

8<sup>th</sup> ETH Conference on Combustion Generated Nanoparticles  
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# Particle size resolved analysis of PAHs in diesel soot

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CU.....  
TEC

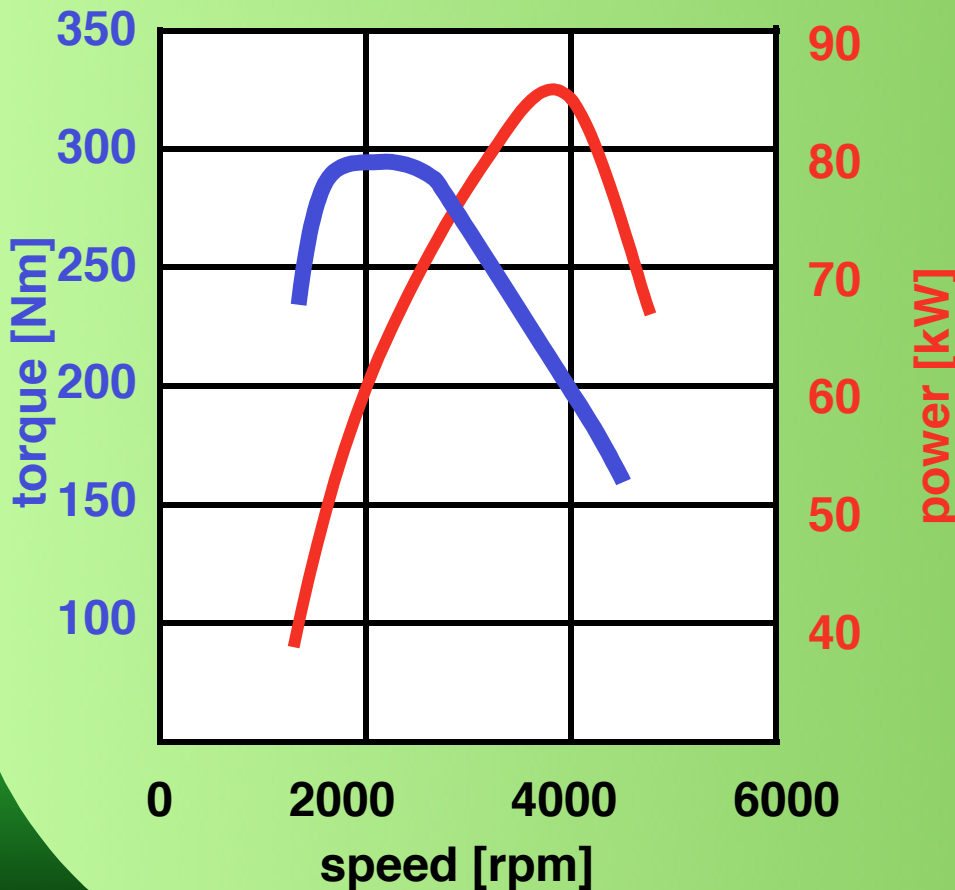
# agenda

- **equipment @ CUTECH to**
  - **generate soot particle**
  - **measure soot particles**
    - **size**
    - **composition (PAH)**
- **test conditions & results**
  - **PAH species distribution to particle size**
  - **PAH spectrum @ impactor stage / soot mass**
  - **PAH spectrum @ particle surface**
- **conclusion**

equipment @ CUTE<sup>TEC</sup> to generate soot particles

# engine

**VW TDI-PUI 4 cylinder 1.9 L, 85 kW, 285 Nm, EURO 3**



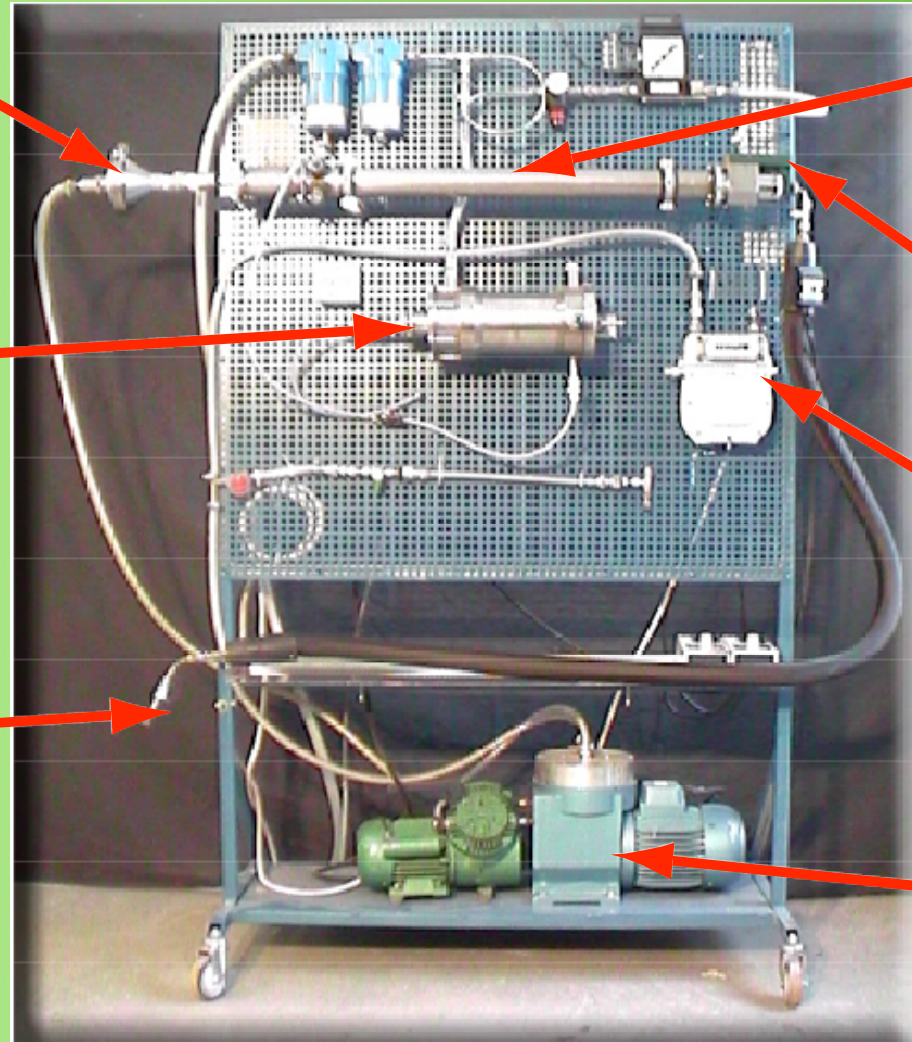
equipment @ CUTE<sup>TEC</sup> to measure soot particle size

# micro dilution tunnel

*filter holder  
or impactor*

Second injector  
dilution ratio:  
1:5 - 1:30

heated hose



micro  
dilution  
tunnel

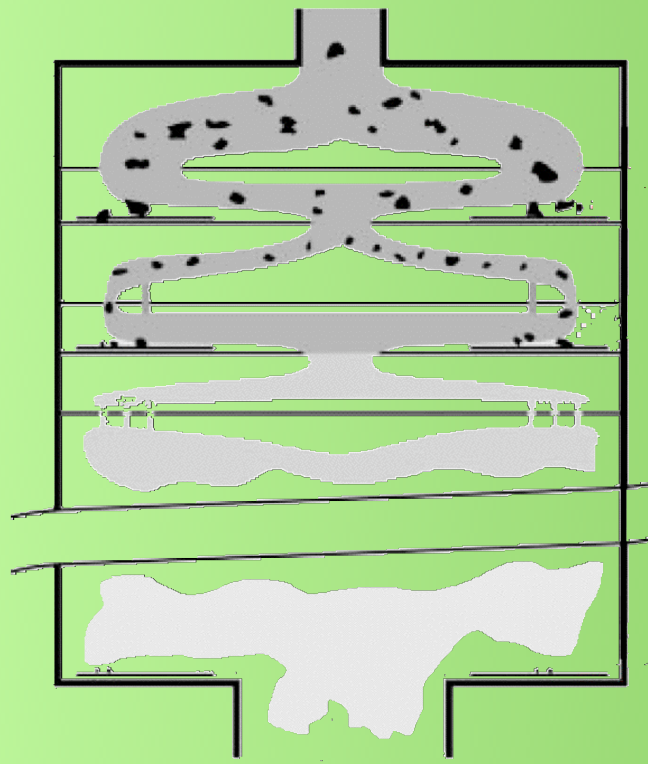
injector  
dilution ratio:  
1:7 - 1:10

flow meter

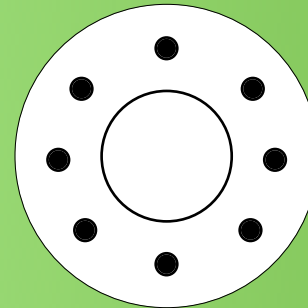
pump

equipment @ CUTEC to measure soot particle size

## 12-stage low pressure impactor LPI (Berner)



$x_{ae, \max}$  : 16000 nm



substrate for soot deposition  
& PAH analysis:

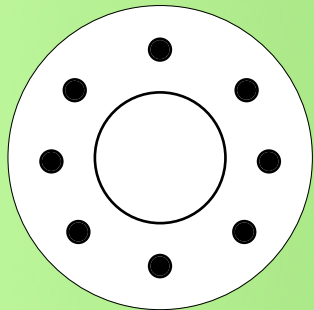
blue ribbon paper filter

$x_{ae, \min}$  : 9 nm

equipment @ CUTEC to measure soot particle composition (PAH)

