

室内半挥发性有机物(SVOCs) 传质与净化机理的研究

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清华大学建筑环境检测中心

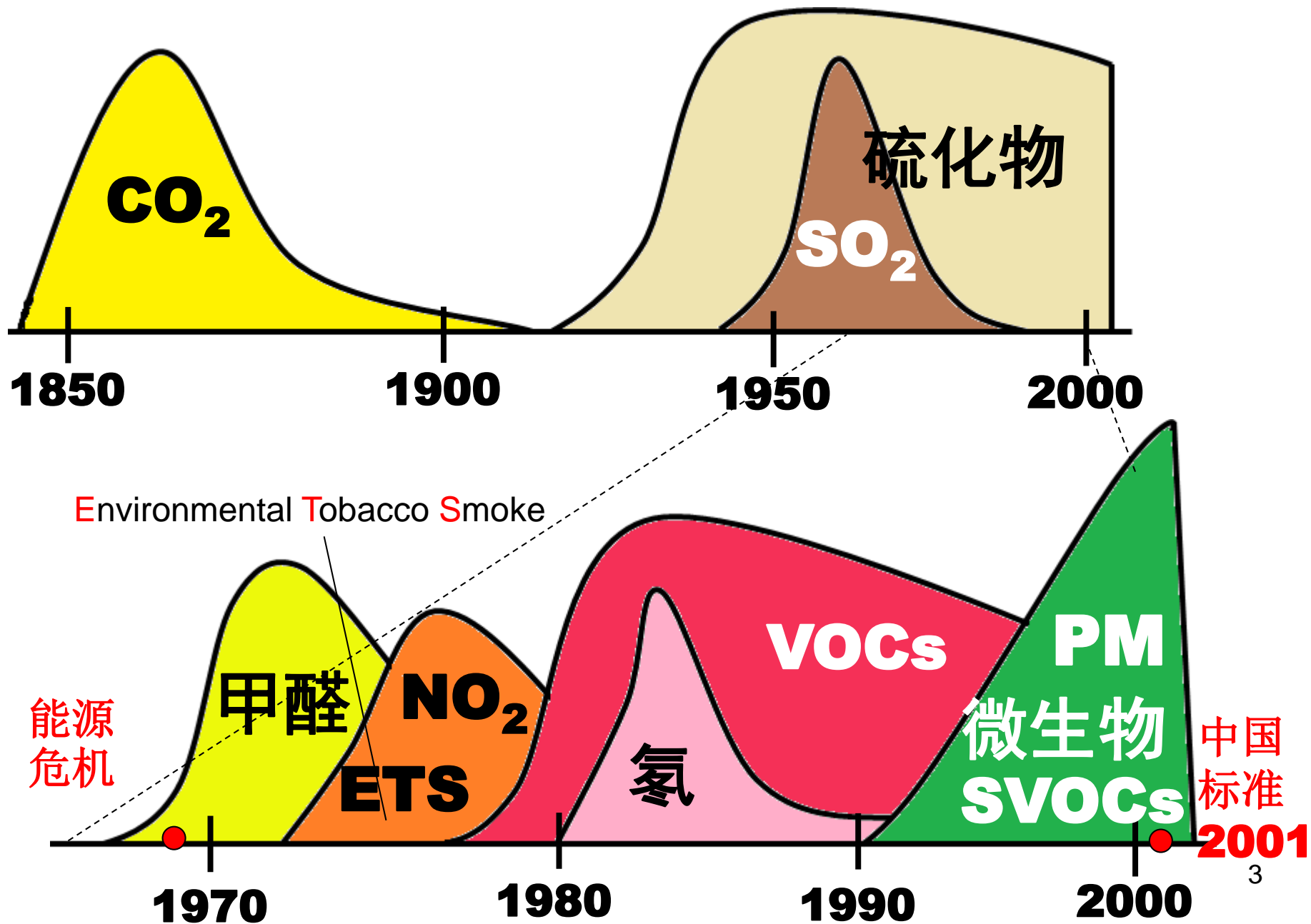
2019年11月10日

汇报内容

- 1. SVOCs研究背景**
- 2. SVOCs的发生方法**
- 3. 气相SVOCs净化方法**
- 4. SVOCs与颗粒物耦合污染净化尝试**

室内空气污染物的变迁

源自251次香山会议-潘小川



世界卫生组织(WHO)对室内有机污染物的分类

VOC: Volatile Organic Compounds

- VVOC: Very ~ 极易
- SVOC: Semi- 半

有机物分类	沸点 (°C)
极易挥发的有机化合物 (VVOC)	<0 到50~100
有机挥发性化合物 (VOC)	50~100 到240~260
半挥发性有机化合物 (SVOC)	240 ~ 260 到 380 ~ 400

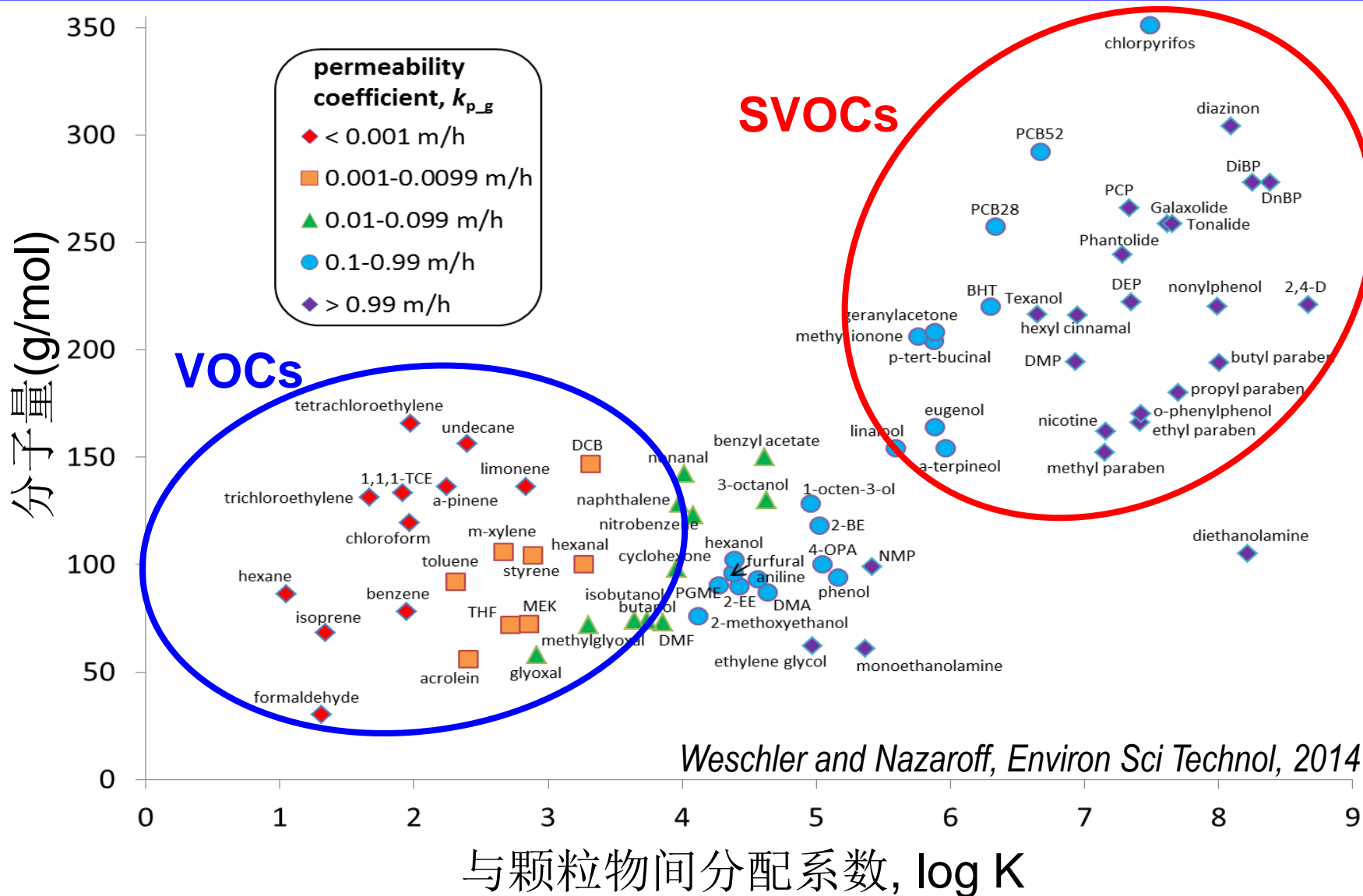
SVOC和VOC性能比较

饱和蒸气压 p_{vap}

VOC或SVOC C_0

名称	VOC (例如甲苯)	SVOC (例如DEHP)
沸点	很低(<50°C)、易挥发	很高(>250°C)、不易挥发
p_{vap} (Pa)	高 (6.9×10^3)	低 (2.5×10^{-5})
存在状态	绝大部分以气态存在于室内空气中	绝大部分吸附在室内材料、物品内；或吸附在室内环境的降尘或飘尘中
比喻	像酒精	像猪油

半挥发性有机物 (SVOCs, 沸点>250°C) 极易与PM_{2.5}附着



问题: SVOCs与PM_{2.5}的复合污染是否危害更大? 形成机制不清晰

室内SVOCs主要可分两类

❖ 阻燃剂 (Flame retardant)

- 为了防火；
- 溴系和氯系阻燃剂具有持久的；
生物积累毒性；
- 部分是致癌物，诱变物，再生毒物。

❖ 增塑剂 (Plasticizer)

- 加入材料中以改进可塑性；
- 影响人体荷尔蒙系统，特别是对成长中的青少年生长和发育不利；
- 引起哮喘、鼻炎；使啮类动物的肝脏致癌。



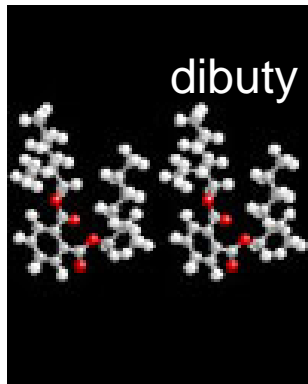
from Dr. Blum



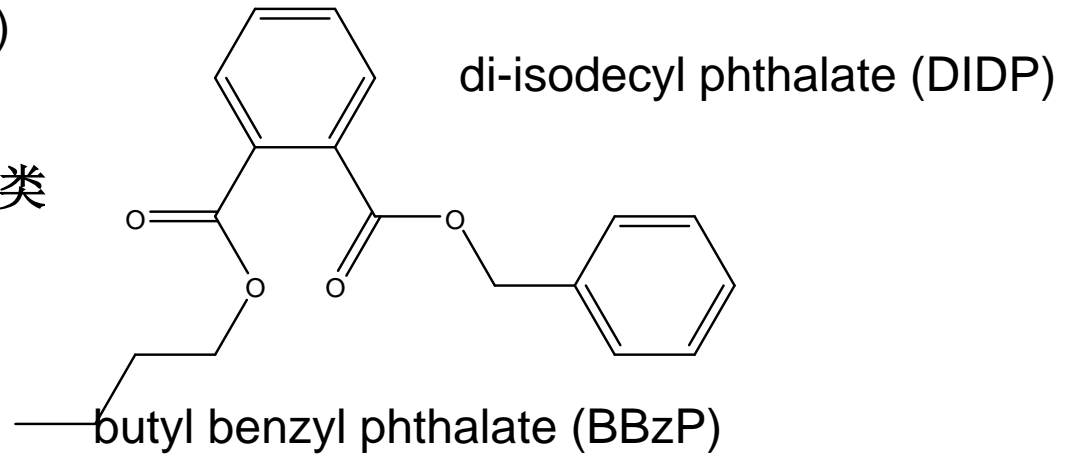
from Prof. Little

增塑剂

di-isononyl phthalate (DINP)



