

含碳气溶胶：研究进展与控制建议

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主要内容

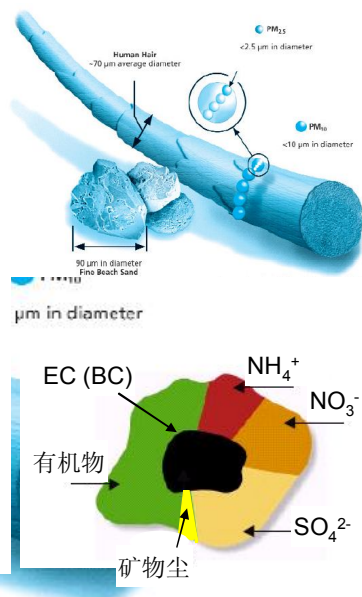
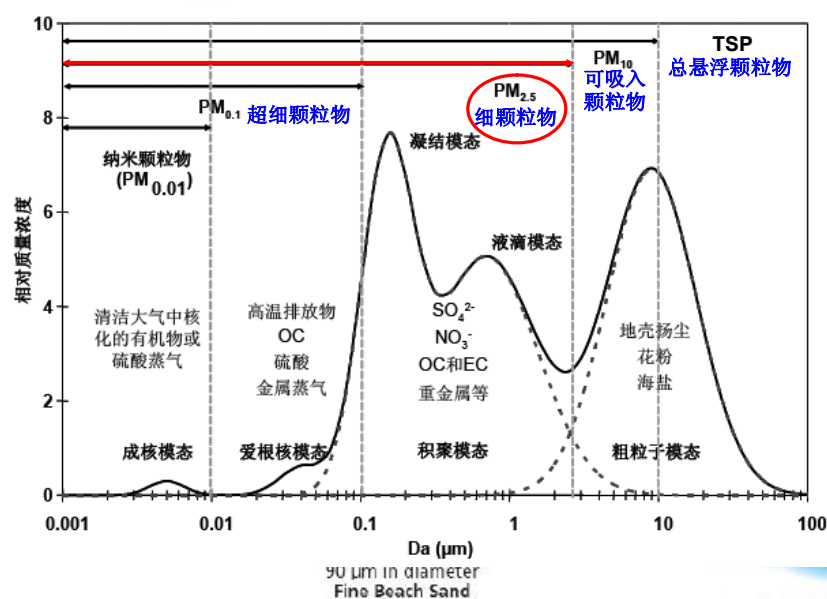
一. 问题背景

二. 研究进展

三. 控制策略

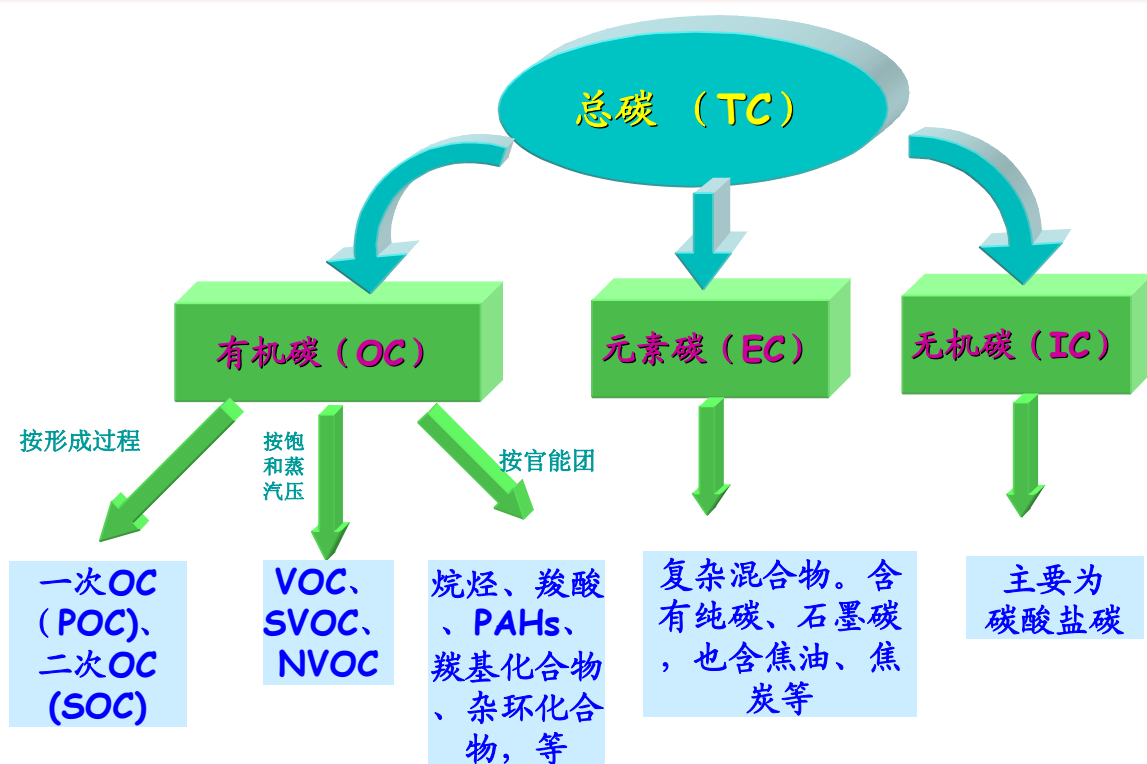
什么是“大气气溶胶”

大气气溶胶——若干细微固体颗粒和液滴的混合物



大气颗粒物质量浓度模态分布

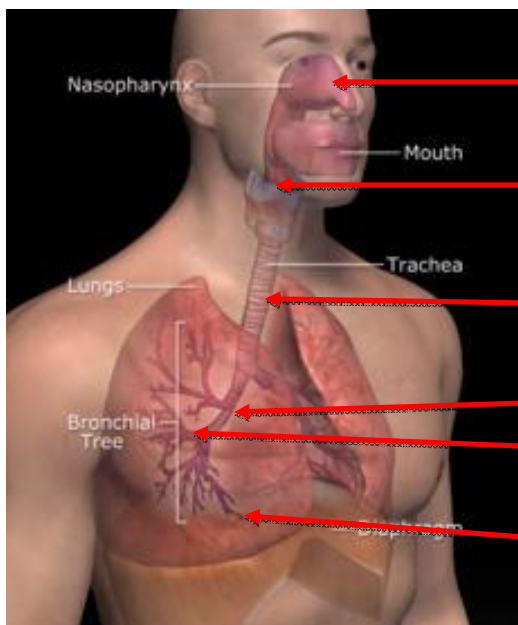
含碳气溶胶：代表了大气气溶胶的重要性与复杂性



Impacts of Atmospheric Components

	 health	 Haze	 Acid rain	 ABC	 Climate
SO_4^{2-}					
NO_3^-					
OC					
BC					
O_3					

PM2.5: Health Impacts



• 7-10 μm : 可以进入鼻腔

• 4.7 - 7 μm : 可以进入咽喉

• 3.3-4.7 μm : 可以进入气管和 支气管

• 2.1-3.3 μm , 可以进入中支气管

• 1.1 - 2.1 μm , 可以进入支气管终

• 0.65 - 1.1 μm , 可以进入肺泡

● 研究表明, $\text{PM}_{2.5}$ 可能引发整个人体范围的疾病。这是监测、评价和控制 $\text{PM}_{2.5}$ 污染的最重要原因!

突破鼻腔、深入肺部、渗透血液

含碳气溶胶：能见度的影响



EPA, RHR1
PM_{2.5}
(Malm et al., 2000)

$$b_{ext, PM_{2.5}} = 3f(RH)[SO_4^{2-}] + 3f(RH)[NO_3^-] + 4[\text{有机物}] + 10[\text{吸光碳}] + 1[\text{土壤}] + 0.6[\text{粗粒子}] + 10 \text{ (表瑞利散射)}$$

EPA, RHR2*
PM_{2.5}
(Pitchford et al., 2007)

$$b_{ext, PM_{2.5}} = 2.2f_s(RH)[\text{小}(NH_4)_2SO_4] + 4.8f_L(RH)[\text{大}(NH_4)_2SO_4] + 2.4f_s(RH)[\text{小}NH_4NO_3] + 5.1f_L(RH)[\text{大}NH_4NO_3] + 2.8f_s(RH)[\text{小有机物}] + 6.1f_L(RH)[\text{大有机物}] + 1.7f_{ss}(RH)[\text{海盐}] + 10[\text{吸光碳}] + 1[\text{土壤}] + 0.6[\text{粗粒子}] + \text{各地区瑞利散射特征值}$$

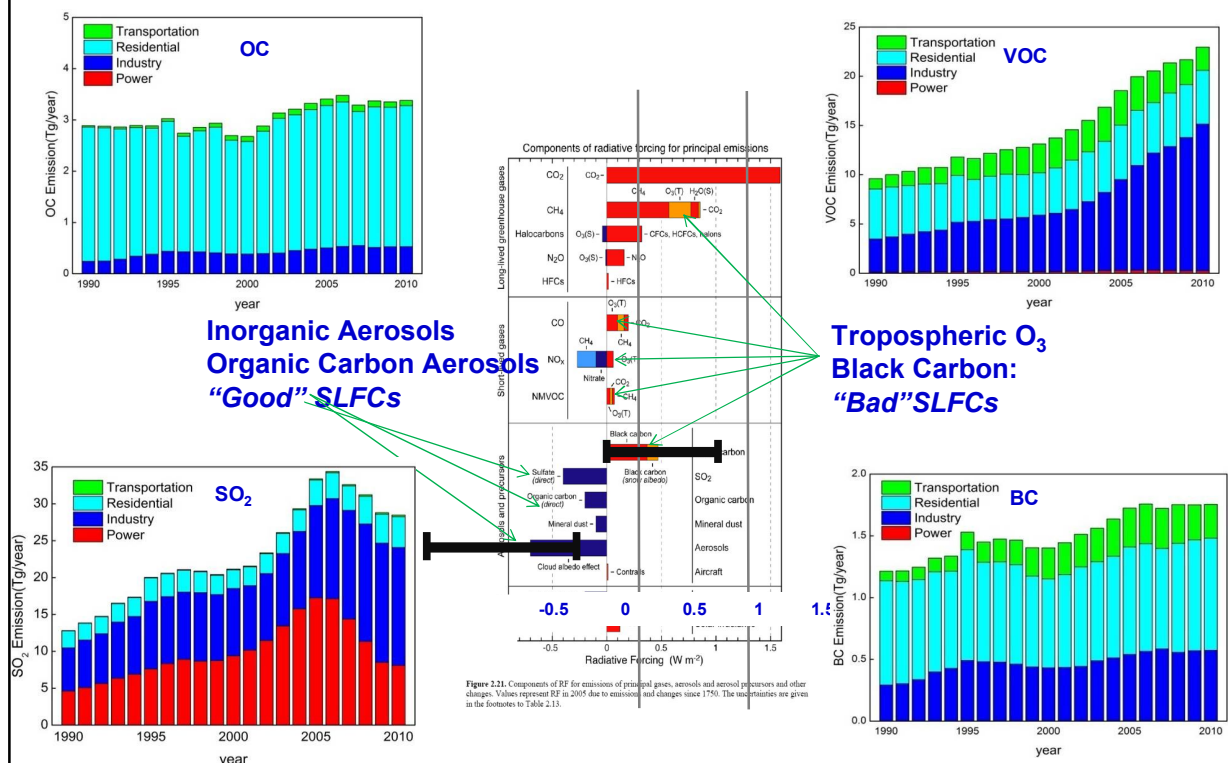
深圳
冬季, PM₁
(姚婷婷 等, 2010)

$$b_{ext, PM_1} = 2.28f(RH)[(NH_4)_2SO_4] + 2.33f(RH)[NH_4NO_3] + 4.53[\text{有机物}] + 9.18[EC] + 6.53 \text{ (表颗粒物其它组分影响)} + 0.33[NO_2(ppb)] + 13 \text{ (表瑞利散射)}$$