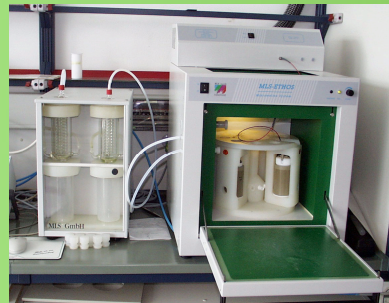
## PAH determination

filter



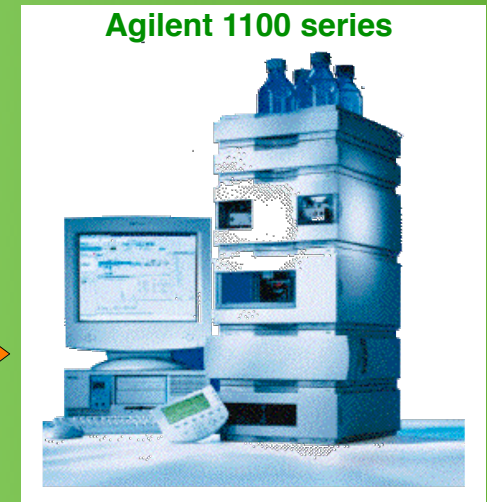
0.03 - 2 mg soot

Microwave assisted  
extraction  
T = 70 °C



solvent: 30 mL  
dichloromethane

HPLC



peak height

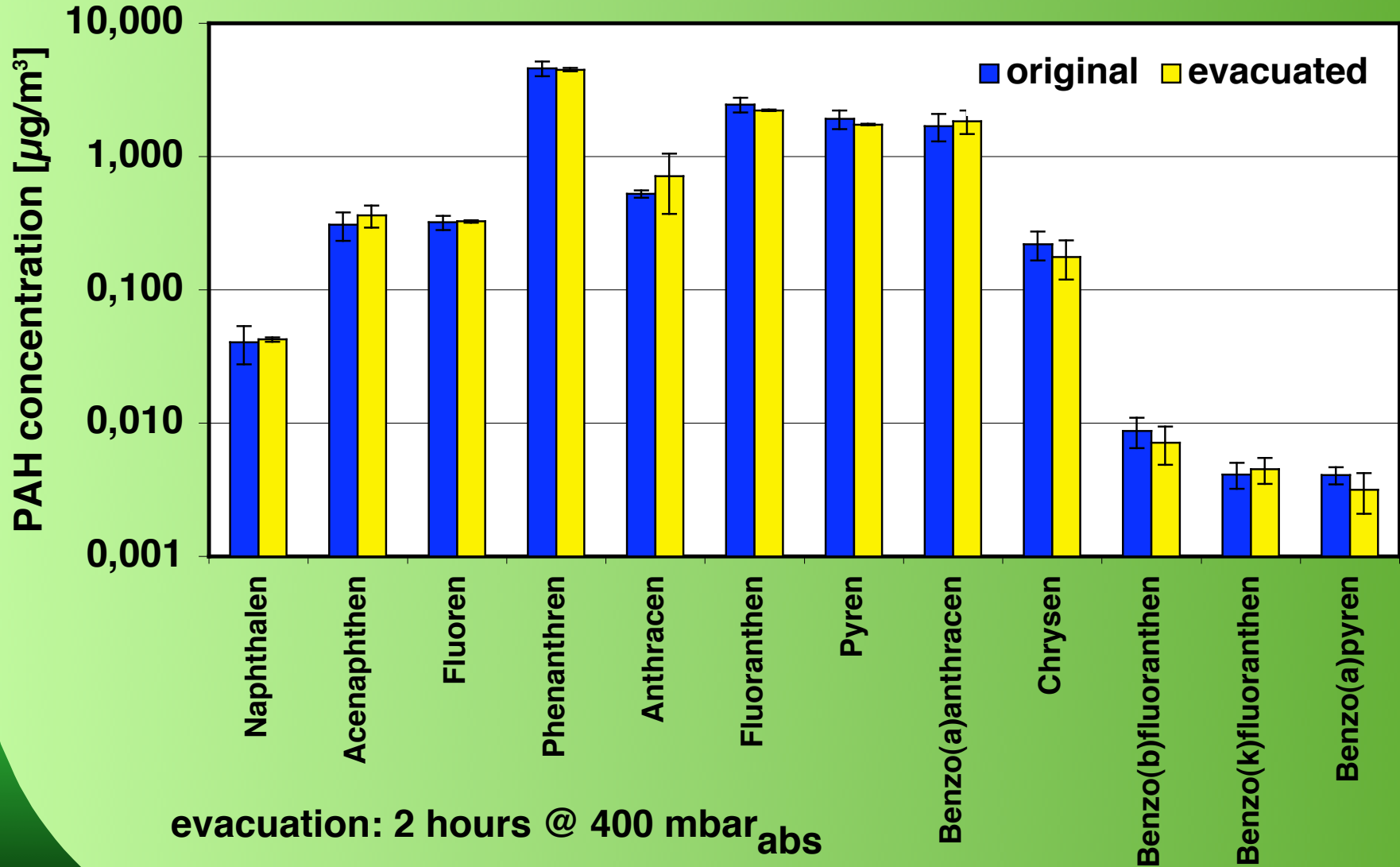
preliminary test results @ CUTEC

## detection limits for PAH


	PAH	Calibration [pg] / [ng/ml]	limit blank filter [pg] / [ng/ml]
1	Naphthalene	$\geq 20 / \geq 1$	$\geq 20 / \geq 1$
2	Benzo(k)fluoranthene		
3	Benzo(a)pyrene		
4	Dibenzo(a,h)anthracene		
5	Benzp(g,h,i)perylene		
6	Acenaphthalene		$\geq 40 / \geq 2$
7	Chrysene		
8	Benzo(b)fluoranthene		
9	Fluorene		$\geq 200 / \geq 10$
10	Anthracene		
11	Fluoranthene		
12	Pyrene		
13	Phenanthrene		$\geq 660 / \geq 33$
14	Benzo(a)anthracene		
15	Indendo(1,2,3-cd)pyrene		$\geq 200 / \geq 10$