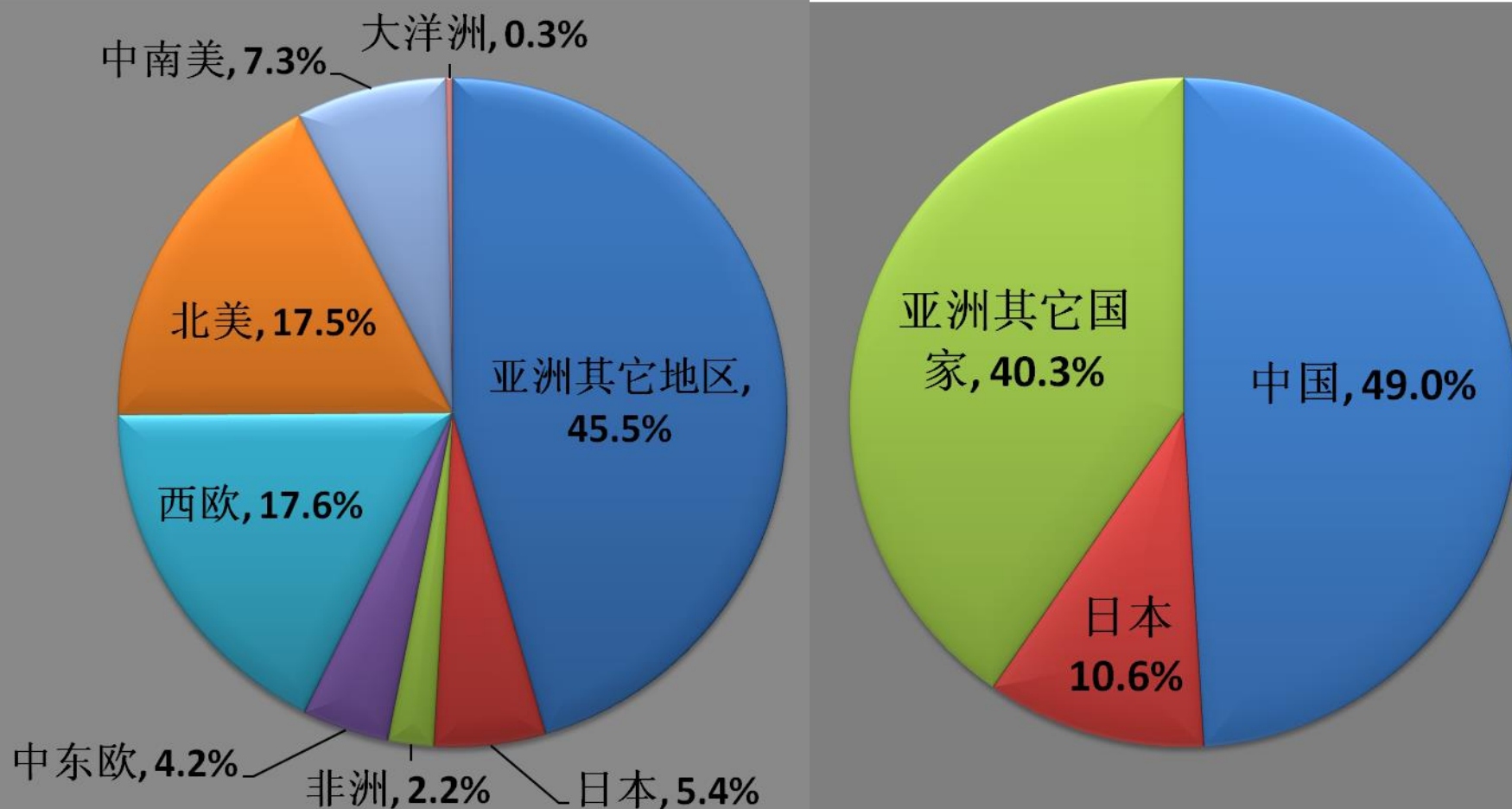
邻苯二甲酸酯类



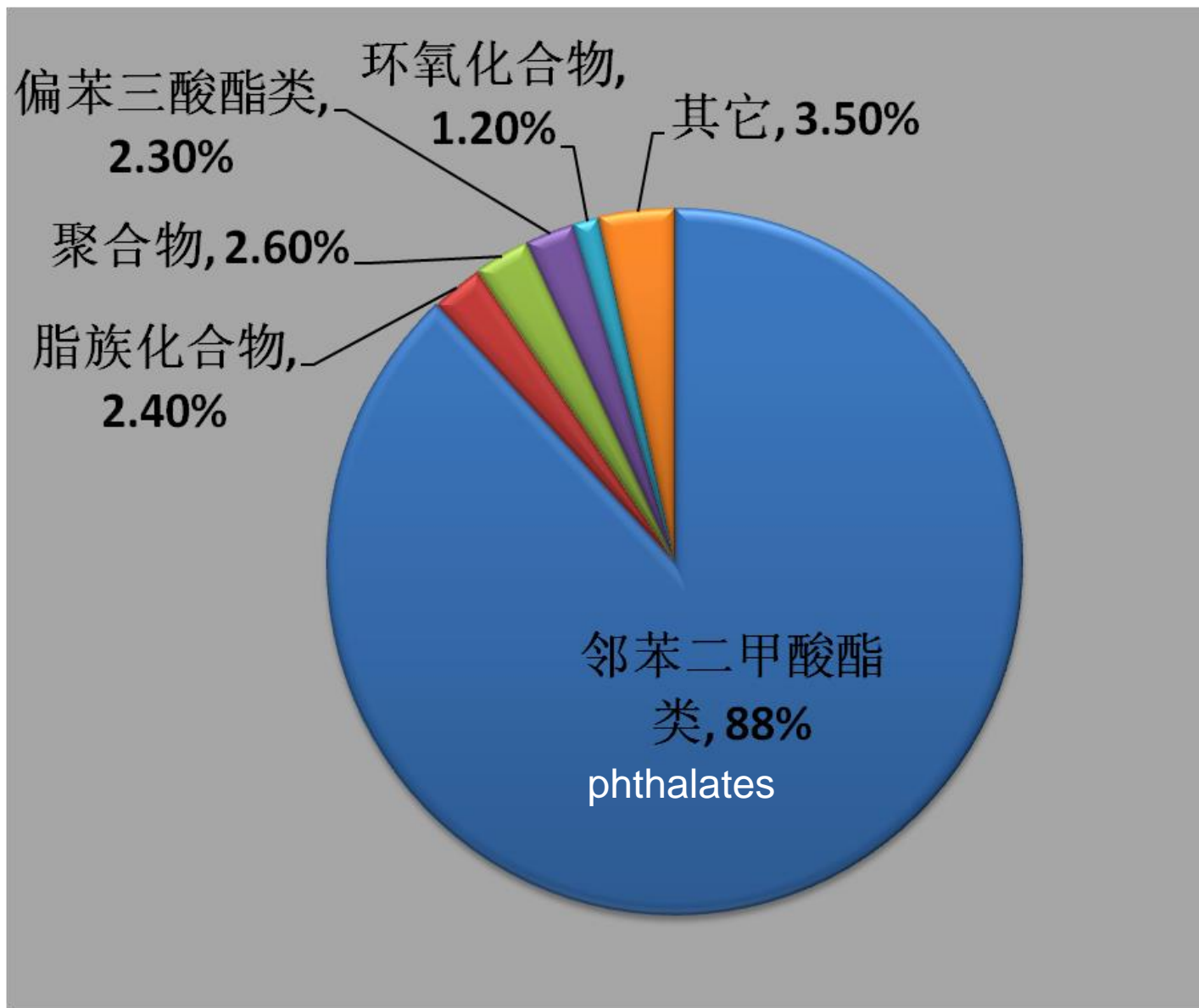
di(2-ethylhexyl) phthalate (DEHP)



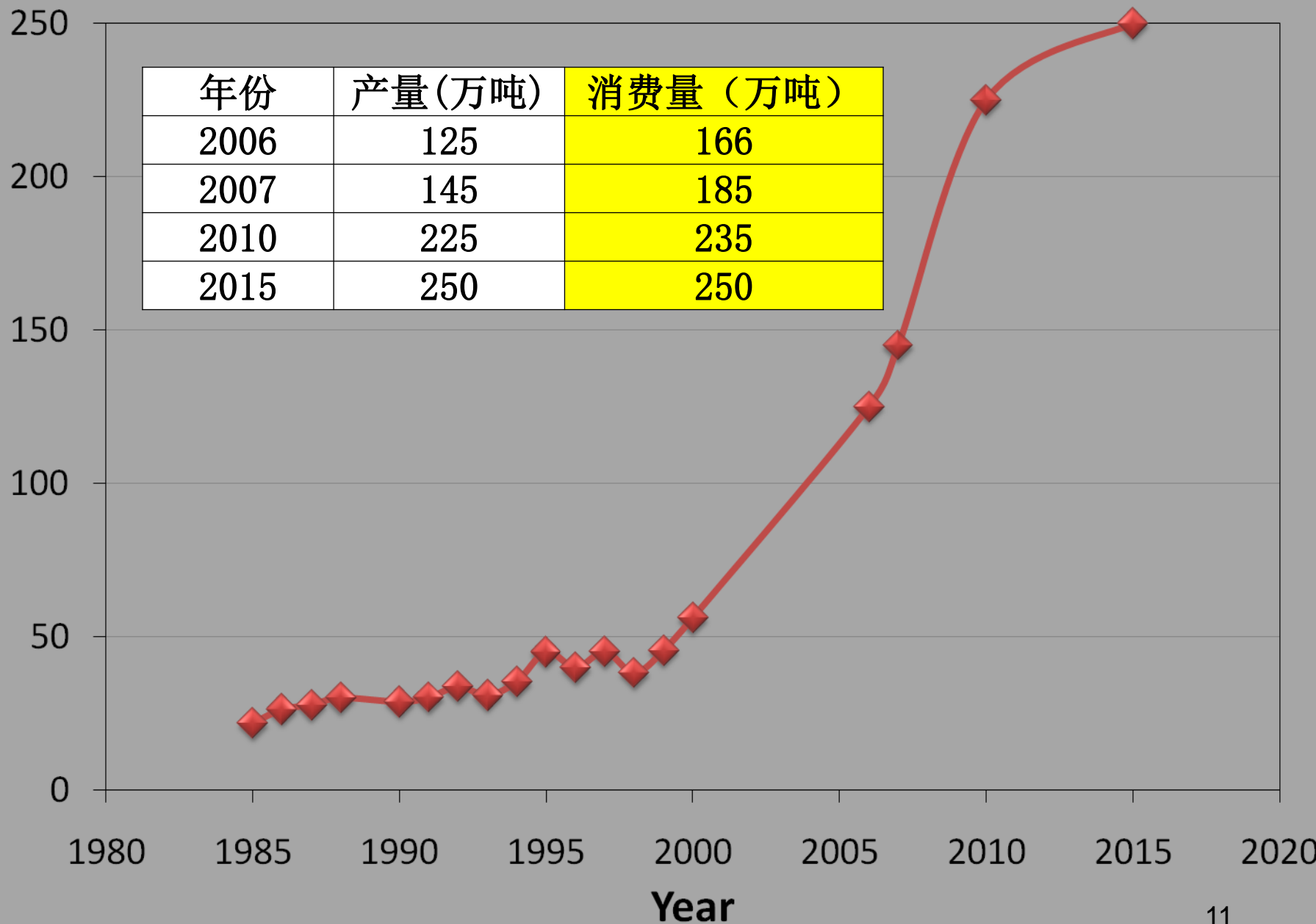
2006年全球增塑剂按地区消费比例



2006年世界增塑剂按品种消费比例



中国增塑剂年产量(万吨)



广泛存在于日常用品中

化妆品



PVC桌垫

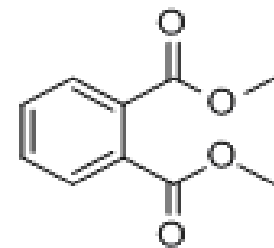
杀虫剂



药品

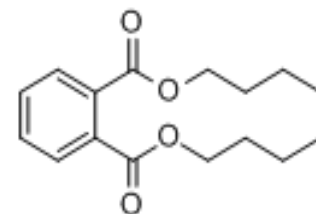


食品袋



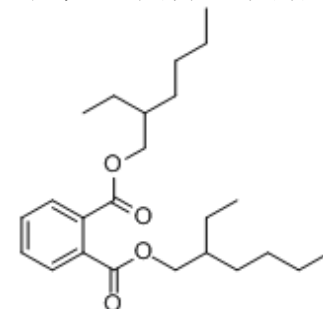
DMP

邻苯二甲酸二甲酯



DBP

邻苯二甲酸二丁酯



DEHP

邻苯二甲酸二(2-乙基)己酯

作为内分泌干扰素， 主要导致慢性疾病



呼吸系统疾病，
过敏，哮喘



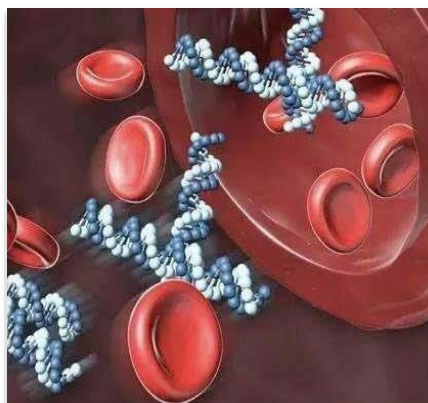
肥胖



出生体重偏低，早产



自闭症



生殖毒性



抗雄激素效应
肛门和生殖器距离过短 (AGD)

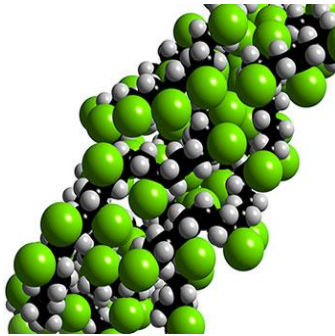
国际著名期刊EHP(IF=8.443): SVOC引发哮喘、癌症和生殖疾病!

- Bornehag et al., *Environ. Health Persp.*, 2004;
- Jaakkola et al., *Environ. Health Persp.*, 2006.

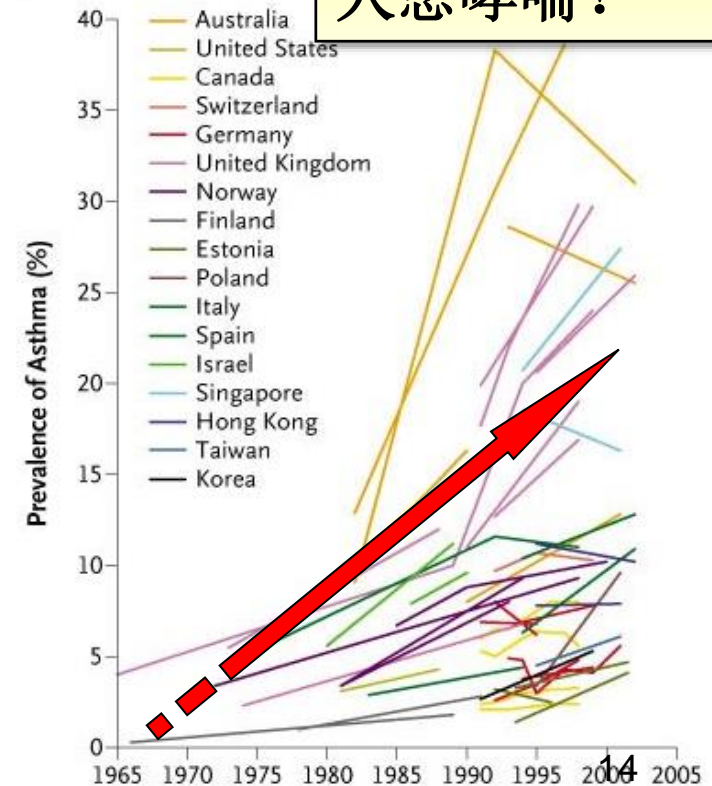
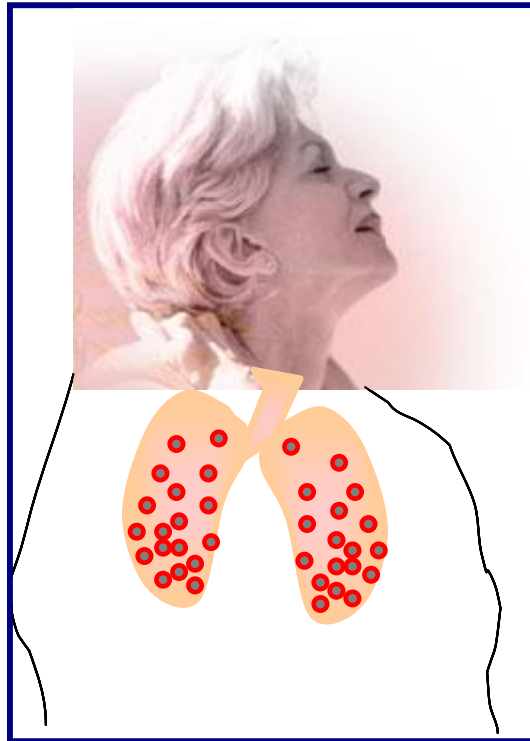


10%以上美国人患哮喘!

