中国科学院广州地球化学研究所
Guangzhou Institute of Geochemistry, Chinese Academy of Sciences

Bridging the gap between modelled and observed SOA: implications from chamber simulation and field campaigns

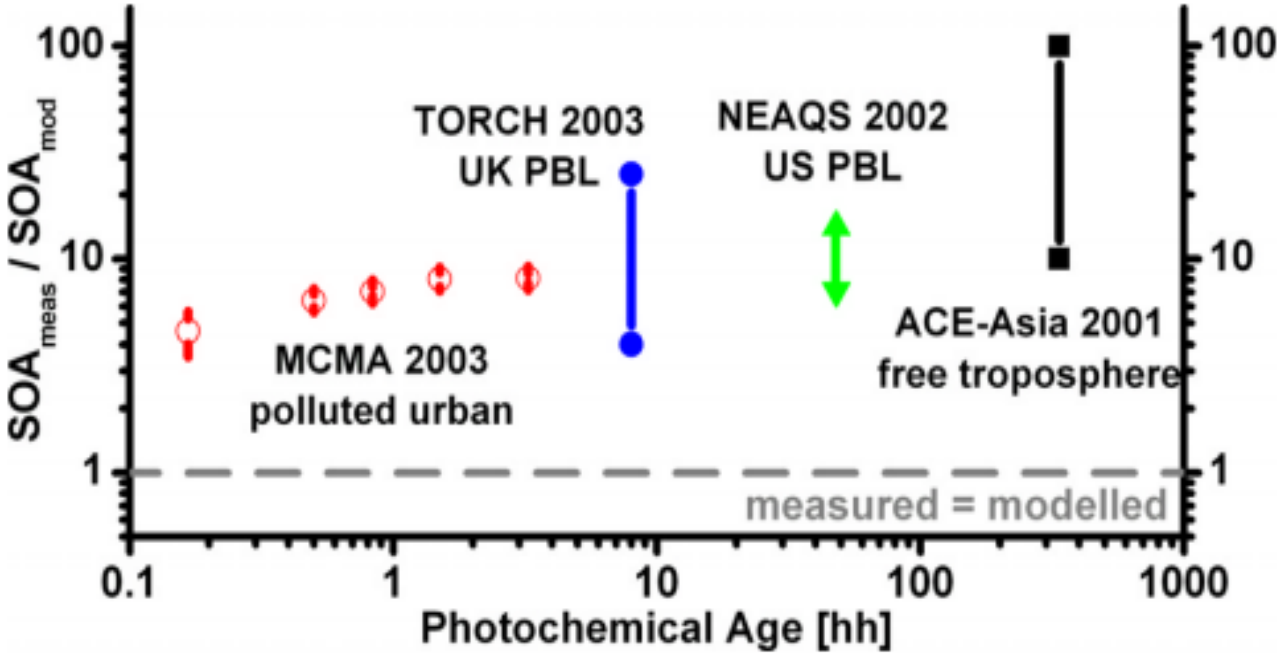
Xinming Wang, Xiang Ding and Yanli Zhang

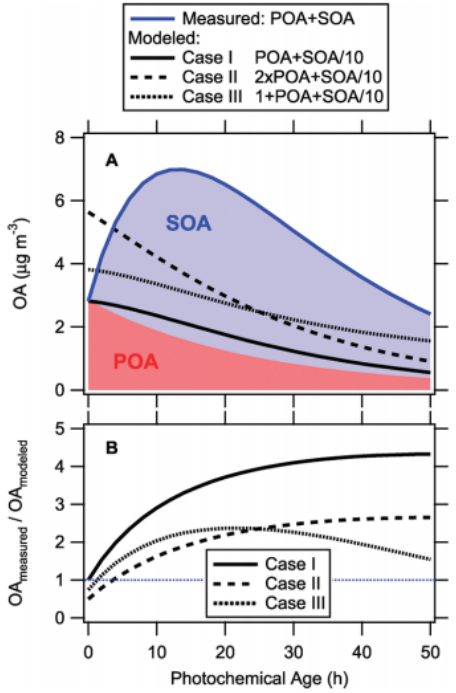
State Key Laboratory of Organic Geochemistry,
Guangzhou Institute of Geochemistry, Chinese Academy of Sciences

2018. 05@Nanjing

Secondary Organic Aerosols (SOA)

- Gap between modeled and measured SOA: models underestimate SOA by a factor up to 10





(*Volkamer et al., 2006, GRL; de Gouw and Jimenez, 2009, EST*)

SOA Observed
(offline: EC-tracer; online: AMS-OOA)

$$OC_{pri} = (OC/EC)_{pri} \times EC$$

$$OC_{sec} = OC_{tot} - OC_{pri}$$

OC/EC from biomass burning

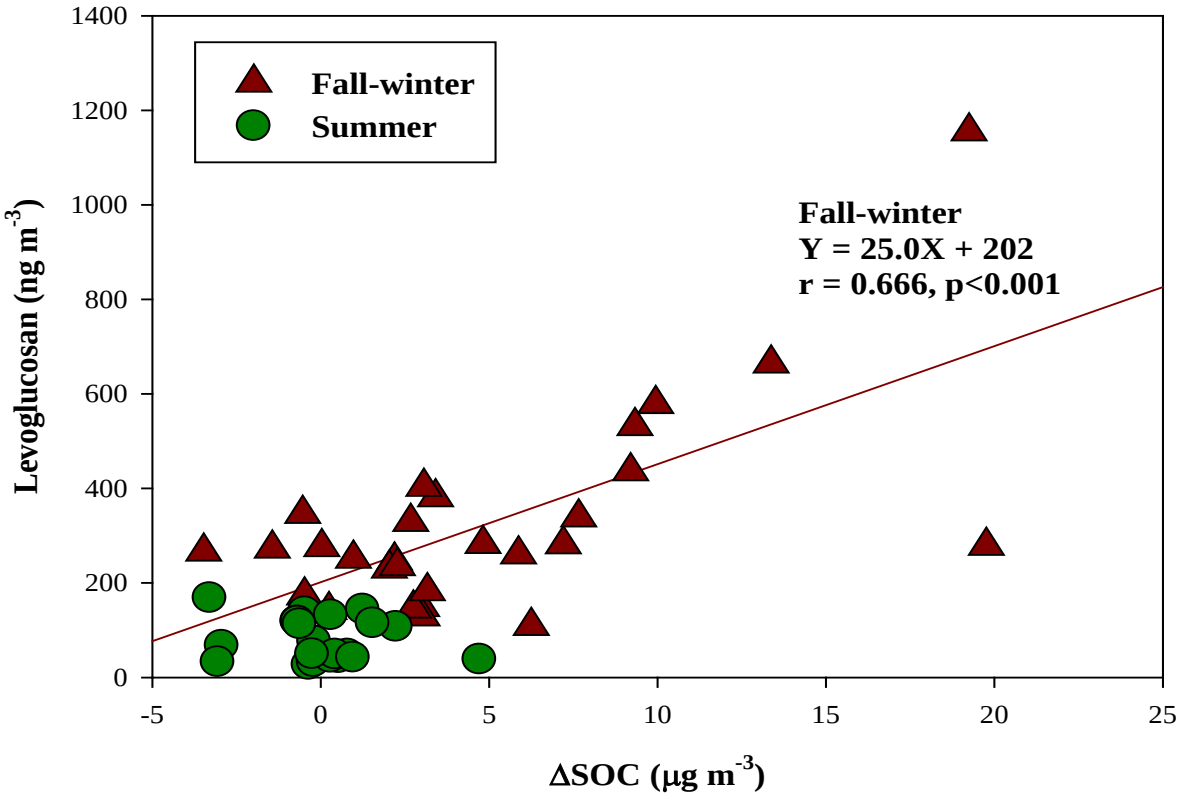
Wood burning

2.3 – 23.0 (12.7) Fine at al., 2001 (Northern US)
5.6 – 61.8 (23.4) Fine et al., 2002 (Southern US)

Cereal straw burning

OC/EC > 7 （Zhang et al., 2007）

SOA observed by tracer methods



$$\Delta SOC = SOC_{EC\text{-}tracer} - SOC_{SOA\text{-}tracer}$$

Overestimated under the influence of biomass burning

(Ding et al., JGR, 2012)

SOA observed

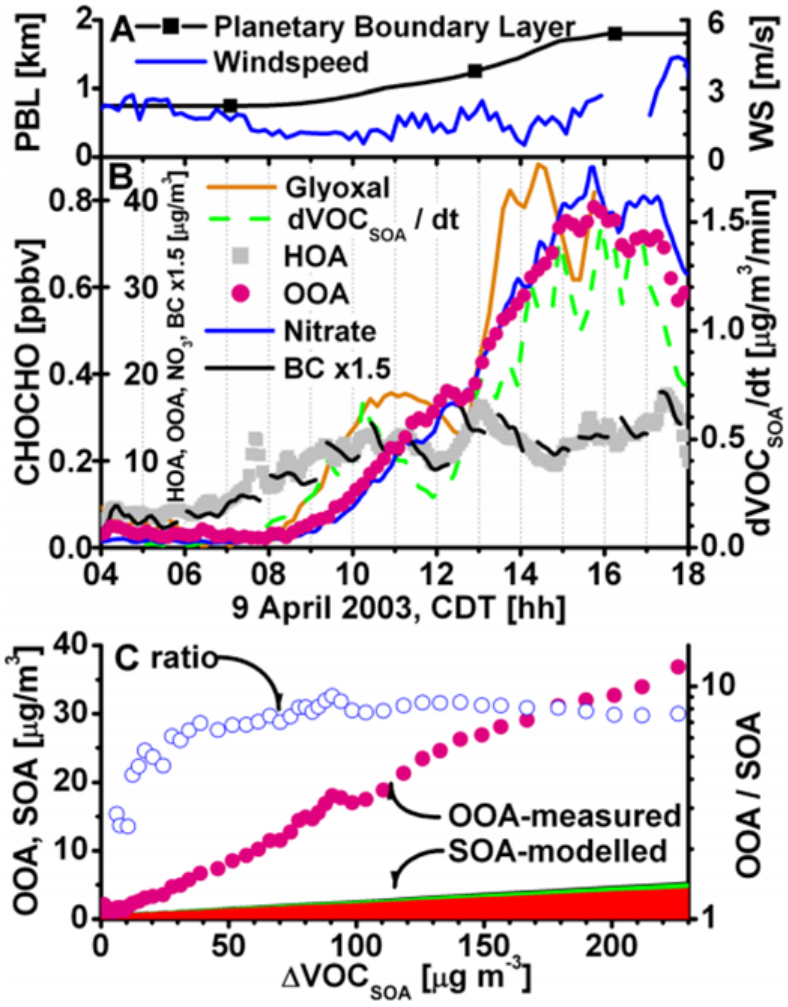
Table 15. Major Differences in BC and OC Predicted by Current and Previous Emission Factors (in Order of Greatest Absolute Difference in BC Inventory)[a]

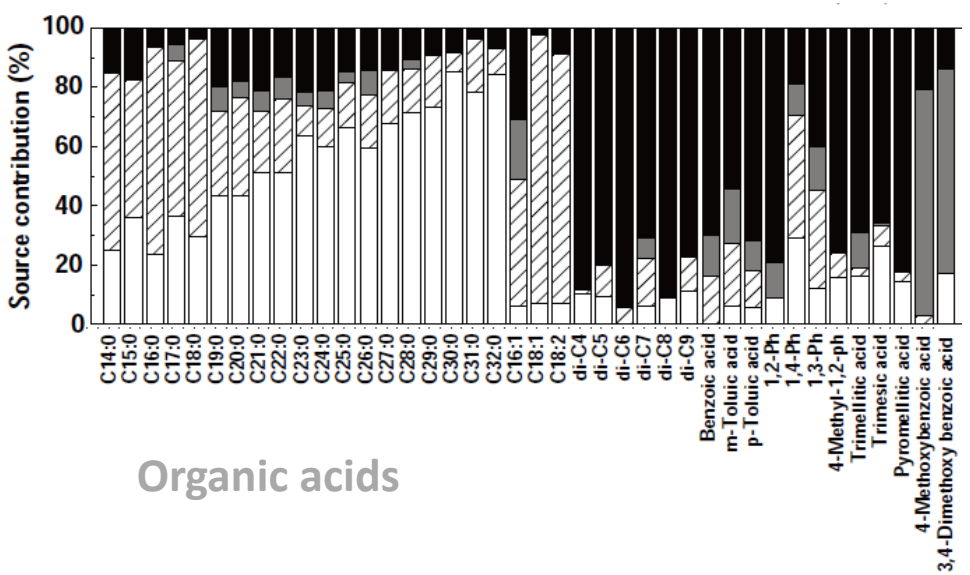
	Black Carbon			Organic Carbon		
Fuel/Sector	This Work	Previous96	Difference	This Work	Previous96	Difference
Open burning						
Open burning/forest	1238	2966	−1728	11,239	22,875	−11,636
Open burning/savanna	1715	2894	−1179	12,147	18,935	−6788
Open burning/crop resid	328	356	−28	1567	1519	48
Contained combustion						
Coal/power generation	7	1606	−1599	5	2359	−2354
Diesel fuel/on-road	792	2179	−1387	292	1278	−986
Wood/residential	880	1921	−1041	3506	11,537	−8031
Agricultural waste/residential	393	90	303	1492	1231	261
Animal waste/residential	208	417	−209	750	5465	−4715
Coal/industry[b]	642	1181	−539	450	1253	−803
Diesel fuel/residential	85	369	−284	28	185	−157
Coal/residential	480	761	−281	422	1716	−1294
Diesel fuel/off-road	579	691	−112	288	469	−181
Gasoline/transport	125	50	75	904	201	703
Other	478	524	−46	776	1242	−466
Total	7950	16,005	−8055	33,866	70,265	−36,399

[a]Units are Gg/yr based on 1996 fuel-use data (for contained combustion) or annual averages (for open burning).
[b]Includes coking, which accounts for 380 Tg BC, 270 Tg OC in this work; 320 Tg BC, 320 Tg OC in Previous96.

Bond et al., 2004, JGR

SOA observed





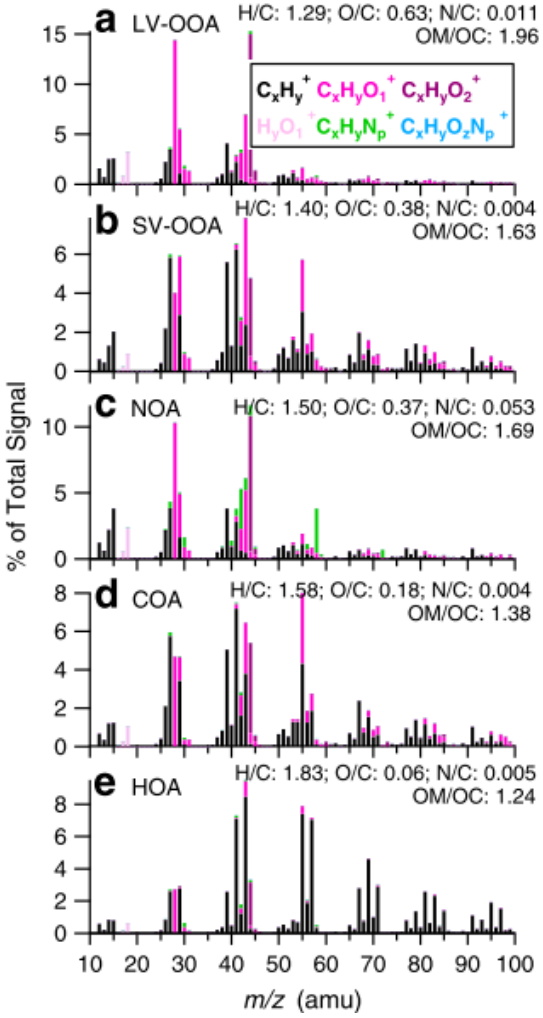
Organic acids

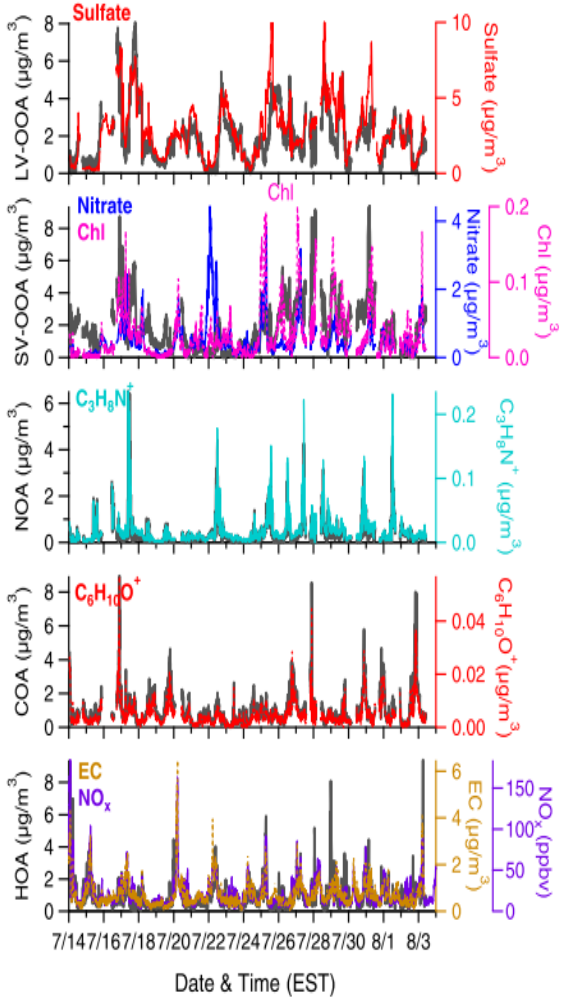
Many OOA might be primary

Volkamer et al., 2006, GRL
Zhang et al., 2005, EST; Zhang et al., 2007, GRL

Zhao et al., 2014, JES; 2015,JAC

SOA observed





LV-OOA：Sulfate
SV-OOA：Nitrate
HOA：NOx，EC
COA：$C_5H_8O^+$, $C_6H_{10}O^+$, $C_7H_{12}O^+$
BBOA：levoglucosan
CCOA: ……
NOA:……
…….