珠三角 (新垦)
秋季PM₁
(Cheng et al., 2008)

$$b_{ext, PM_1} = 7.5f(RH)[SO_4^{2-}] + 8.0f(RH)[NO_3^-] + 7.1[\text{有机物}] + 11.0[EC] + 4.4f_{ss}(RH)[\text{海盐}] + 6.2 \text{ (表颗粒物其它组分影响)} + 0.33[NO_2(ppb)] + 11.3 \text{ (表瑞利散射)}$$

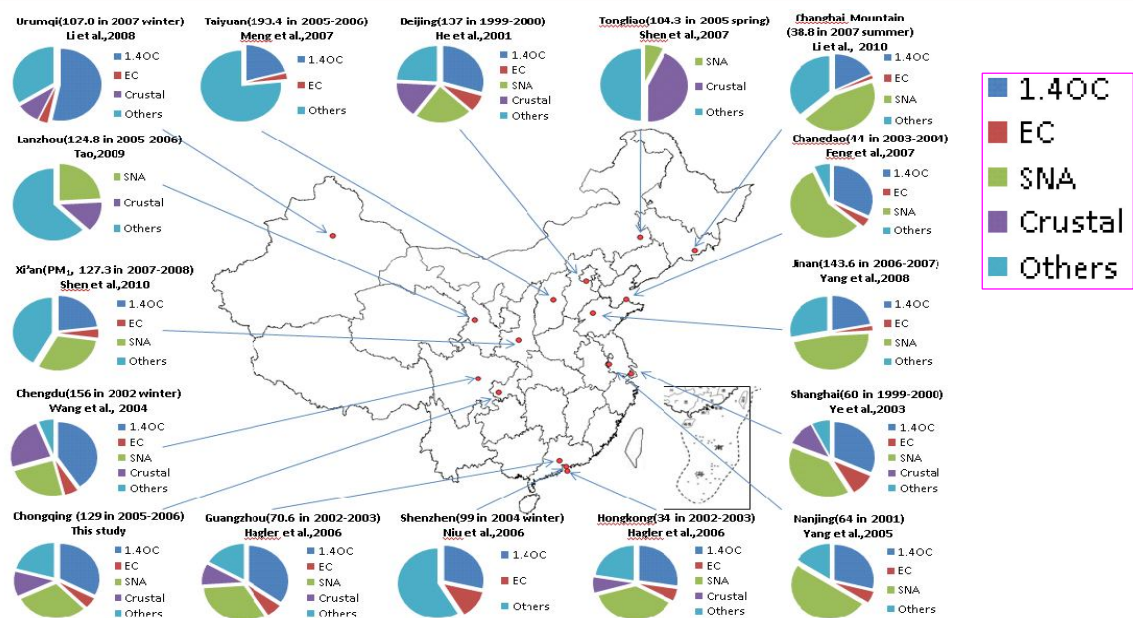
历史排放的辐射强迫



Inorganic Aerosols
Organic Carbon Aerosols
"Good" SLFCs

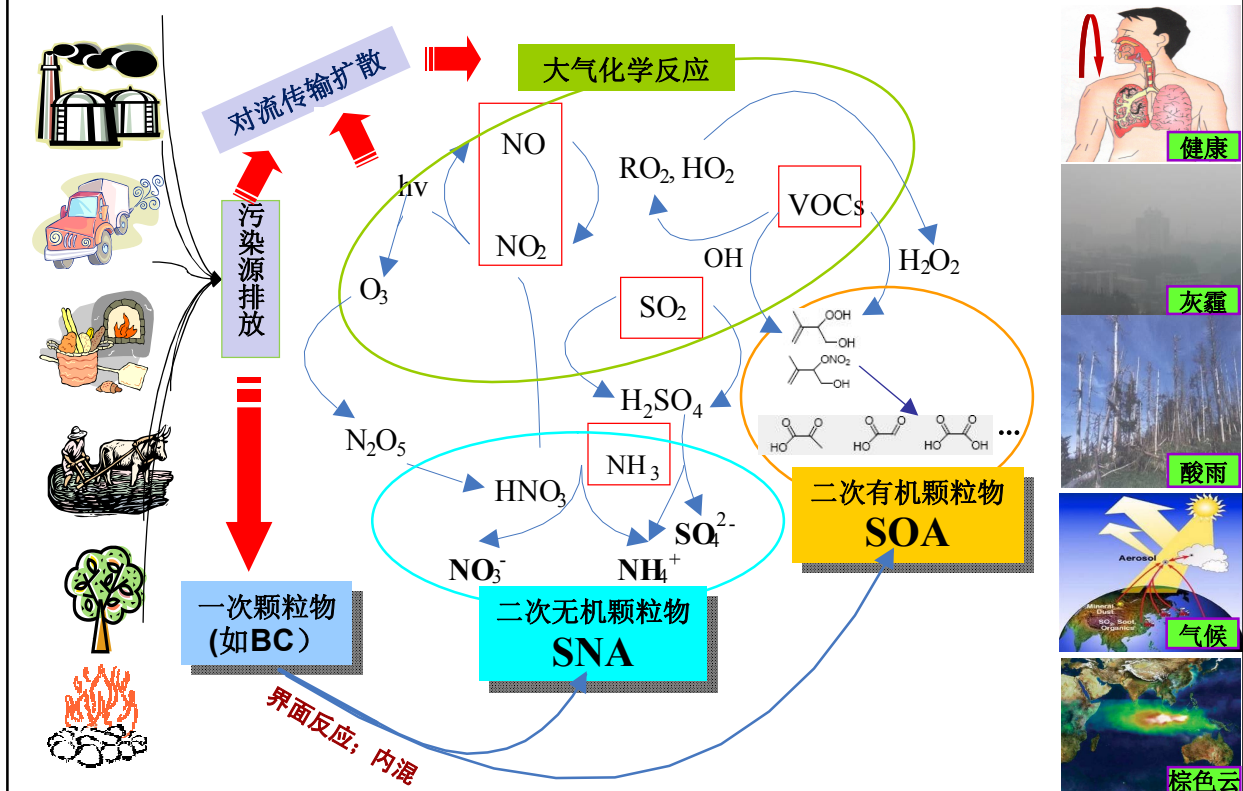
Tropospheric O₃
Black Carbon:
"Bad" SLFCs

污染特征1：含量高



➤ OC是城市地区和非城区PM_{2.5}中的主要成分，平均占 20%-70%

污染特征2：来源与形成机制复杂



主要内容

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1、一次含碳气溶胶排放特征

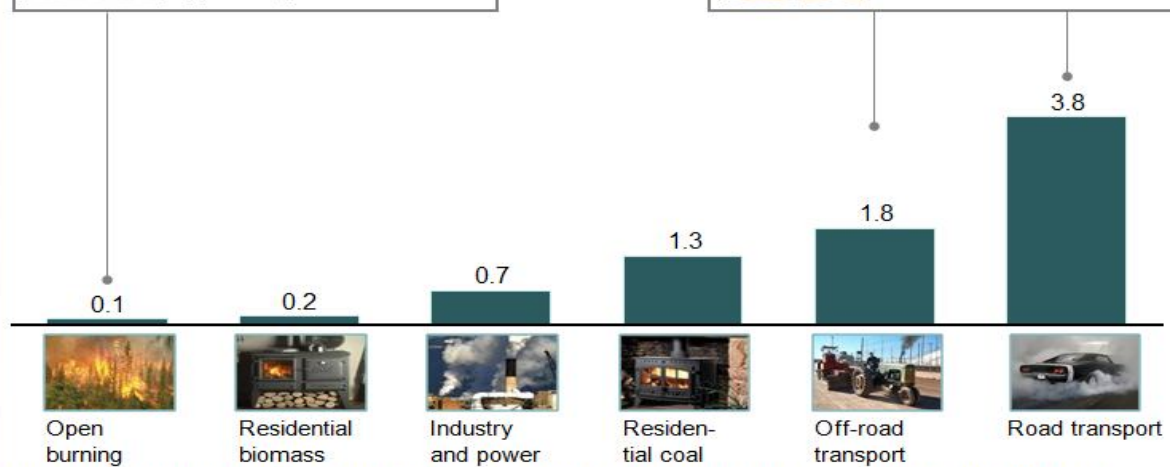
Ratio of black carbon to organic carbon



Smoke from open burning of biomass or wildfires appears gray because of the high ratio of OC which scatters sunlight and therefore appears light colored



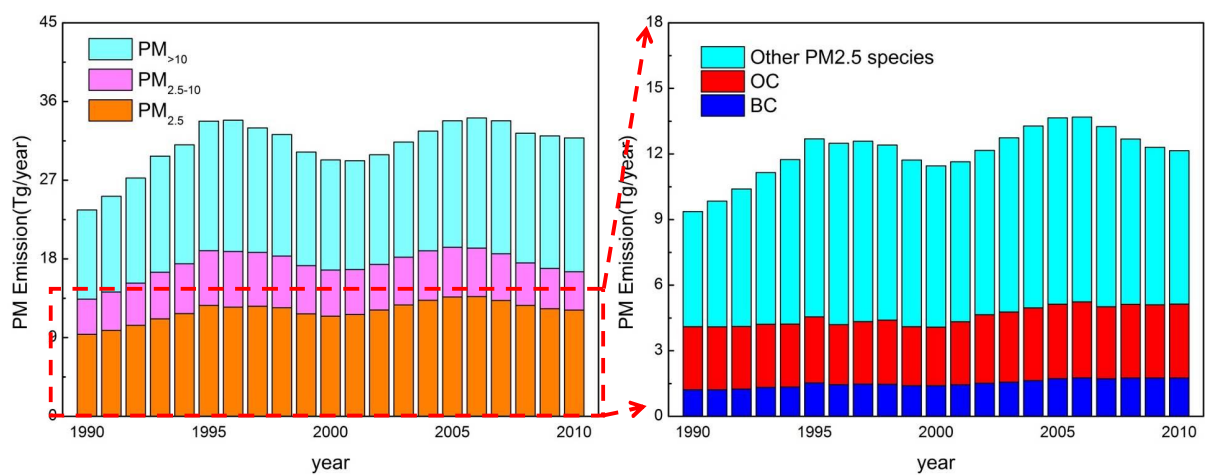
Soot from diesel combustion appears black because of its high content of black carbon, the light-absorbing component of aerosols



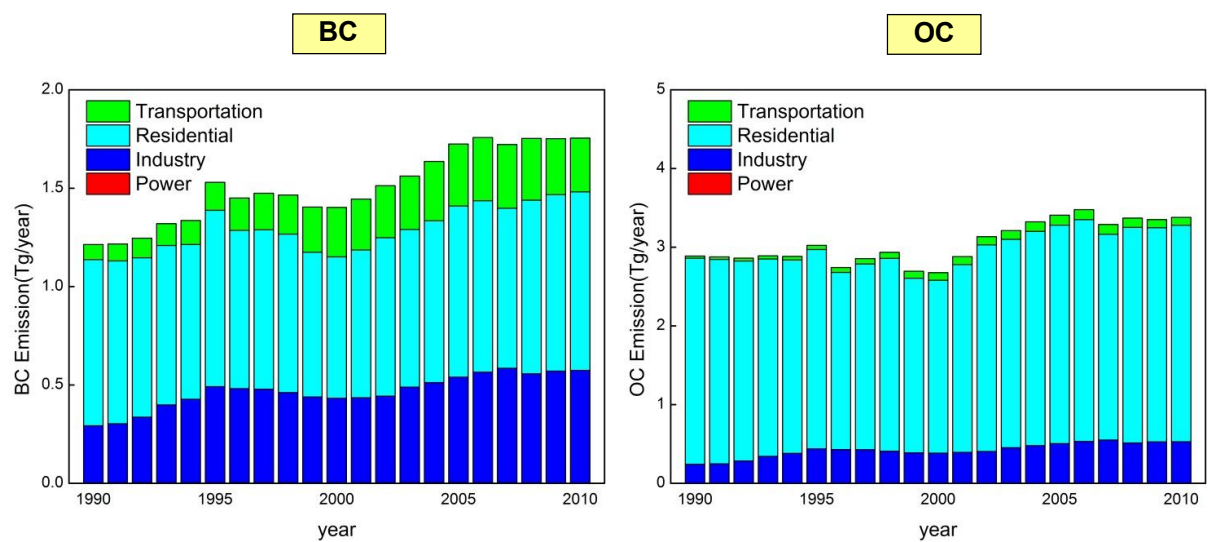
Note: All sources emit significant quantities of other pollutants that may warm or cool the climate, including CO₂ (warming), NO_x (ozone and N₂O warming, nitrate cooling), and SO₂ (sulfate cooling)