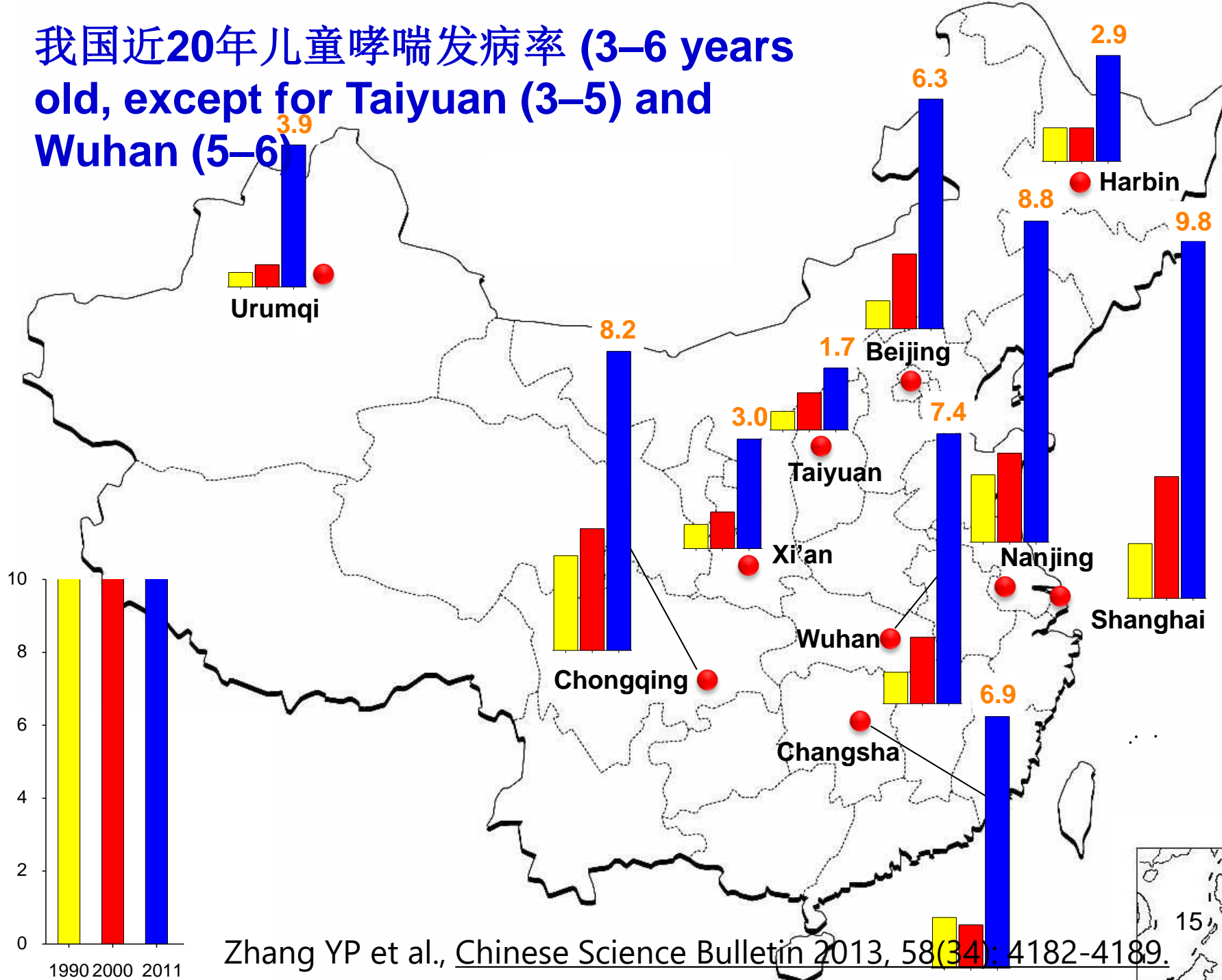
SVOC



增塑剂
阻燃剂等



我国近20年儿童哮喘发病率 (3–6 years old, except for Taiyuan (3–5) and Wuhan (5–6))

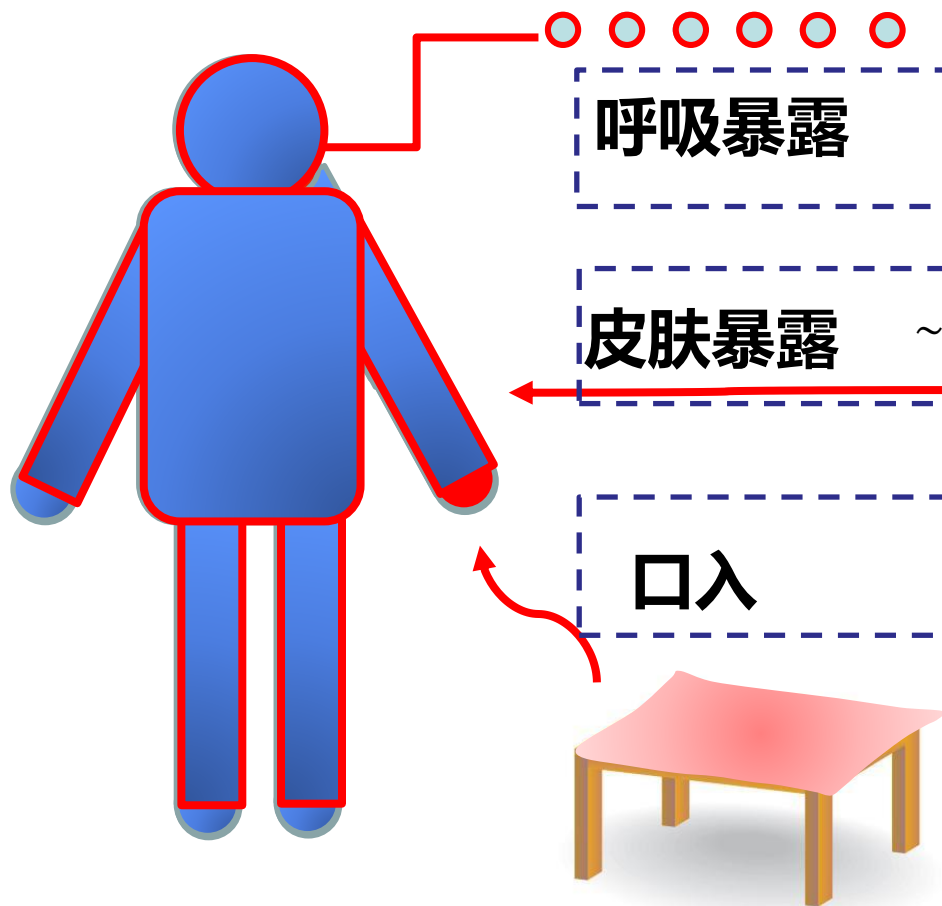


汇报内容

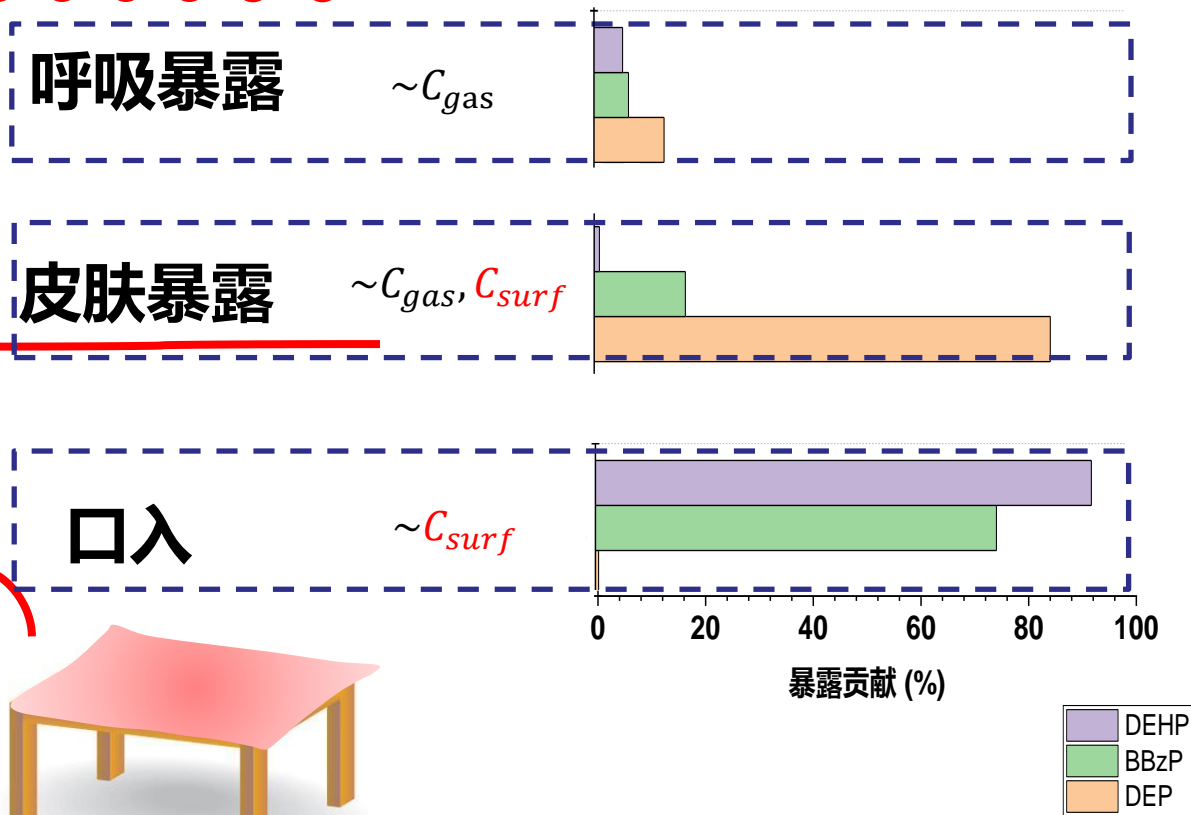
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塑化剂暴露特征与界面处浓度紧密相关

暴露途径



不同暴露途径对PAEs暴露的贡献比例^[1] (%)



塑化剂吸附与暴露特征的研究

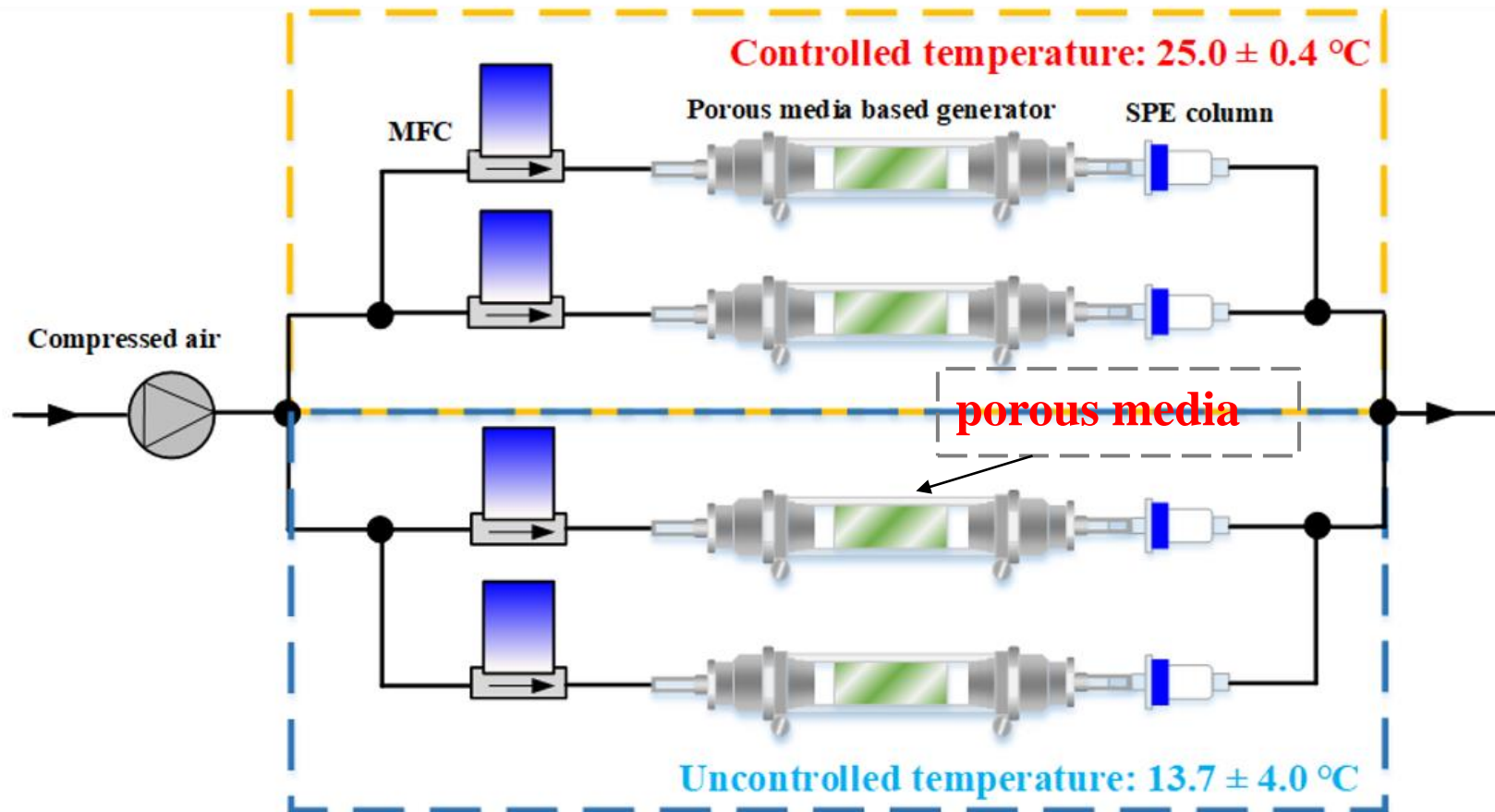
PAEs

皮肤吸附

口入

稳定的SVOC发生源

稳定的SVOC发生源

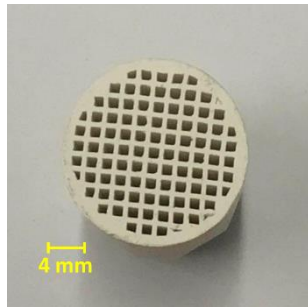
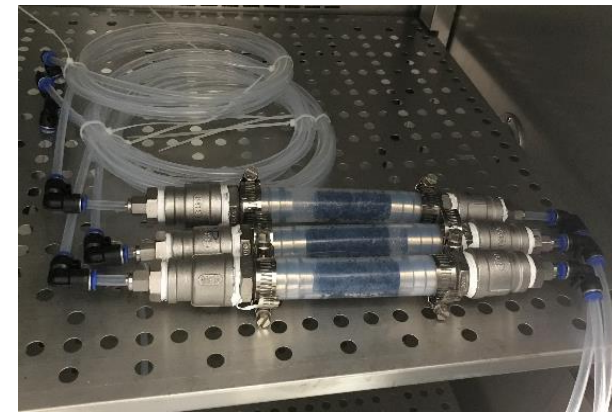


