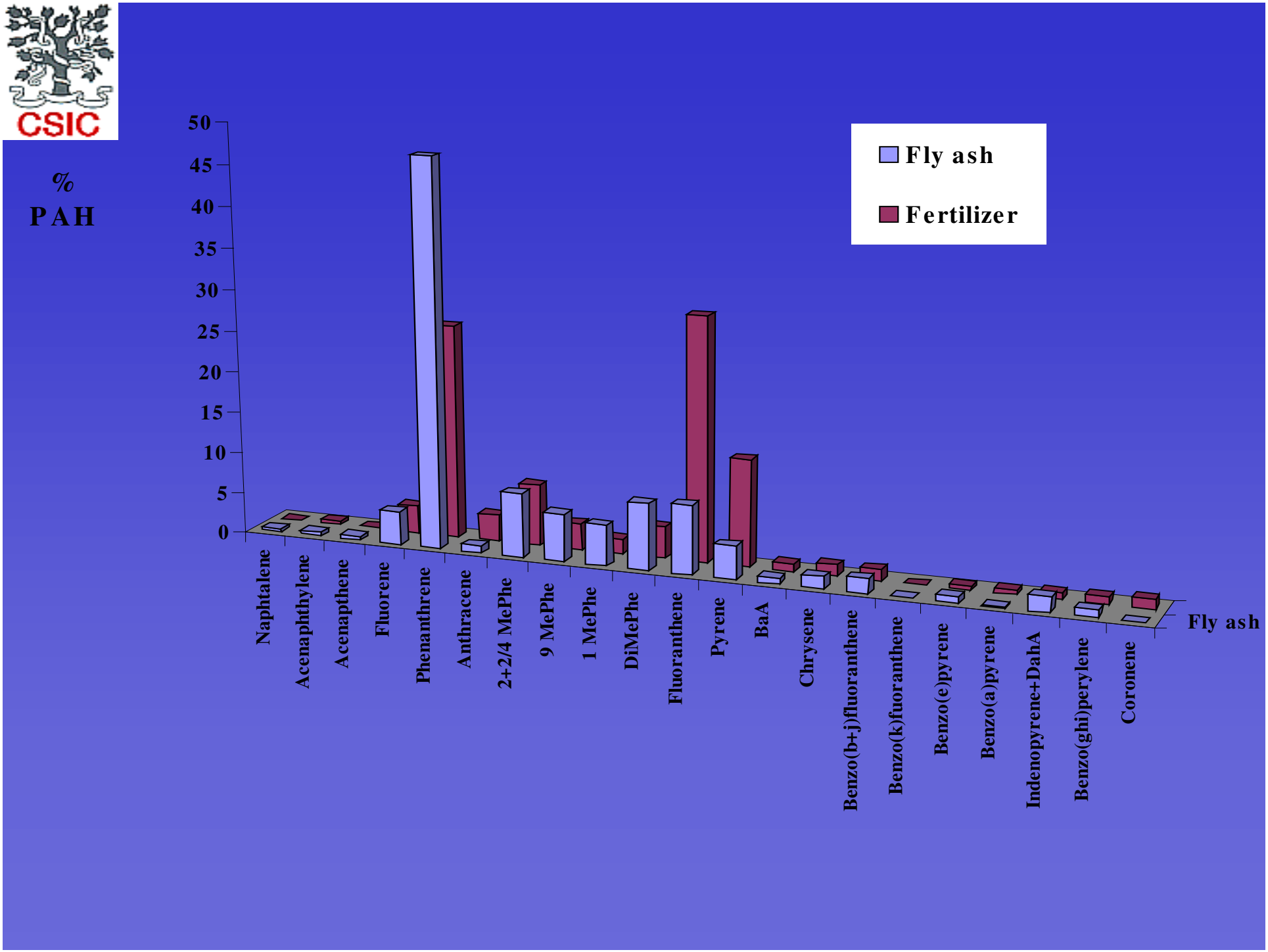
EB on PAH formation and emisions from:

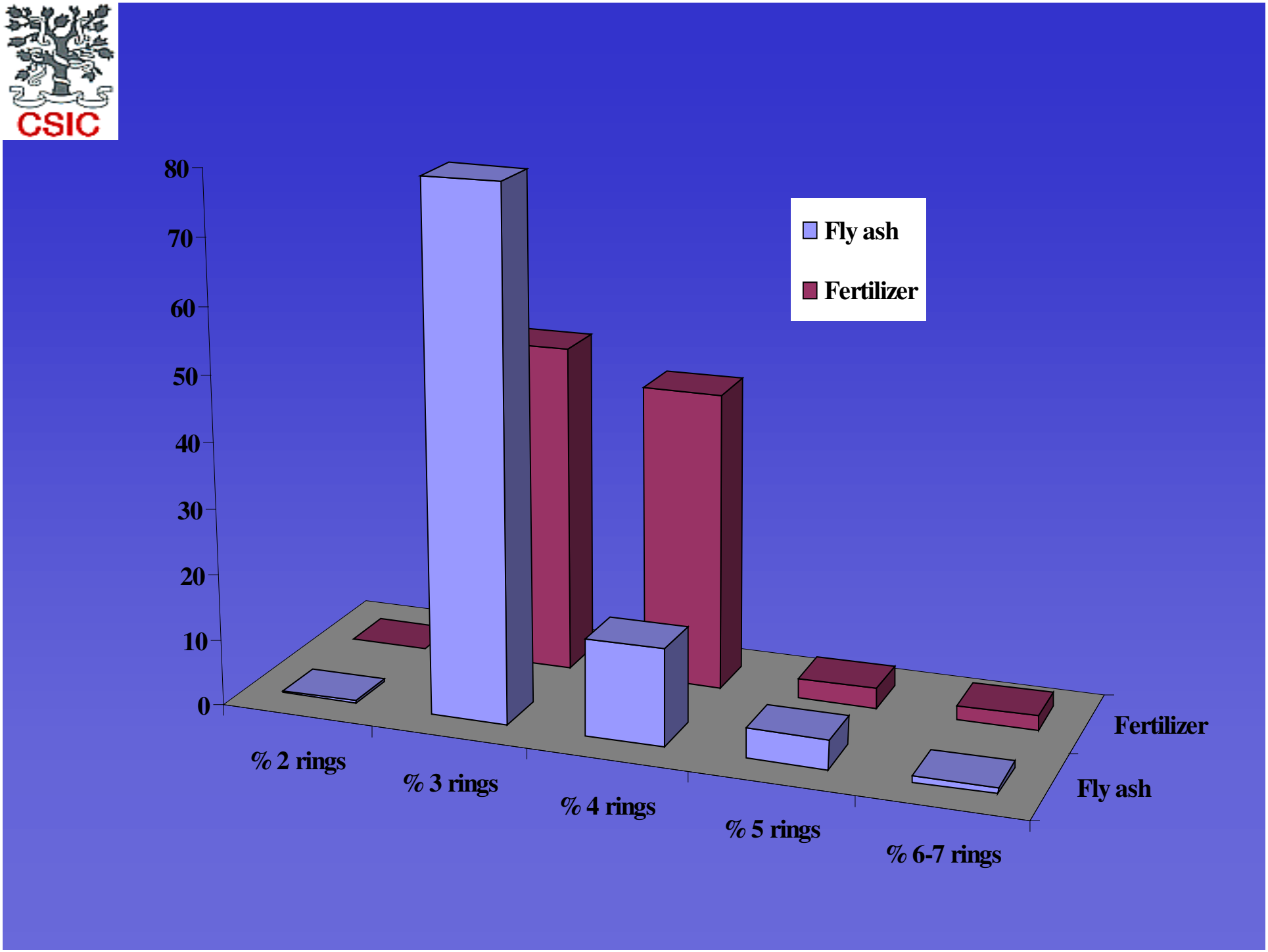
---gas samples from coal combustion power station provided with EBT