SOURCE: Non-CO₂ Climate Forcers Report (2010), Bond (2007), GAINS

1990年-2010年中国人为源气溶胶排放趋势

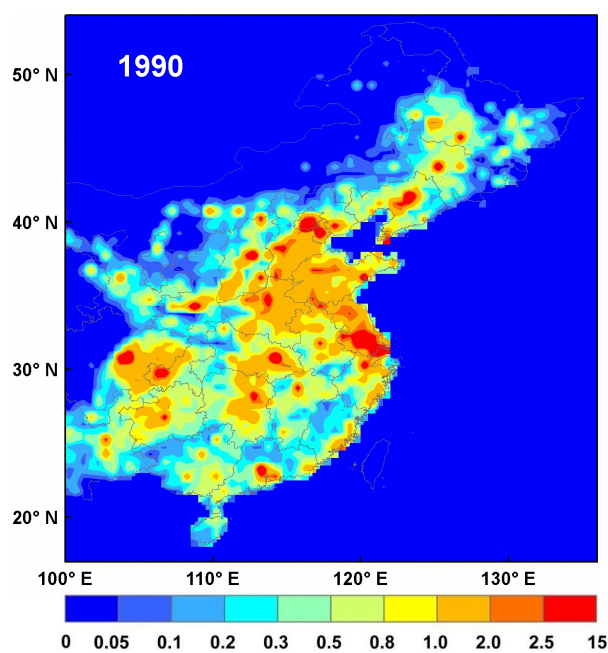


1990年-2010年中国人为源含碳气溶胶排放趋势

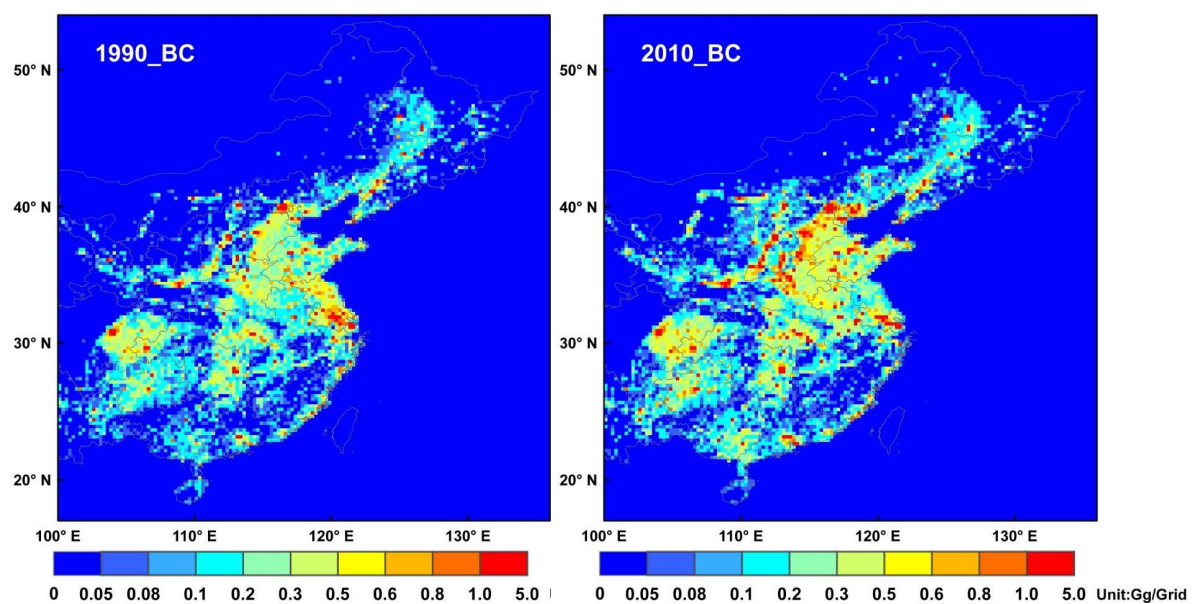


20年间中国黑碳气溶胶排放呈上升趋势

中国BC排放空间分布(单位:Gg/Grid)

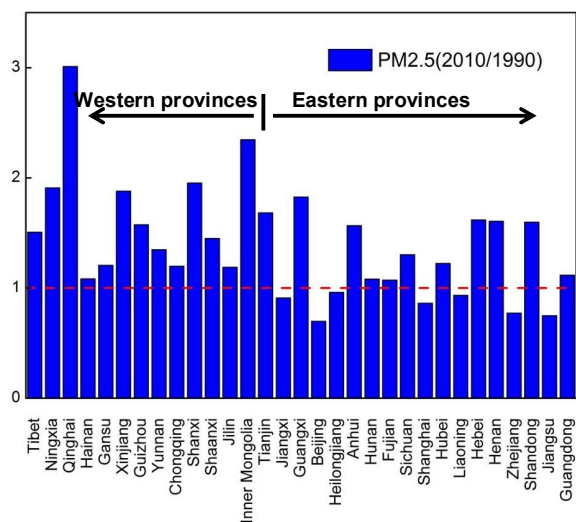


黑碳气溶胶高排放区在华北地区逐渐扩大

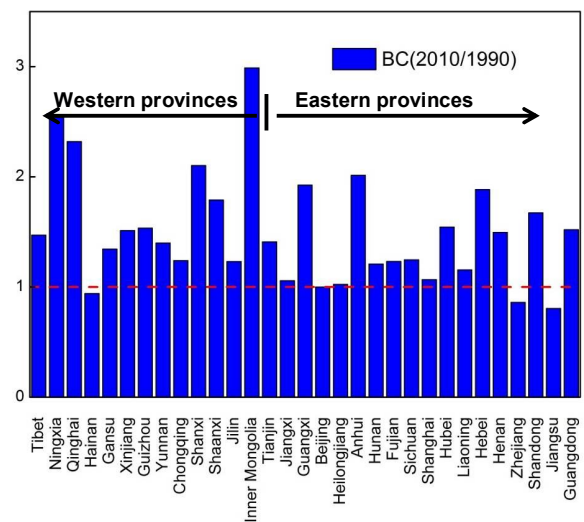


西部各省人为源气溶胶排放增长较快

中国PM_{2.5}排放(2010/1990)

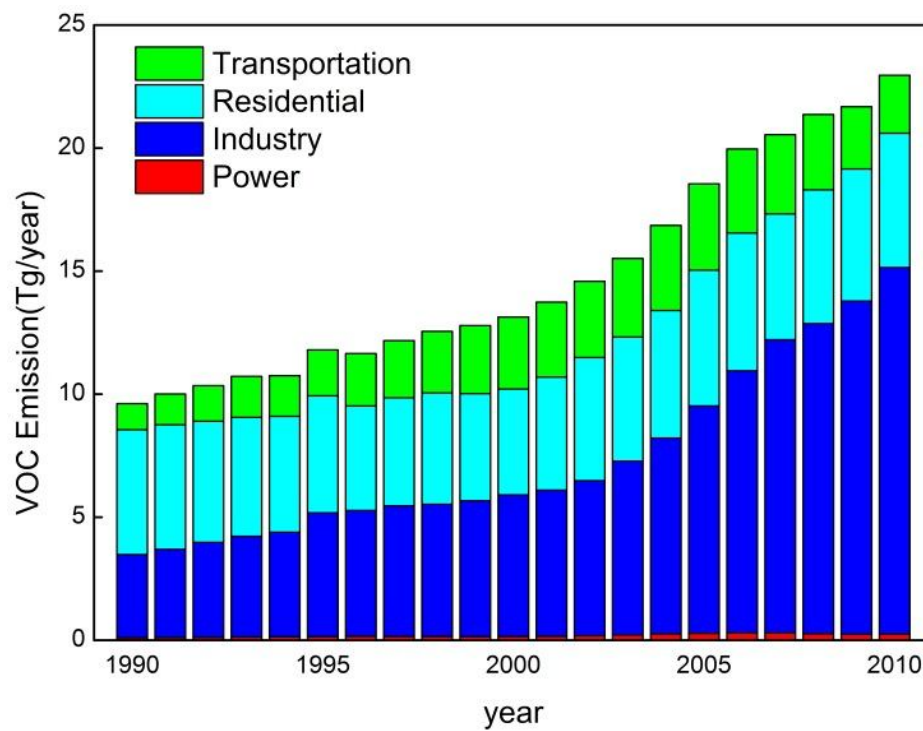


中国BC排放(2010/1990)