preliminary test results @ CUTEC

# PAH detection

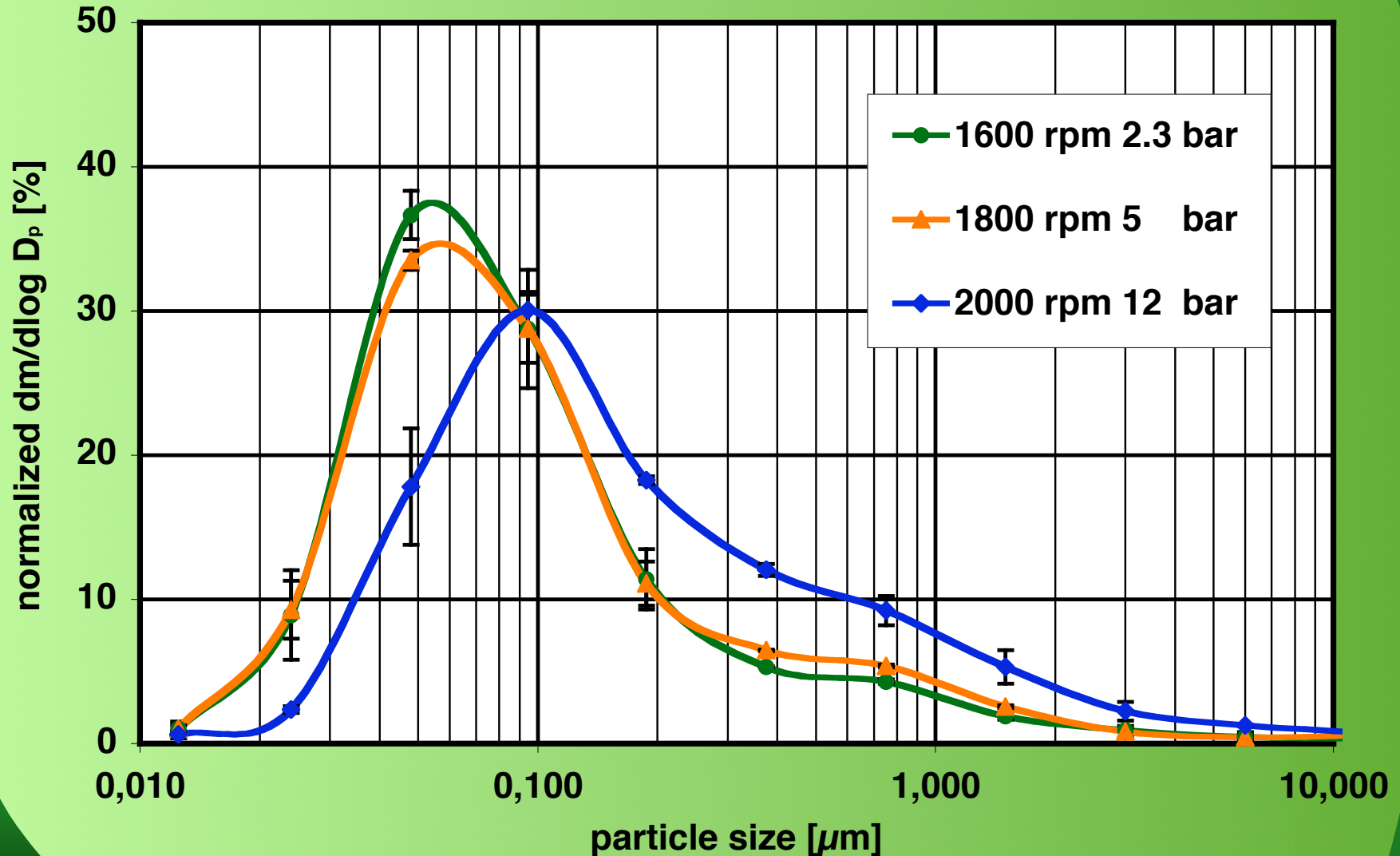




**test conditions @ CUTEC****engine settings**

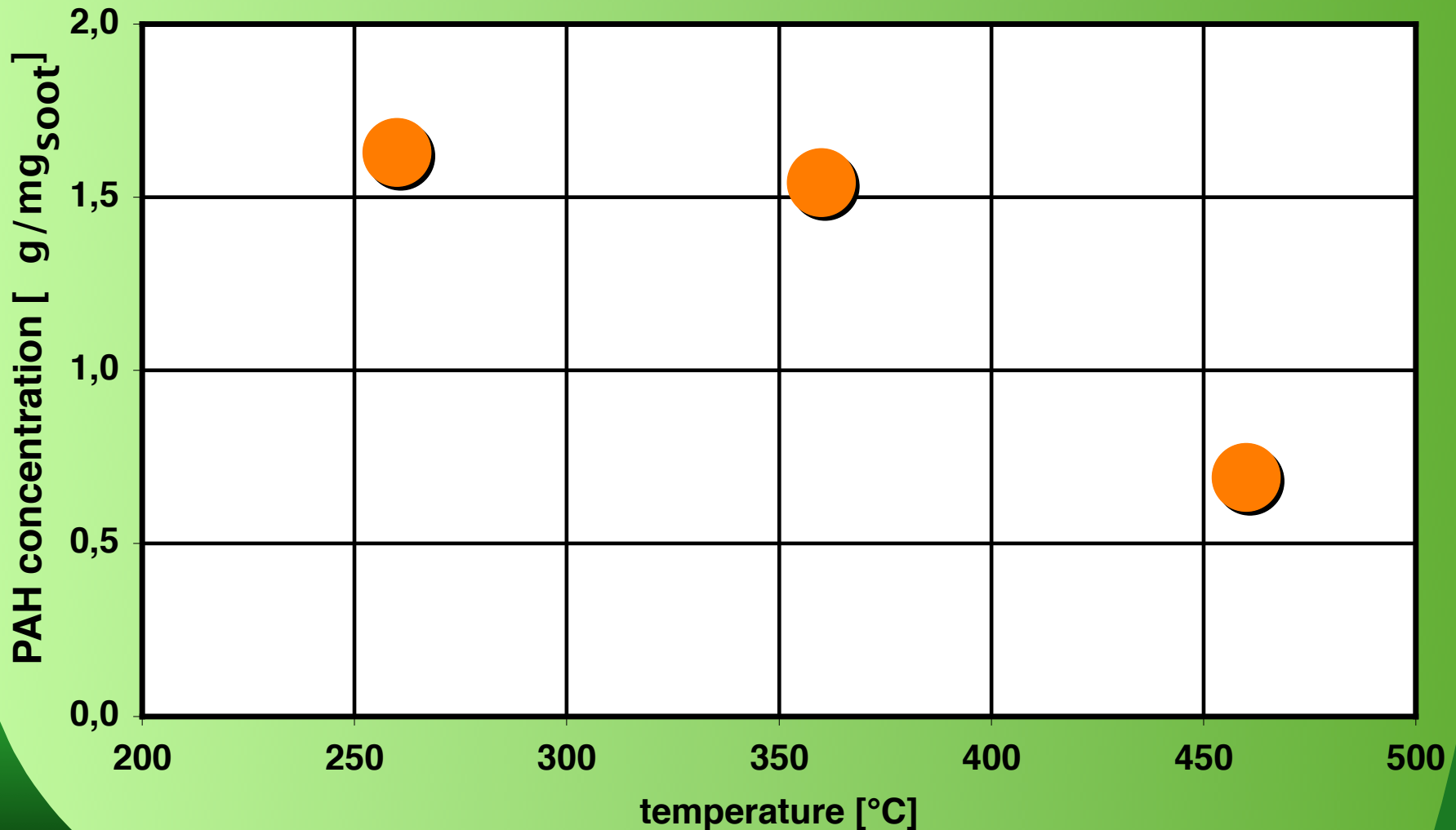
<b>speed [rpm]</b>	<b>torque [Nm]</b>	<b>BMEP [bar]</b>	<b>exhaust gas temperature [ °C]</b>
<b>1600</b>	<b>34</b>	<b>2.3</b>	<b>260</b>
<b>1800</b>	<b>80</b>	<b>5</b>	<b>360</b>
<b>2000</b>	<b>186</b>	<b>12</b>	<b>460</b>

# particle mass distribution



test results @ CUTEC

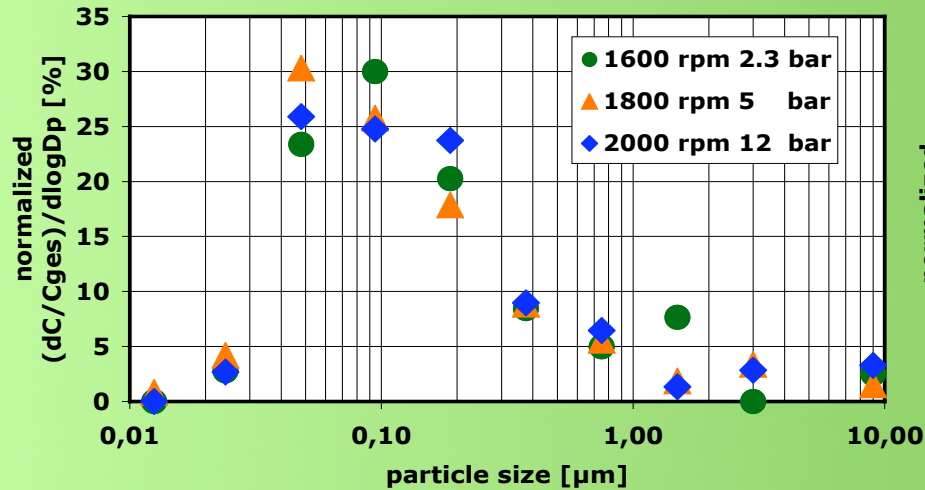
$$\Sigma \text{PAH} = f(\text{temperature})$$