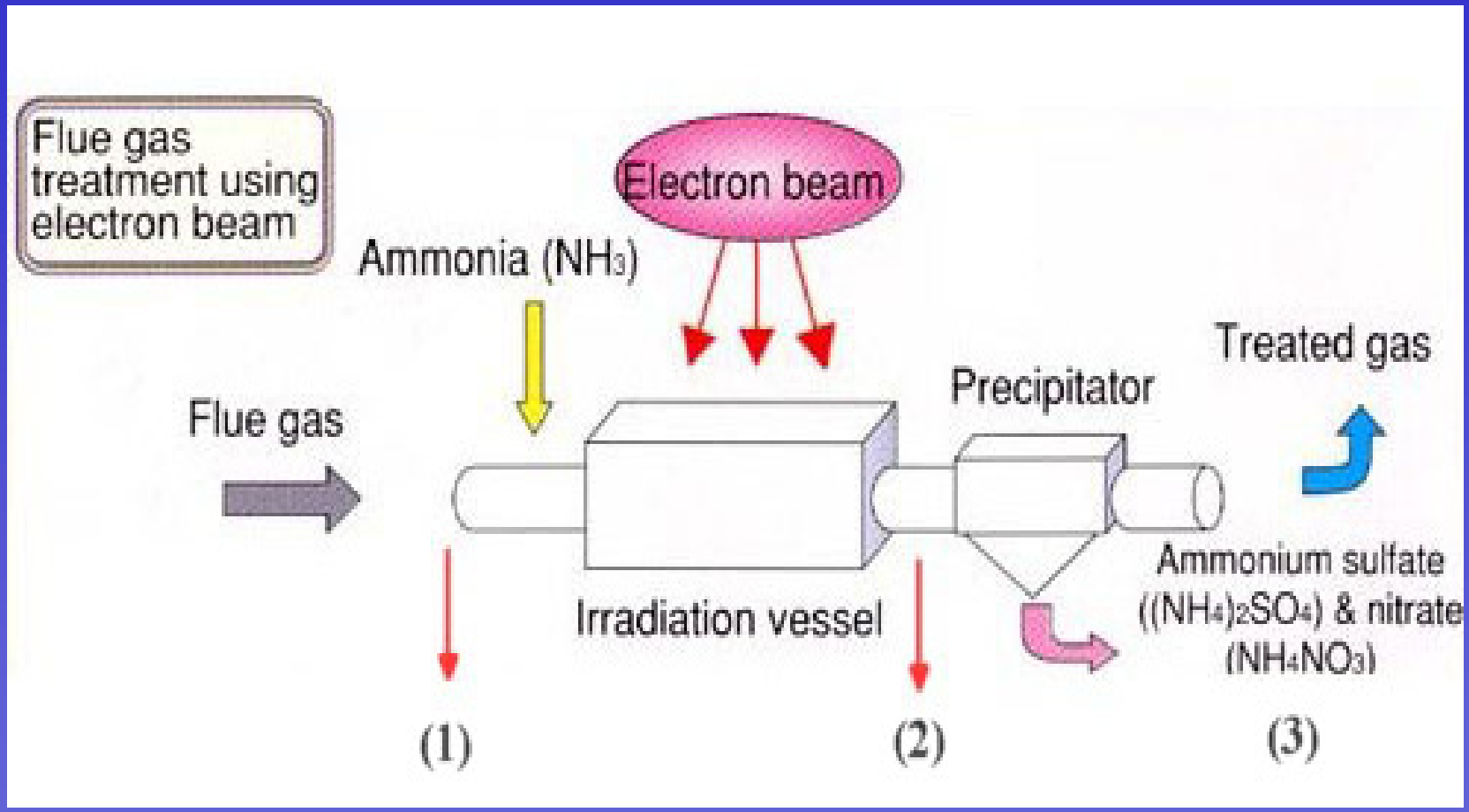
---solid samples: fly ash and residue after EBT


CSIC
Inlet
Outlet
80
70
60
50
40
30
20
10
0
%2 rings
%3 rings
%4 rings
%5 rings
%6-7 rings
Outlet
Inlet


PAH removal efficiency (%)
100
50
0
-50
-100
-150
-200
-250
-300
Naphtalene
Acenaphthylene
Acenapthene
Fluorene
Phenanthrene
Anthracene
2+2/4 MePhe
9 MePhe
1 MePhe
DiMePhe
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b+j)fluoranthene
Benzo(k)fuoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Indendpyrene
Dibenzo(a,h)anthracene
Benzo(ghi)perylene
Coronene


CSIC
%
PAH
50
45
40
35
30
25
20
15
10
5
0
Fly ash
Fertilizer
Naphtalene
Acenaphthylene
Acenapthene
Fluorene
Phenanthrene
Anthracene
2+2/4 MePhe
9 MePhe
1 MePhe
DiMePhe
Fluoranthene
Pyrene
BaA
Chrysene
Benzo(b+j)fluoranthene
Benzo(k)fuoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Indenopyrene+DahA
Benzo(ghi)perylene
Coronene
Fly ash


CSIC
80
70
60
50
40
30
20
10
0
Fly ash
Fertilizer
% 2 rings
% 3 rings
% 4 rings
% 5 rings
% 6-7 rings
Fertilizer
Fly ash



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EMISSIONS IN POWER GENERATION

Inorganics:

- CO_x
- NO_x
- SO_x
- TRACE ELEMENTS
- PARTICULATE MATTER (PM)

Organics:

- PARTICULATE MATTER (PM)
- VOLATILE ORGANIC COMPOUNDS:
  - Dioxins
  - Furanes
  - PAH

Fuel composition: C, H, N, S, O

- **Combustion chemical reactions**

$C + O_2 \longrightarrow CO_X$ (CO, CO_2)

$H_2 + O_2 \longrightarrow H_2O$

$N + O_2 \longrightarrow NO_X$

$S + O_2 \longrightarrow SO_X$

$C + C \longrightarrow$ SOOTS (polyaromatics)