Experimental conditions:

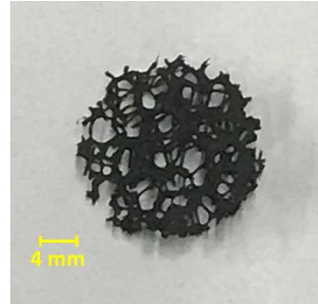
- Carrier gas: **air**
- Flow rate: **100 mL/min**
- Air sampling: **SPE column**
- Concentration analysis : **GC-MS**

变量控制

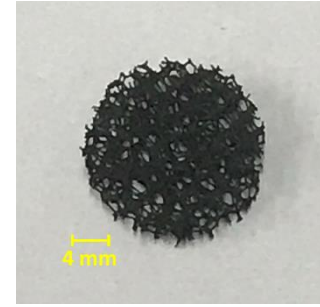
- Temperature states
 - Controlled (25.0 ± 0.4 °C);
 - Uncontrolled (13.7 ± 4.0 °C)
- Materials of porous media



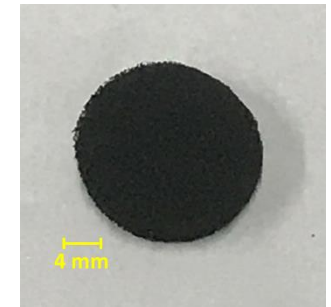
14 ppi honeycomb ceramics



20 ppi carbon sponges



30 ppi carbon sponges



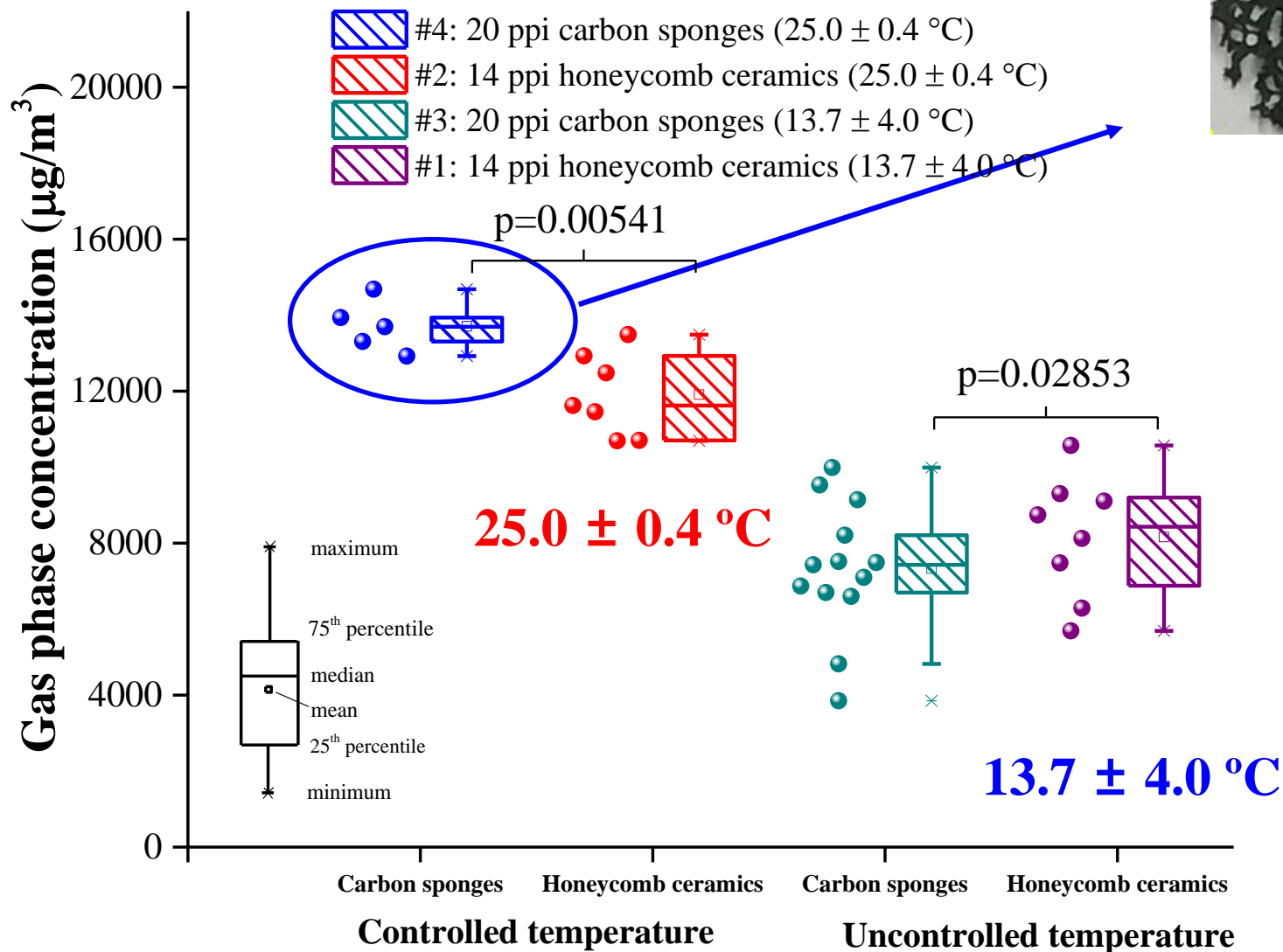
40 ppi carbon sponges

- Types of PAEs

- **DMP**, **DiBP**, **DEHP**

结果与讨论

• Influence of temperature and materials



Influence of temperature on vapor pressure

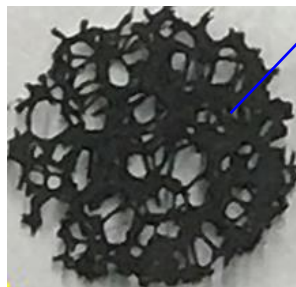
Phthalates		15 ° C	20 ° C	25 ° C
DMP	Vapor pressure (Pa)	1.11×10^{-2}	2.51×10^{-2}	5.67×10^{-2}
	Saturated concentration ($\mu\text{g}/\text{m}^3$)	286.60	610.83	1335.63
DiBP	Vapor pressure (Pa)	9.50×10^{-5}	2.19×10^{-4}	5.09×10^{-4}
	Saturated concentration ($\mu\text{g}/\text{m}^3$)	11.04	25.01	57.15
DEHP	Vapor pressure (Pa)	1.82×10^{-8}	5.11×10^{-8}	1.42×10^{-7}
	Saturated concentration ($\mu\text{g}/\text{m}^3$)	0.0030	0.0082	0.022

SPARC on-line calculator (<http://sparc.chem.uga.edu/sparc/>)

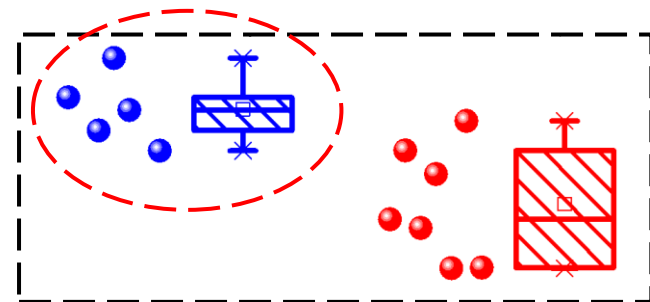
Materials to guarantee stably generating

Straight tubes

Cylindrical disturbed flow (more disturbance)



$$q_m = h_m A_{in} (y_0 - \bar{y}_g) \quad h_{m,HC} < h_{m,CS}$$

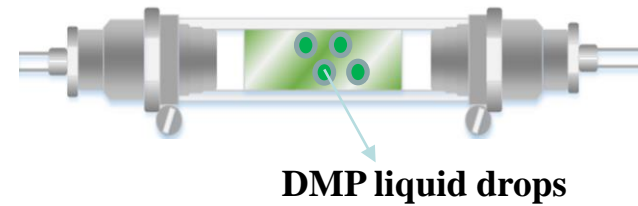
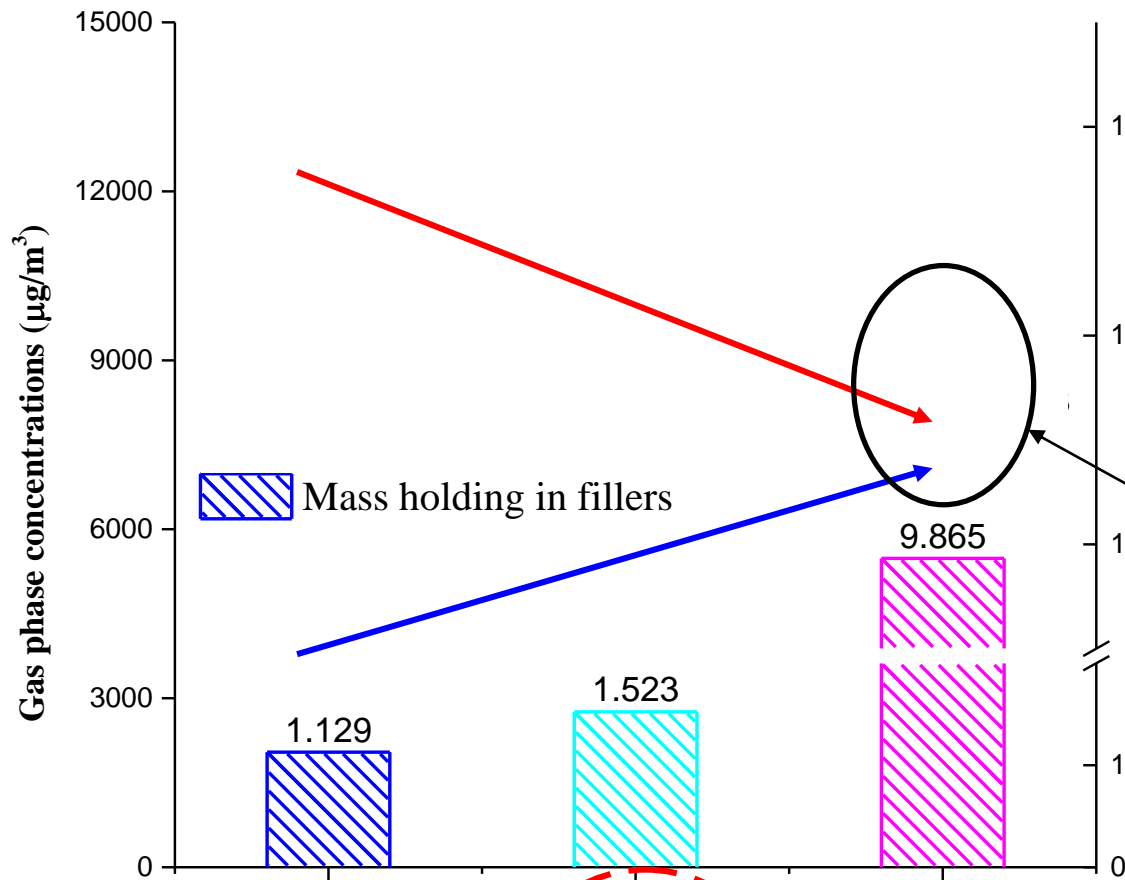


Higher concentration and more stable

honeycomb ceramics
(HC)

carbon sponges
(CS)

• Influence of carbon sponges pore size

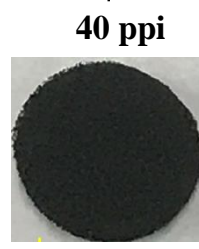
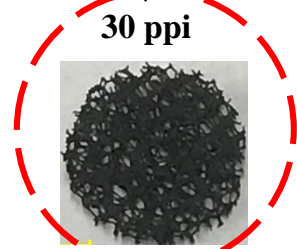
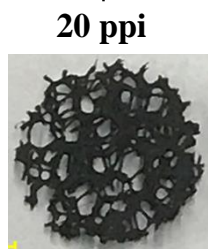