Online VS Offline?

mz 44: OOA
mz 41,43,55,57: HOA

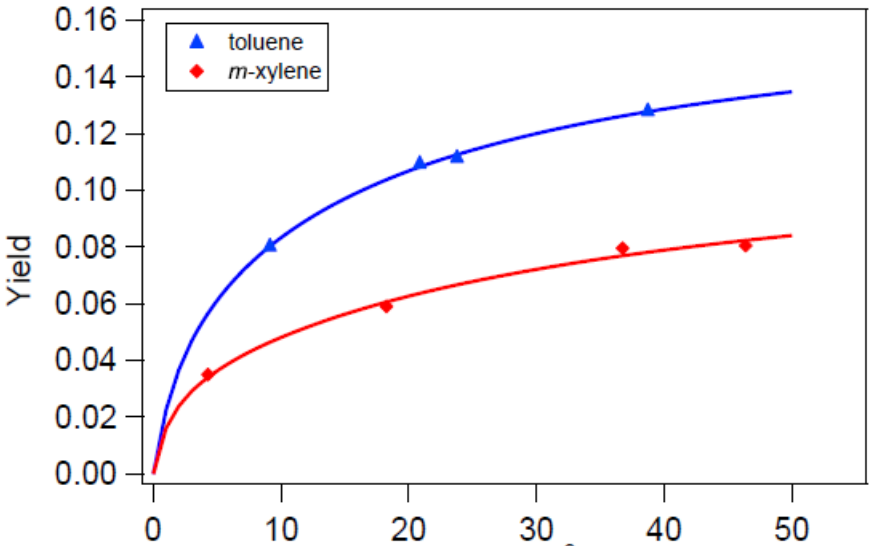
Zhang et al., 2011, ABC

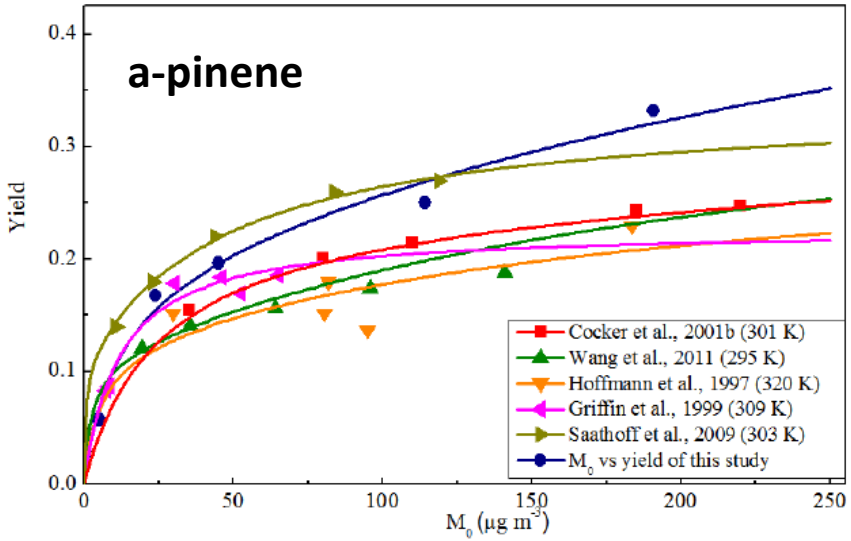
Predicted SOA matched the observed in chamber studies?

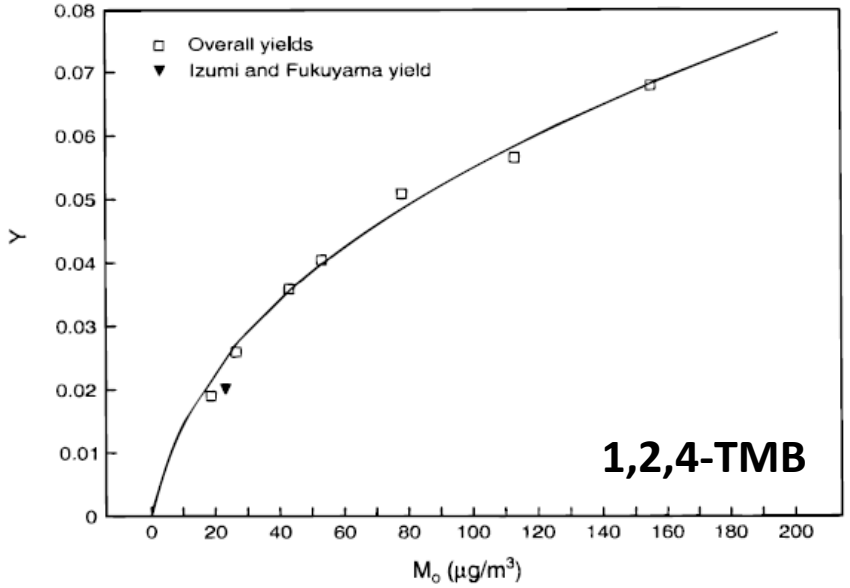
Chamber studies: emission and meteorological factors are excluded

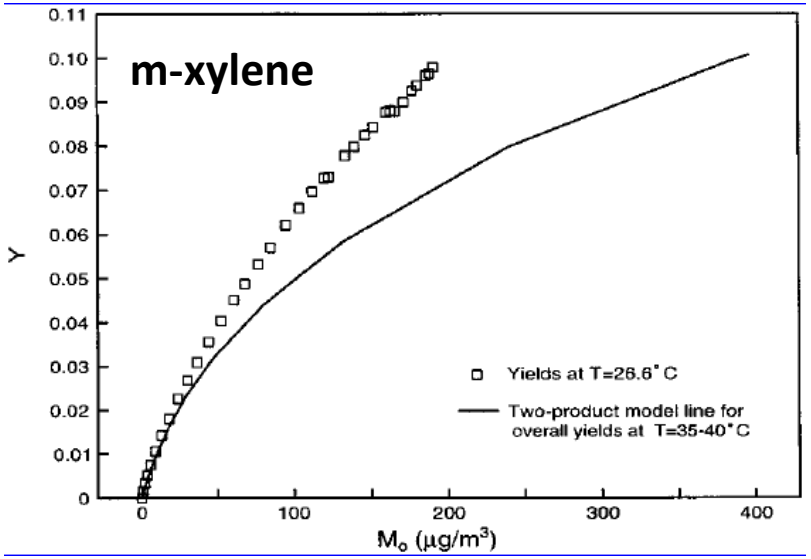
SOA formation from individual VOC in SMOG chamber

Two product model









Odum et al., 1996; Ng et al., 2007; Wang et al., 2014

SOA formation from gasoline vapor in chamber

- SOA yield curves of 17 individual aromatic species from smog chamber gasoline experiments.
- These yield curves, interpreted within the framework of a gas/aerosol absorption model, are used to quantitatively account for the SOA that is formed from the whole vapor of 12 different reformulated gasolines.
- The total amount of secondary organic aerosol produced from the atmospheric oxidation of whole gasoline vapor can be represented as the sum of the contributions of the individual aromatic molecular constituents of the fuel.

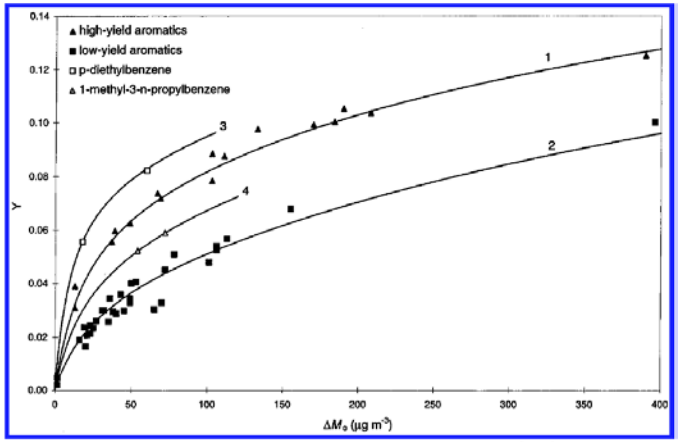


TABLE 4. Results for Gasoline Experiments

date	fuel	ΔROG (μg m^{-3})	ΔAromatic (μg m^{-3})	max O_3 (ppb)	actual ΔM_o (μg m^{-3})	predicted ΔM_o (μg m^{-3})	pred/actual
7/26/96	RF-A	3642	1742	1668	160	113	0.71
7/29/96	RF-A	3554	1725	1733	110	94	0.85
8/21/96	RF-A	2601	1178	1248	64	53	0.83
7/26/96	C2	3203	1200	1536	36	47	1.31
7/29/96	C2	3551	1421	1687	54	63	1.17
9/06/96	C2	2072	814	1012	18	21	1.17
8/19/96	RF-L	1876	907	1156	130	60	0.46
8/23/96	RF-L	1784	846	1269	95	52	0.55
8/21/96	RF-F	2326	823	1084	22	26	1.18
8/26/96	RF-F	1826	627	540	18	17	0.97
9/04/96	RF-F	1648	551	469	15	13	0.87
8/26/96	RF-G	3088	1407	1476	110	98	0.89
9/02/96	RF-G	3134	1459	1484	108	102	0.94
9/06/96	RF-K	2638	1409	1328	84	90	1.07
9/02/96	RF-O	3348	1549	1479	118	115	0.97
9/04/96	RF-P	2918	777	1371	35	29	0.83
8/28/96	RF-1B	2663	788	1513	28	28	1.00
8/30/96	RF-2B	3273	1556	1595	64	76	1.19
8/28/96	RF-3B	2243	678	1482	17	18	1.06
8/30/96	RF-4B	2534	1270	1564	56	58	1.04
						av = 1.00 ± 0.16	

Odum et al., 1997; EST

SOA formation from whole gasoline vapor in chamber

The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor

J. R. Odum, T. P. W. Jungkamp, R. J. Griffin, R. C. Flagan, J. H. Seinfeld*

A series of sunlight-irradiated, smog-chamber experiments confirmed that the atmospheric organic aerosol formation potential of whole gasoline vapor can be accounted for solely in terms of the aromatic fraction of the fuel. The total amount of secondary organic aerosol produced from the atmospheric oxidation of whole gasoline vapor can be represented as the sum of the contributions of the individual aromatic molecular constituents of the fuel. The urban atmospheric, anthropogenic hydrocarbon profile is approximated well by evaporated whole gasoline, and thus these results suggest that it is possible to model atmospheric secondary organic aerosol formation.

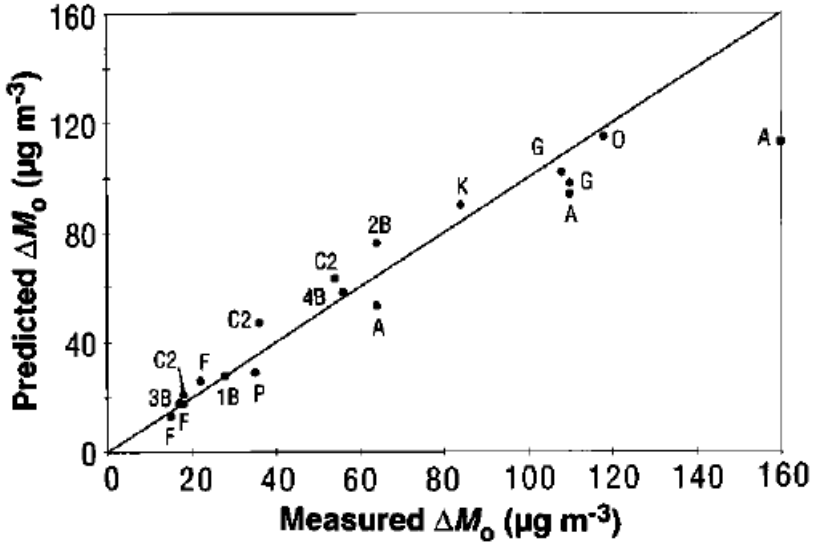
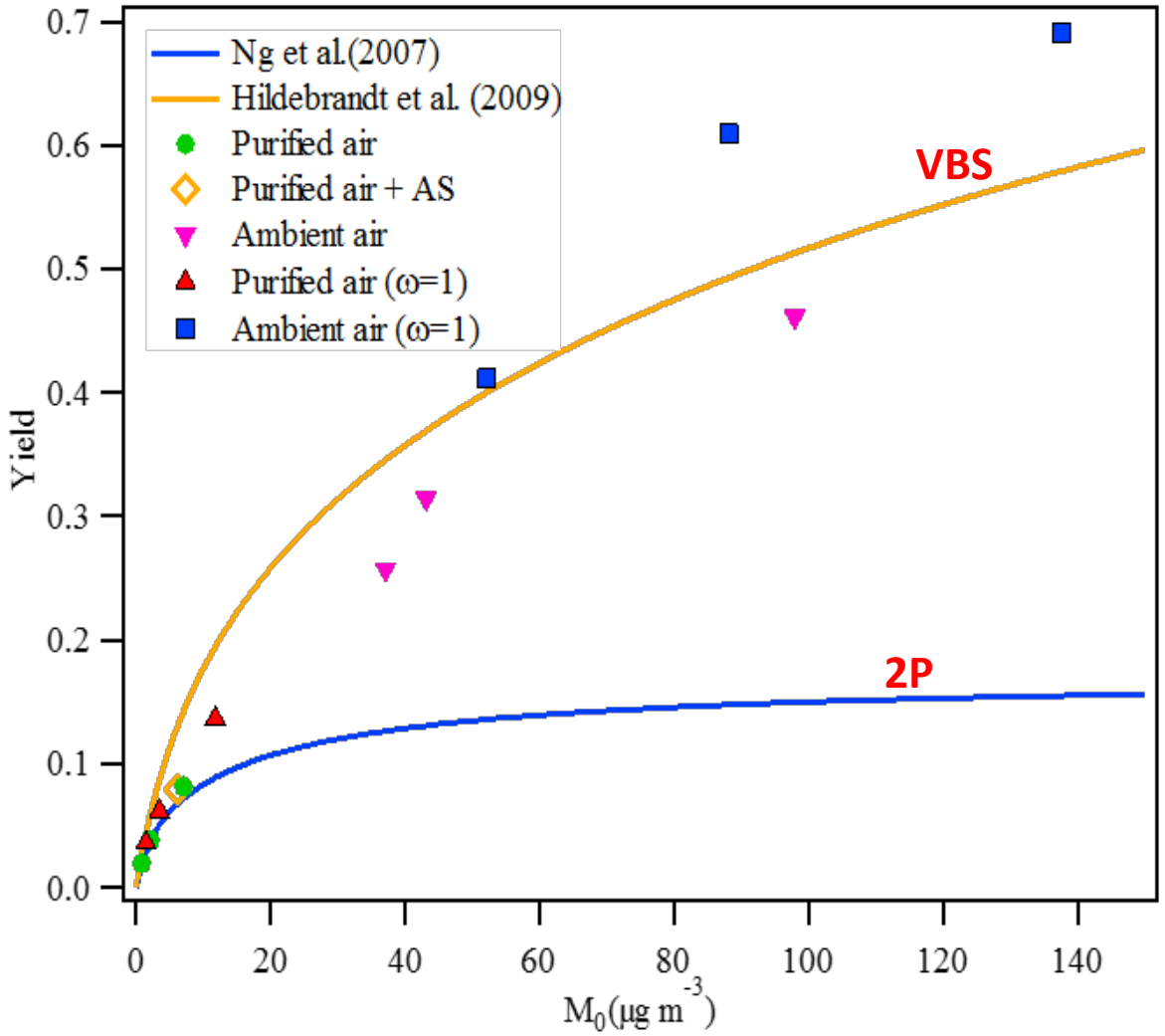


Table 2. Properties of AQIRP reformulated gasolines. MTBE = the fuel additive methyl tertiary butyl ether; the fuel identification code is derived from A (a) = high (low) aromatics, M (m) = high (low) MTBE, O (o) = high (low) olefins, T (t) = high (low) T_{90}, RMH = medium and heavy reformate cut (predominantly C_9 and C_{10} aromatics), and AH = heavy alkylate cut (heavy paraffins).