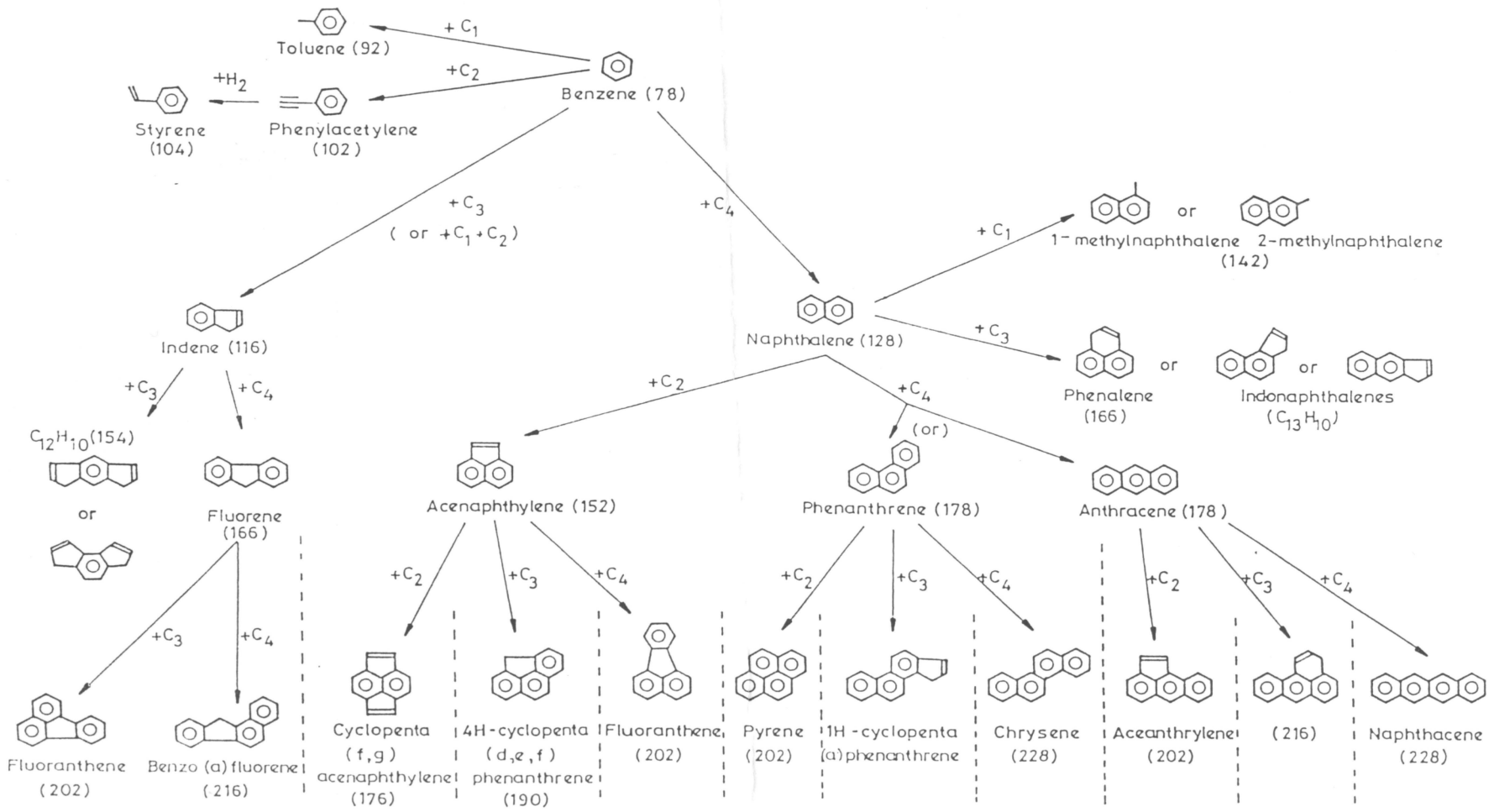
chem. bonds-chem. breakings

A : B E_1 energy bond
by applying $E_2 > E_1$

A* + B* homolitic breaking = radicals
(AA, AB, BB, AAA, AAB….and so on)
Radical reactions (very fast, high TºC, lots of side reactions)