Block inner holes

- **Lower concentrations**

Carry DMP drips out

- **Larger error bar**



Larger

inner area

increase

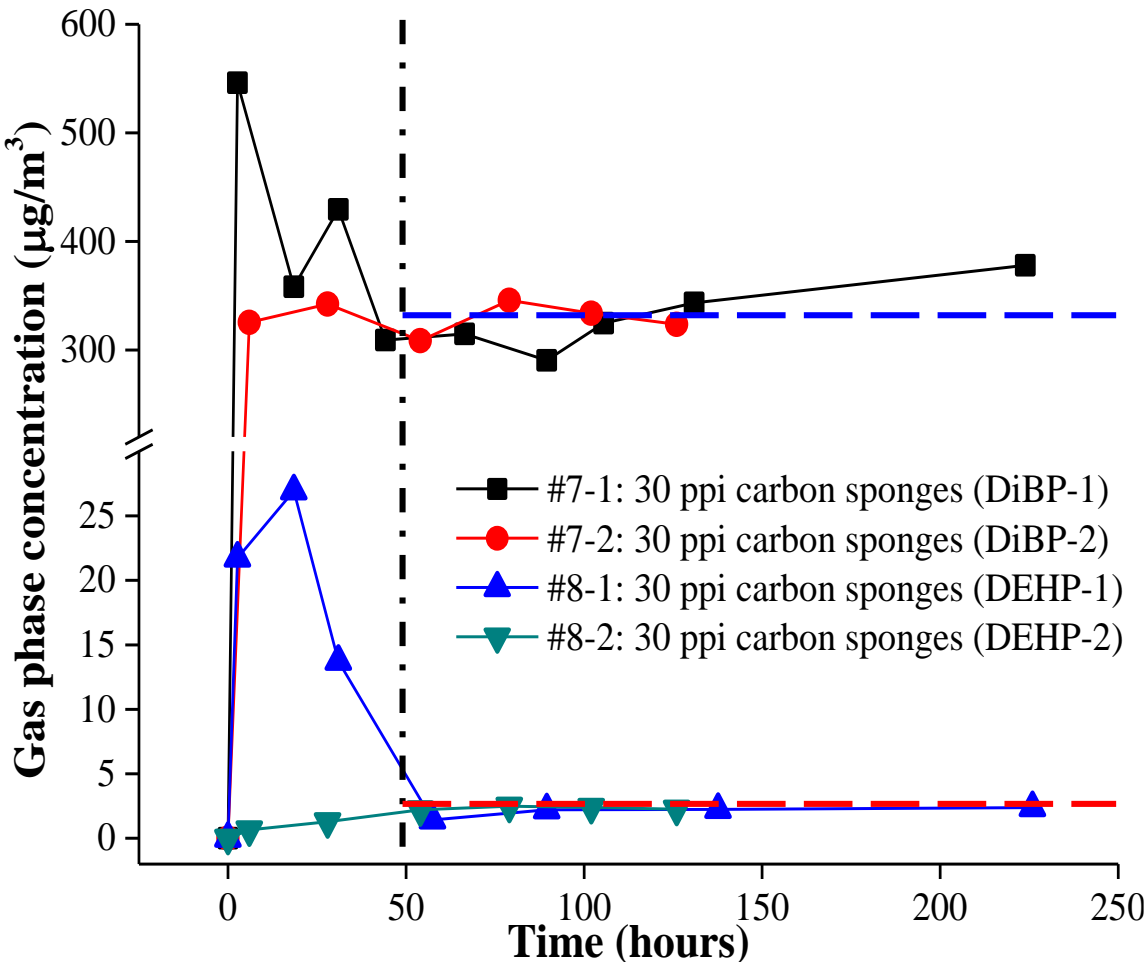
The most suitable filler

Generating DiBP and DEHP stably (t-test)

$$y_{g,i} = a \tau_i + b, i = 0, 1, 2, \dots, n$$

$$t = \frac{\hat{a}}{S(\hat{a})}$$

$$S(\hat{a}) = \sqrt{\frac{\sum_{i=1}^n (y_{g,i} - \bar{y}_g)^2}{(n-2) \sum_{i=1}^n (\tau_i - \bar{\tau})^2}}$$



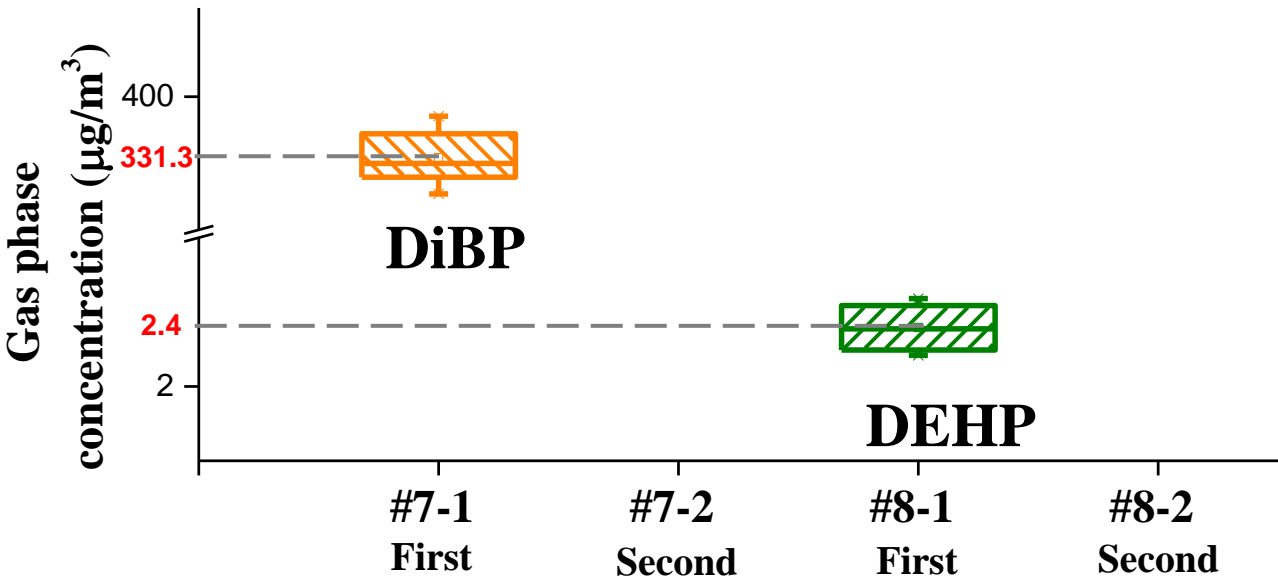
if $t_{0.05/2(n-2)} > t$: stable

Sample	$t_{0.05/2(n-2)}$	a	b	S(a)	t
#7-1	2.6	0.2	309.5	1.2	0.2
#7-2	2.8	0.0	329.9	2.2	0.0
#8-1	3.2	0.0	2.5	0.0	0.0
#8-2	4.3	0.0	2.3	0.0	0.0

Generations of DiBP and DEHP are stable

- Controlled temperature
- 30 ppi carbon sponges

- **Generating DiBP and DEHP repeatedly**



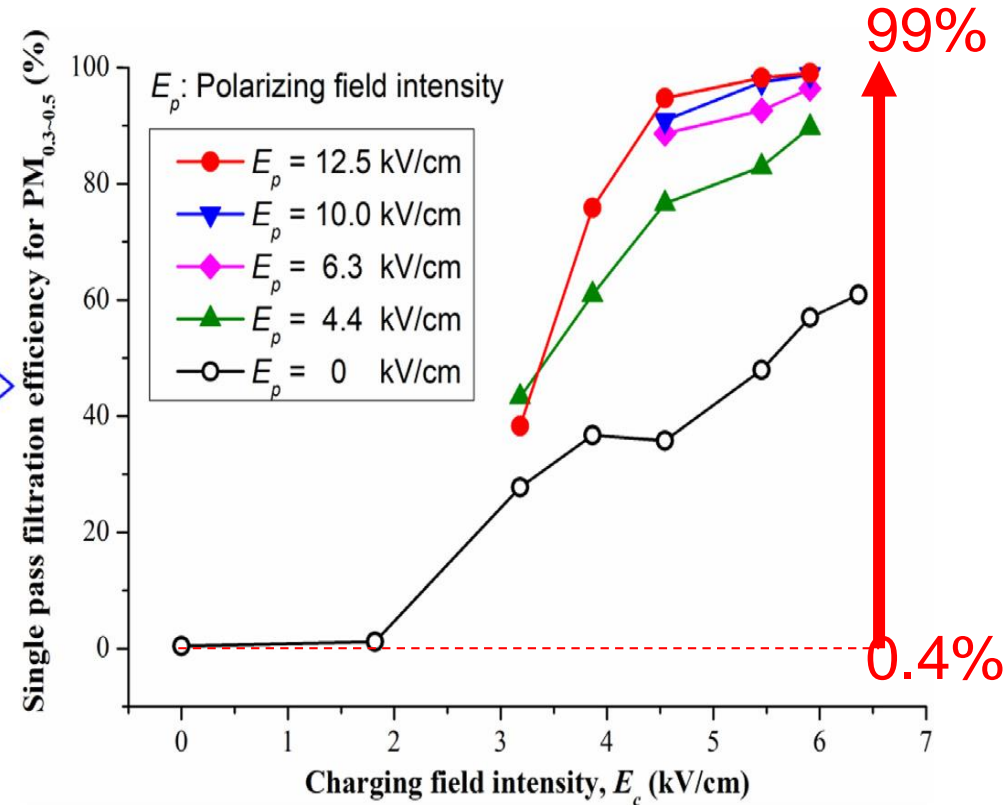
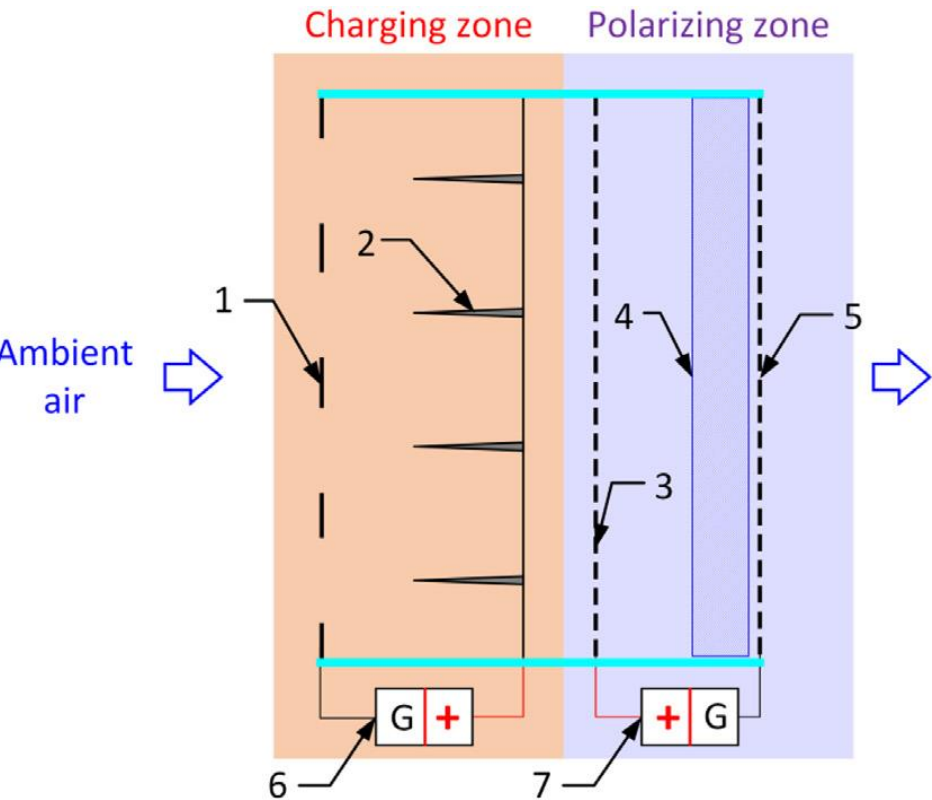
- **Controlled temperature**
- **30 ppi carbon sponges**

- **Test generating performance twice: C₁, C₂**

汇报内容

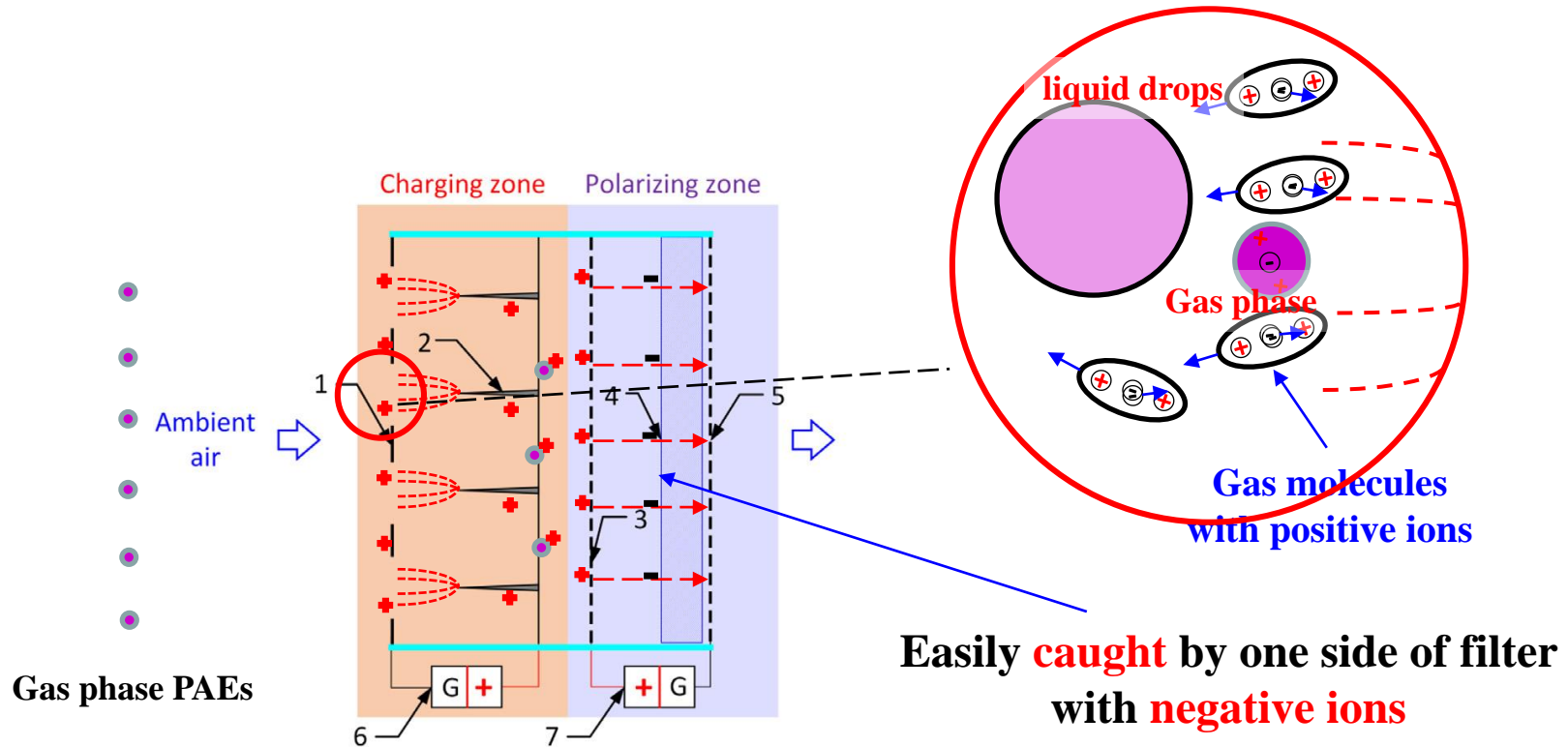
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静电增强过滤去除颗粒物