Fuel code	AQIRP phase	Fuel ID	Aromatics (vol %)	MTBE (vol %)	Olefins (vol %)	T_{90} (°C)
A	I	Industry average	32.0	0.0	9.2	166
F	I	amot	20.0	0.0	3.2	137
G	I	AmOt	44.3	0.0	17.4	141
K	I	Amot	45.7	0.0	4.9	146
L	I	AmOT	47.8	0.0	17.7	181
O	I	AMOt	46.7	14.6	19.3	139
P	I	amOt	20.3	0.0	18.3	140
C2	II	California phase II	25.4	11.2	4.1	145
1B	II	Matrix B base	25.3	11.2	15.0	131
2B	II	Base + RMH	35.1	10.4	11.2	157
3B	II	Base + AH	22.1	10.4	13.3	148
4B	II	Base + AH + RMH	32.2	10.2	10.7	168

Matrix effect: purified air VS ambient air

SOA from "SO_2+NO_x+toluene"



Ng et al., 2007; Hildebrandt et al., 2009; Deng et al., 2017

Combustion sources are important and far more complex with emission of organics from very volatile organic compounds to low- and non-volatile organic compounds that all potentially contribute to SOA formation.

Globally important: biomass burning

Important in urban areas: vehicle exhaust (diesel in particular)

SOA formed from these important sources can be predicted with traditinal precursors?

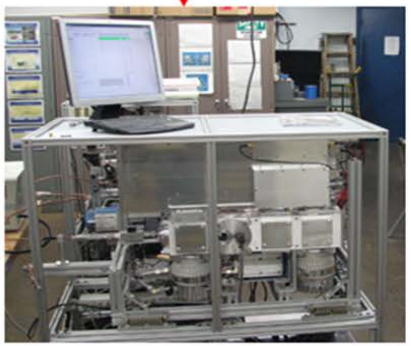
GIG Smog chamber (30m^3)

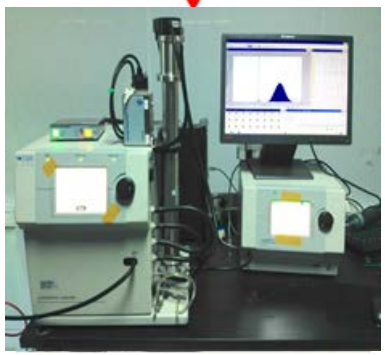
Gas/Dies

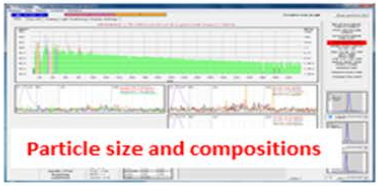
Vehicle exhaust

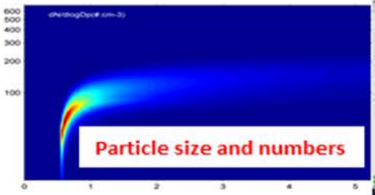
C/W/R

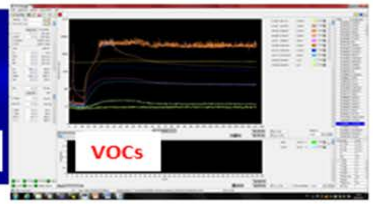
Biomass burning

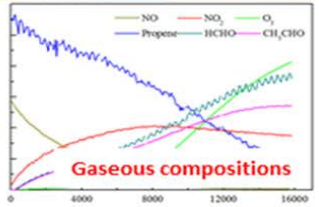








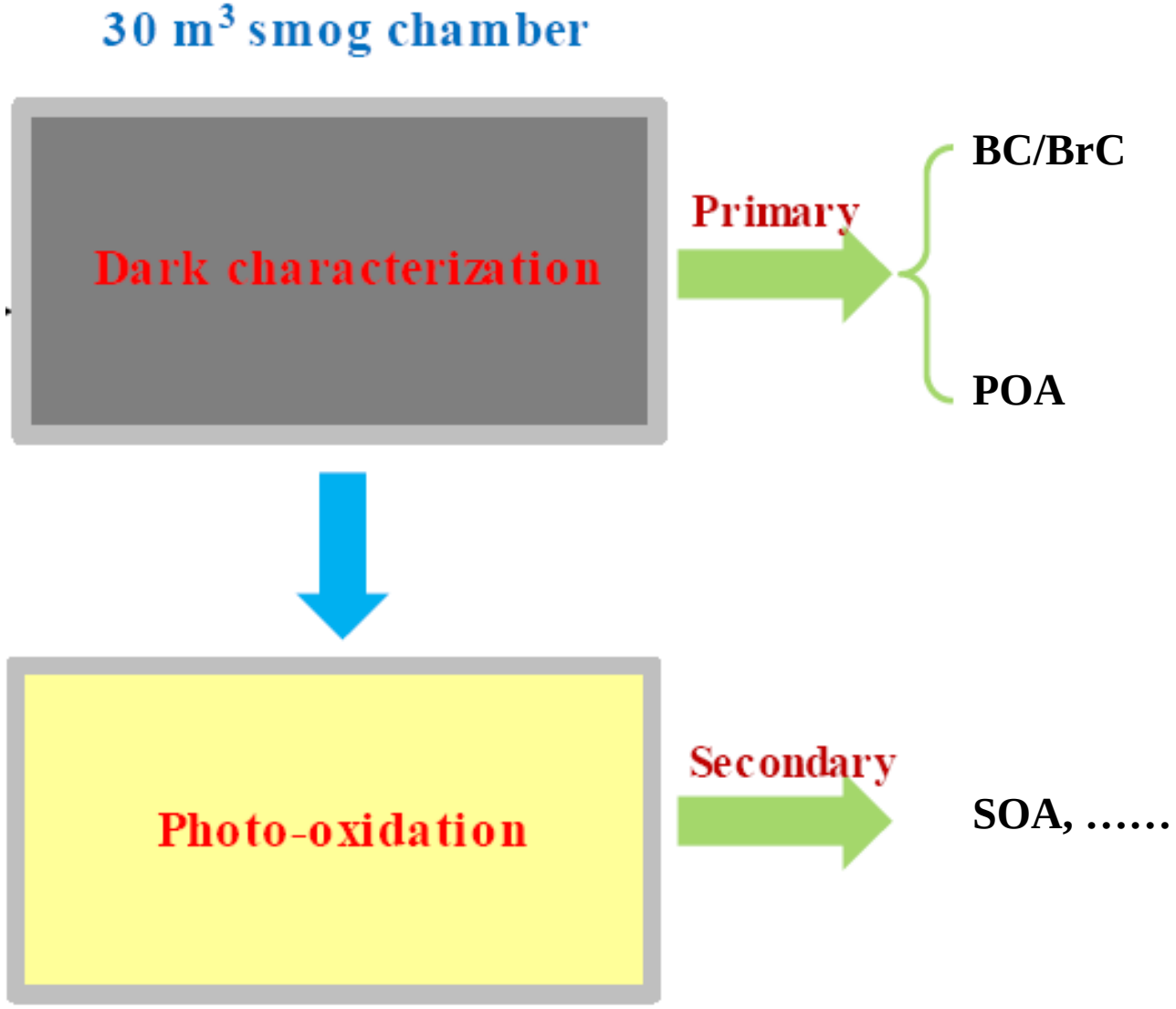




中国科学院广州地球化学研究所

Guangzhou Institute of Geochemistry Chinese Academy of Sciences

Experimental design



Biomass burning： open or quasi-open combustion of any non-fossilized vegetative or organic fuel

Forest

Grassland

Crop residue

Peat/Charcoal

Biomass pellet

Garbage

(Andreae and Merlet, 2001, GBC; Akagi et al., 2011, ACP)

Biomass burning: globally important pollution source

Table 15. Major Differences in BC and OC Predicted by Current and Previous Emission Factors (in Order of Greatest Absolute Difference in BC Inventory)[a]

	Black Carbon			Organic Carbon		
Fuel/Sector	This Work	Previous96	Difference	This Work	Previous96	Difference
Open burning						
Open burning/forest	1238	2966	−1728	11,239	22,875	−11,636
Open burning/savanna	1715	2894	−1179	12,147	18,935	−6788
Open burning/crop resid	328	356	−28	1567	1519	48
Contained combustion						
Coal/power generation	7	1606	−1599	5	2359	−2354
Diesel fuel/on-road	792	2179	−1387	292	1278	−986
Wood/residential	880	1921	−1041	3506	11,537	−8031
Agricultural waste/residential	393	90	303	1492	1231	261
Animal waste/residential	208	417	−209	750	5465	−4715
Coal/industry[b]	642	1181	−539	450	1253	−803
Diesel fuel/residential	85	369	−284	28	185	−157
Coal/residential	480	761	−281	422	1716	−1294
Diesel fuel/off-road	579	691	−112	288	469	−181
Gasoline/transport	125	50	75	904	201	703
Other	478	524	−46	776	1242	−466
Total	7950	16,005	−8055	33,866	70,265	−36,399

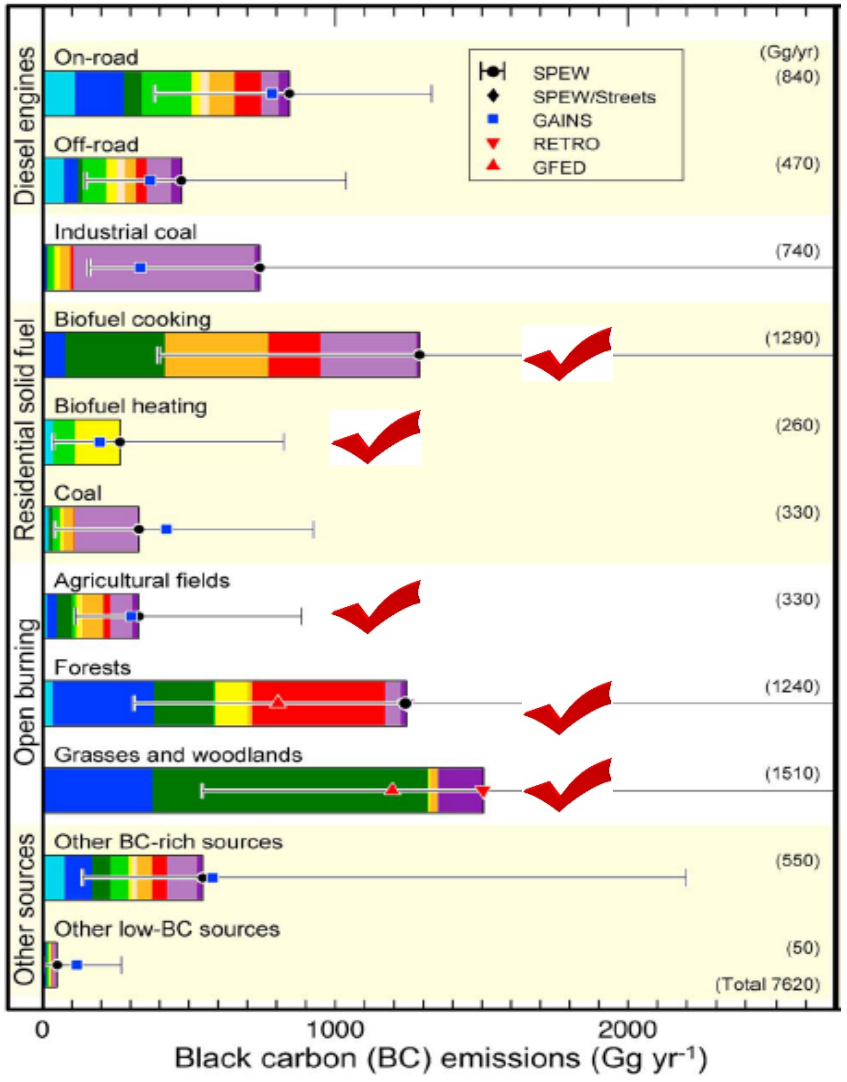
More than 90% of global primary organic carbon

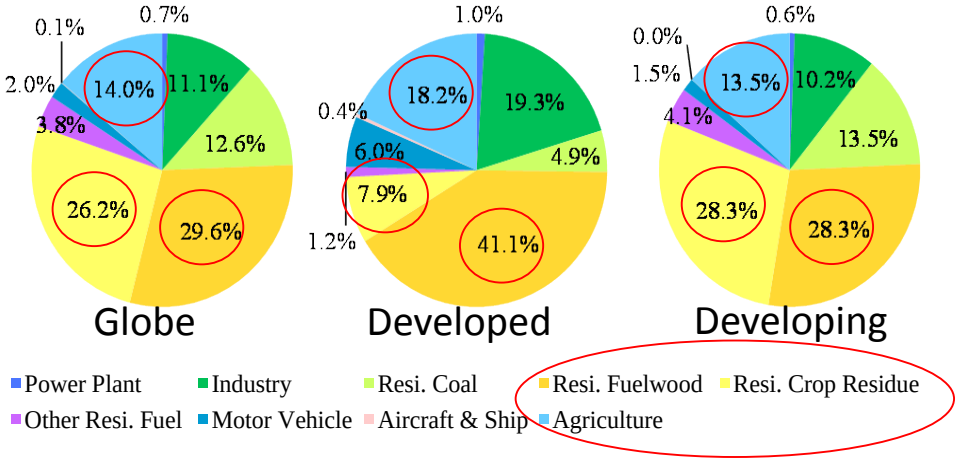
More than 60% of global black carbon

(Bond et al., *JGR*, 2004)

Biomass burning: globally important pollution source

Biomass burning: the largest BC and OC source





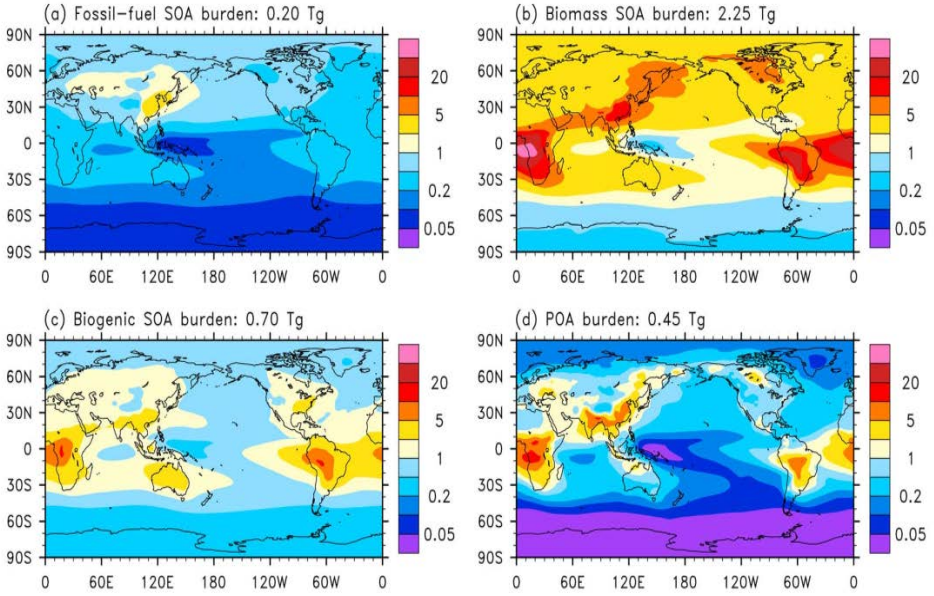
Global OC emission

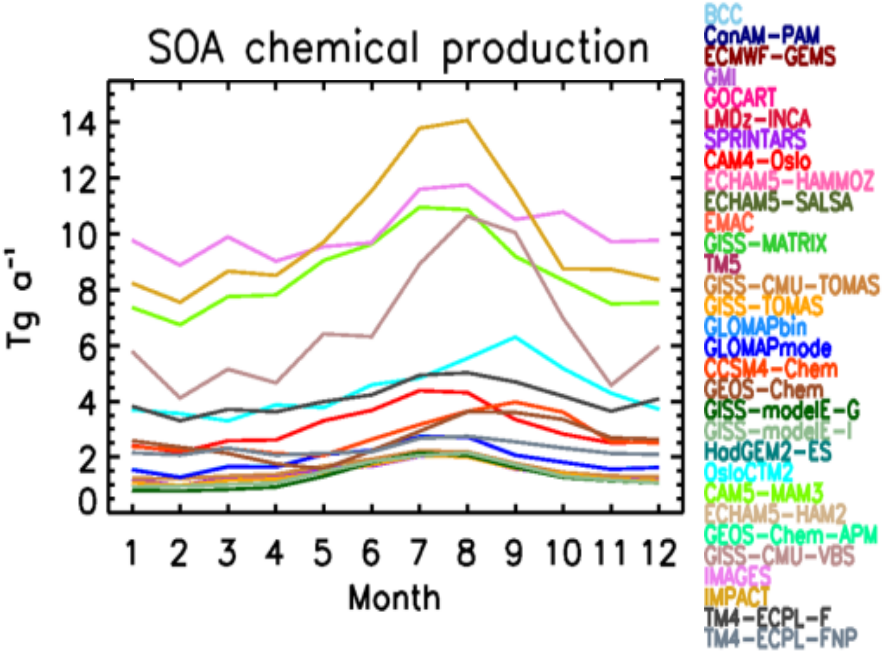
(Bond et al., 2013, JGR; Huang et al., 2015, AE)