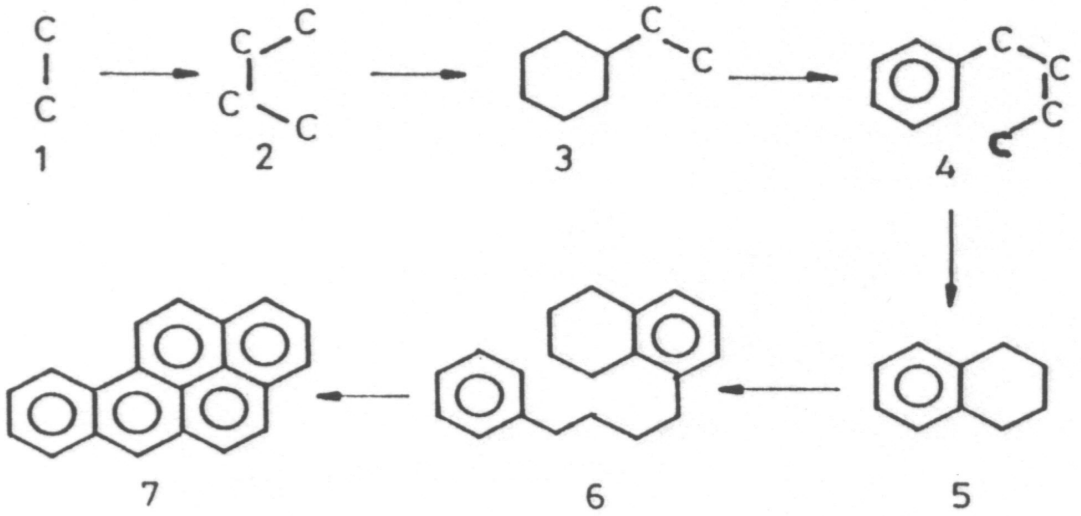
A^+ + B^- heterolitic breaking = ions
(AB)
Ionic reactions (longer times, lower temperatures, few side reactions)

General mechanisms of PAH formation and growth



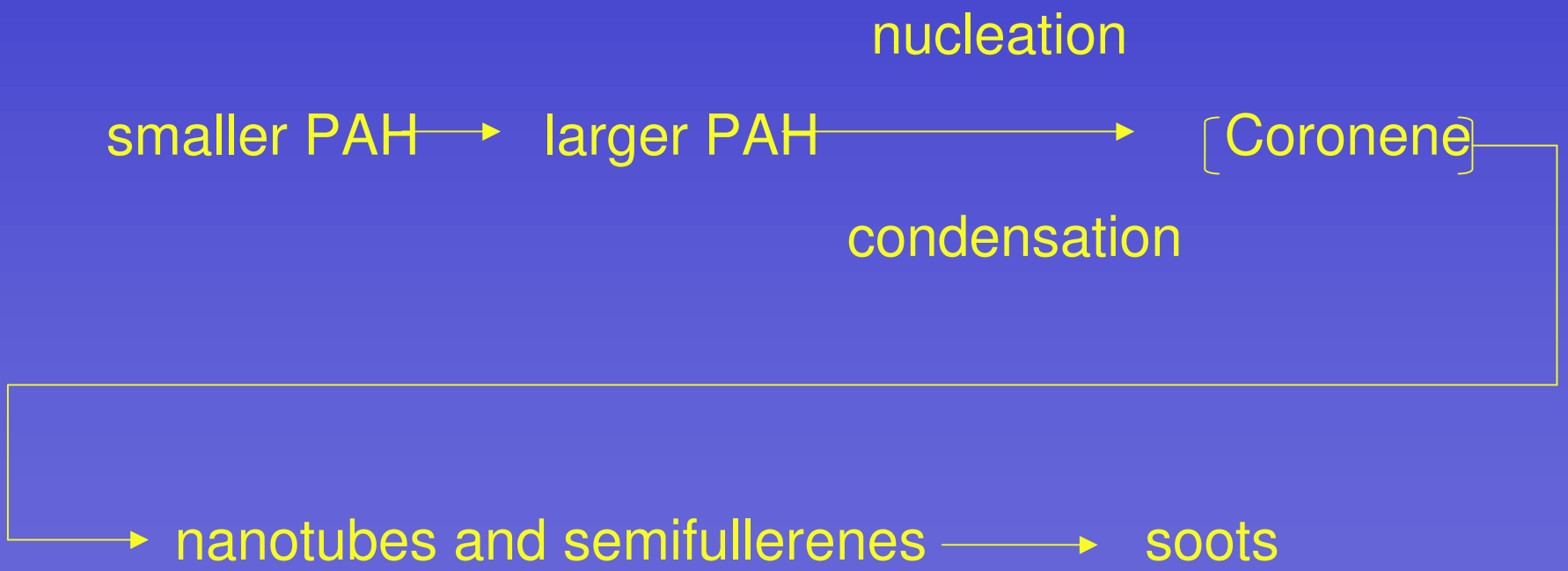
Mechanisms of PAH formation and growth. The numbers in parenthesis are the molecular weights.

Pyrolytic formation of BaP



Pyrolytic formation of benzo(a)pyrene.