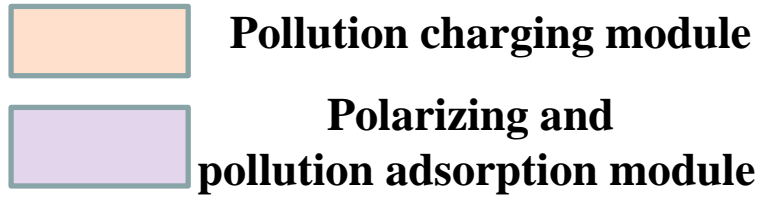
Single-pass removal efficiency for particle can be enhanced

Electrostatically assisted air (EAA) filtration^[1]:

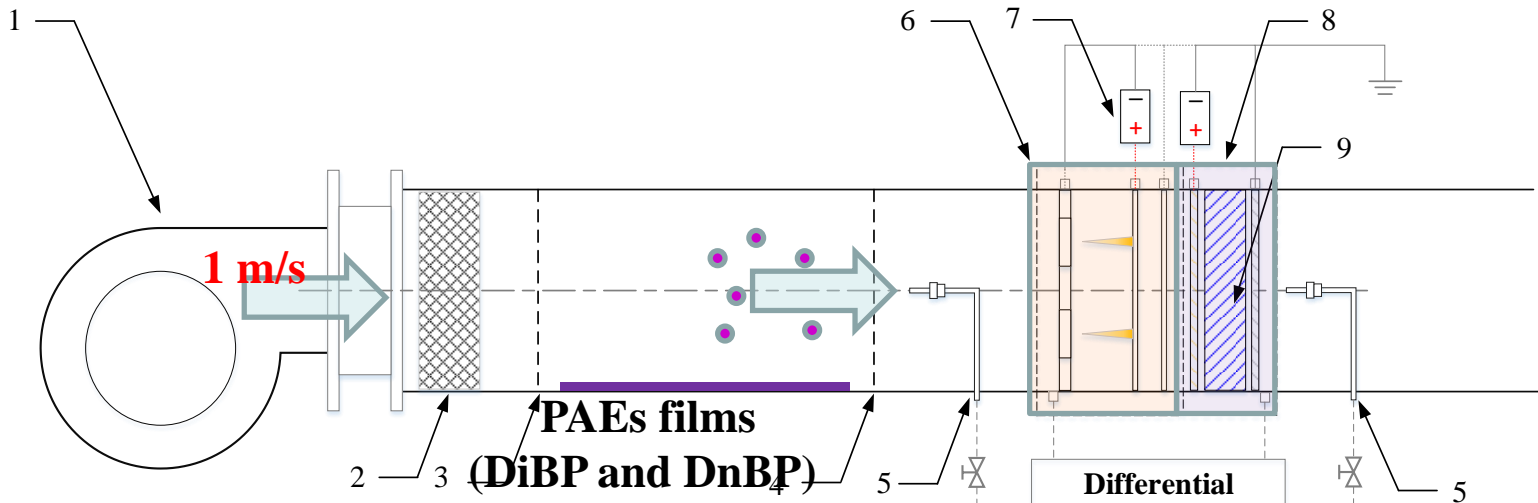


Enhance the PAEs adsorption on filters through EAA filtration?

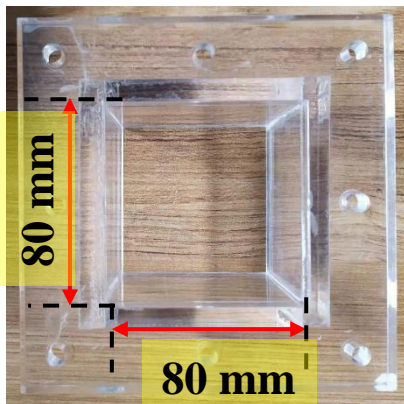
实验平台



- | | |
|---------------------------------|----------------------|
| 1: Centrifugal fan | 6: Charging module |
| 2: HEPA filter | 7: HVDC power |
| 3,4: Perforated diffusion plate | 8: Polarizing module |
| 5: Sampler | 9: EAA filter |



- Differential Pressure device
- Ozone monitor
- Tenax tubes

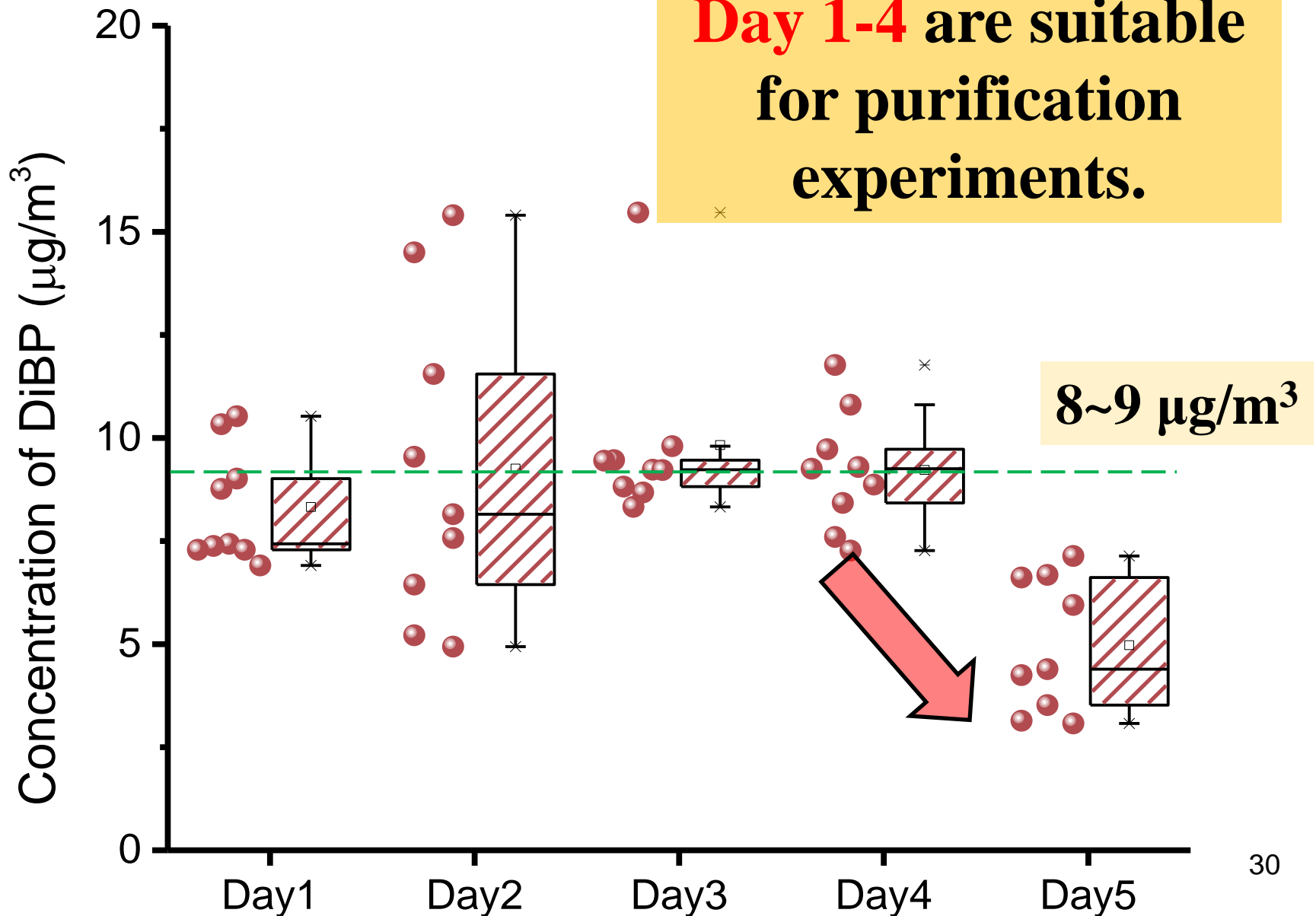


(Model 205, 2B Tech. Boulder, USA)

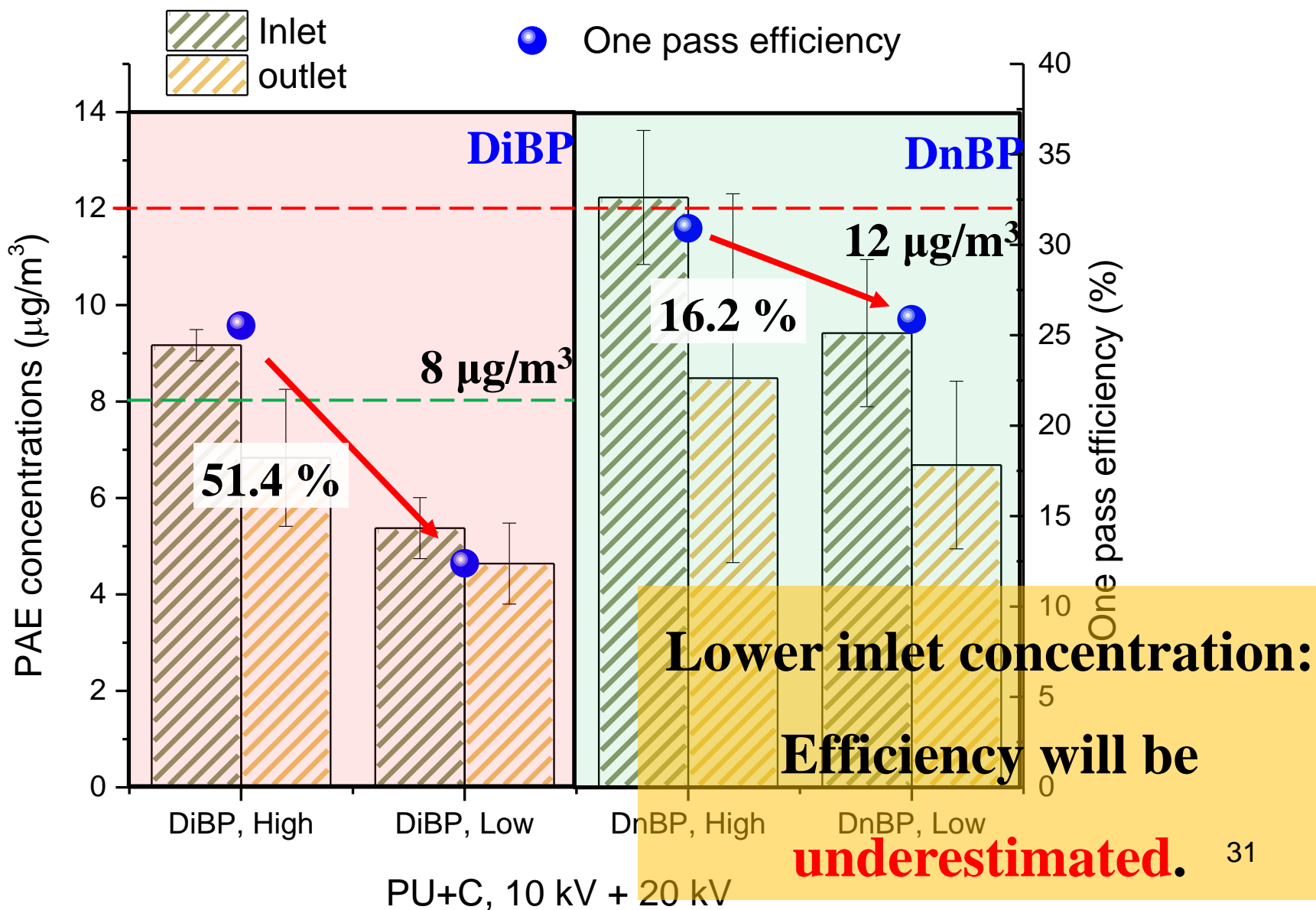


(DP-CALC5825, TSI Inc. Shoreview, USA)

浓度发生稳定性



入口浓度对效率的影响



控制变量

Filters



PU
(polyurethane)



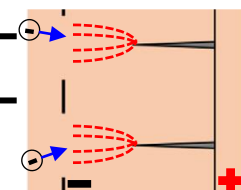
PU+Activated carbon
(adsorbent)



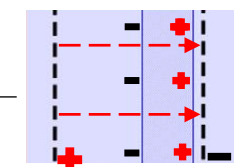
PU+MnO₂
(catalyst)

Electrical conditions

	con1	con2	con3	con4	con5
Charging (kV)	0	10	10	13	13
Polarizing (kV)	0	0	20	0	20
Sample ID	0 kV + 0 kV	10 kV + 0 kV	10 kV + 20 kV	13 kV + 0 kV	13 kV + 20 kV