Secondary organic aerosol budget

BBSOA: 71% in global SOA burden

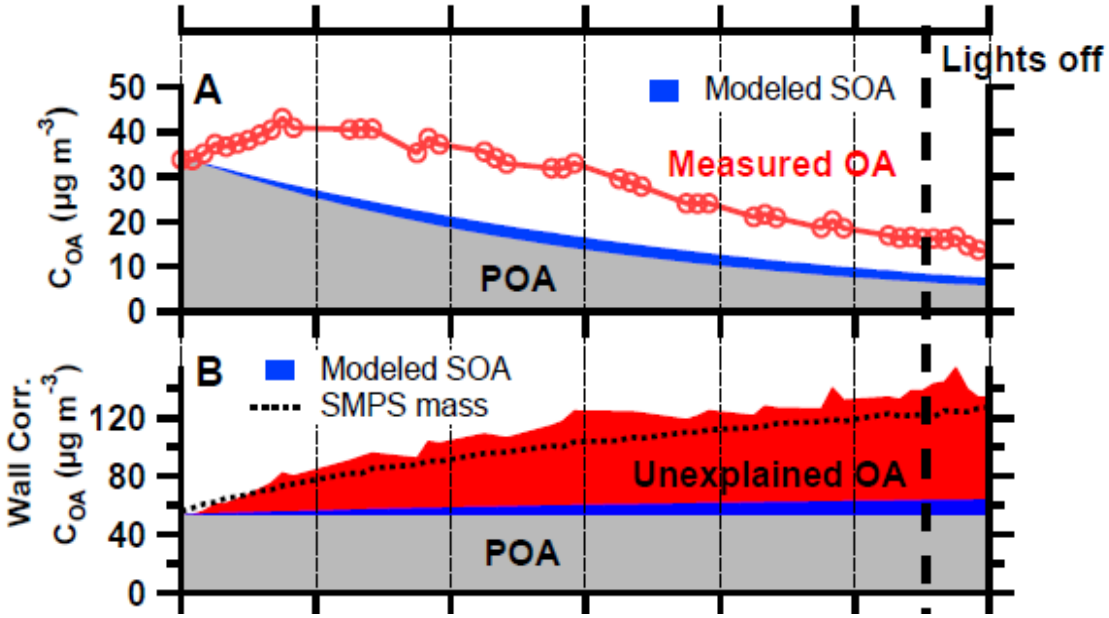
Global seasonal SOA production: peaks when BB is at its maximum in the North Hemisphere

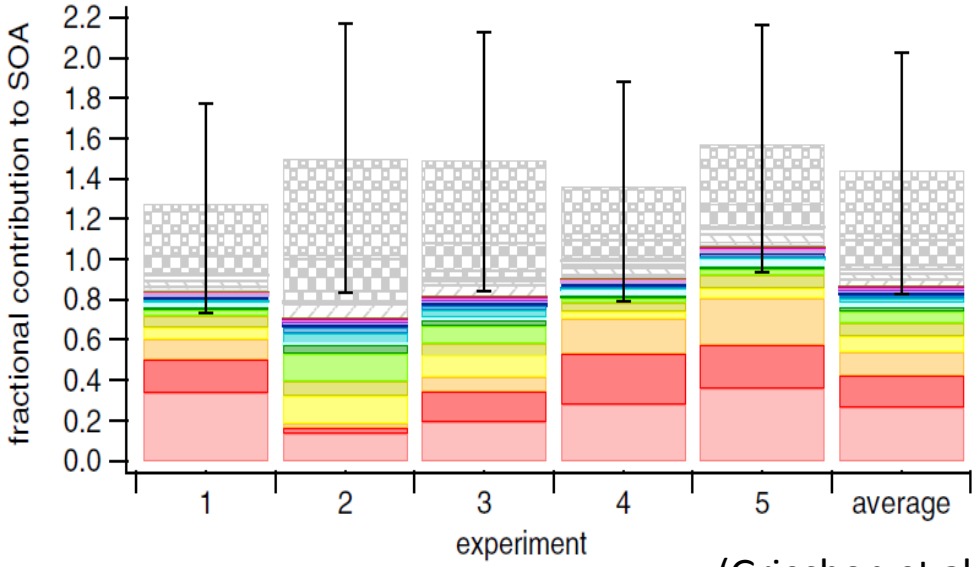




(Tsigaridis et al., 2014, ACP; Shrivastava et al., 2015, JGR)

SOA mass prediction





Aromatic and biogenic hydrocarbons: explain <20% formed SOA in oak and pine burning plume

22 NMOGs (11 containing O): explained 84-116% formed SOA in beech burning plume

How about agricultural residue burning?

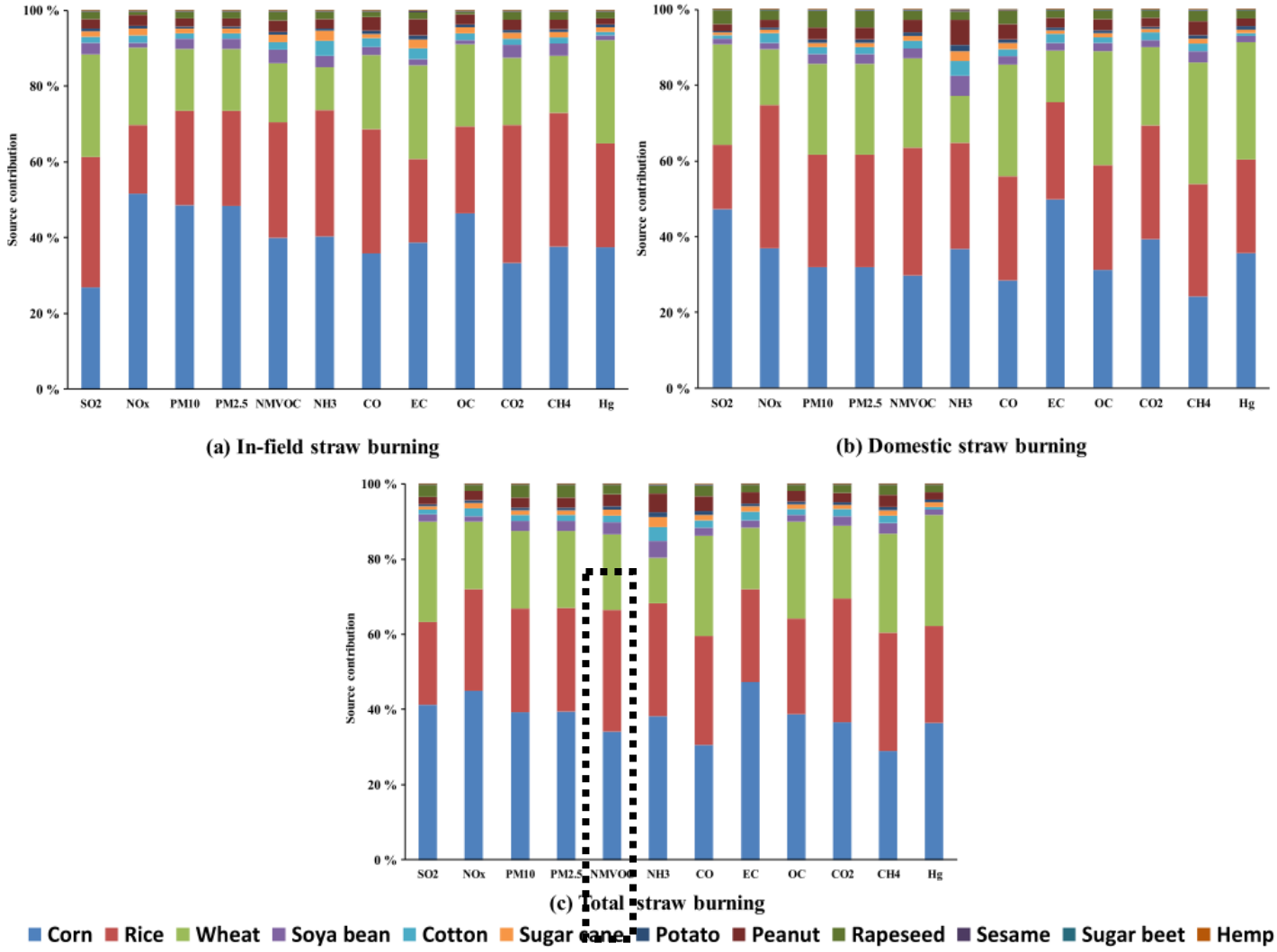
(Grieshop et al., 2009, ACP; Bruns et al., 2016, Sci. Rep.)

Previous chamber work on BBSOA

Author	Year	Fuels	Relative humidity（%）	UV light	Time（h）	OA enhancement ratio
Grieshop et al.	2009	Pine, oak	~5	Yes	5-6	1.5-2.8
Heringa et al.	2011	Beech	50	Yes	5	4.1±1.4
Hennigan et al.	2011	Wildfire fuels	19	Yes	3-4.5	1.7±0.7
Ortega et al.	2013	16 unique biomasses	30	Yes	3-120	1.4±0.4
Bruns et al.	2016	Beech	55	Yes	4-6.5	~3-7
Tiitta et al.	2016	Birch, beech, spruce	60±5	Yes/No	4.5-16	1.6-2.6
Tkacik et al.	2017	Pine, spruce	Not reported	Yes/No	~3.5	1.8±0.9

Reported BBOA enhancement ratios during the photoaging process: 0.7-6.8

Corn, Rice, Wheat contributed most to BB emissions in China



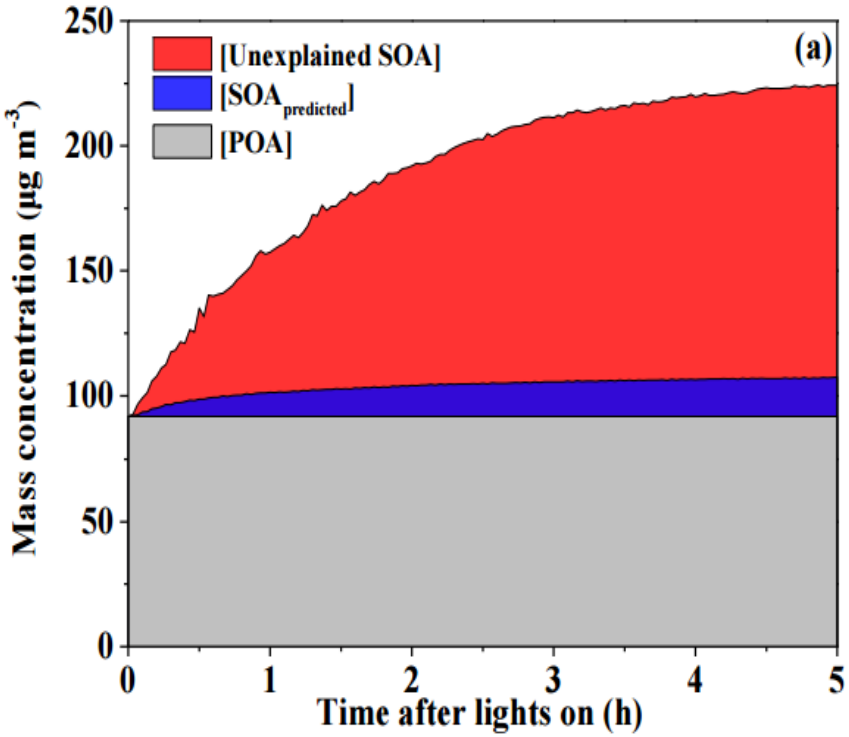
Zhou et al., 2017, ACP

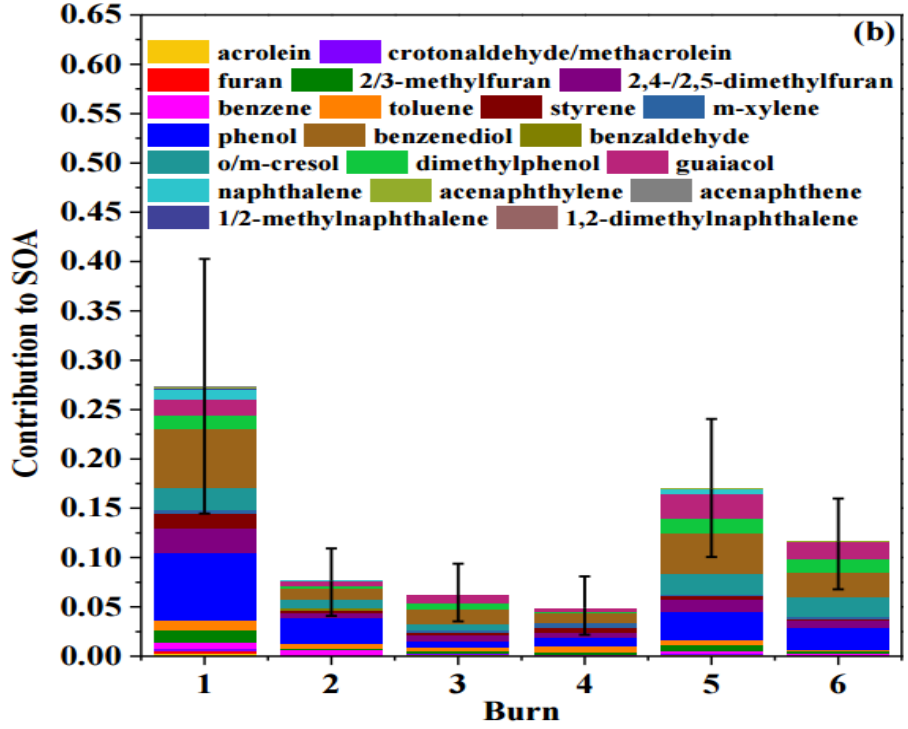
SOA precursors—straw burning

rice, corn, wheat

$$SOA_{predicted} = \sum_i \Delta X_i \times Y_i$$

Reacted VOC ← ΔX_i ; Y_i → SOA yield





- Biomass Burning: 20 NMHCs and OVOCs only account for 5.0-27.3% of formed SOA

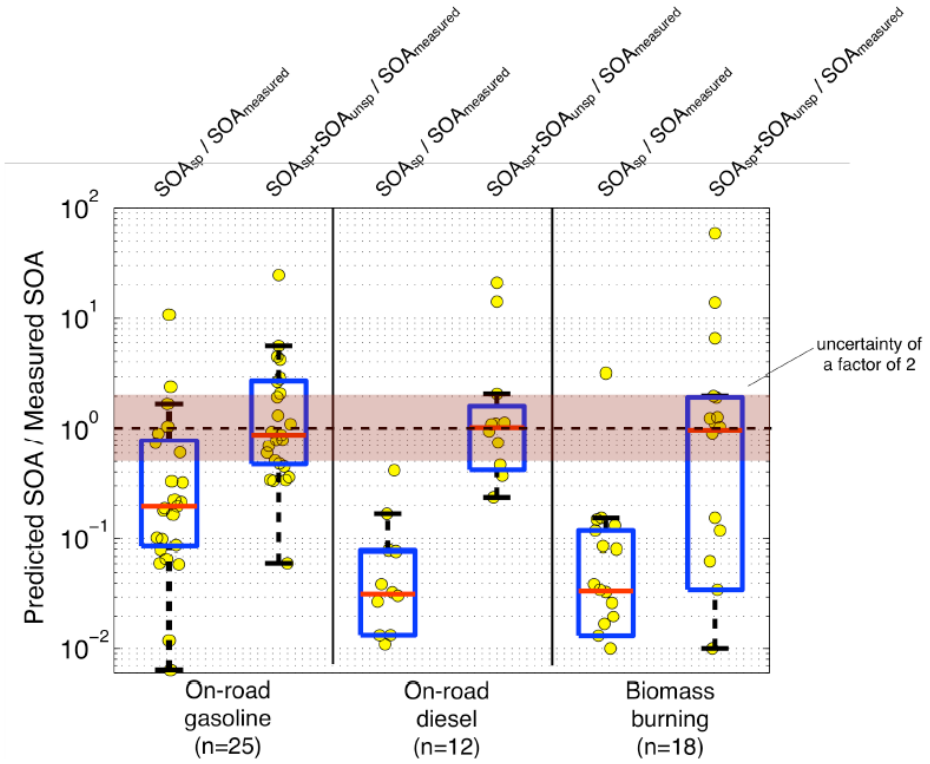
(*Fang et al., 2017, ACP*)

Considering unspeciated organics

SOA yiled$_{unsp}$=[Unexplained SOA]/[Unspeciated organics], then SOA surrogate was determined according to the SOA yield$_{unsp}$

Source	SOA surrogate	C* (μg m^{-3})			
		0.1	1	10	100
Biomass burning/Wood burning	*n*-pentadecane (C_{15})	0.044	0.071	0.41	0.30
On- and off-road gasoline	*n*-tridecane (C_{13})	0.014	0.059	0.22	0.4
On- and off-road diesel	*n*-pentadecane (C_{15})	0.044	0.071	0.41	0.30