Gaseous PAH / Solid PAH



Atmospheric PAH Origin

- **Natural Sources:** e.g. Volcanos, spontaneous fires, etc
- **Antropogenic Sources:**
  - stationary sources: POWER STATIONS
  - mobile sources: TRANSPORT

Human exposure to PAH

Inhalation

active smoking
pasive smoking
air

Retention

Adding to the caronogenic risk

Ingestion

vegetables-roots-leaves
sea food

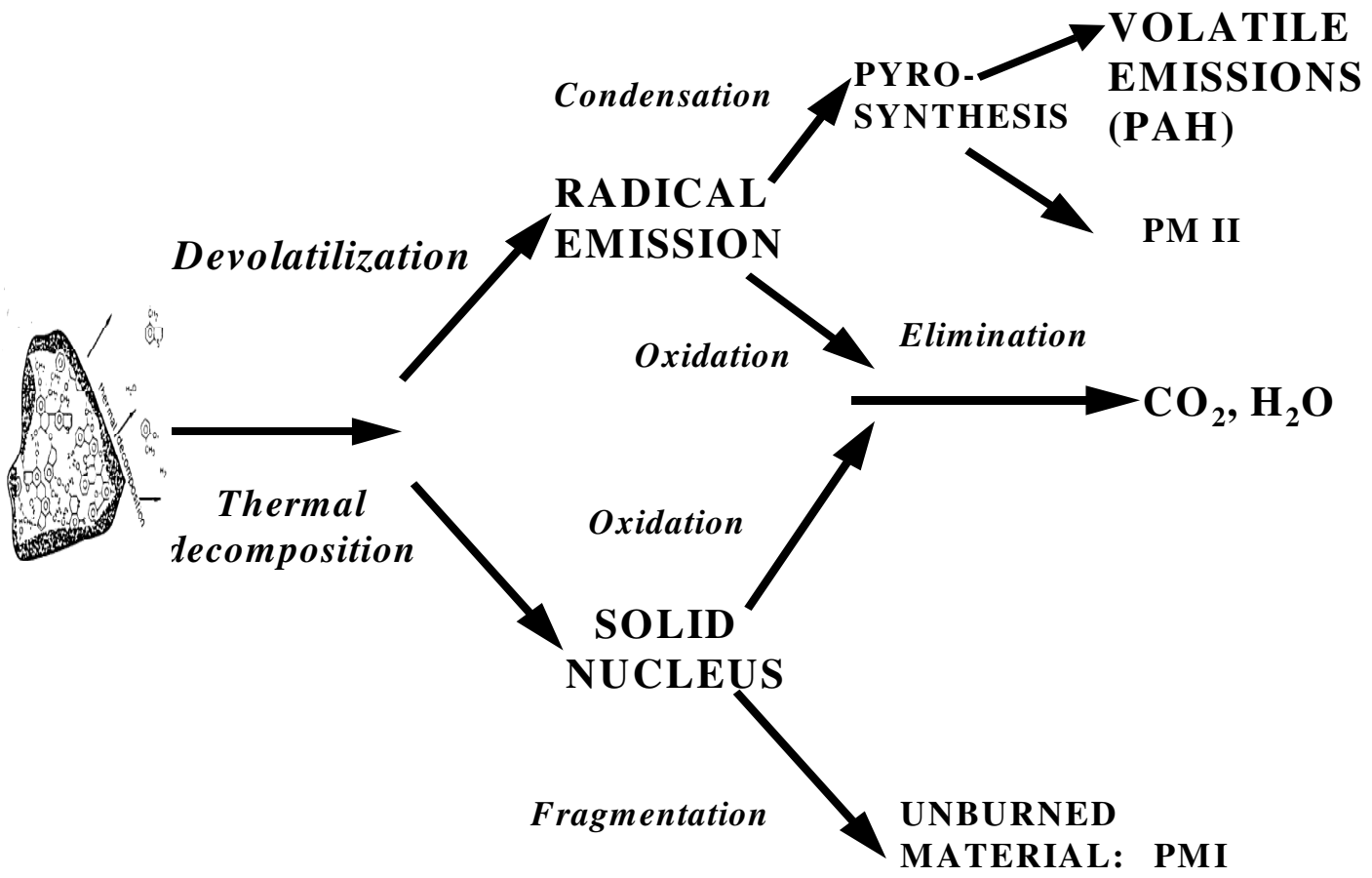
meat and fish (smoked, fried, grilled and broiled)

drinks, including water

Waste

urine
faeces

PAH formation and emission



Mastral et al., Environ. Sci. & Technol. 33(18),3177, 1999

BaP EU directive proposal

- According to the European Parlament, the BaP annual mean value should not be higgher than 1ng/m^3

  (UK, 0,25 ng/m^3; NL, 0,50 ng/m^3;
  Italy, 1 ng/m^3)

$B(a)P_{eq}$=B(a)P+BFx0.07+B(a)Ax0.06+D(a,h)Ax0.6+Ipx0.08

PAH Removal in Energy Generation

- **During combustion**:
  - improving combustion efficiencies by variables optimization
- **Post combustion :**
  - **Solid Phase**:
    - By trapping in cyclons, electrostatic precipitators, scrubbers, etc
  - **Gas Phase** (laboratory tests):
    - **by adsorbents**
    - by catalysts
    - by EB treatment

CONCLUSIONS

- Results showed that PAH gas emissions from coal combustion are influenced by the EBT showing a reduction of the most volatile PAH and an increase in PAH with higher molecular weight when EBT is applied.