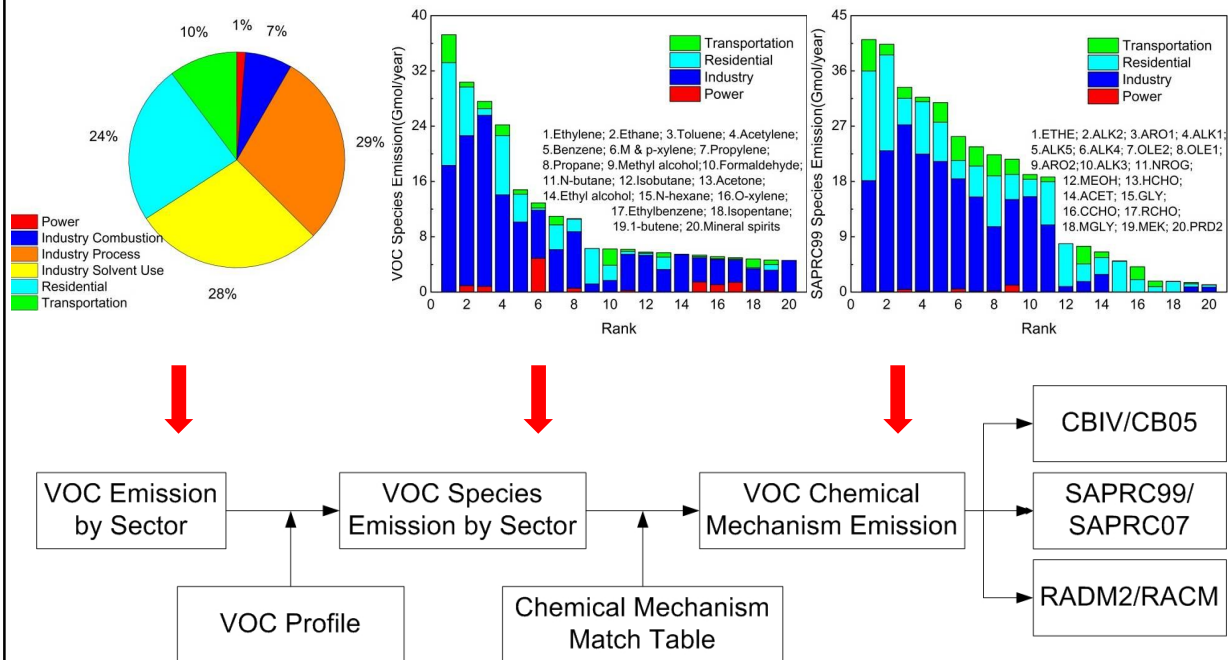


Ranked by province GDP in 2010

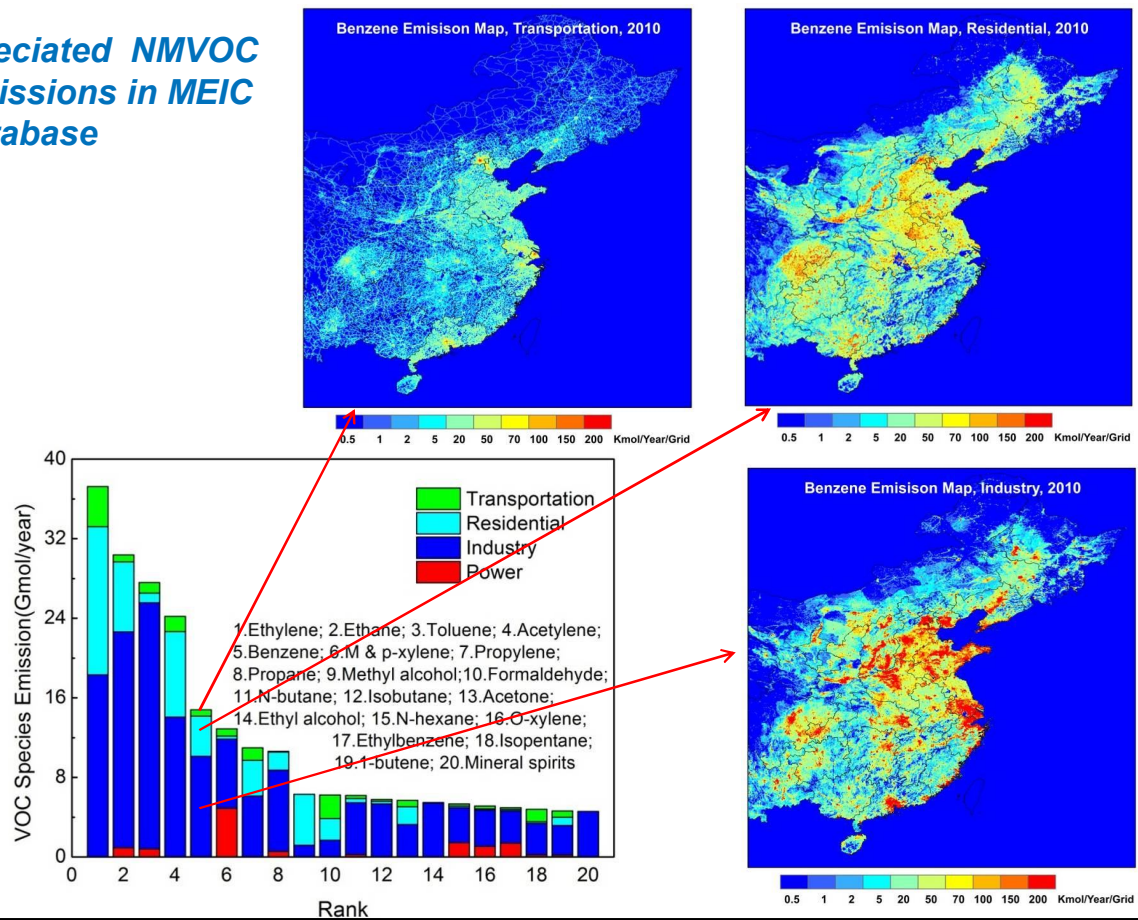
2、二次含碳气溶胶前体物排放特征



Speciated NMVOC emissions in MEIC database

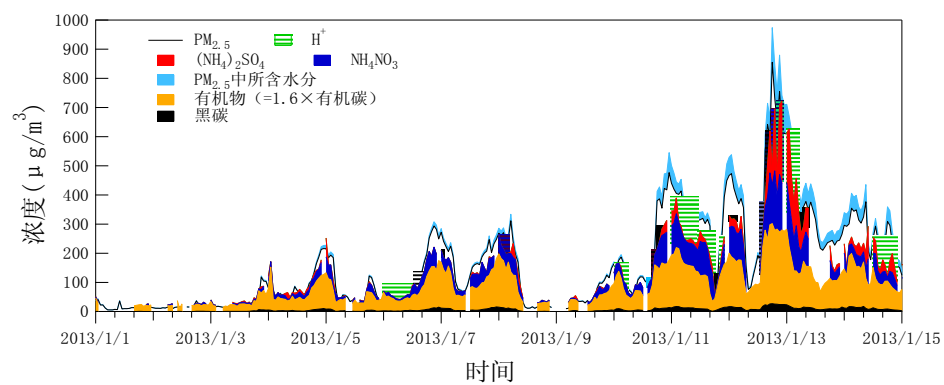
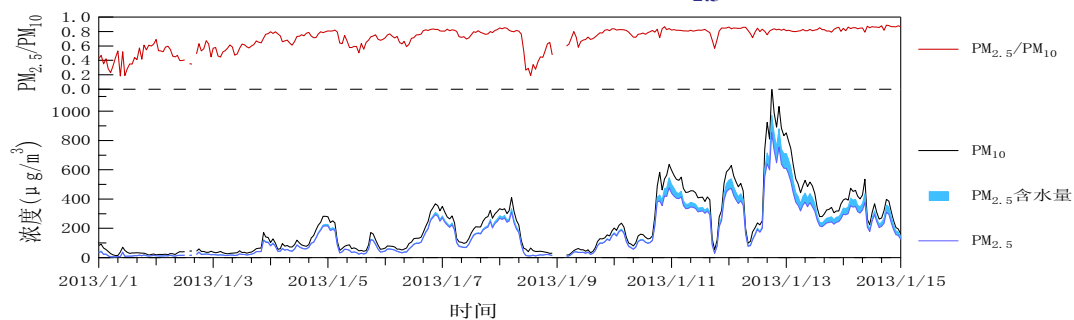


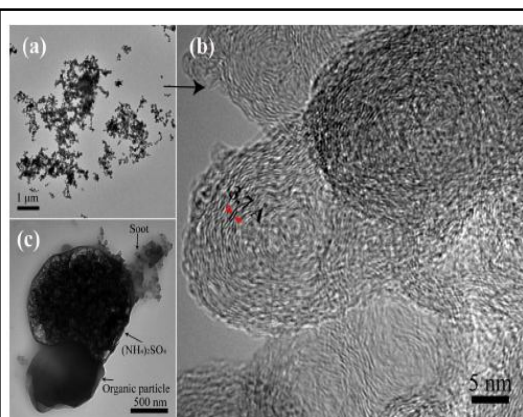
Speciated NMVOC emissions in MEIC database



3、雾霾污染中含碳气溶胶的污染特征

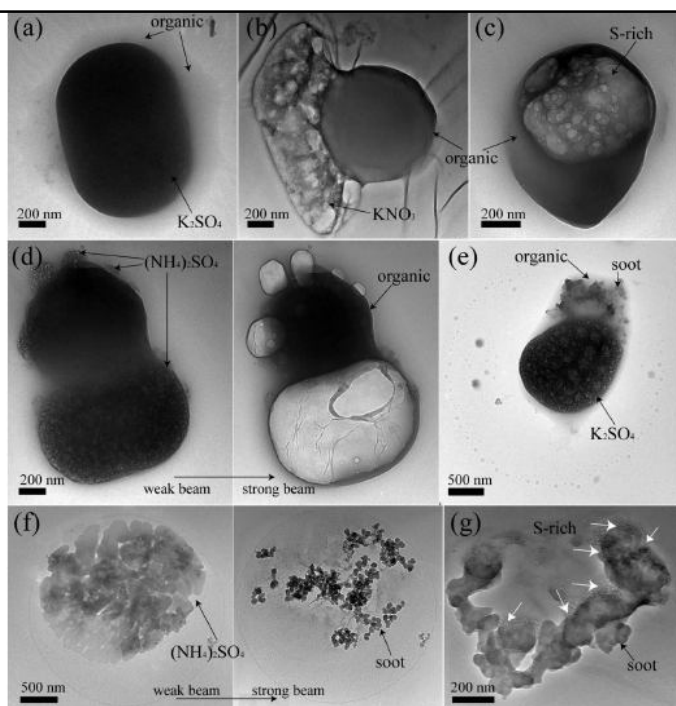
2013年1月我国东部雾霾期间北京PM_{2.5}观测结果





扫描电镜下雾霾污染中的soot

(a) 链状聚集体 (b) 似洋葱结构
不规则石墨层 (c) 有机碳、
soot与的 $(\text{NH}_4)_2\text{SO}_4$ 混合体



雾霾/非雾霾污染中含碳气溶胶的微观形貌存在差异

Li WJ, et al., Atmos. Chem. Phys., 10, 8119–8130, 2010

大气中OC/EC采样与分析

OC的大气环境采样存在误差

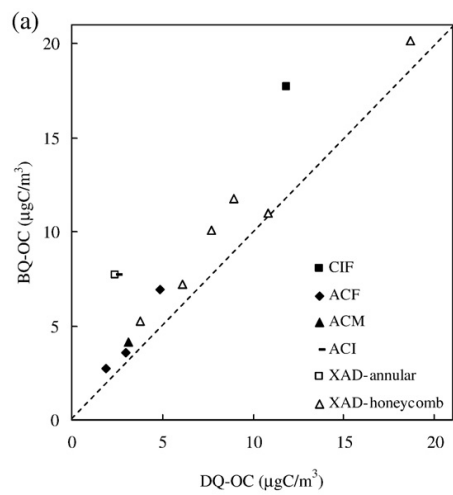


Table 2
Carbonaceous components measured by organic denuder-based samplers

Denuder/filter pack ^b	Sampling site	Sampling period	NVOC	SVOC
CIF ^a /Q+ CIF or CIG	Lawrence, TN	Jul, 1997	2.0	1.5
	Riverside, CA	Sep, 1997	19.8	14.3
	Bakersfield, CA	Feb-Mar, 1998	3.9	9.1
	Rubidoux, CA	Jul, 2003	16.6	17.5
	Fresno, CA	Dec, 2003	11.0	14.9
	Provo, UT	Dec, 1998	8.7	4.6
	Salt Lake City, UT	Dec, 2000-Jan, 2001	15.8	5.8
	Salt Lake City, UT	Jul, 2001	9.7	3.0
	Bountiful, UT	Dec, 2000-Jan, 2001	10.5	3.1
	Philadelphia, PA	Jul, 1999	14.3	11.1
	Pittsburgh, PA	Aug, 2000	5.8	5.3
	Atlanta, GA	Aug, 1999	11.4	5.3
ACF ^a /Q+Q	Seattle, WA	Apr-May, 1999	4.9	3.8
	Bily Kriz, Czech	Jun-Jul, 2003	2.62	0.04
	Kpuszta, Hungary	Jun-Jul, 2003	3.4	0.06
	Ghent, Belgium	Jun-Jul, 2004	1.9	-0.08
	Barcelona, Spain	Jul-Aug, 2004	3.0	0.2
	Barcelona, Spain	Nov-Dec, 2004	4.9	0.9
ACM ^a /Q+CIF	Pittsburgh, PA	Jul-Aug, 2001	2.8	0.3
ACI ^a /Q	Seattle, WA	May, 2001	2.5	-
XAD annular ^a /Q+XAD-Q	Toronto, Canada	July, 2001	4.14	2.38
	Toronto, Canada	Mar, 2003	3.09	2.22
	Vancouver, Canada	Aug, 2001	2.50	0.30
XAD honeycomb ^a /Q+Q	Pasadena, CA	Aug, 2001	6.02	0.05

对石英膜和溶蚀器—石英膜—后置滤膜样品的OC/EC分析表明：

- OC的正偏差可达10~30%
- OC的负偏差可达10~50%

Cheng Y., He K. B., et al., ENVIRON. INT., 2009

OC/EC测定实验室分割不一致

不同升温程序测定的EC 浓度有数倍的差别

TABLE 2. Temperature Programs Used in the Two Studies^a

step	gas	hold time (s)	temperature (°C)			
			base case	alternate 1	alternate 2	alternate 3
1	He	60	340	275	200	120
2	He	60	500	400	325	250
3	He	60	615	550	500	450
4	He	90	870	750	650	550
5	He	45	oven heaters turned off to cool oven			
5	He:O ₂ ^b	45	550	550	550	550
6	He:O ₂ ^b	45	625	625	625	625
7	He:O ₂ ^b	45	700	700	700	700
8	He:O ₂ ^b	45	775	775	775	775
9	He:O ₂ ^b	45	850	850	850	850
10	He:O ₂ ^b	120	900	900	900	900

^a The base case program was the only program used for the laboratory intercomparison study. ^b Actual gas composition: 98% He + 2% O₂. Lab H used 99%He + 1% O₂.