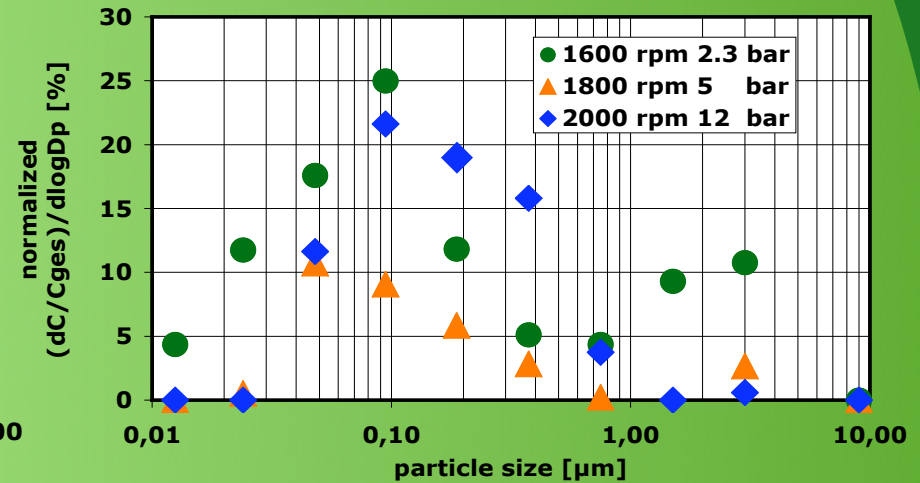
test results @ CUTEC

# [PAH] = f (particle size, temperature)

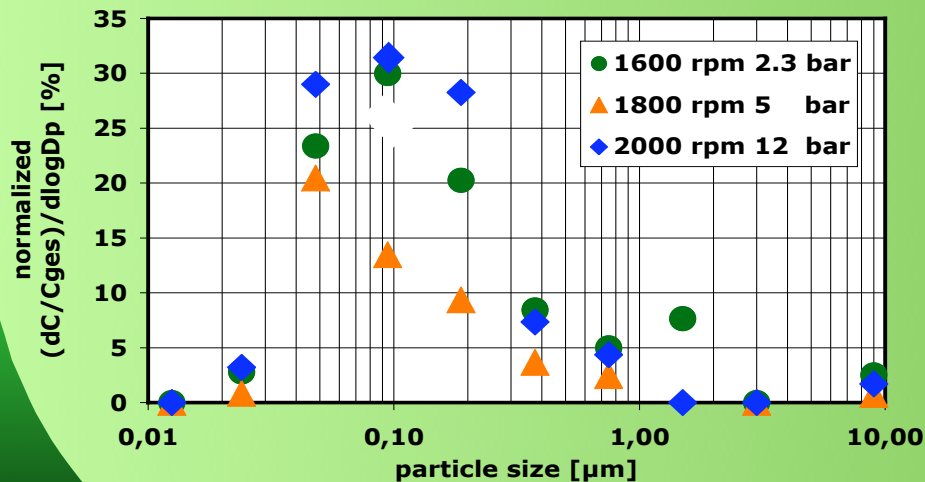
Pyrene



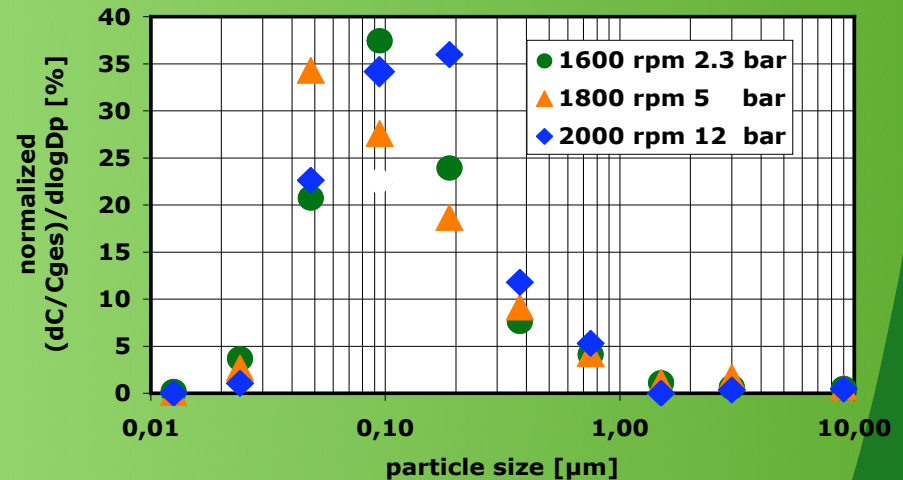
Anthracene



Benzo(a)anthracene

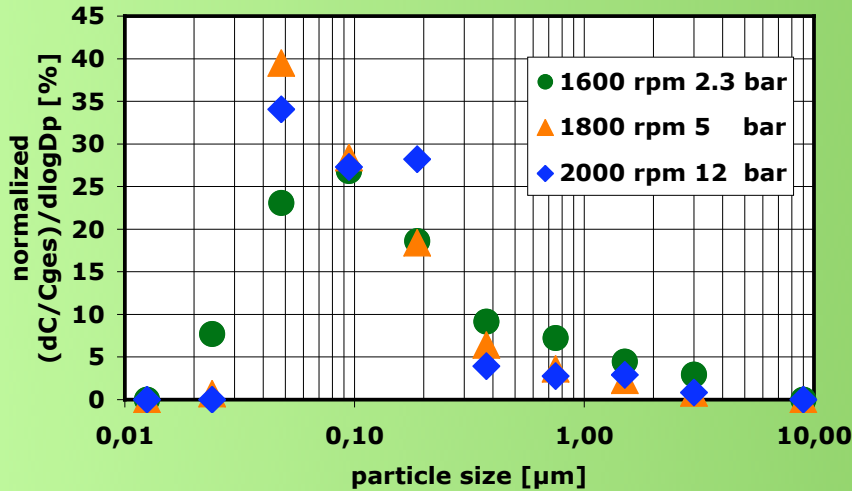


Phenanthrene

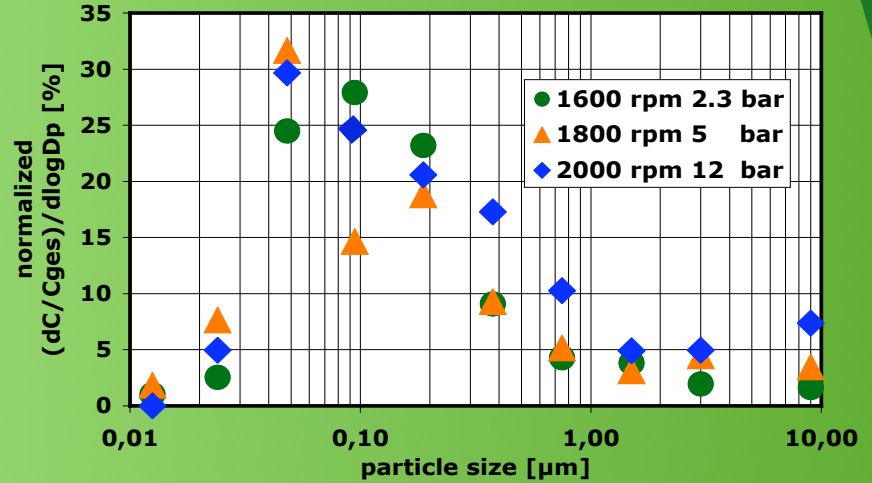


# [PAH] = f (particle size, temperature)

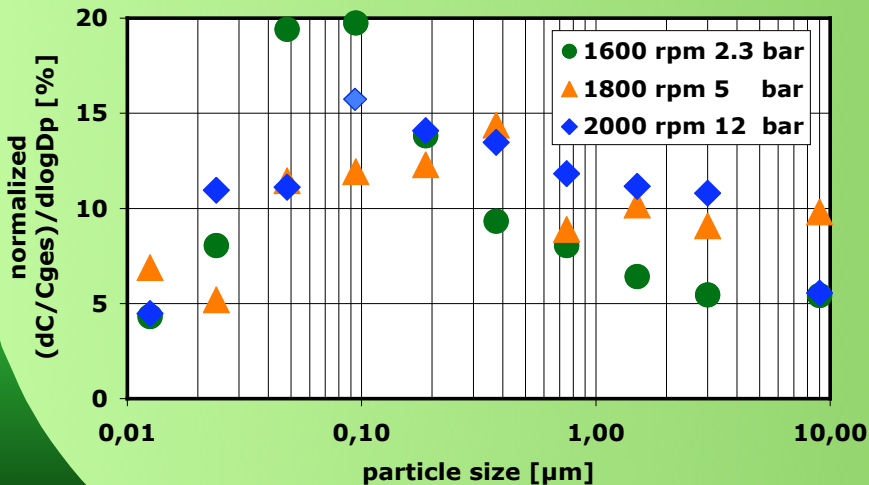