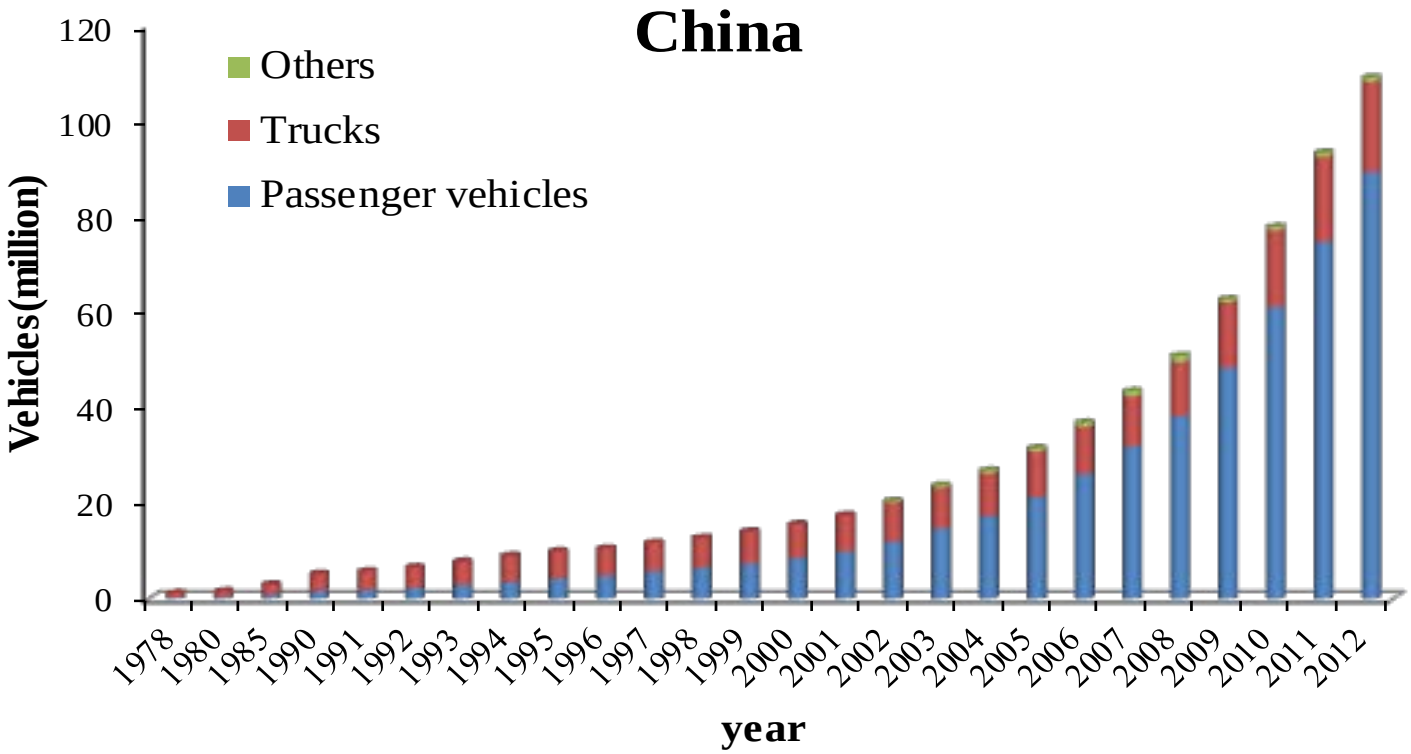
SOA prediction improved with unspeciated organics accounted:



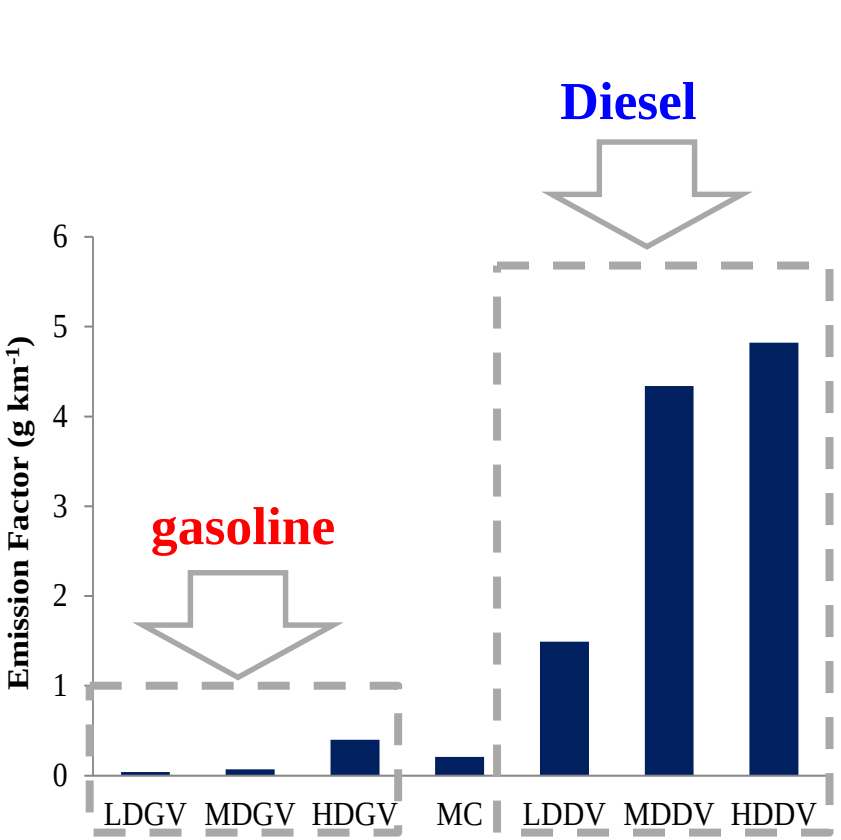
(Jathar et al., 2014, PNAS)

Autos in China

- China overtook USA as the largest auto market in 2010；
- Increasing at a rate over 20% per year in the recent years
- Passenger cars dominates

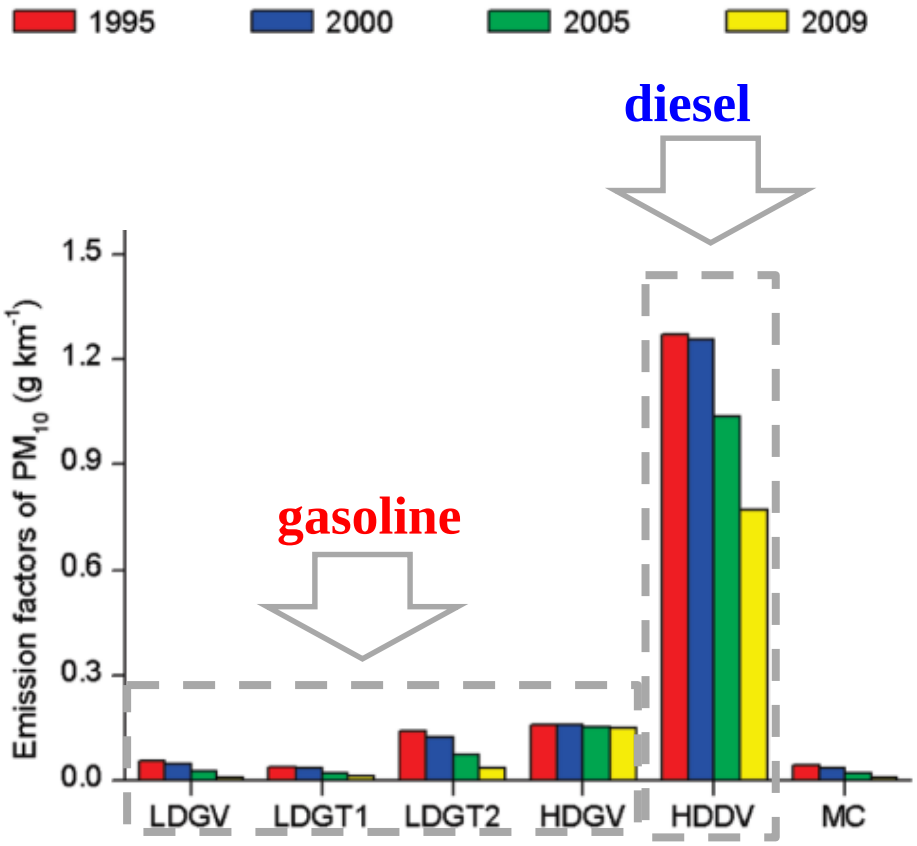


Primary emissions from vehicles



广州

(Che et al., 2006)



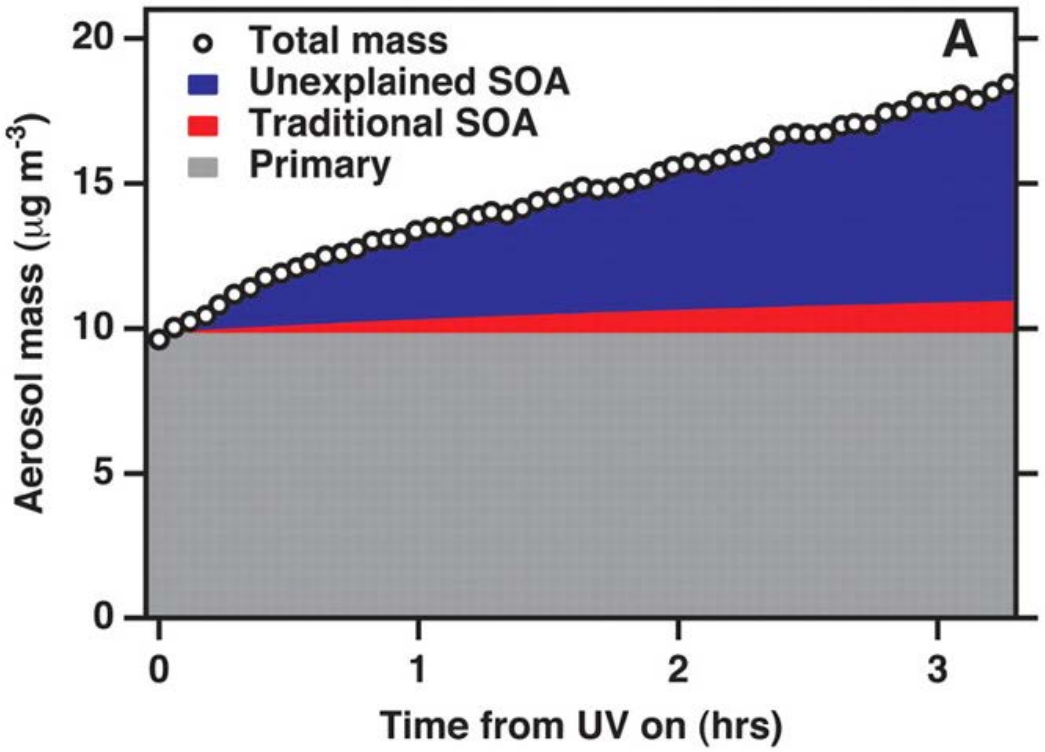
北京

(Wu et al., 2011)

Vehicle emission of primary PM: over 90% by diesel

(中国机动车环境管理年报，2017)

SOA formation from diesel vehicle exhaust



SOA/POA：~3

(Robinson et al., 2007)

SOA formation from diesel vehicle exhaust

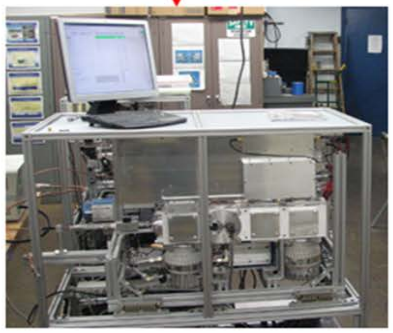
Conditions	country	literatures
idle	USA	Weitkamp et al., 2007
idle	USA	Robinson et al., 2007
idle，60 km/h	Switzerland	Chirico et al., 2010
idle，UDDS，UC	USA	Gordon et al., 2014; Zhao et al., 2014; 2015
idle	USA	Presto et al., 2014

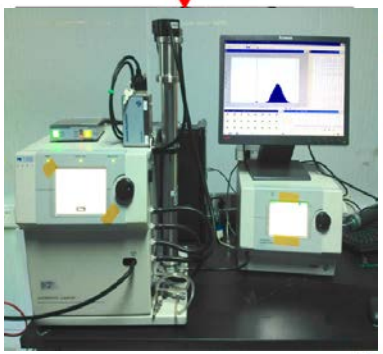
SOA from diesel vehicle exhaust

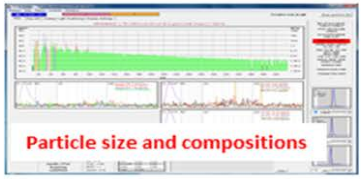
Idle
20 km/h
40 km/h

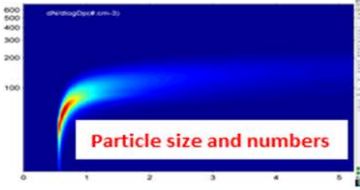
Diesel
Exhausts

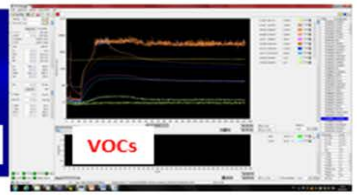
25 ˚C,
< 5%,
VOC/NOx≈ 3

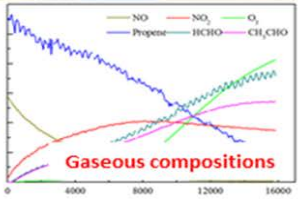












SOA from diesel vehicle exhaust: precursors

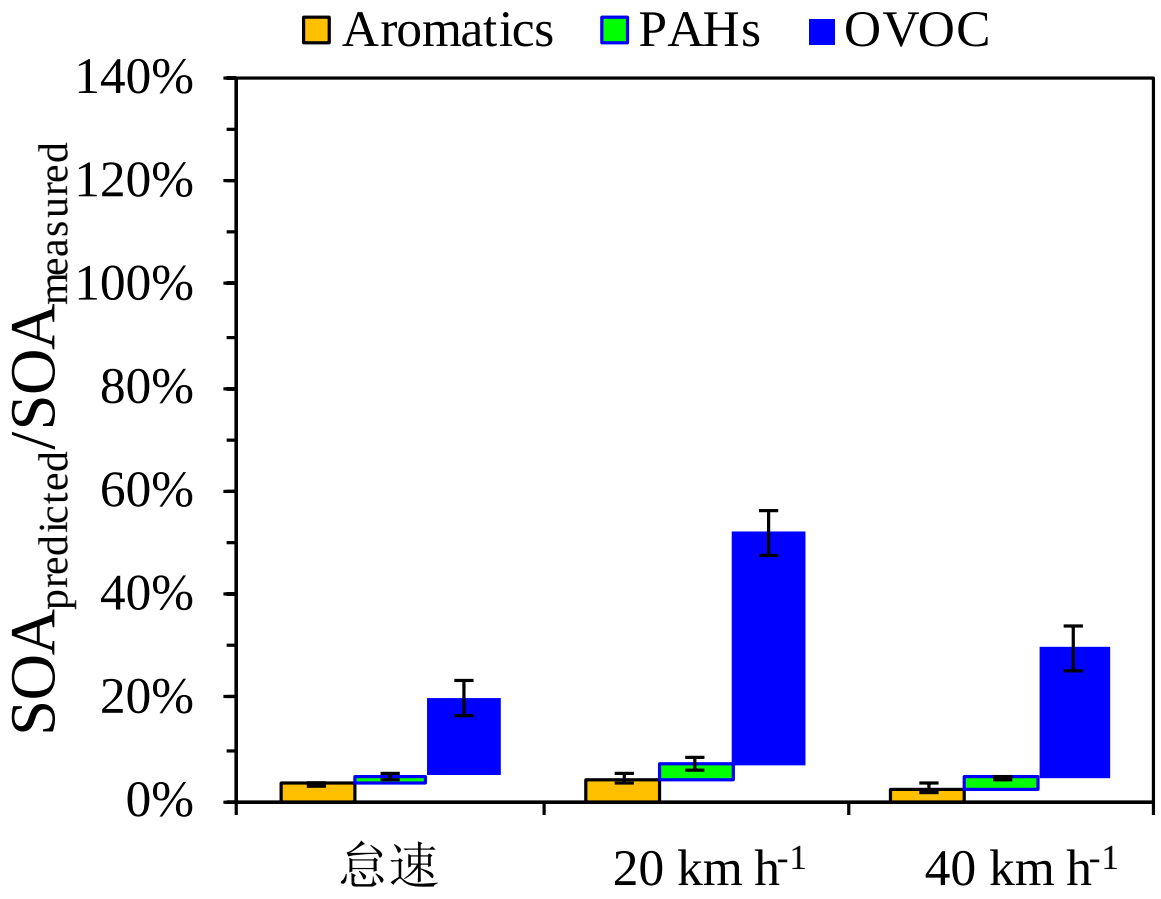
$$SOA_{predicted} = \sum_i \Delta X_i \times Y_i$$

VOC consumed ← ΔX_i ; Y_i → yield

Expt. No.	Predicted SOA (μg m^{-3})							Predicted SOA/ Measured SOA[a]
	Benzene	Toluene	C_2-benzene	C_3-benzene	C_4-benzene	Alkanes	Alkenes	
1	0.015	0.019	0.022	0.081	0.085	0.022	0.080	2.6%
2	0.202	0.028	0.050	0.068	0.114	0.002	0.012	2.2%
3	0.069	0.013	0.051	0.054	0.068	0.038	0.082	1.4%
4	0.127	0.055	0.013	0.007	0.017	0.028	0.013	0.8%
5	0.074	0.012	0.082	0.075	0.108	0.030	0.229	1.6%
6	0.237	0.213	0.496	0.018	0.007	0.029	0.090	3.1%
7	0.164	0.065	0.014	0.052	0.077	0.049	0.019	1.2%
8	0.329	0.072	0.067	0.124	0.229	0.052	0.34	2.3%