OC、EC缺乏标准测定方法。不同测定方法之间、甚至相同测试方法不同实验室之间EC的数据一致性较差，不同实验室之间的相对标准偏差则分别为37%、46%。

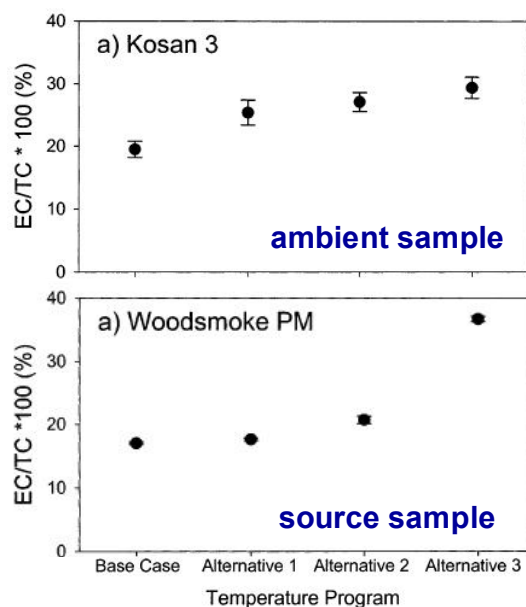
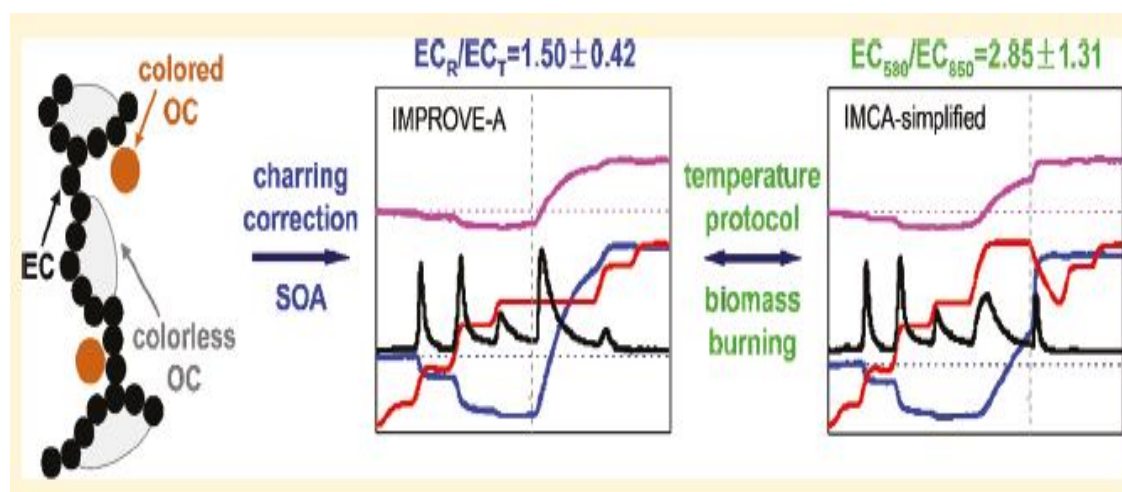


FIGURE 3. Pooled (Caltech and UW-Madison) elemental carbon (EC) levels as measured for the ambient particulate matter samples for the selected source samples using the four different temperature programs for ECOC analysis

Source: Schauer et al., ES & T, 2003

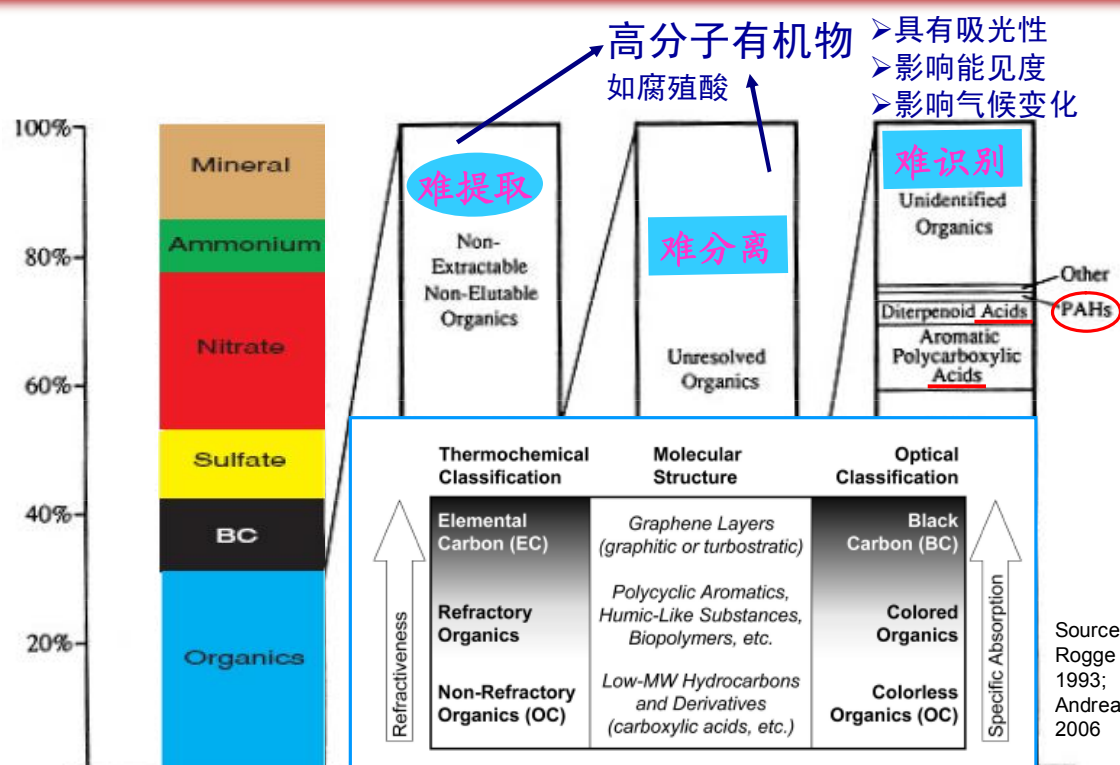
探讨OC/EC准确测定的影响因素



样品来源与**SOA**是影响**OC/EC**准确分割的重要因素

Cheng Y et al., ES&T, 2011, 45 (23), pp 10117–10123

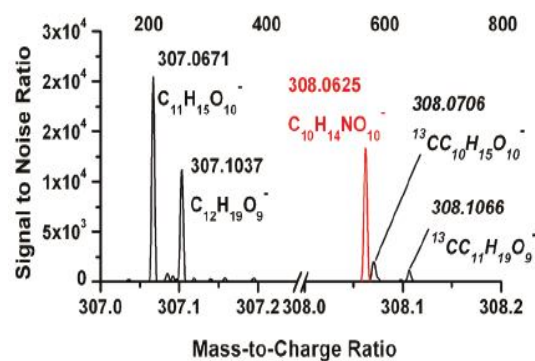
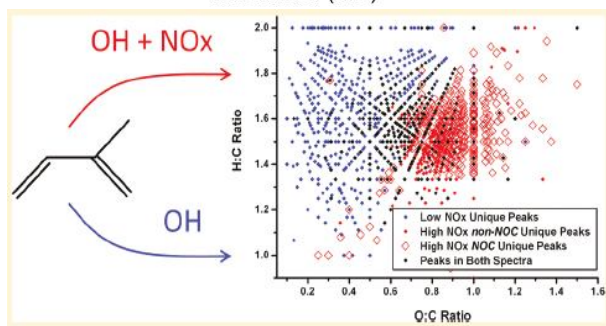
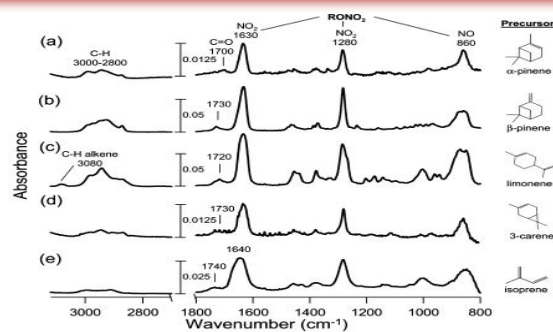
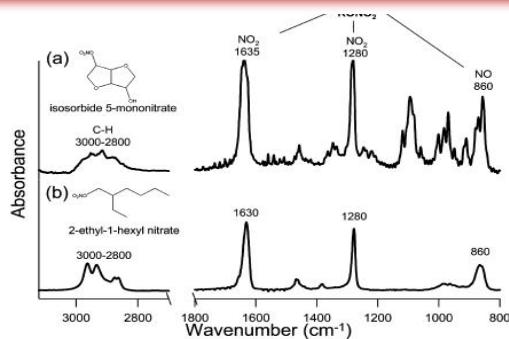
单体有机物的识别困难



Source:
Rogge et al,
1993;
Andreae et al
2006

单体有机物的研究多数限于正构烷烃、多环芳烃和部分有机酸

拓宽有机单体分子识别范围



- 联合多种分析手段（高分辨质谱、FTIR等），不断识别新的有机分子。

Bruns EA et al. ES&T, 2010, 44, 1056–1061

Nguyen TB, et al. ES&T, 2011 45: 6908-6918

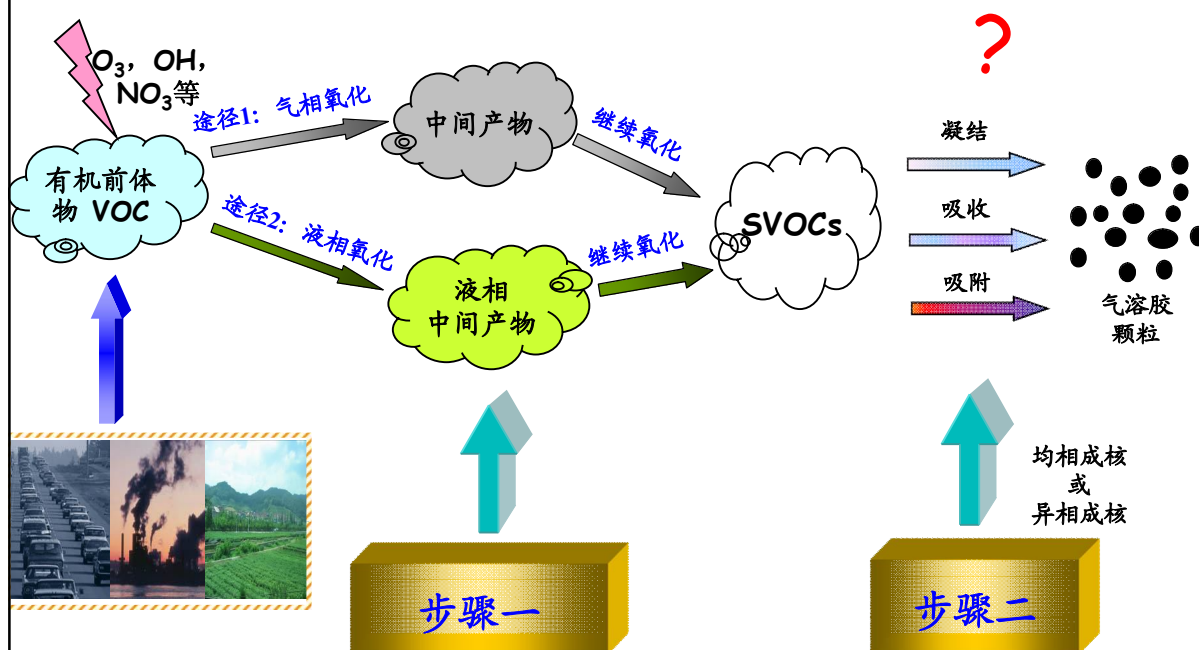
OC/EC测量

OC中仅有很小一部分（<15%）被定量解析为单个有机化合物，绝大多数OC用目前的色谱方法无法识别

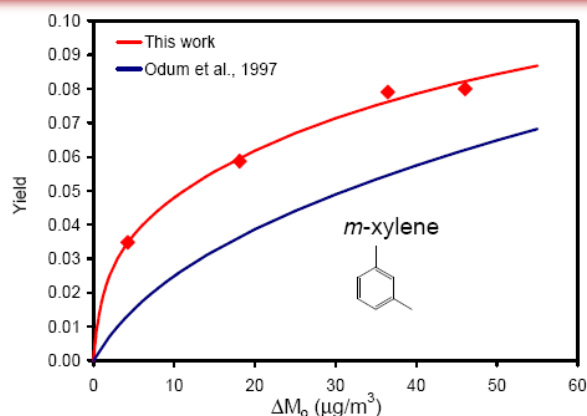
- ✧前处理过程繁琐
- ✧痕量分析
- ✧耗时长
- ✧花费高
- ✧.....