Chrysene



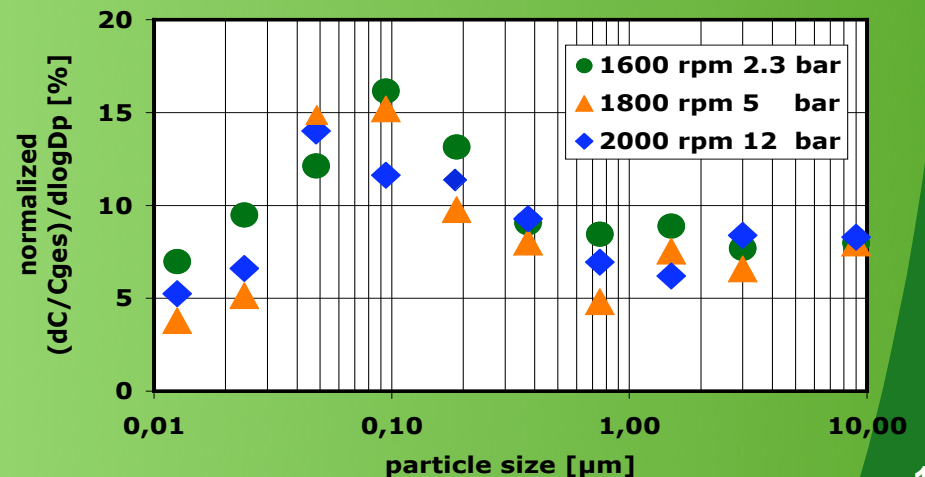
Fluoranthene



Benzo(b)fluoranthene



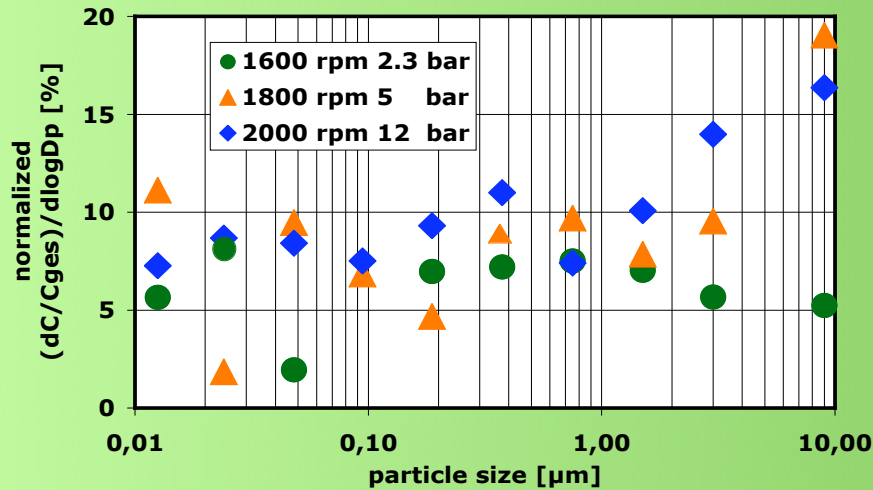
Fluorene



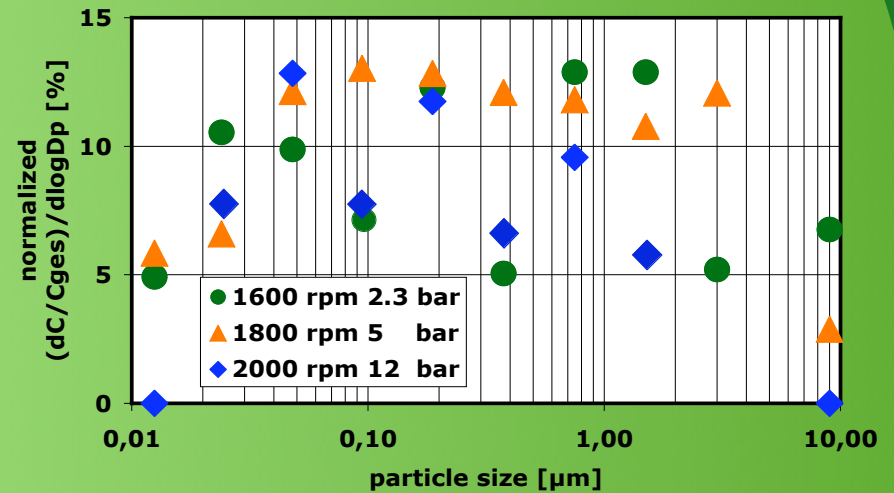
test results @ CUTEC

# [PAH] = f (particle size, temperature)

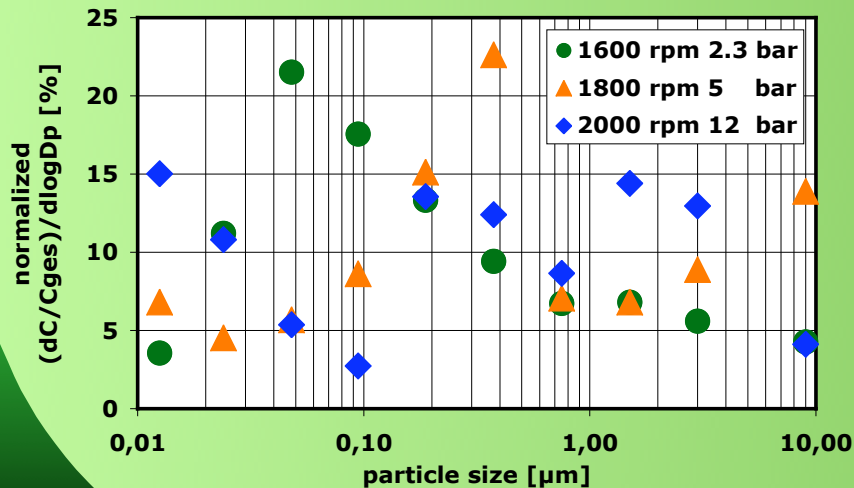
Naphthalene



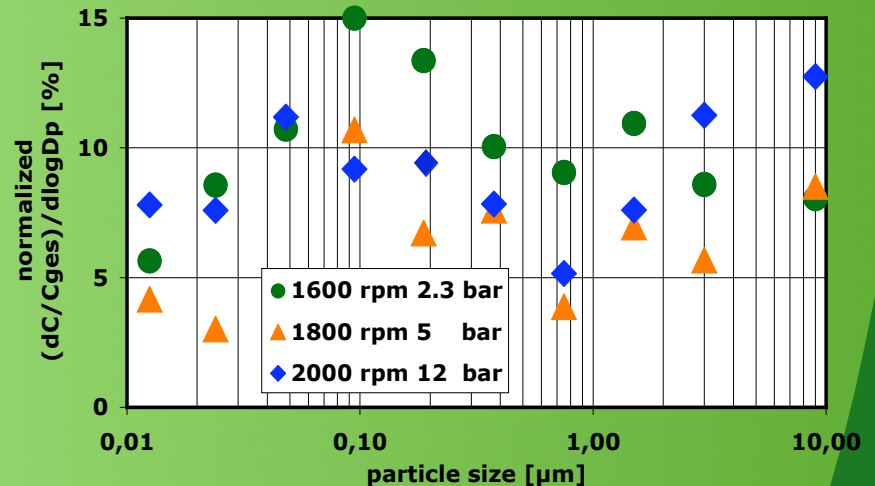