C_2-C_{12} NMHCs: <3% SOA explained;

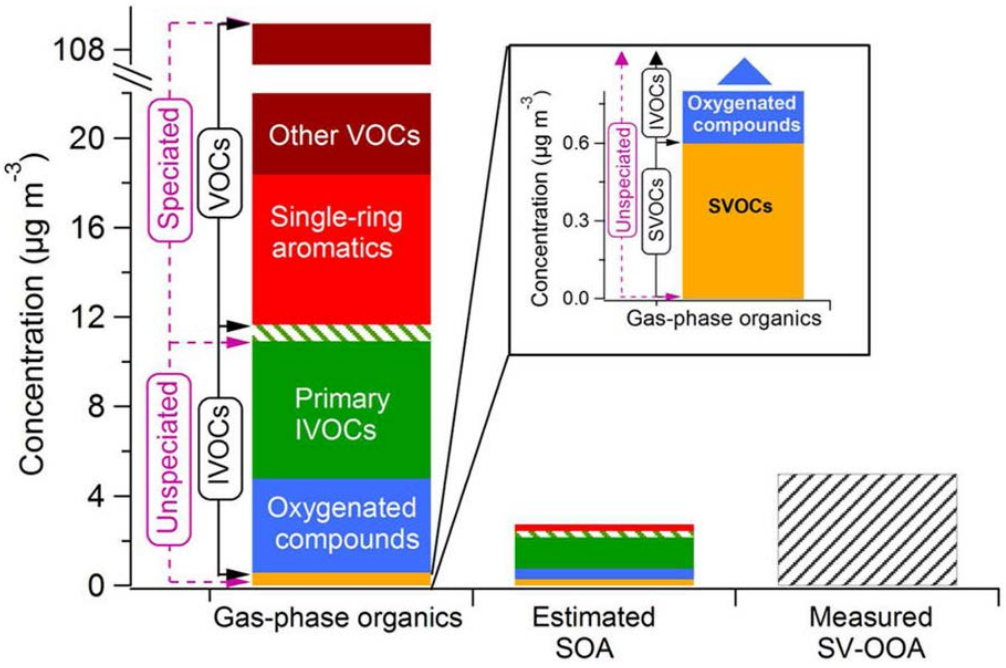
SOA from diesel vehicle exhaust: precursors

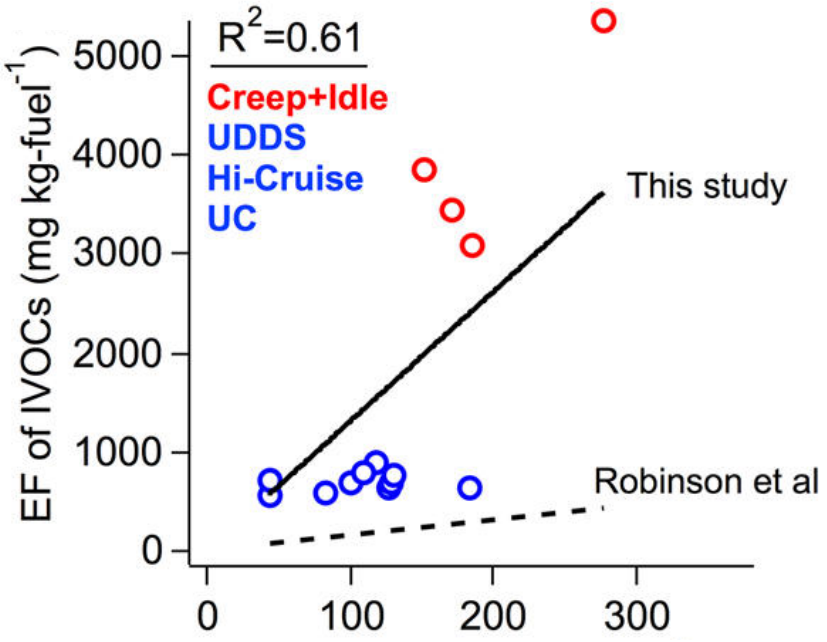


- ✓ **Aromatic hydrocarbons + PAHs: <10% SOA explained;**
- ✓ **OVOCs: 15~45% SOA expalined**

SOA from diesel vehicle exhaust: precursors

IVOC: such like C_{12}~C_{22} alkanes?

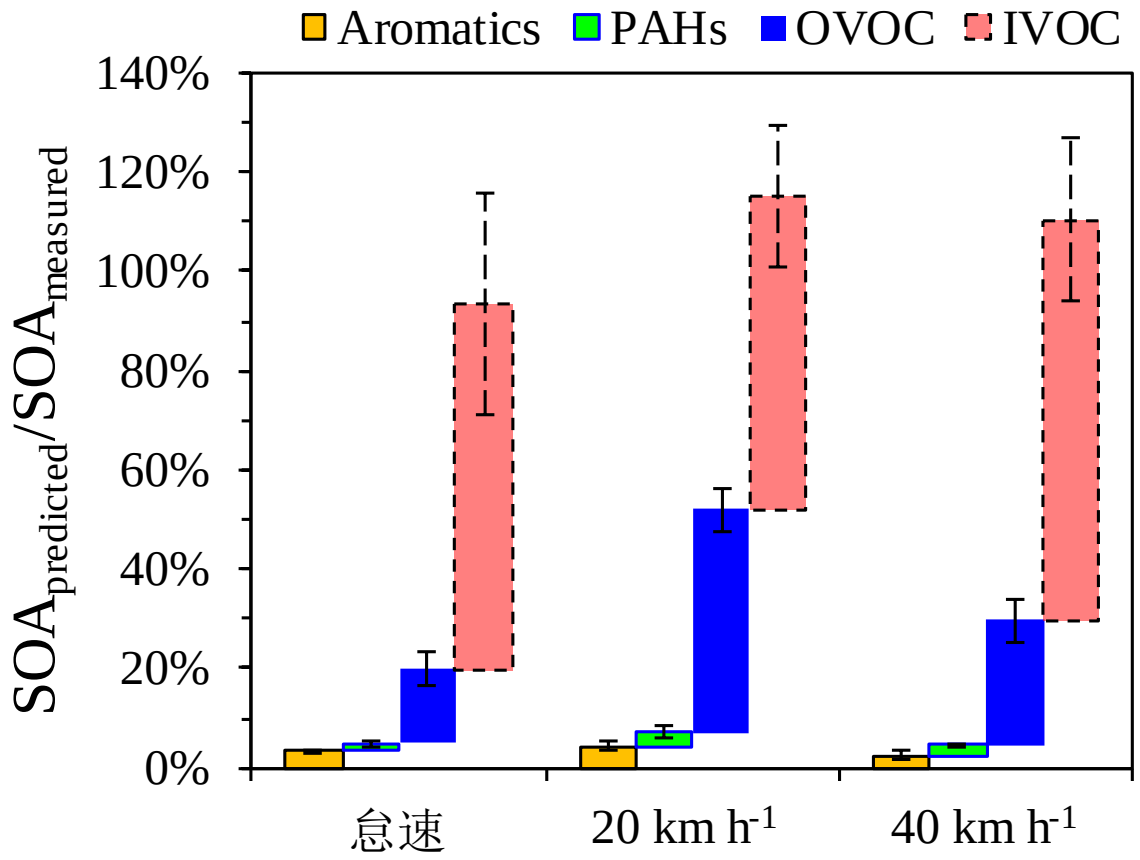




- **idle：IVOC/POA = 20.4±3.7**
- **driving：IVOC/POA = 8.0±3.6**

(Zhao et al., 2014; Zhao et al., 2015)

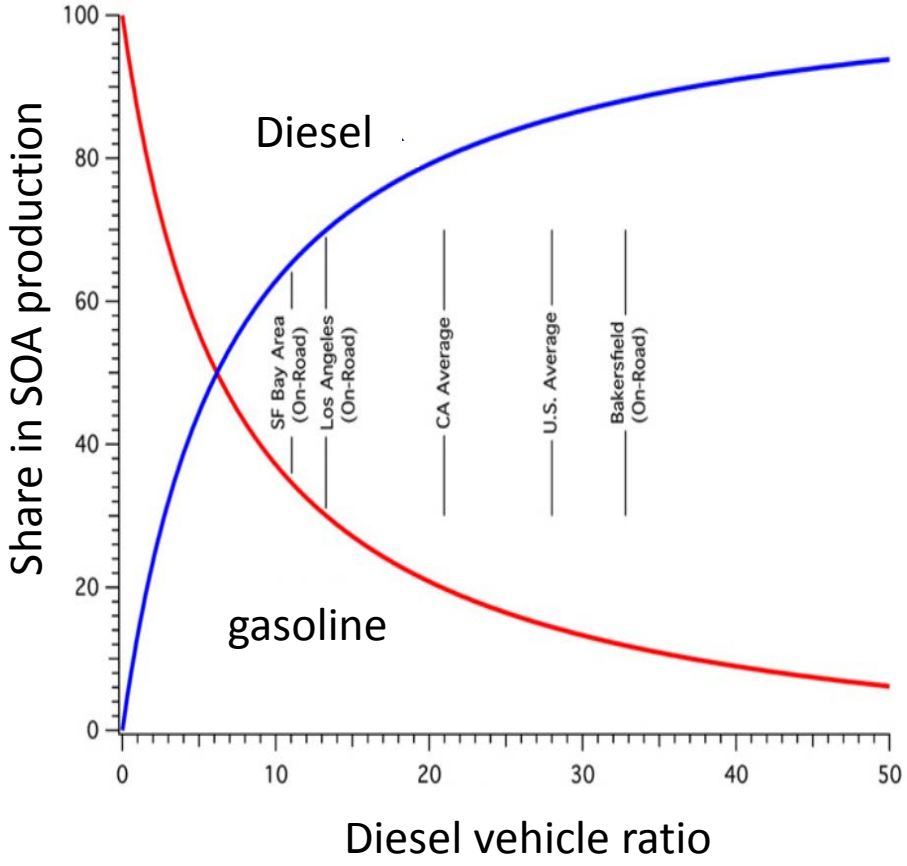
SOA from diesel vehicle exhaust: precursors



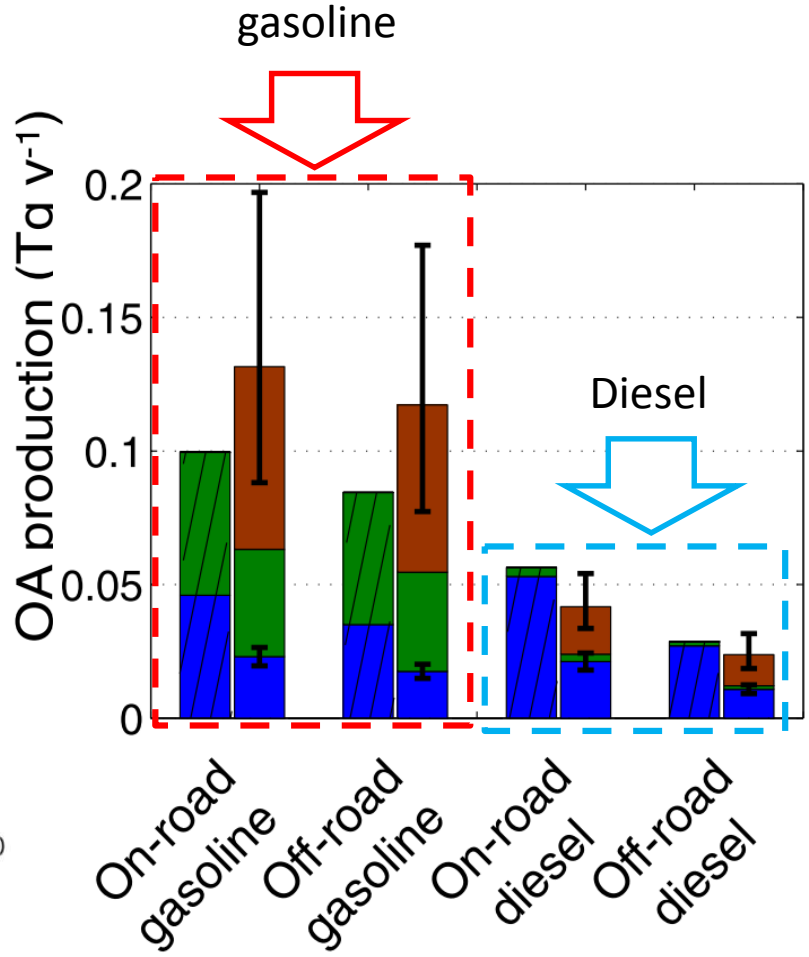
- IVOC: can explain up to 63-81% of formed SOA.

Deng et al., in preparation

SOA from aging of vehicle exhaust

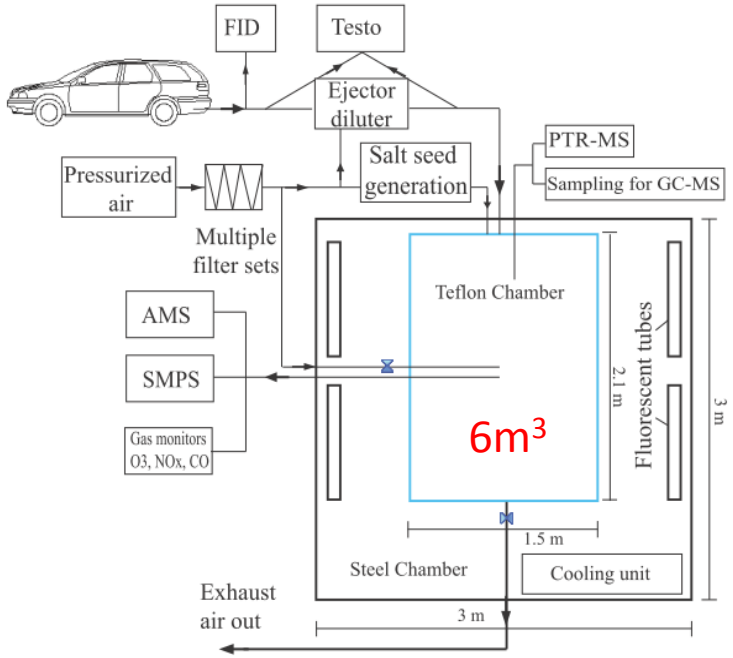


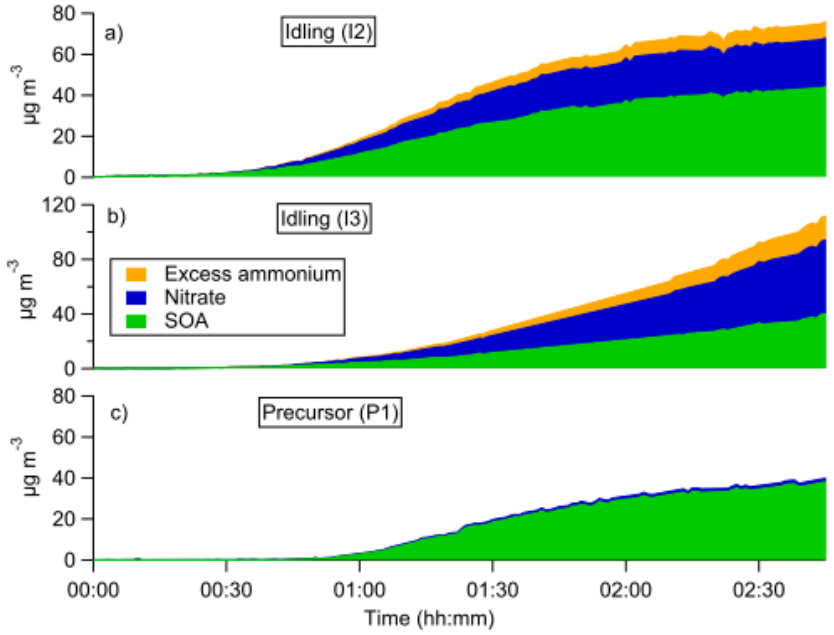
(Gentner et al., 2012,PNAS)



(Jathar et al., 2014, PNAS)

SOA formation from idling gasoline passenger vehicle emissions





EU vehicles

- Injecting the vehicle exhaust into the chamber directly;
- SOA Production factor: 0.005 – 0.09 g kg^{-1}; 0.48 g kg^{-1} for the cold start;
- SOA/POA ratios: 7-510;
- Classic C6-C9 aromatics can explain up to 60% of the formed SOA.