➡对于宏观测量（bulk measurement）而言，需要准确、一致；对于单体有机物测量而言，需多种分析手段的联合，需要示踪物.....

4、SOA形成的复杂机制



观测结果与模拟结果相差大



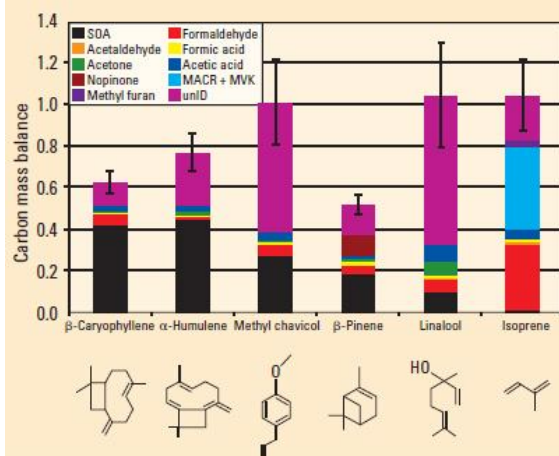
(Source: J.Seinfeld, 2008)

(Goldstein & Galbally, 2007)

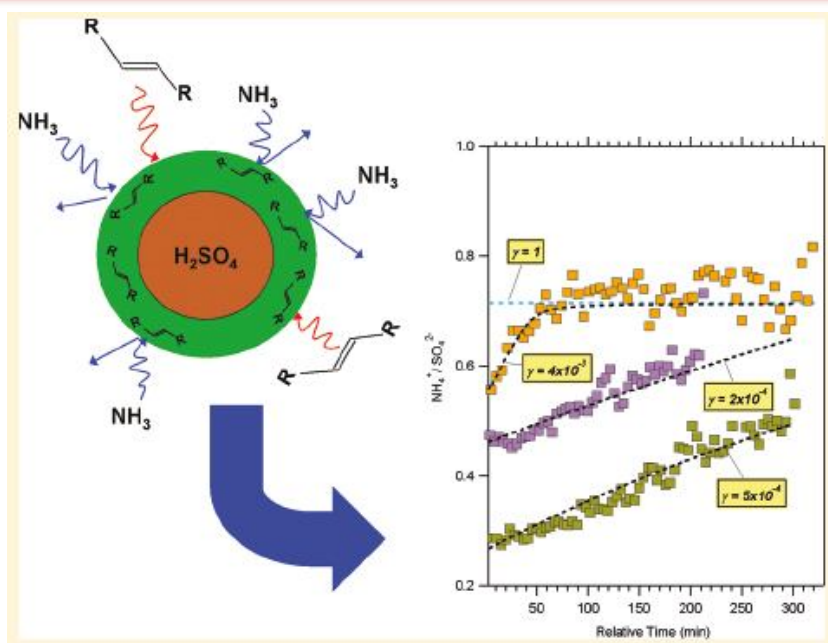
- Atmospheric Observation
- Smog-chamber Study
- Modeling

Carbon mass balance for photochemical oxidation of six different terpenoid compounds

All SOA and gas-phase products detected are included. Compounds measured as m/z ratios by PTR-MS that were not specifically identified are referred to as unID (adapted with permission from Ref. 26).

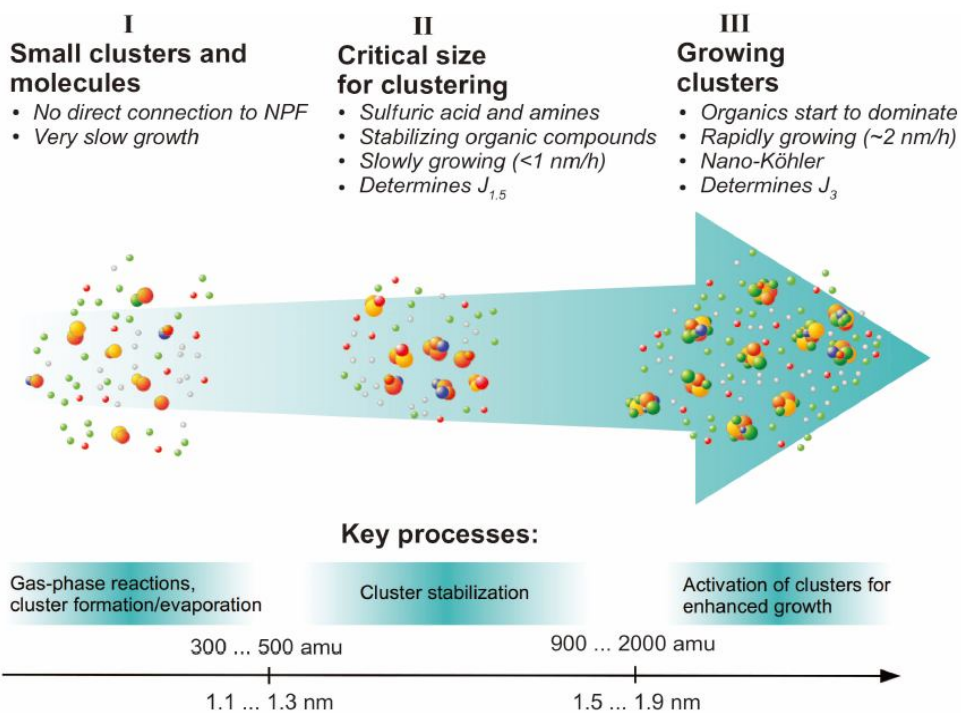


SOA形成机理不断深入与丰富:



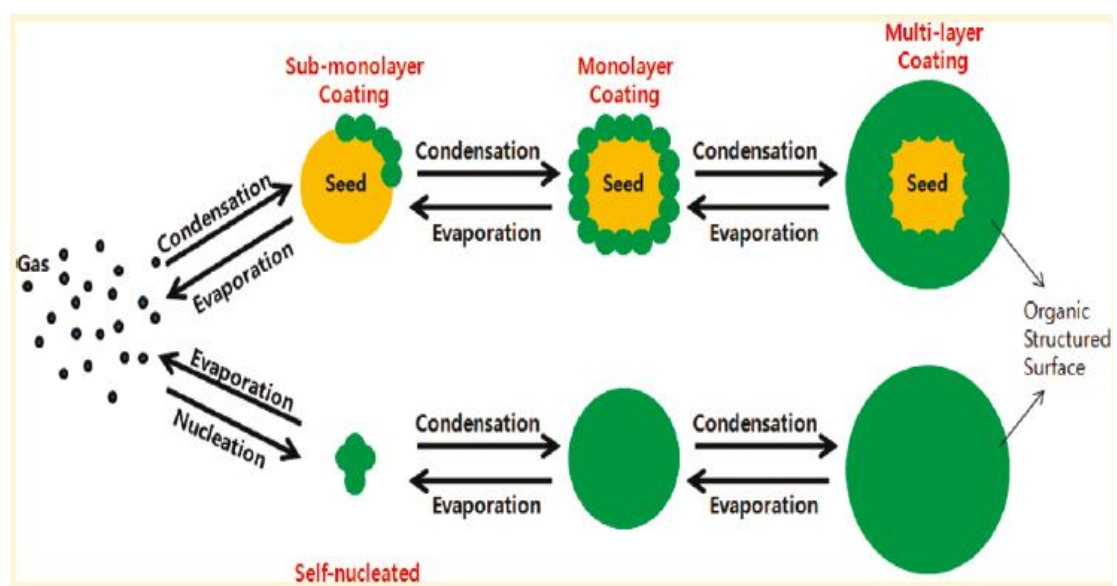
发现界面反应中无机-有机前体物竞争现象

Liggio J et al., ES&T. 2011, 45, 2790–2796



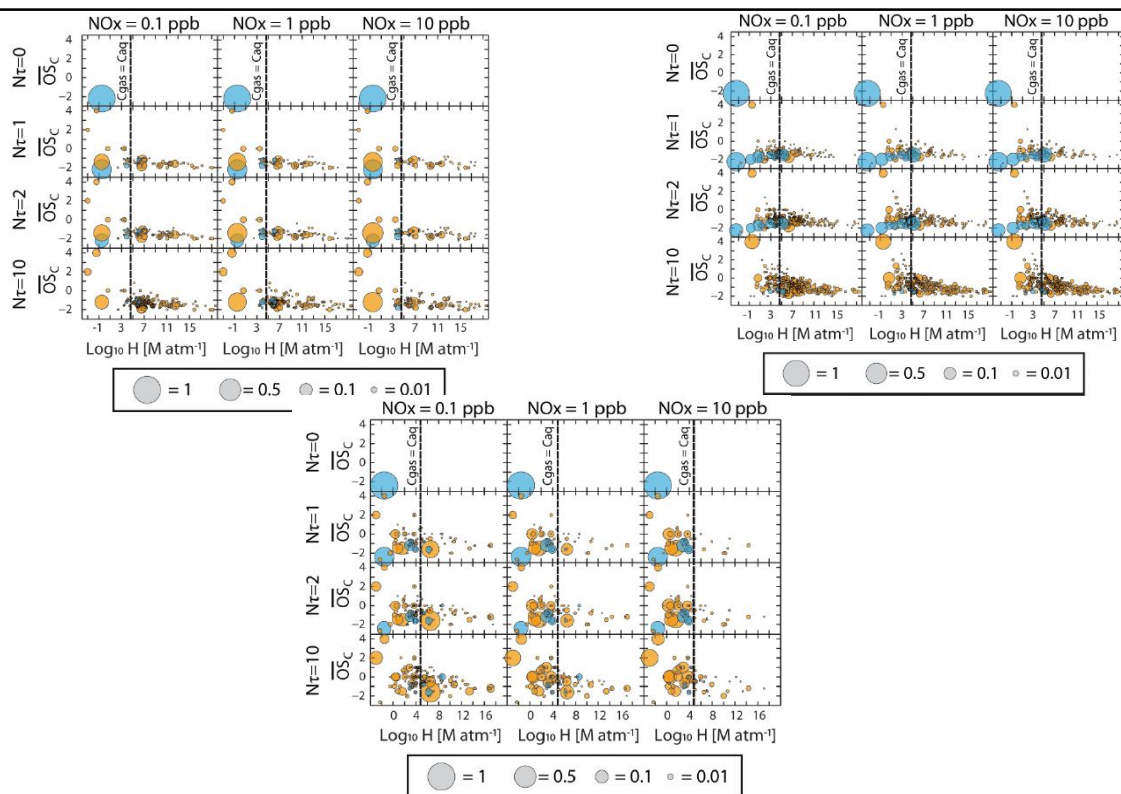
发现新粒子生成的直接证据

Kulmala M *et al. Science* 2013, 339, 943



金属氧化物纳米颗粒种子能够加速新粒子生成速率

Lee J and Donahue NM. ES&T, 2011, 45, 4689–4695

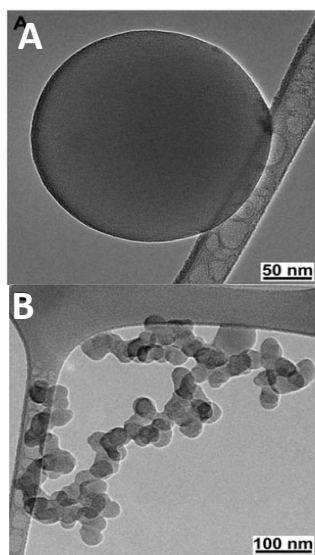


VOCs种类与 NO_x 浓度是影响液相反应速度的关键因素

Vallon CM, et al. Atmos. Chem. Phys., 13, 1023–1037, 2013

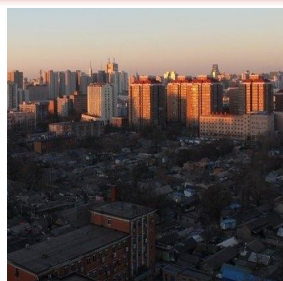
5、棕色碳的性质与环境影响

组成：棕色碳+黑炭

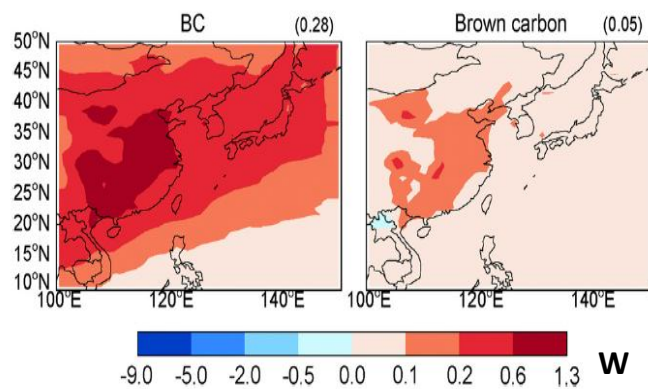


扫描电镜下棕色碳
(A) 与黑炭 (B) 颗粒
(Alexander et al., 2008)

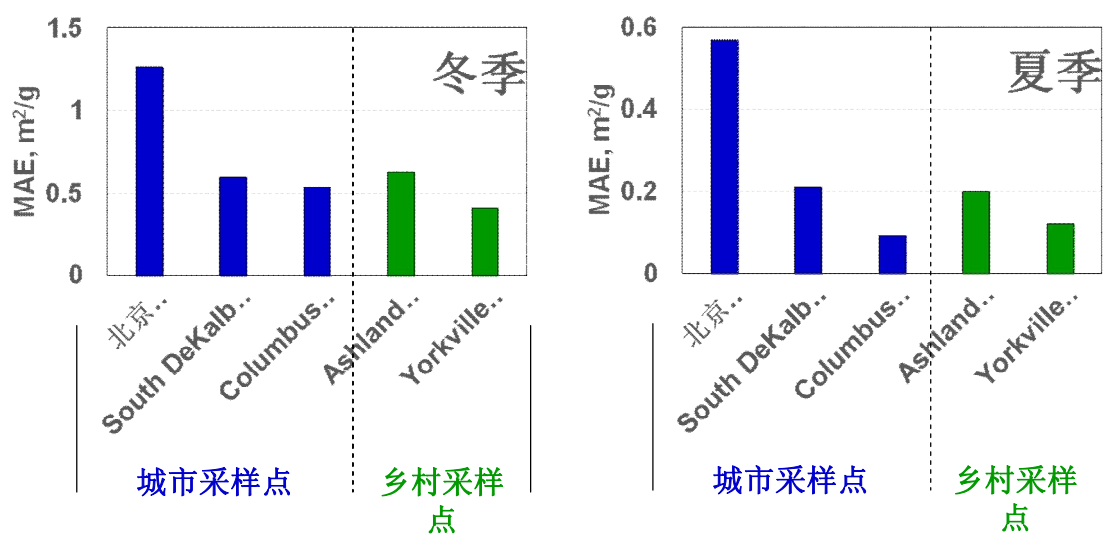
影响



1. 能见度降低



2. 辐射强迫 (Park et al., 2010) W m^{-2}

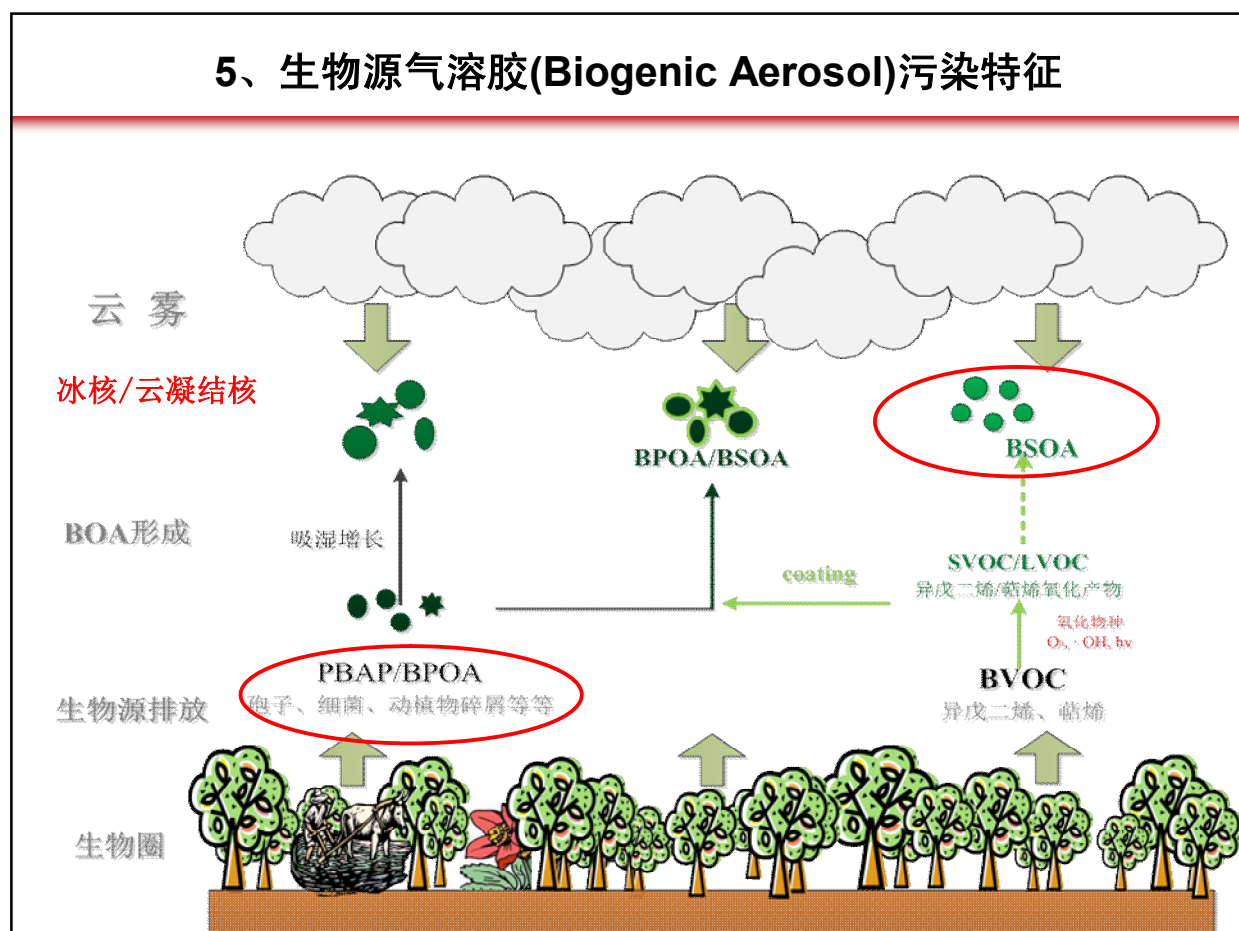


北京市与美国西南部分采样点**WSOC**吸光效率对比

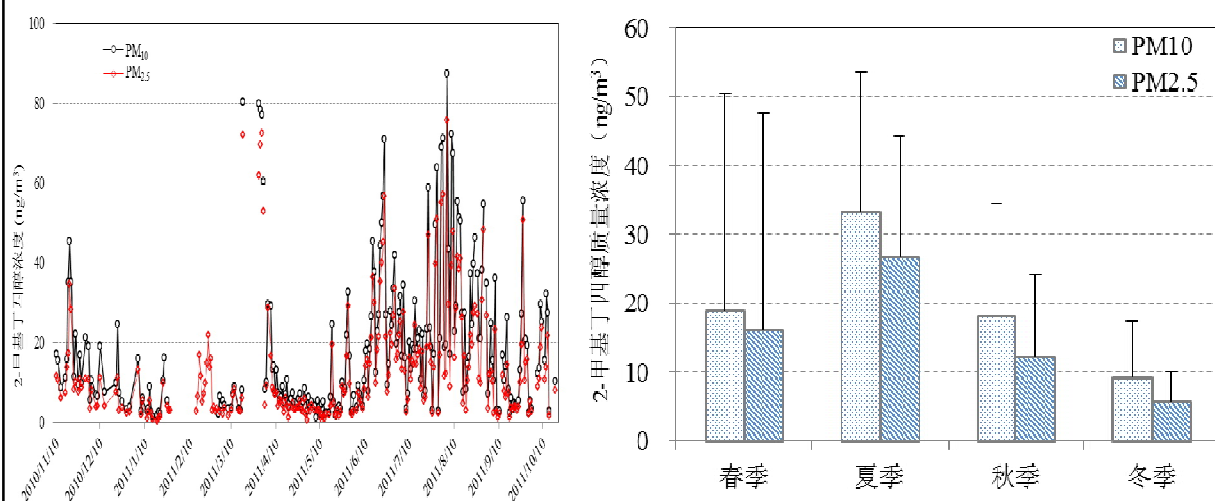
冬夏两季北京市吸光效率均普遍高于美国西南采样点，表明北京市水溶性棕色碳对**WSOC**具有更高的贡献

Du ZY, et al., in preparation

5、生物源气溶胶(Biogenic Aerosol)污染特征



生物源SOA污染特征



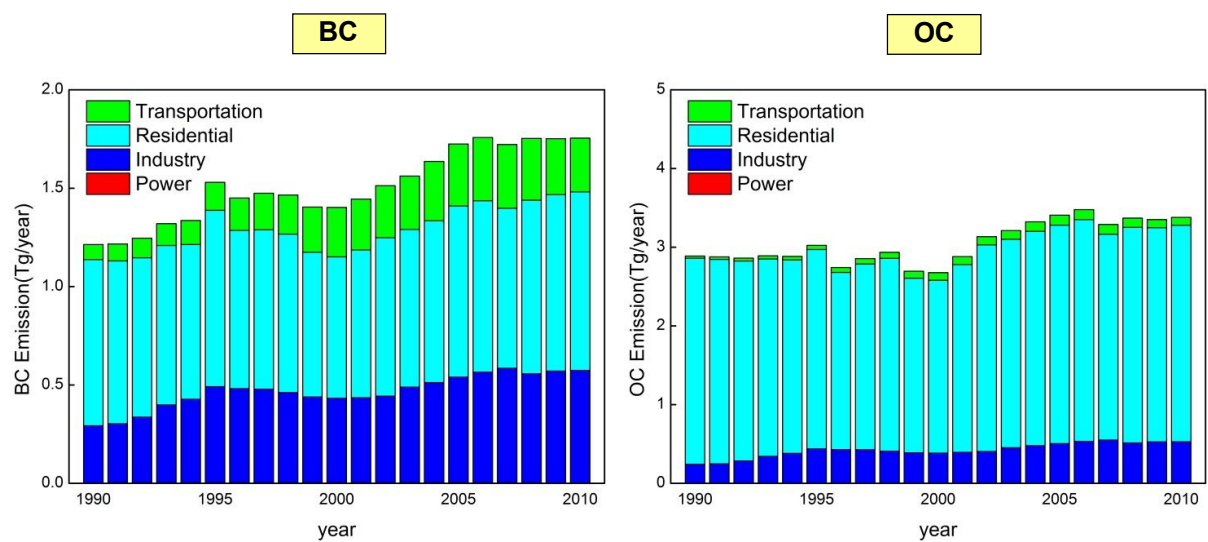
- 异戊二烯SOA主要分布在细颗粒物 $\text{PM}_{2.5}$ 中，占 PM_{10} 的71.94%。
- 北京大气气溶胶中异戊二烯SOA浓度水平呈现了明显的季节变化特征，随夏、春、秋、冬季递减。