Benzo(a)pyrene

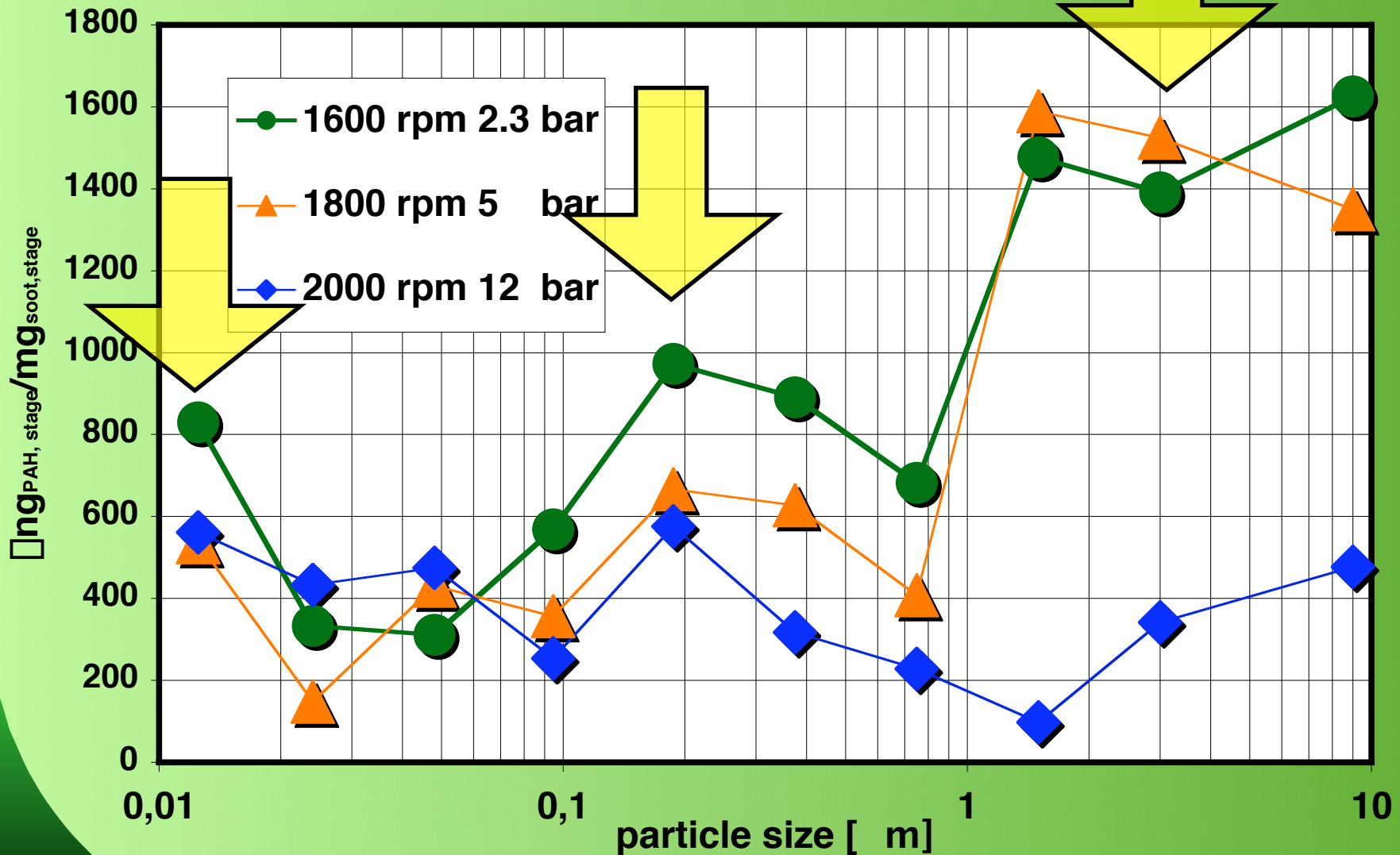


Benzo(k)fluoranthene

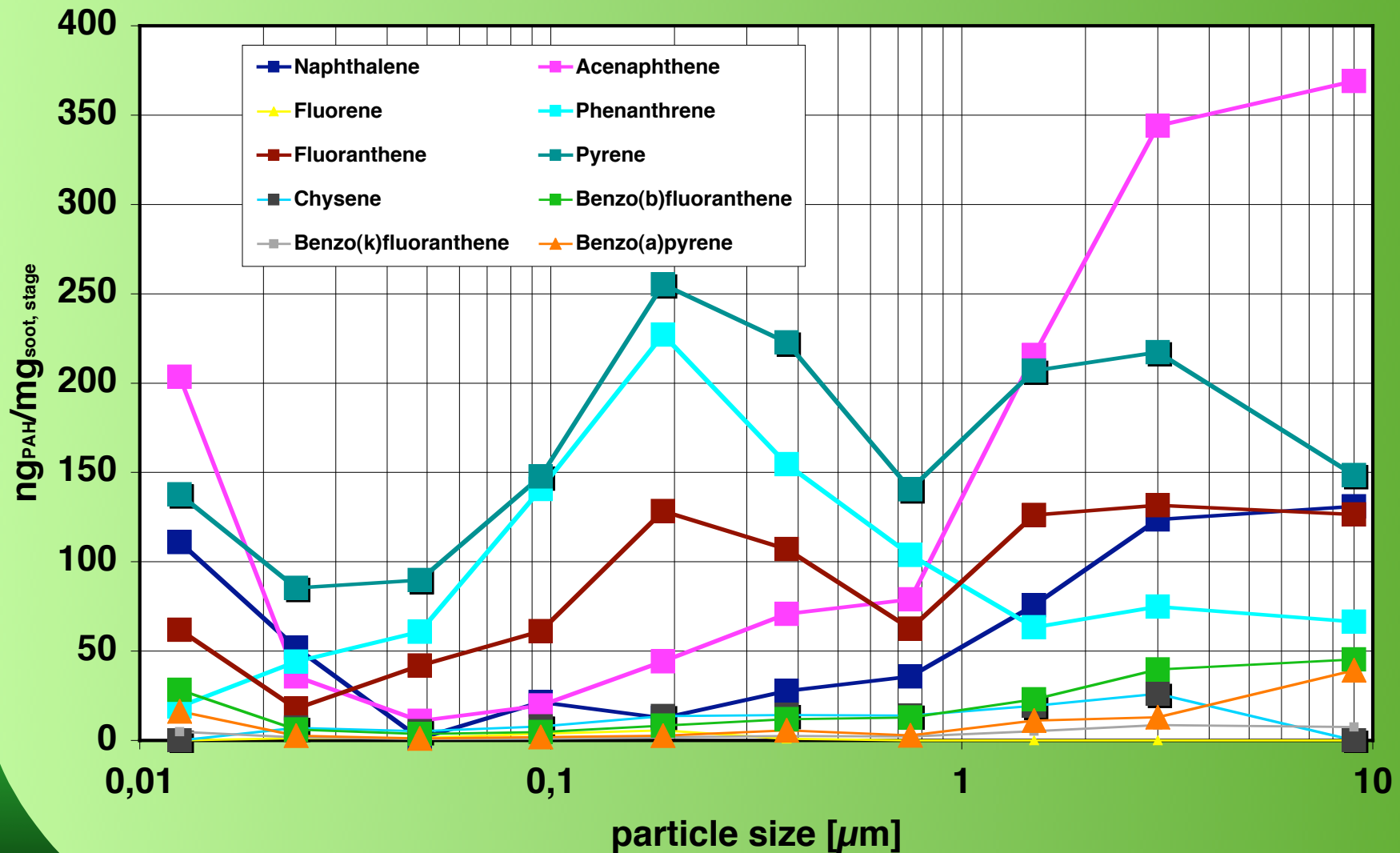


Acenaphthene



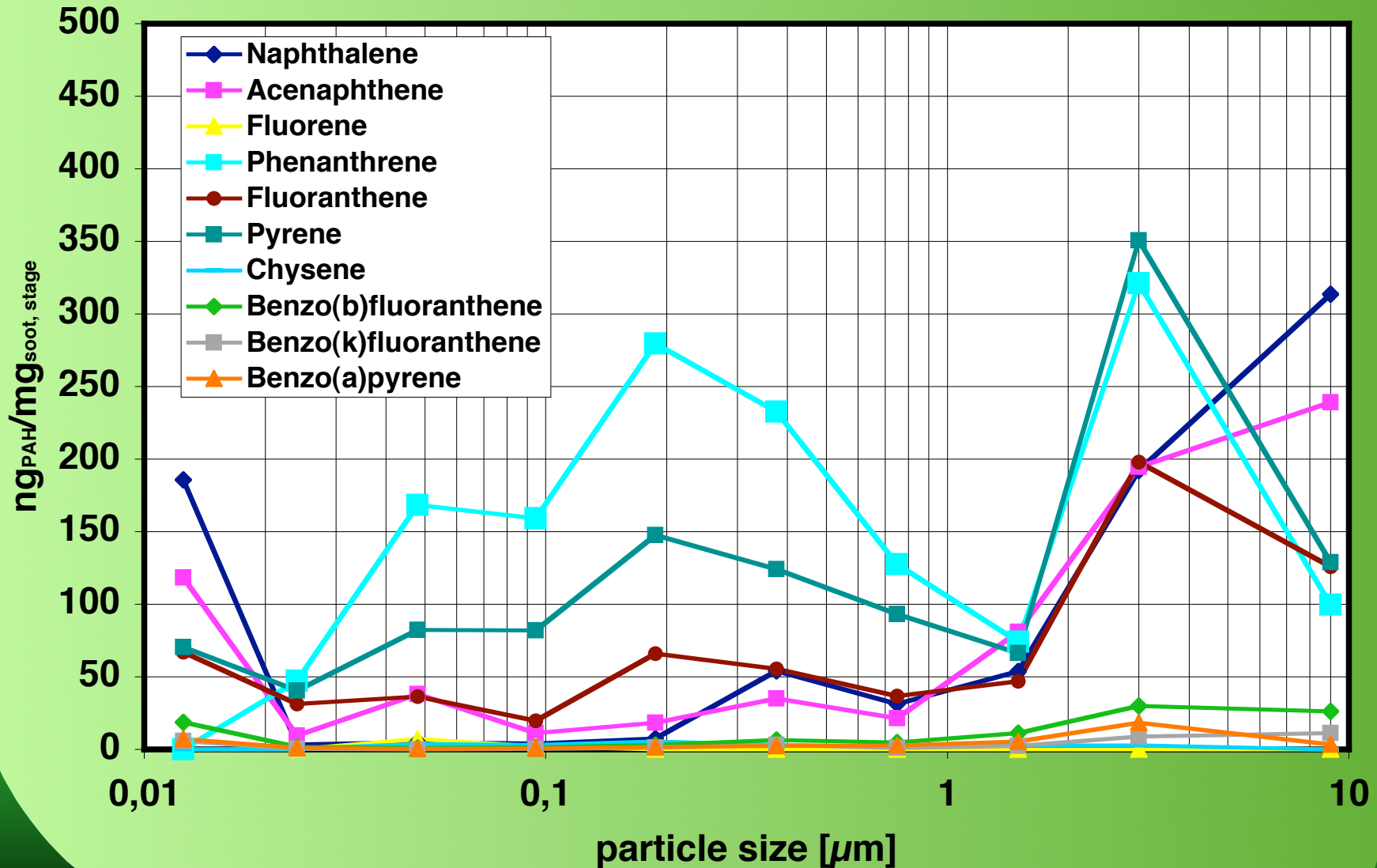
$\Sigma \text{PAH} = f(\text{impactor stage})$ 

test results 1600 rpm 2.3 bar @ CUTEC

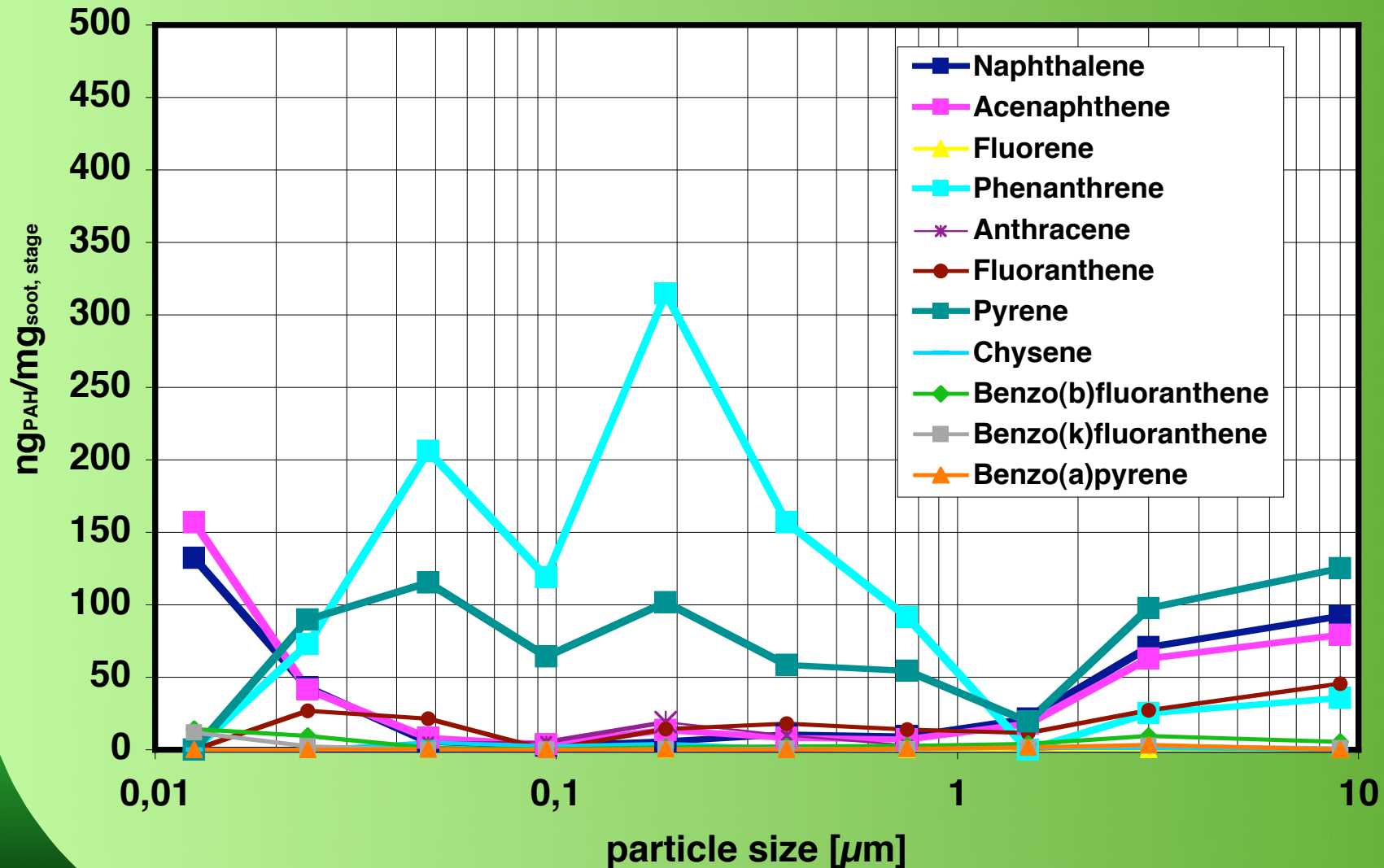
 $PAH = f(\text{impactor stage}) [ng_{PAHi} / mg_{Soot}]$ 