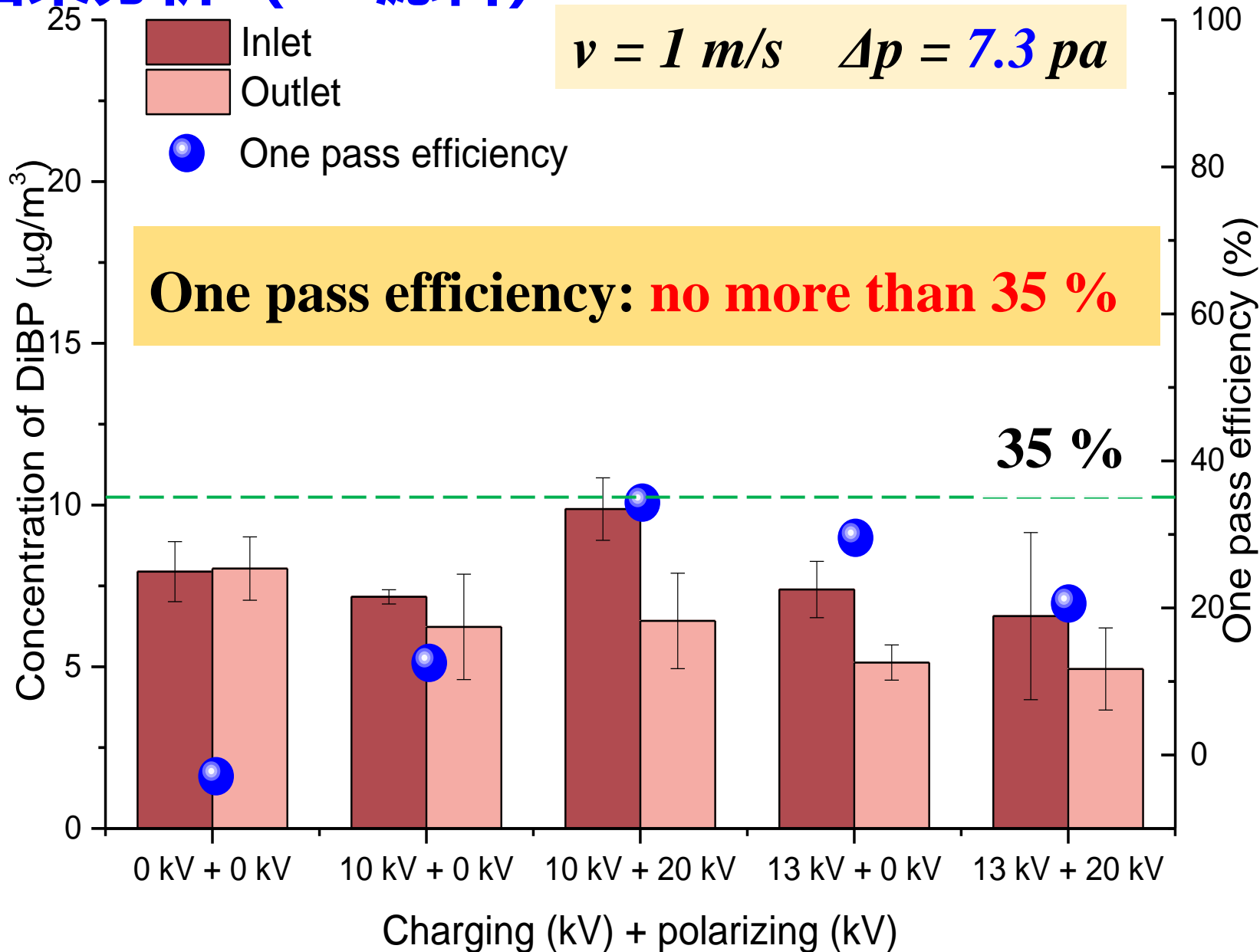


Charging

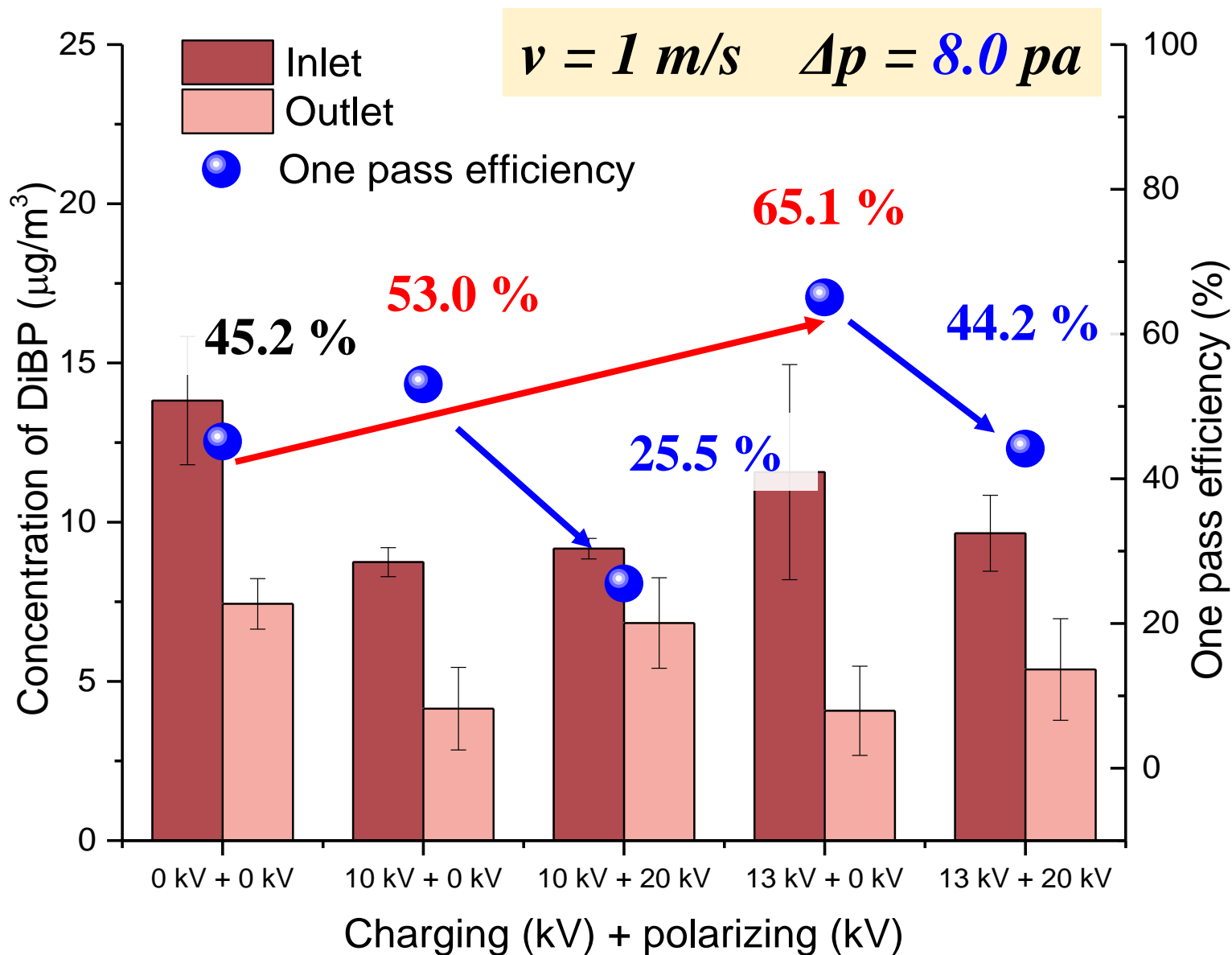


Polarizing

结果分析 (PU滤料)



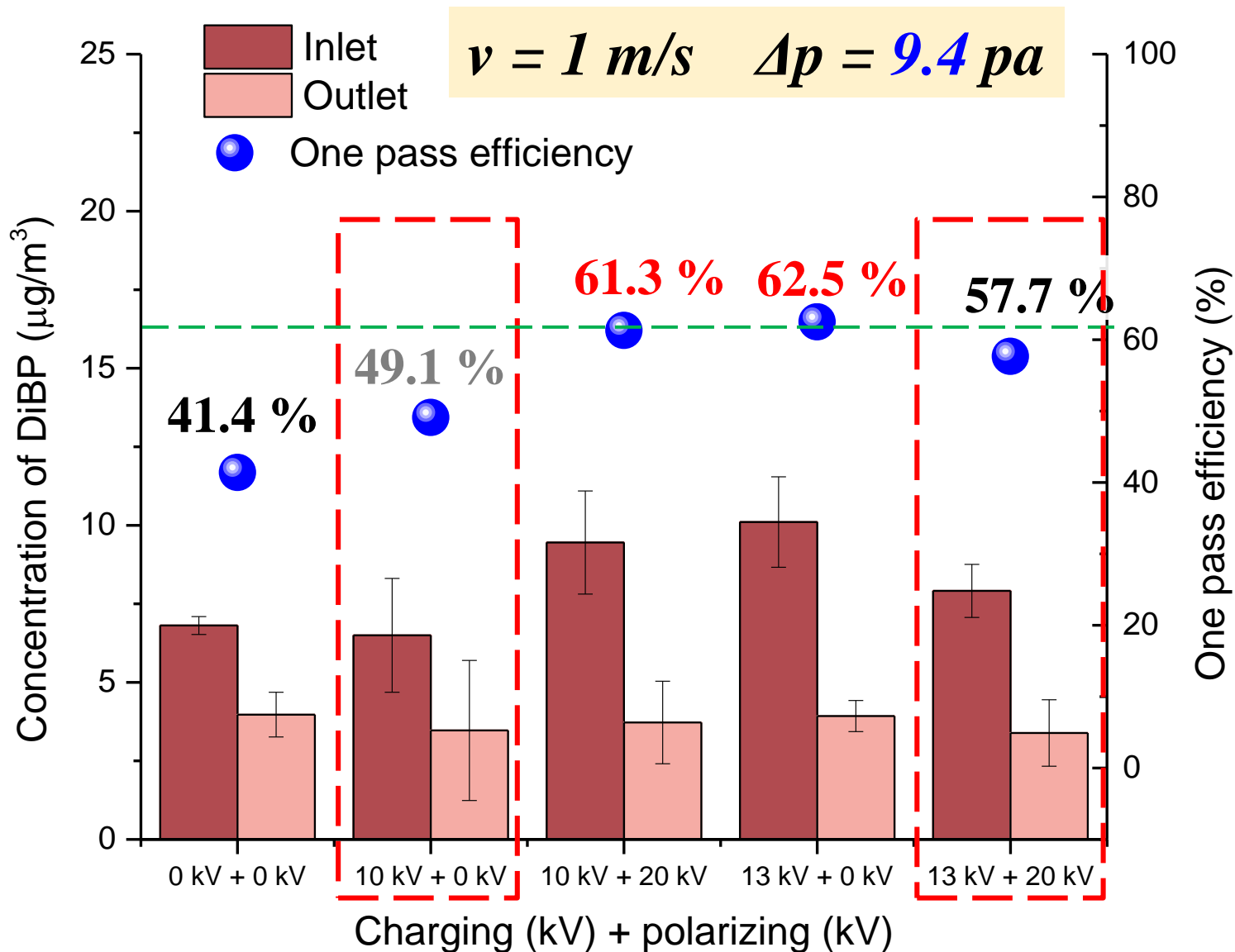
结果分析 (PU+C滤料)



结果分析 (PU+MnO₂滤料)



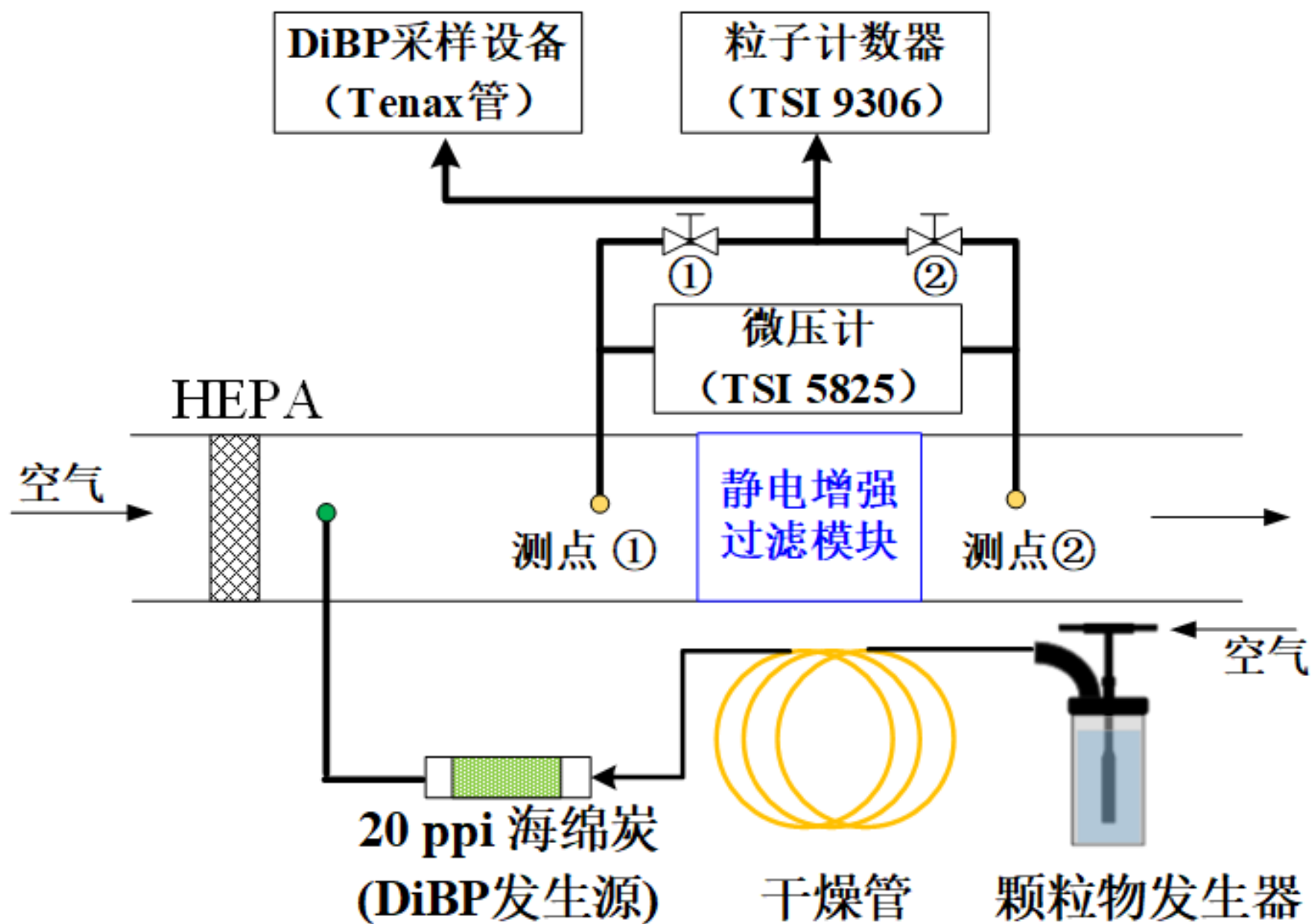
Low concentration (underestimate)