Liang LL, et al., AE, 2012, 59: 376-381

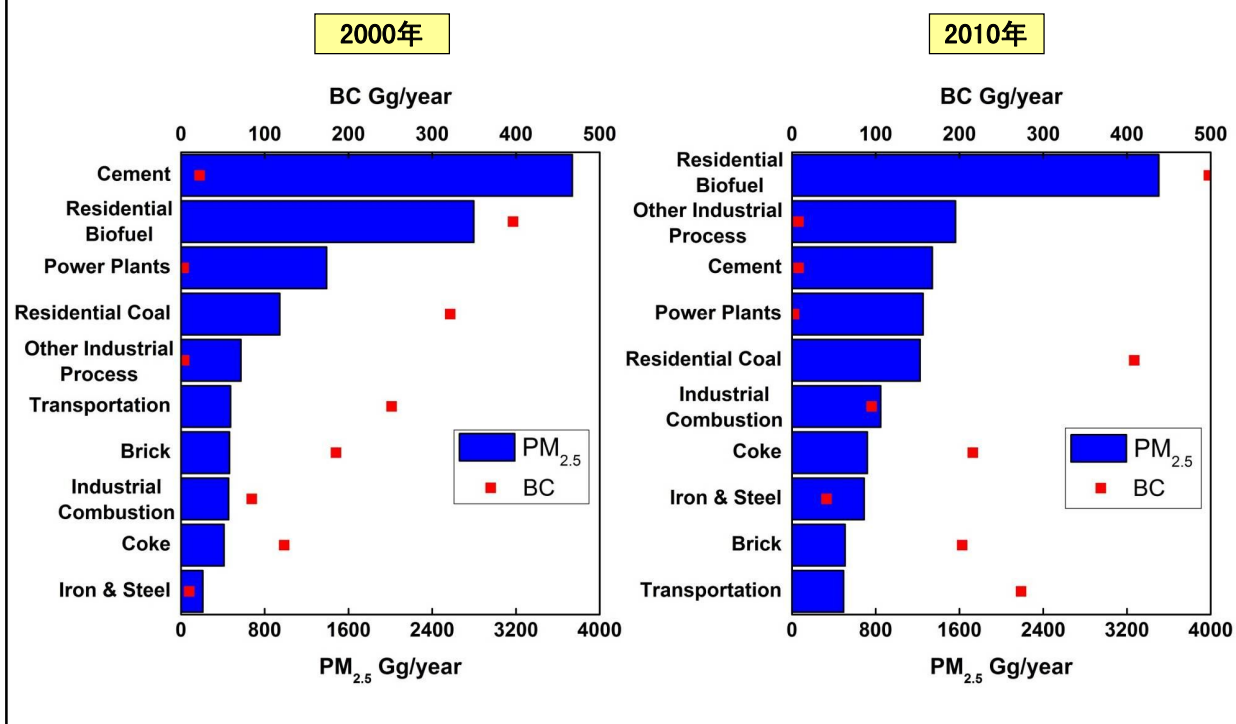
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- 二. 研究进展
- 三. 控制策略

现有的颗粒物控制措施对BC减排效果不明显



PM_{2.5}与BC的协同控制策略

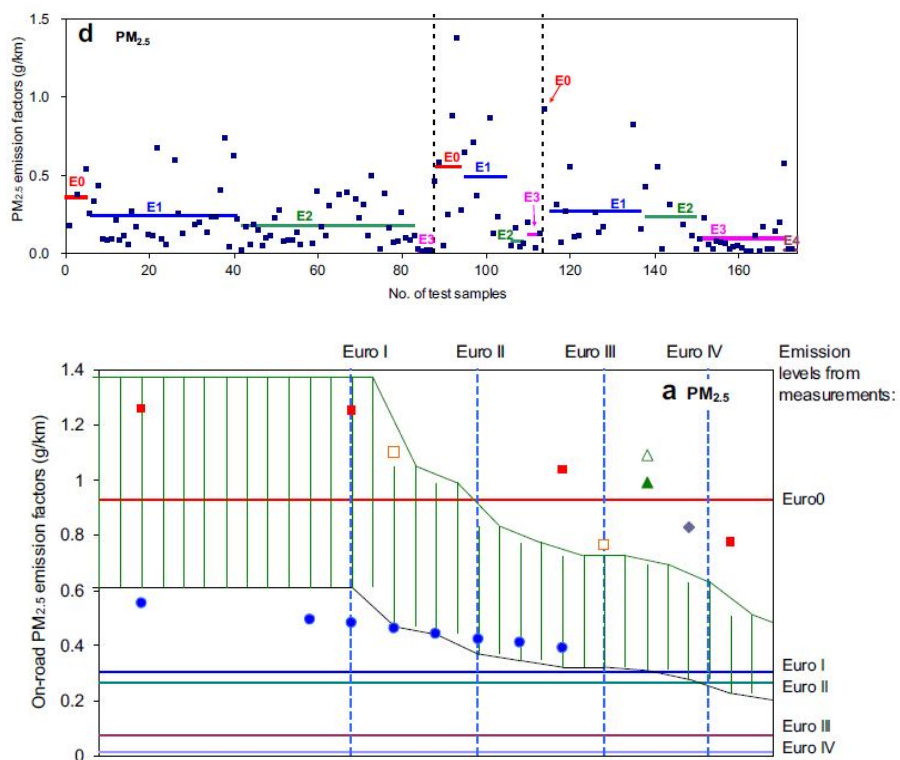


BC与PM_{2.5}及SO₂的协同控制策略

中国2010年不同污染源的一次排放比值

	BC/PM2.5	BC/SO2
电力	0.0021	0.0002
供热	0.0022	0.0004
工业锅炉	0.11	0.0091
工业过程	0.10	0.12
城市民用源	0.28	0.08
农村民用源	0.18	0.42
交通	0.50	0.79

柴油车在路排放因子随标准实施的变化



Abatement options of residential sectors

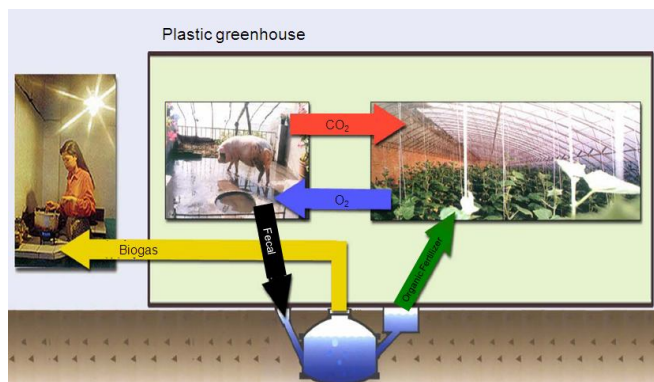
Enhance the usage of improved stoves



Increase the usage of briquette coal

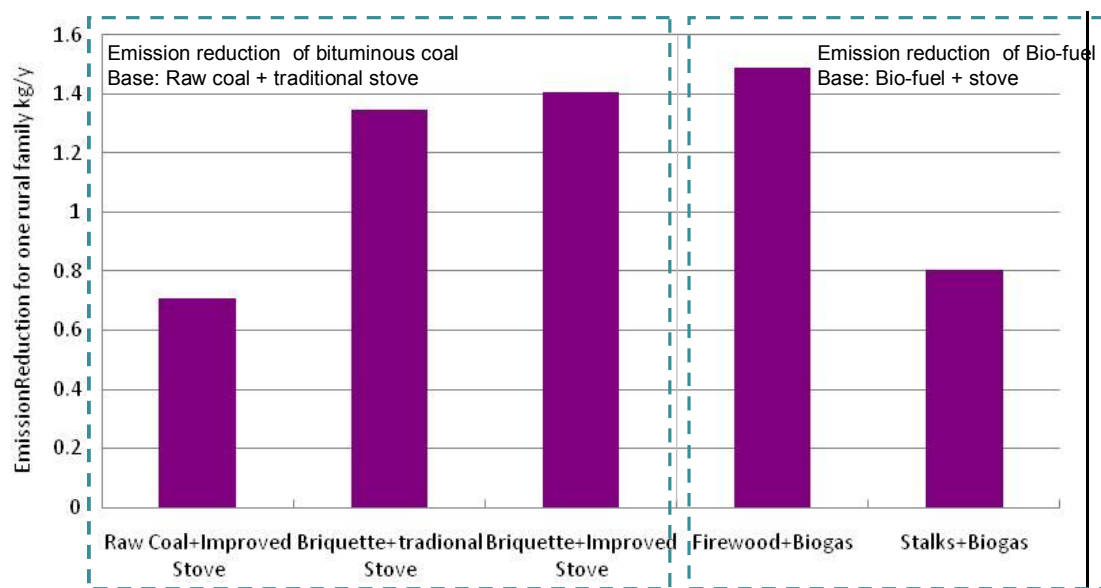


Increase the usage of Biogas

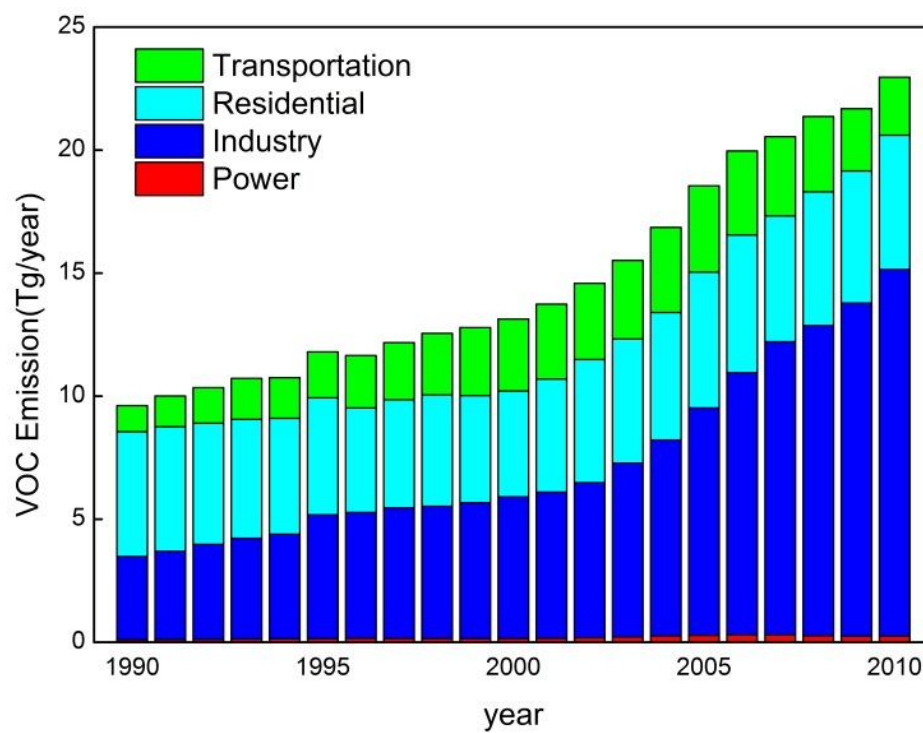


Emission Reduction of BC by using briquette and biogas

BC emission reduction on rural fuel combustion by different technologies
(one family in one year)



20年间中国人为源VOC排放趋势及部门组成



谢 谢！