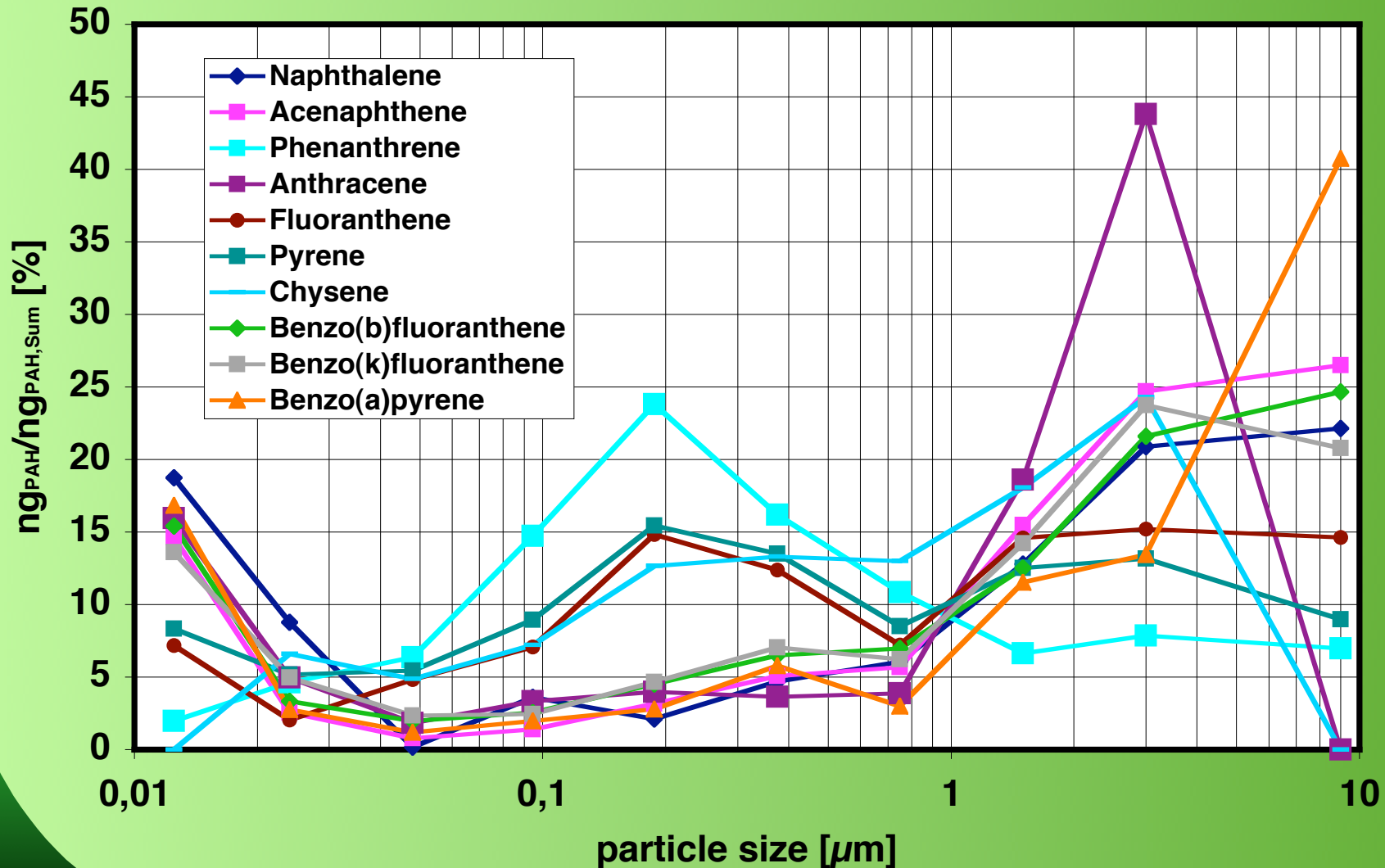
test results 1800 rpm 5 bar @ CUTEC

PAH = f (impactor stage) [ $\text{ng}_{\text{PAHi}} / \text{mg}_{\text{Soot}}$ ]

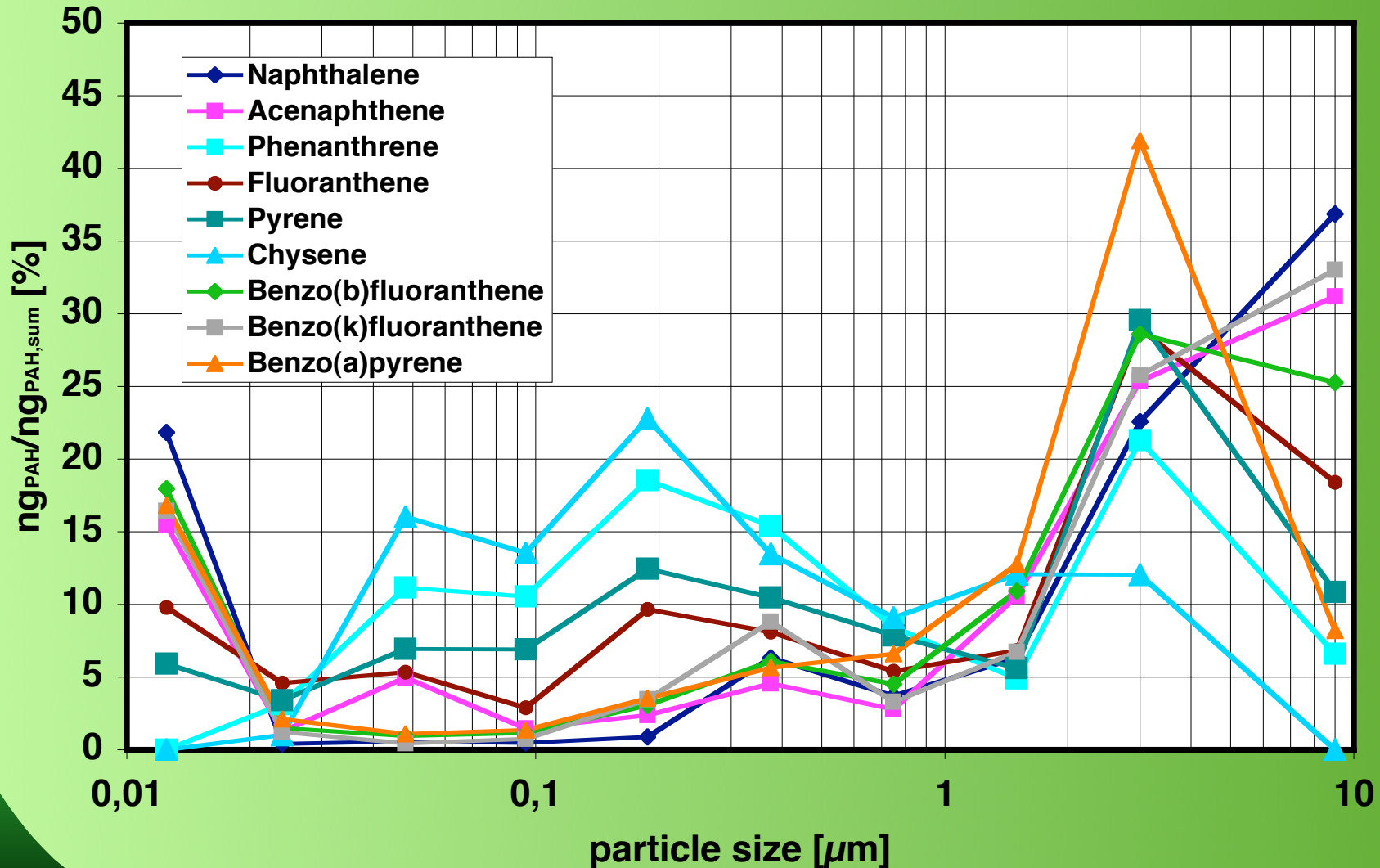
test results 2000 rpm 12 bar @ CUTEC

$$\text{PAH} = f(\text{impactor stage}) [\text{ng}_{\text{PAHi}} / \text{mg}_{\text{Soot}}]$$