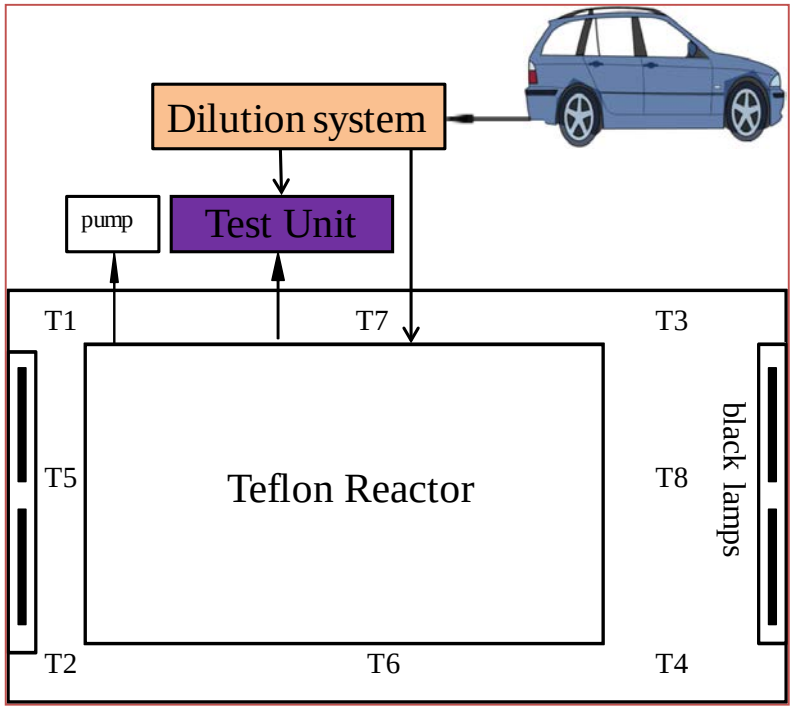
Nordin et al., 2013; ACP

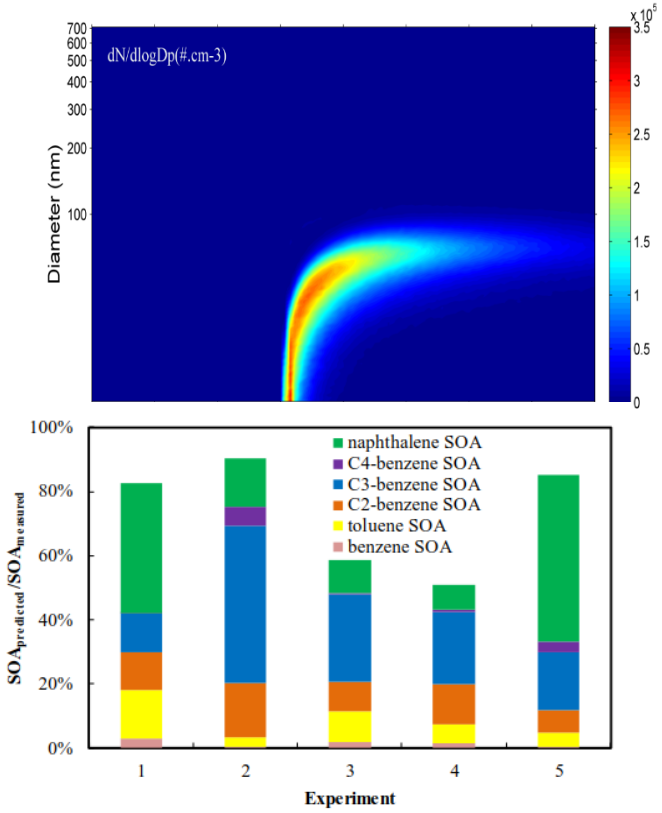
SOA formation from idling gasoline passenger vehicle emissions

GIG

SMOG

CHAMBER



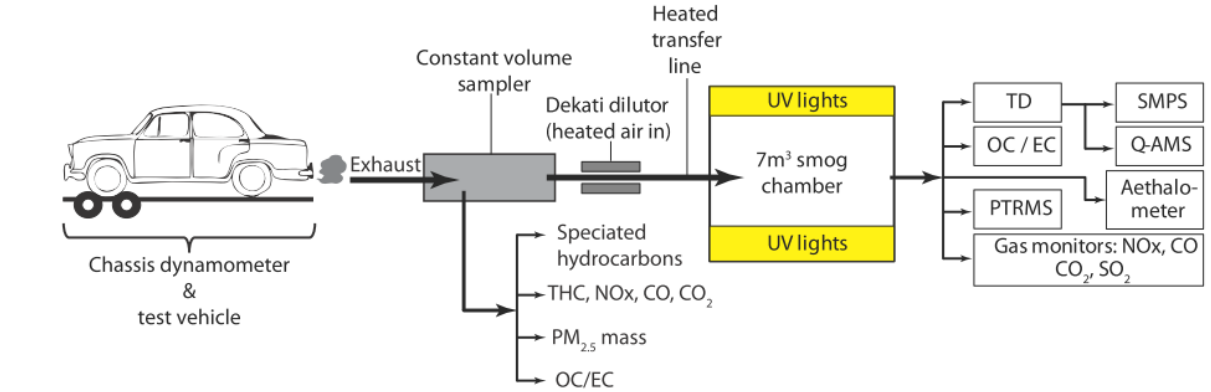


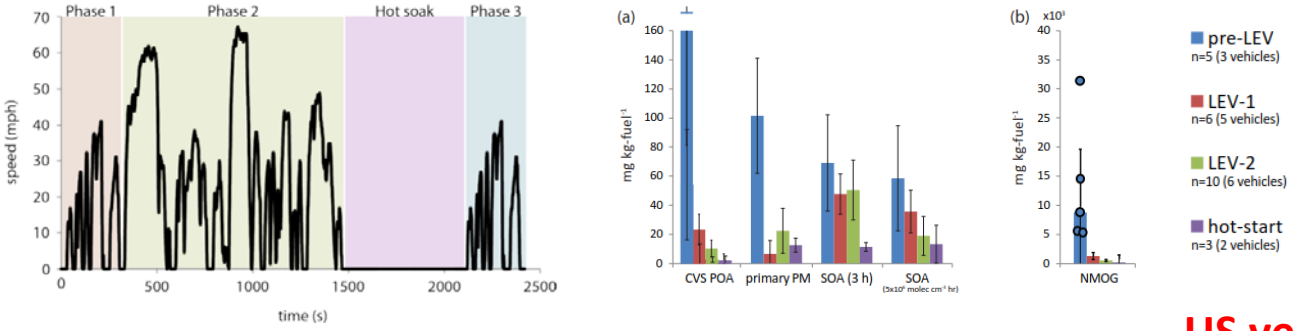
China vehicles

- SOA Production factor: 0.001-0.044 g kg^{-1};
- SOA/POA ratios: 12-259;
- Traditional single-ring aromatics and naphthalene can explain 51-90% of the formed SOA.

Liu et al., 2015, ACP

SOA formation from gasoline vehicles during driving cycle





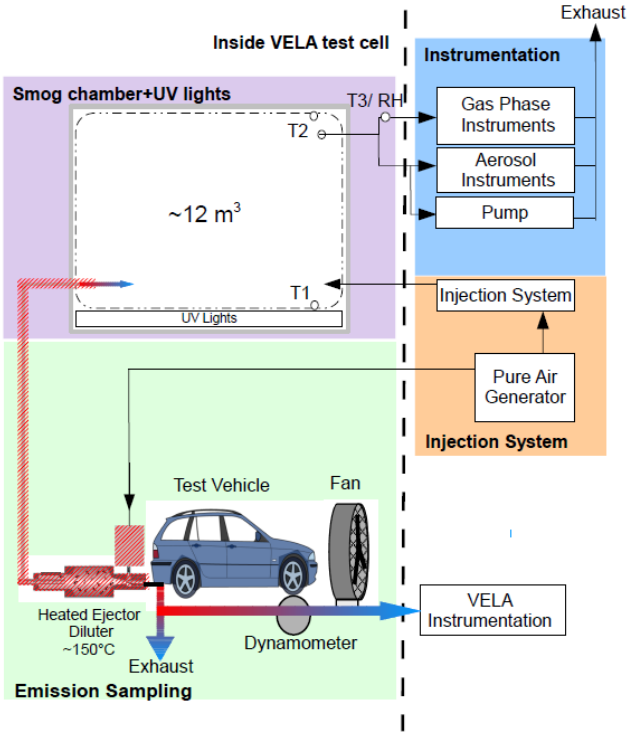
US vehicles

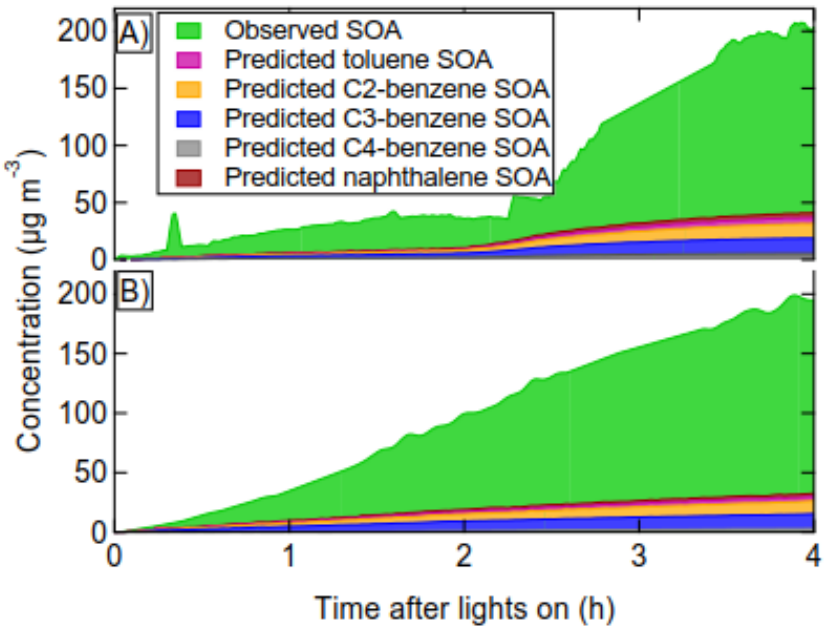
- Pre-LEV, LEV-1, LEV-2; hot-start and cold-start;
- SOA Production factor: 0.02-0.13 g kg^{-1}; SOA/POA ratios: 1-15;
- Except pre-LEV, the SOA production could not be fully explained by the measured traditional SOA precursors.
- About 30% of the NMOGs from news vehicles could not be speciated (IVOCs), which may contribute to SOA formation.

Gordon et al., 2014, ACP

SOA formation from gasoline vehicles during driving cycle

New European Driving Cycles, NEDC



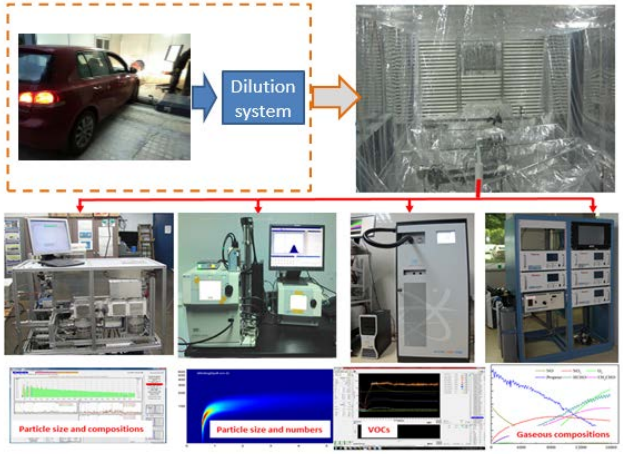


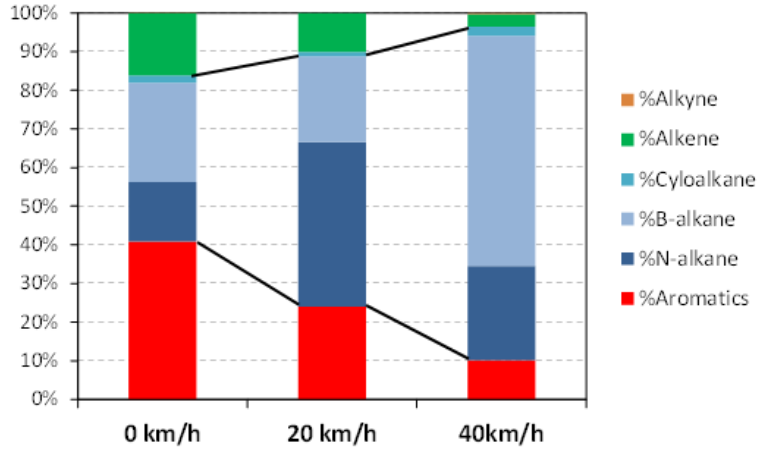
EU vehicles

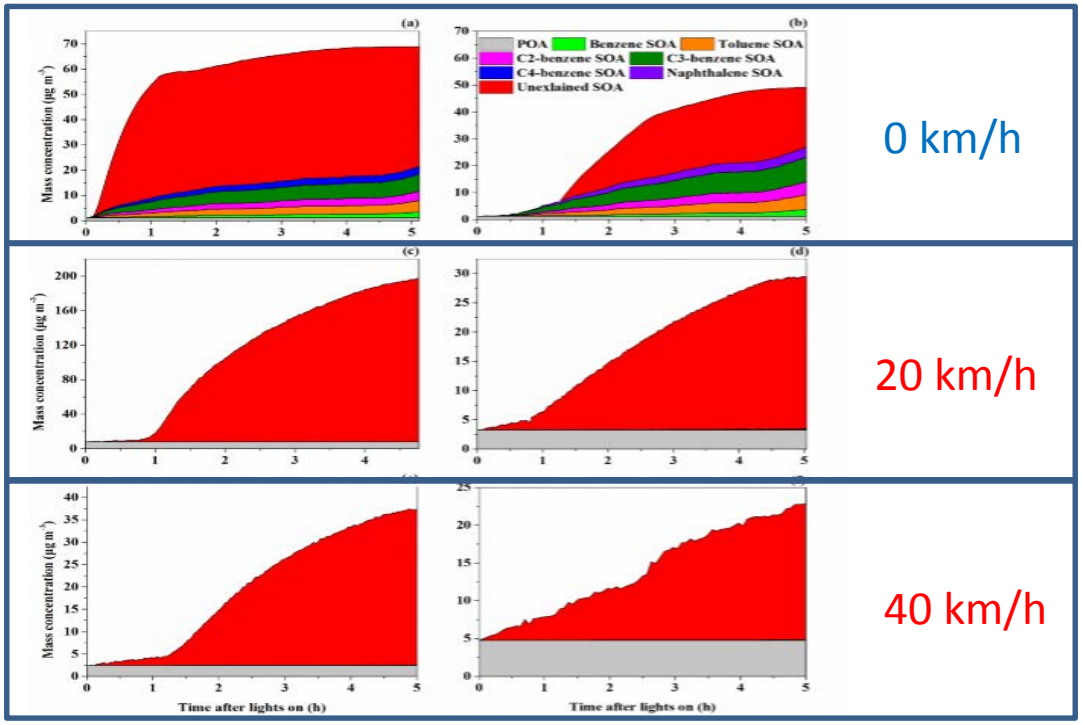
- SOA Production factor: 0.344-0.347 g kg^{-1};
- SOA/POA ratios: 9-15;
- Traditional single-ring aromatics and naphthalene can only explain less than 20% of the formed SOA.

Platt et al., 2013, ACP

Large gaps between measured and calculated SOA



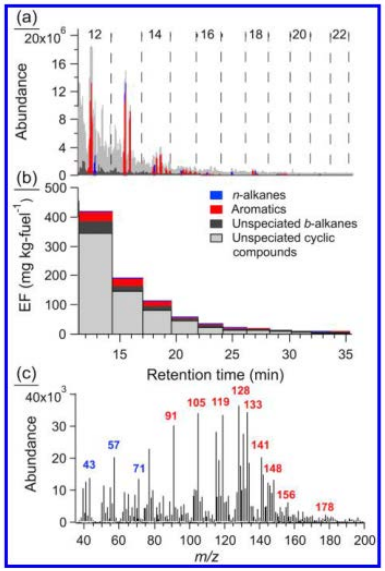


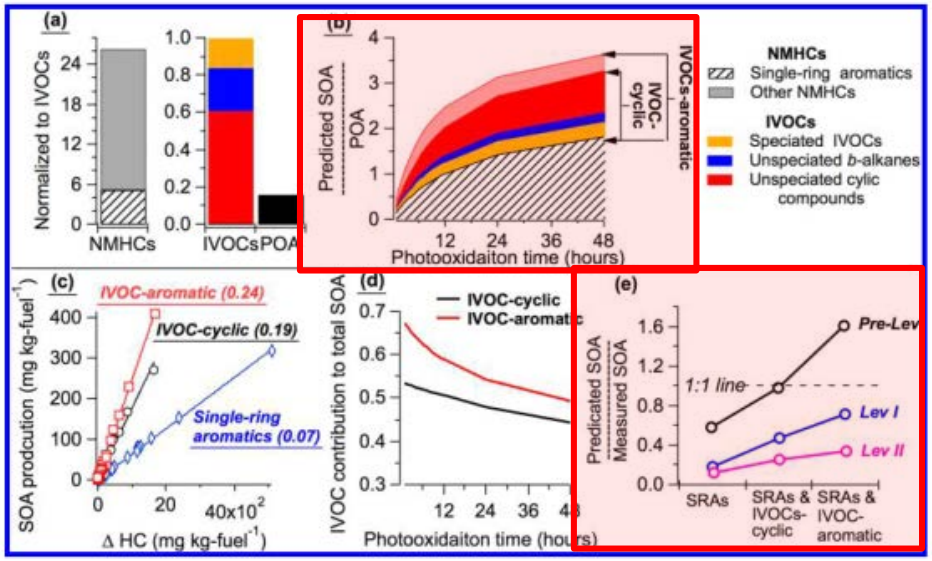


- Idling: 30-55%
- **Driving: Less than 1% !!!**

Zhang et al., in preparation

Predicted SOA formation from gasoline vehicles emissions of IVOC

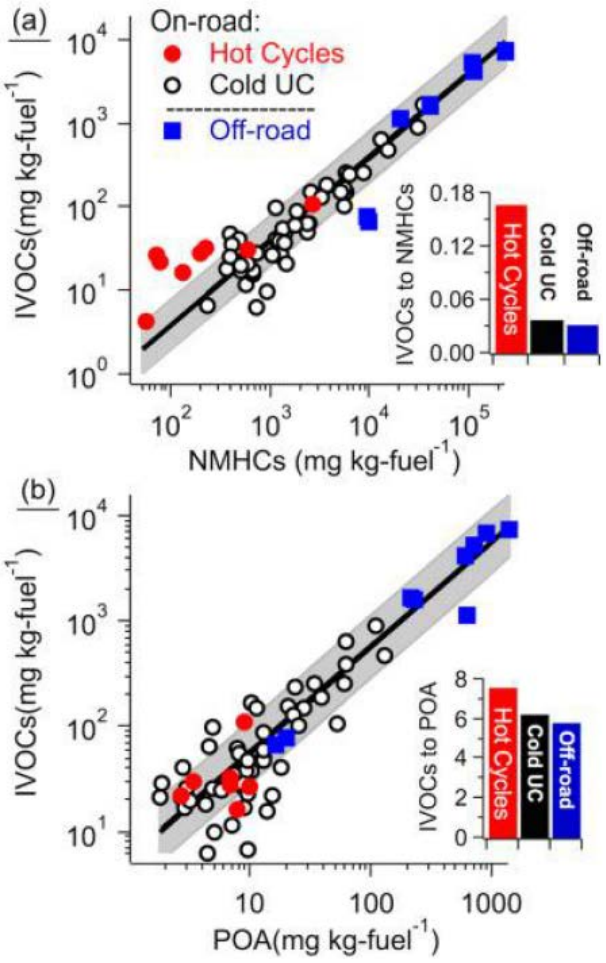




- Using the chassis dynamometer testing at CARB; UC;
- Measured the emission factor of IVOCs from GVs exhaust;
- Estimated the SOA formation by using published SOA yields based on smog chamber;
- IVOC emissions only correspond to approximately 4% of NMHC, but they are estimated to produce as much or more SOA than single-ring aromatics.
- Even adding **IVOC** formed SOA, about 30% and 65% of measured SOA remains unexplained.