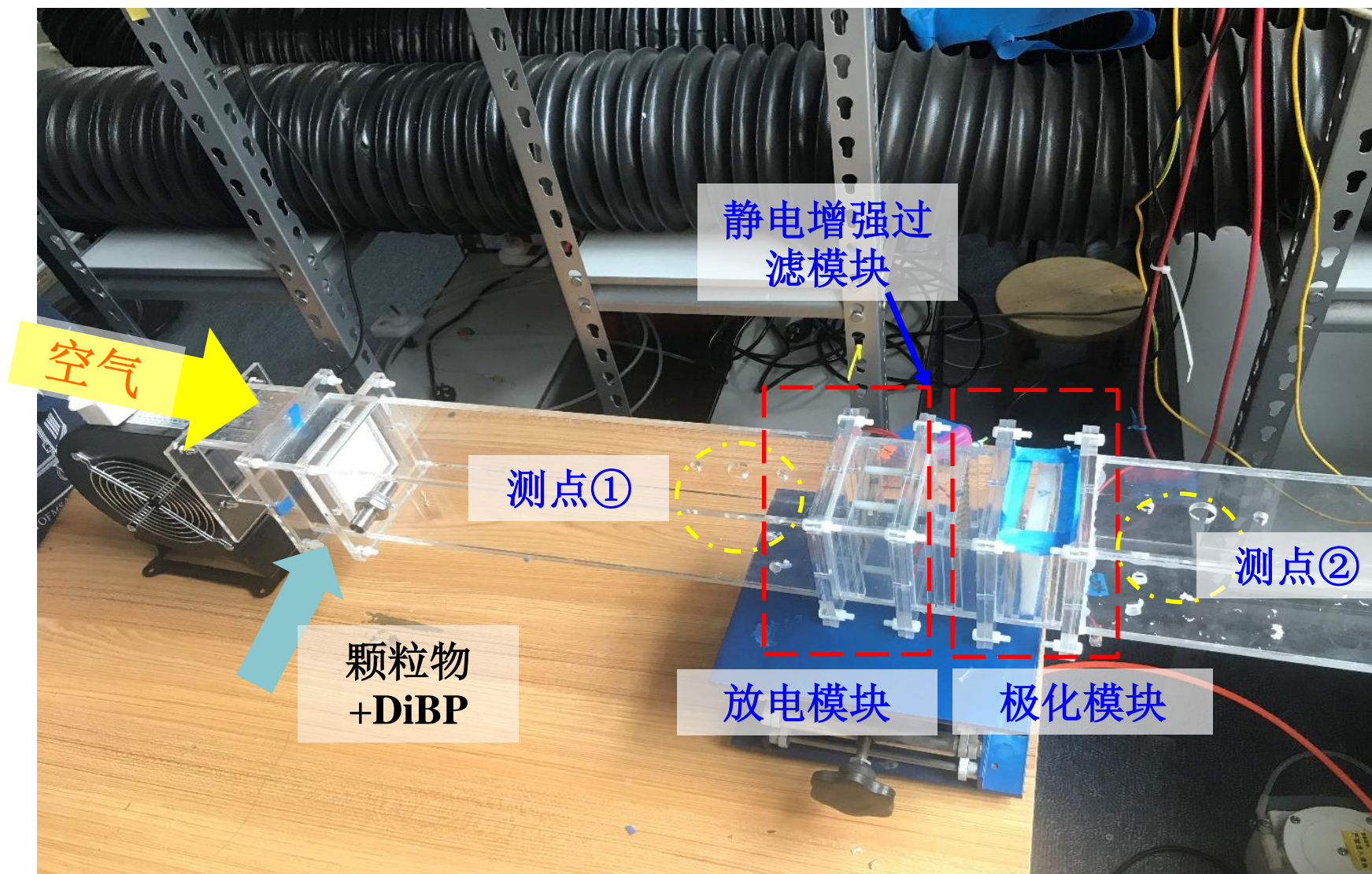
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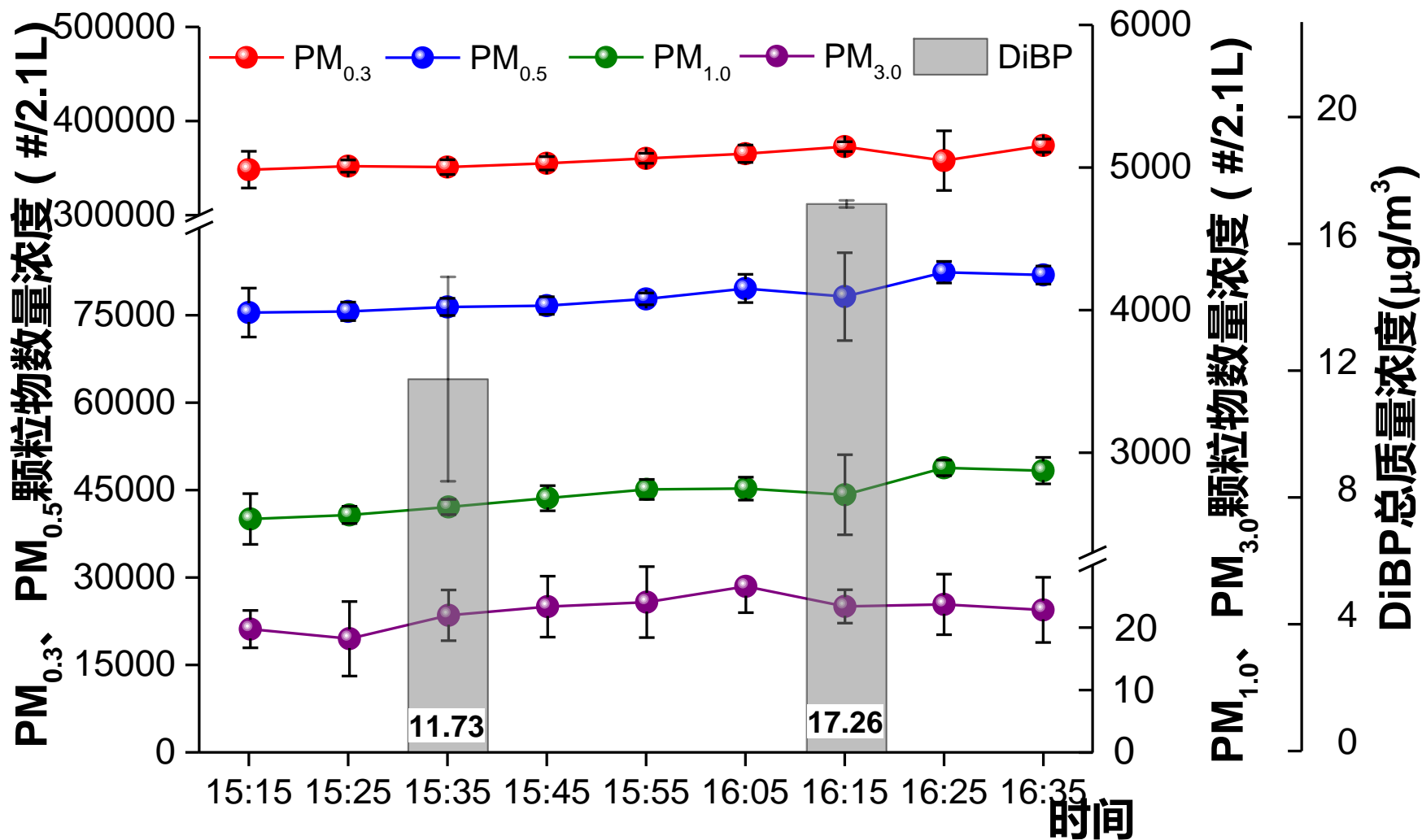
实验平台建立



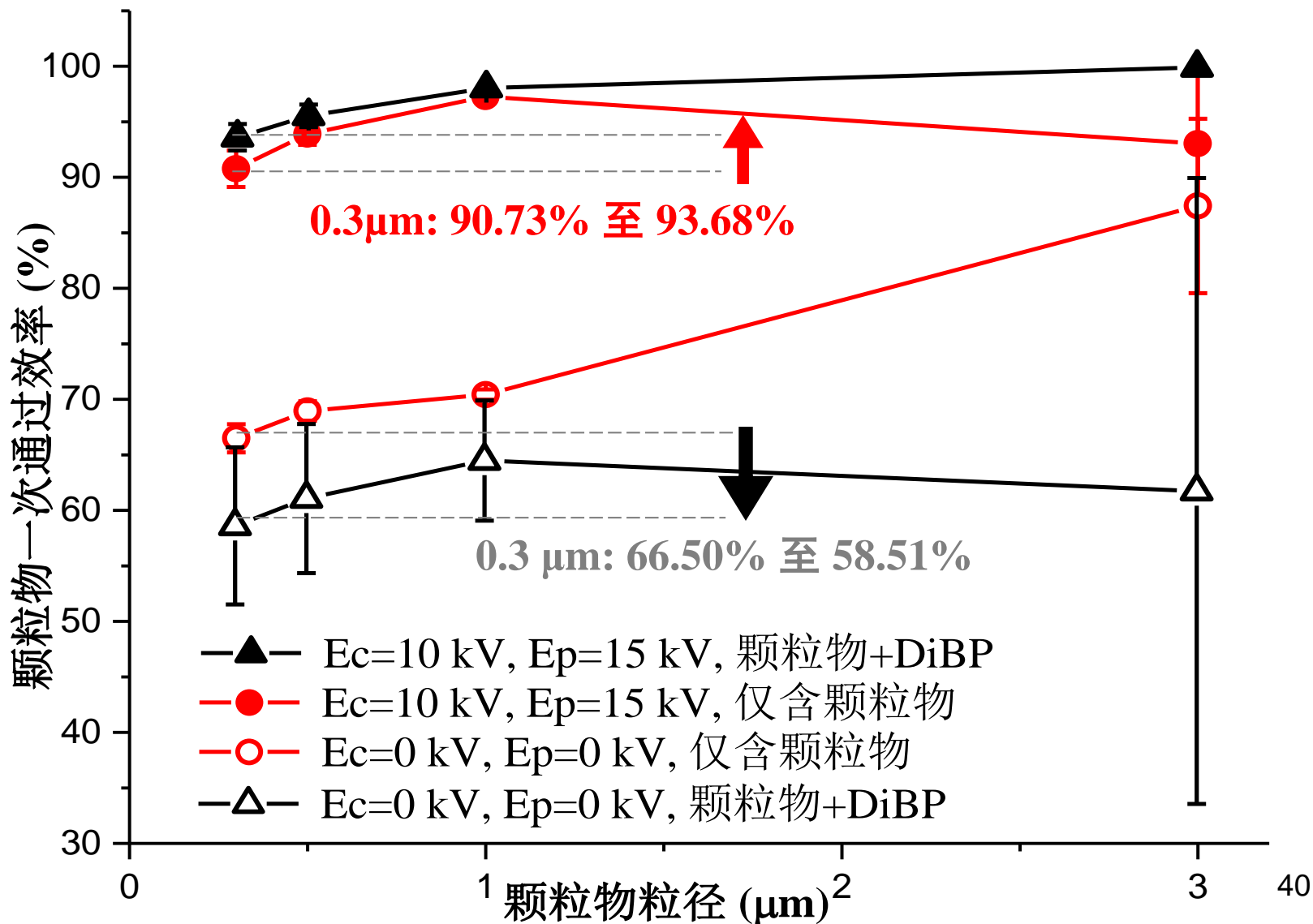
实验平台建立



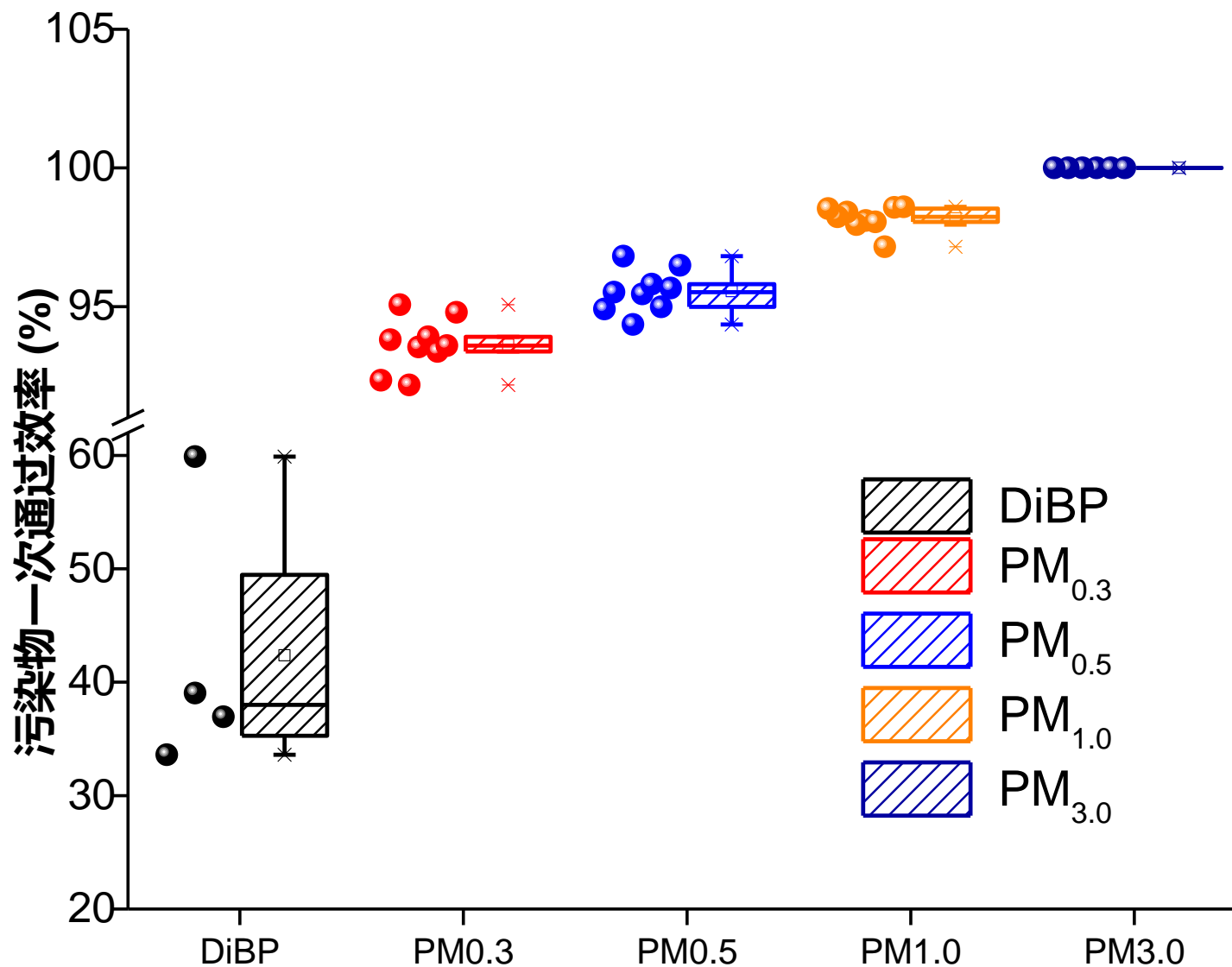
耦合污染源发生特性



SVOC引入对颗粒物静电增强过滤效率的影响



复合污染去除效率



Thank you!