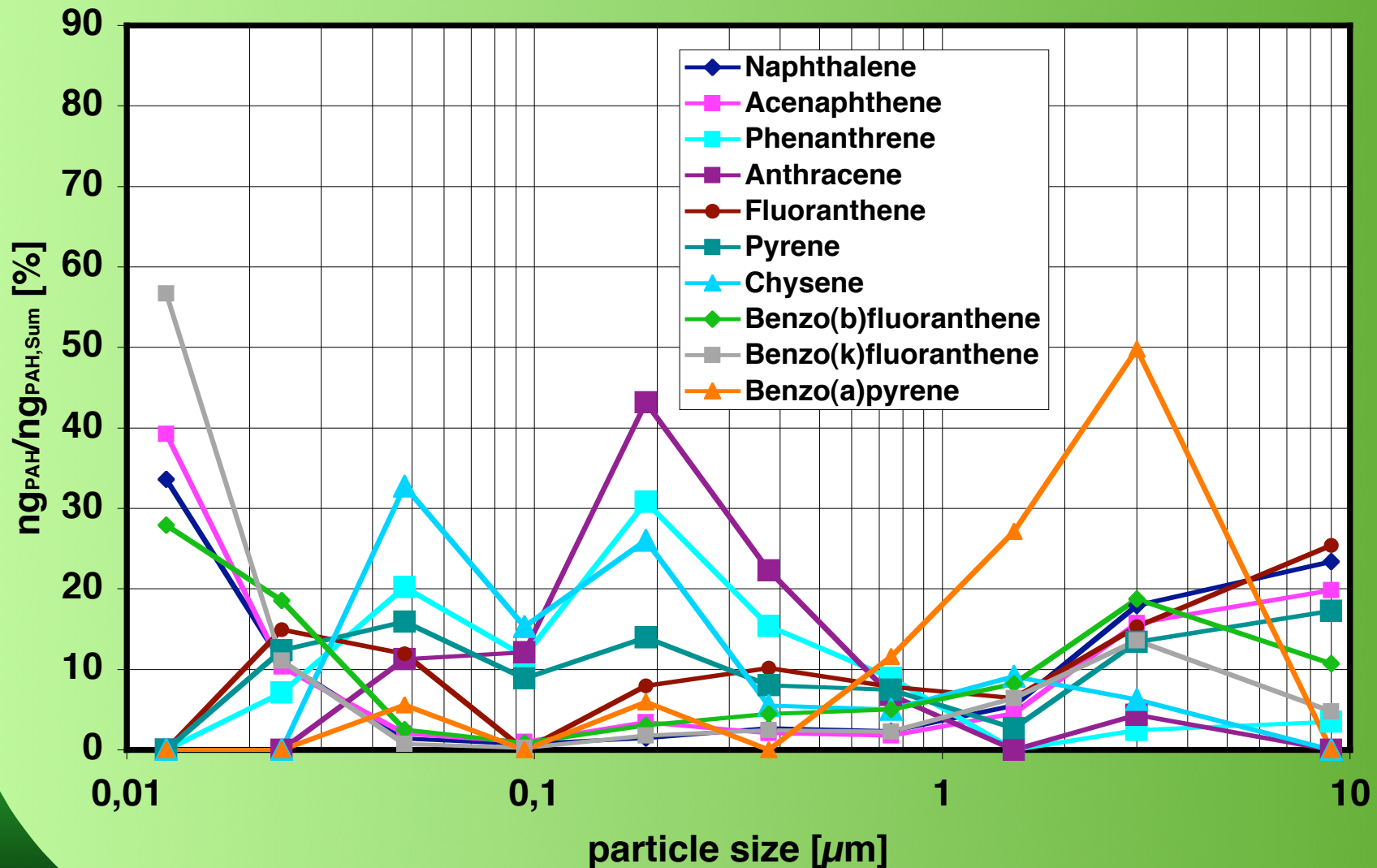
test results 1600 rpm 2.3 bar @ CUTEC

$$\text{PAH} = f(\text{impactor stage}) \left[ \frac{\text{ng}_{\text{PAH}i}}{\sum \text{ng}_{\text{PAH}}} \right]$$


test results 1800 rpm 5 bar @ CUTEC

$$\text{PAH} = f(\text{impactor stage}) \left[ \frac{\text{ng}_{\text{PAH}i}}{\sum \text{ng}_{\text{PAH}}} \right]$$


test results 2000 rpm 12 bar @ CUTEC

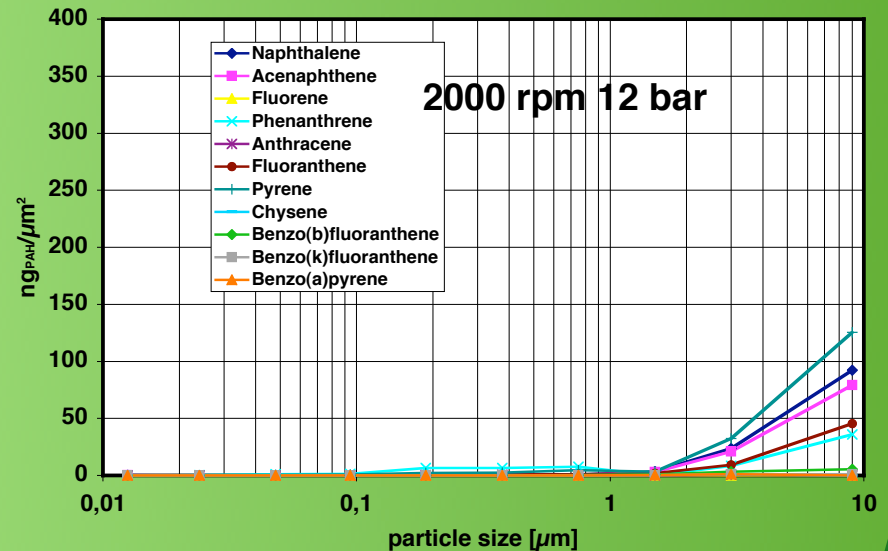
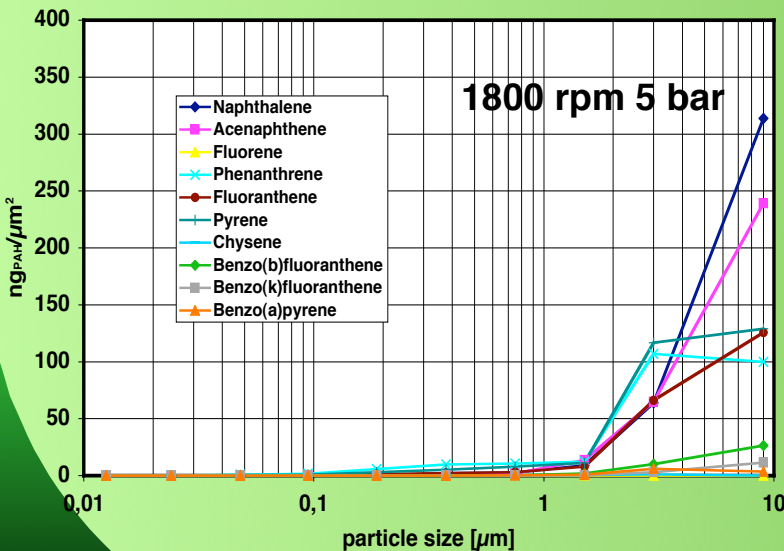
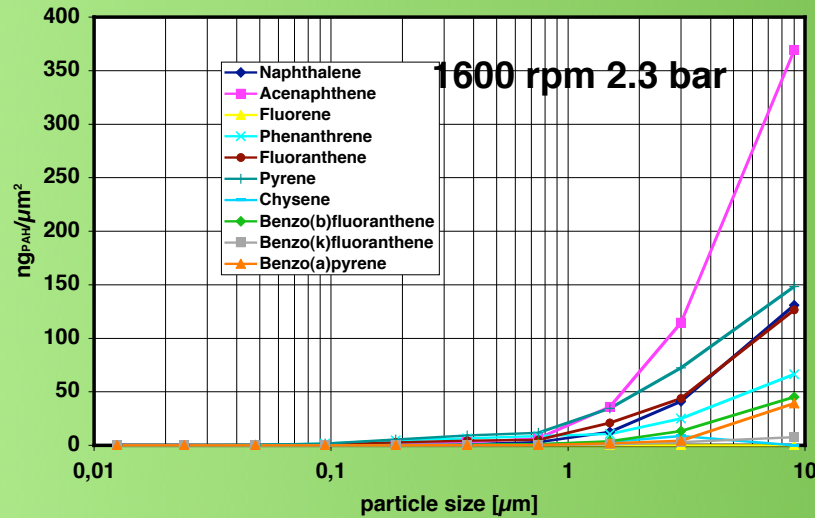
$$\text{PAH} = f(\text{impactor stage}) \left[ \frac{\text{ng}_{\text{PAHi}}}{\sum \text{ng}_{\text{PAH}}} \right]$$


$$\text{PAH} = f(\text{particle surface})$$
$$[\text{ng}_{\text{PAHi}} / \text{m}^2]$$

- simple assumptions
- particles as spheres, no fractals
- constant particle density per size class
- PAH molecules as spheres
- but particles are fractals !!!  $D_f \text{ mean} : 2.4$
- more information
  - B. Benker, A. Wollmann, M. Claussen:  
*Comparison of diesel soot particle size distributions measured with a cascade impactor and a mobility spectrometer*, SAE\_NA 2003-01-55
  - Journal Aerosol Science , EAC 2003 Madrid

PAH = f (particle surface)

$[ng_{PAH} / m^2]$



# conclusion

- high resolution PAH measurement technique
- PAH distribution  $\cong$  particle mass distribution
  - not significant effected by temperature
- PAH accumulation
  - particle  $\leq 20$  nm
  - $100 \leq$  particle  $\leq 200$  nm
  - particle  $\geq 1000$  nm
- PAH condensed on particles  $\geq 1000$  nm



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