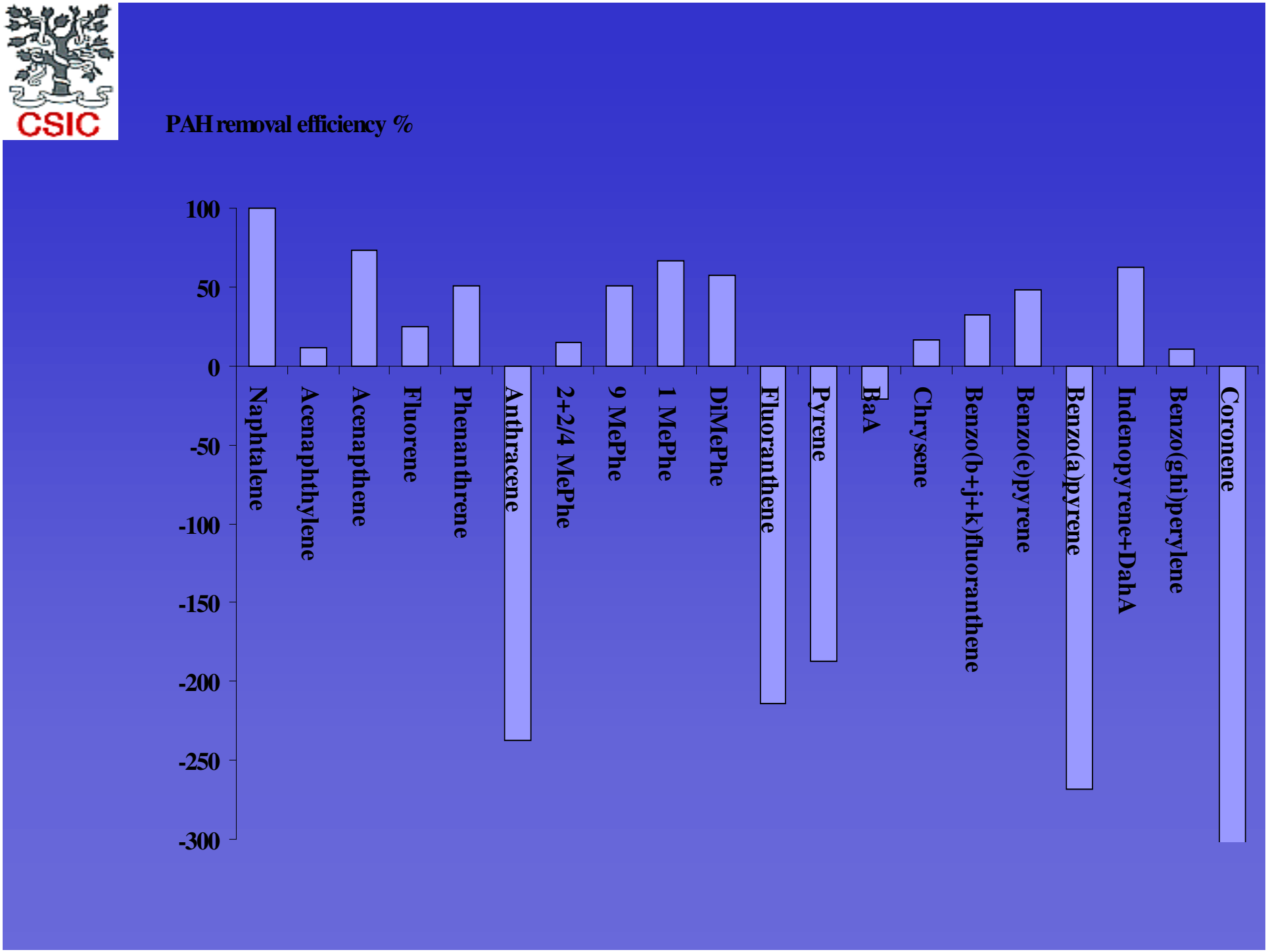
- For a good air quality, this trend could be tried to be addressed to PAH formation in solid phase, easier to control than the gas phase.

ICB Samples preparation and PAH analysis

- After the addition of deuterated internal standards for quantification (acenaphthene-d10, anthracene-d10, benzo(a)anthracene-d12, benzo(a)pyrene-d12, perylene-d12 and benzo(g,h,i)perylene-d12), samples were Soxhlets extracted, concentrated and then purify on silica-gel column with DCM. The eluted was concentrated by N_2 stream and the solvent exchanged to hexane (50 µl).

- Before 1µl injection to the GC-MS-MS, 5 ml of p-terphenyl native was added as internal standard.

To check the analytical accuracy and precission, an appropriate standard reference material (SRM 1649) of NIST was analysed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-50
-100
-150
-200
-250
-300
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Acenapthene
Fluorene
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Anthracene
2+2/4 MePhe
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1 MePhe
DiMePhe
Fluoranthene
Pyrene
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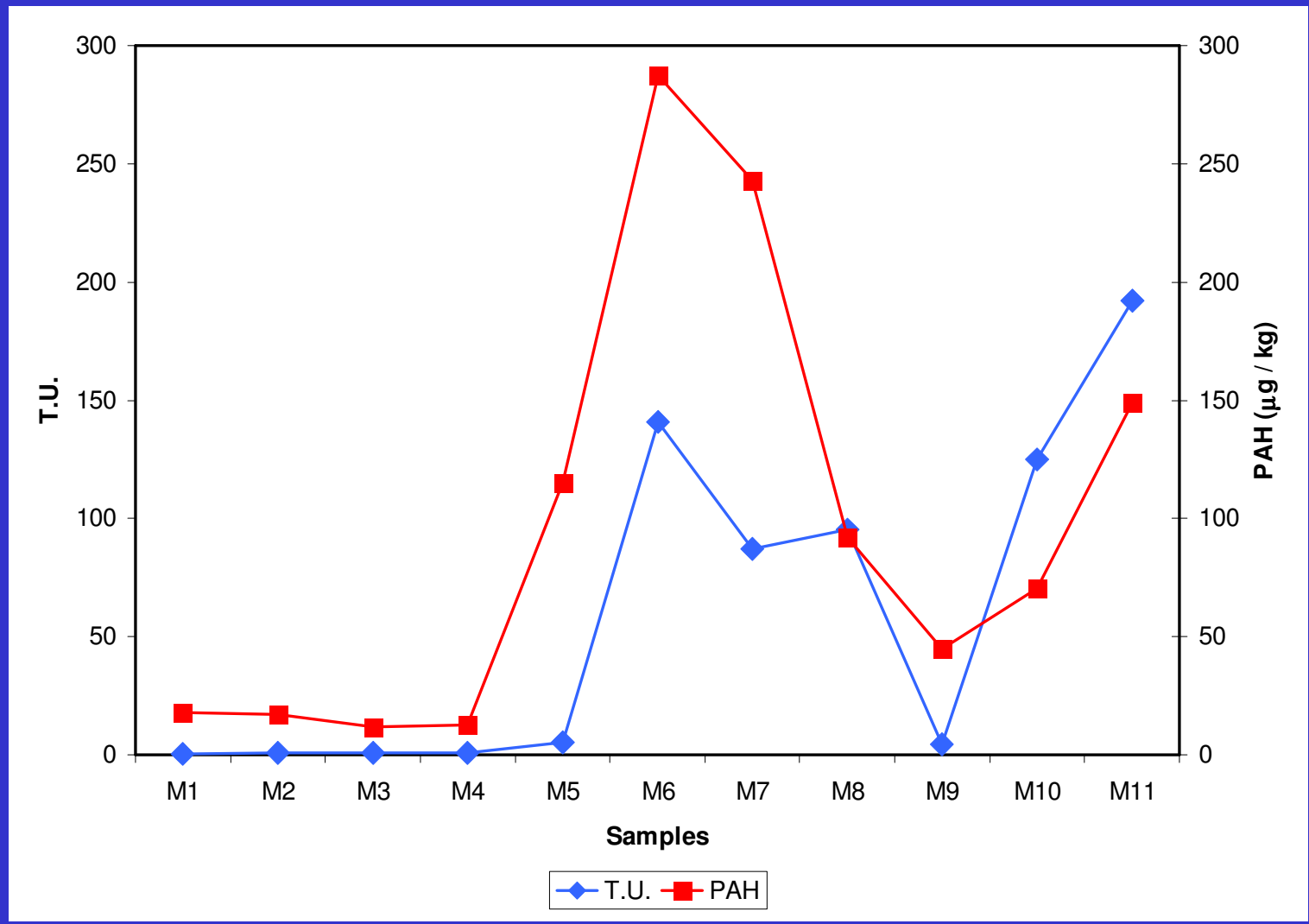
300
250
200
150
100
50
0
T.U.
PAH (µg / kg)
M1
M2
M3
M4
M5
M6
M7
M8
M9
M10
M11
Samples
T.U.
PAH