Zhao et al., 2016, EST

formation of SOA from IVOC?

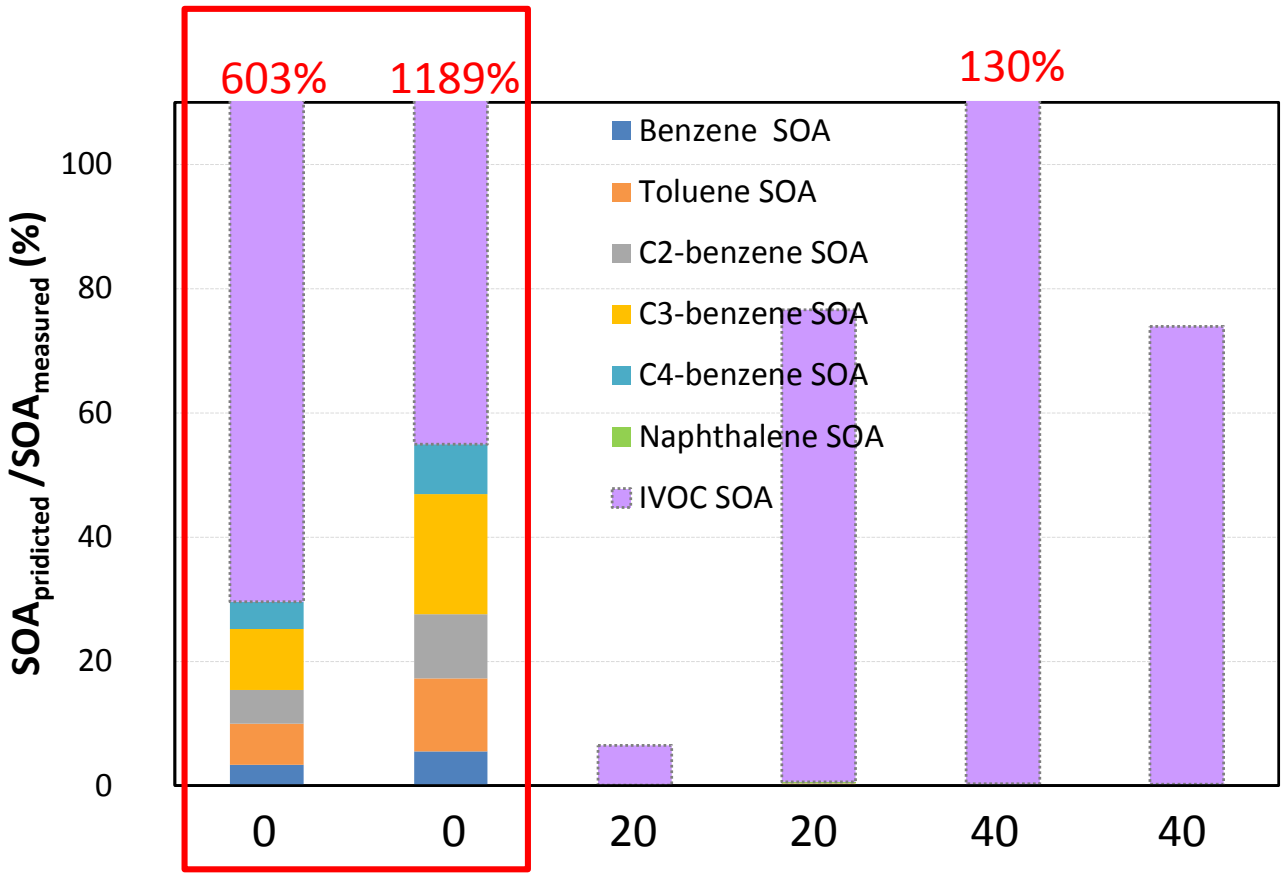


IVOC-to-NMHCs ratios
- Hot Cycles: 0.17
- Cold UC: 0.04

$\Delta M = [HC] \times (1 - e^{-kOH \times [OH] \times \Delta t}) \times Y$

IVOC-to-POA ratios
- Hot Cycles: 8.5
- Cold UC: 7.3

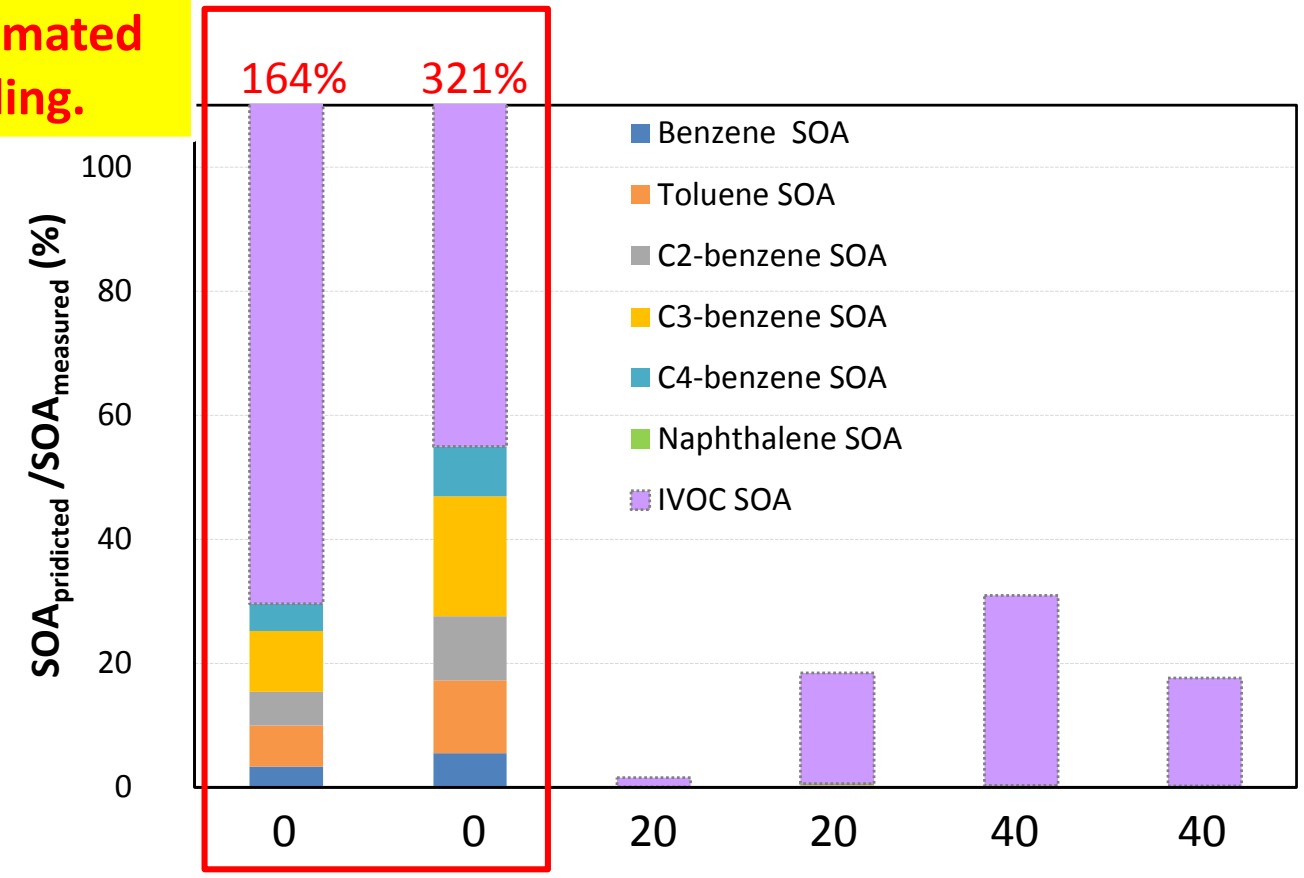
Zhao et al., 2014 EST; 2016 EST



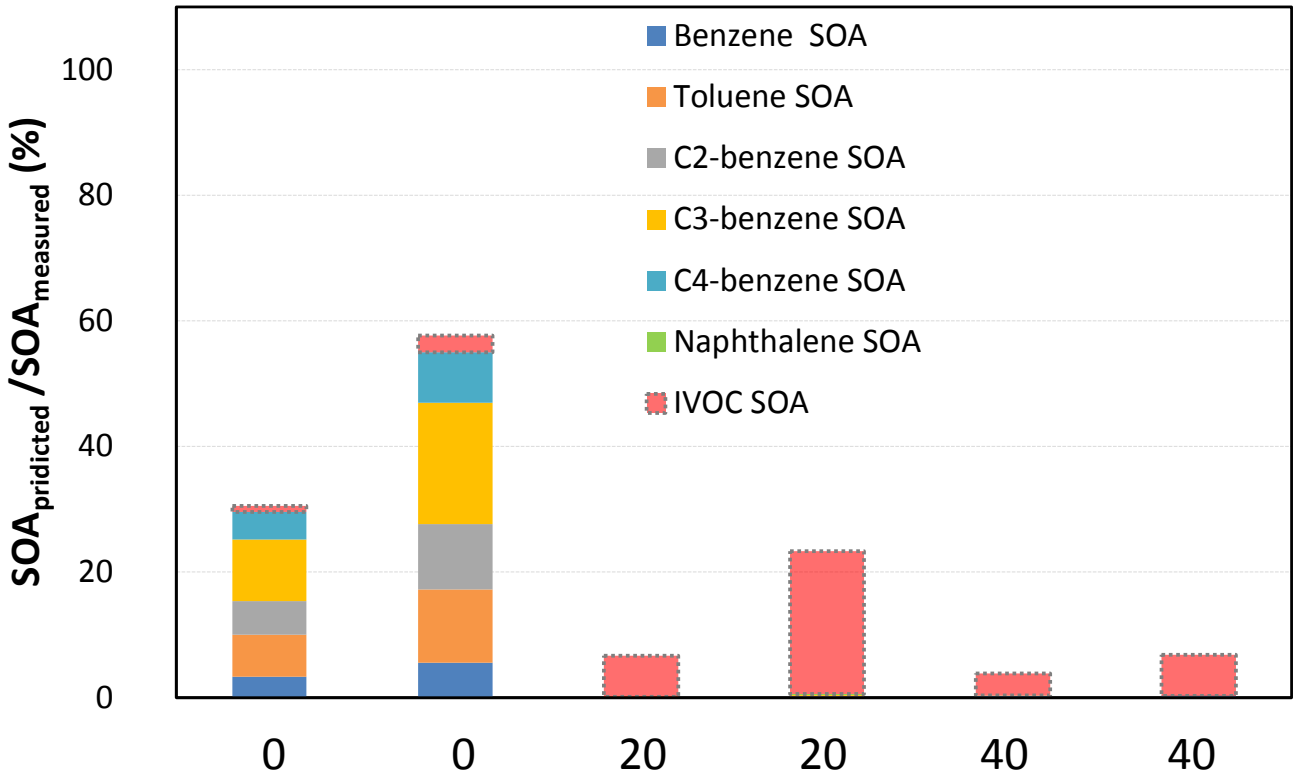
- IVOCs-to-NMHCs ratios: 0.17;
- IVOC SOA contribute: 603-1189% at idling;
- IVOC-SOA contribute 6-130% under driving

Overestimated!

Overestimated for idling.



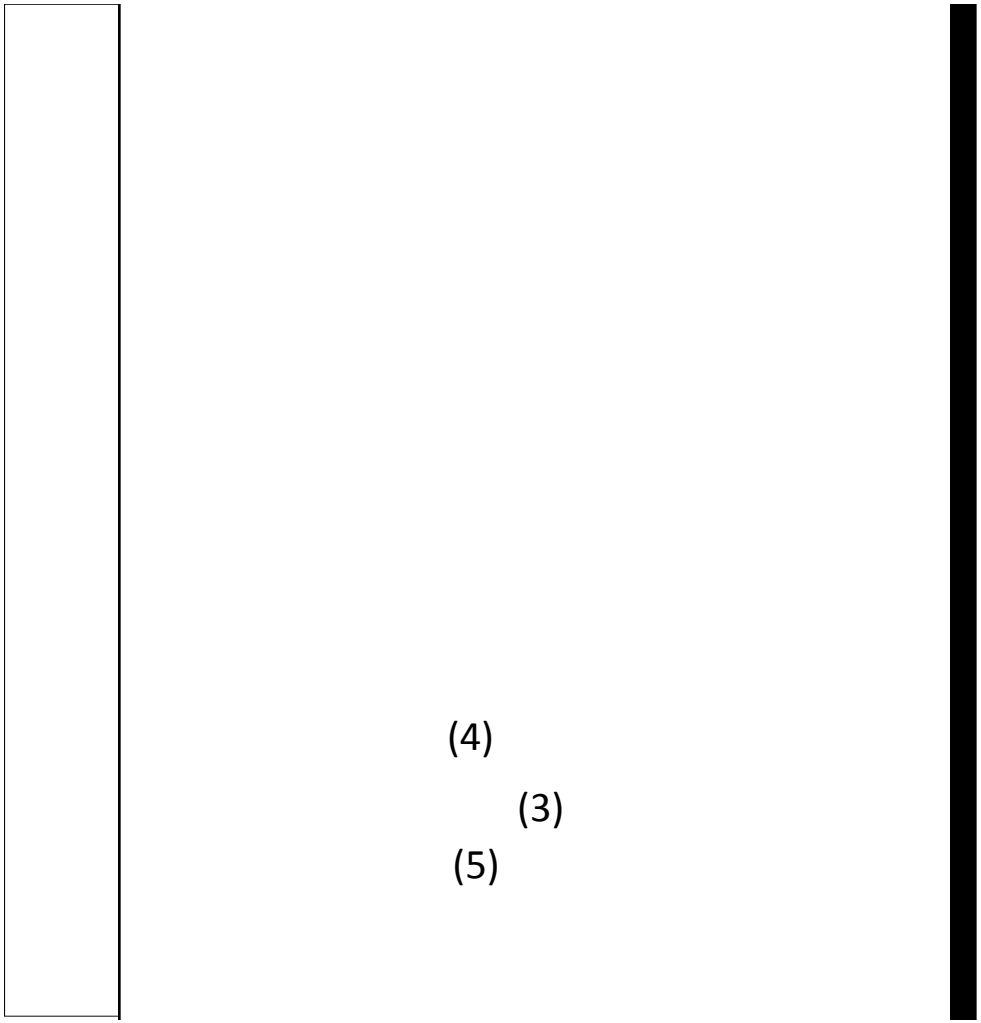
- IVOCs-to-NMHCs ratios: 0.04;
- IVOC SOA contribute: 135-266% at idling;
- IVOC-SOA contribute 2-31% under driving.



- IVOCs-to-POA ratios: 8.5
- IVOC-SOA contribute 1-3% at idling;
- IVOC-SOA contribute 4-22% under driving.
- CARB ratios are not suitable for our cars.

Underestimated!

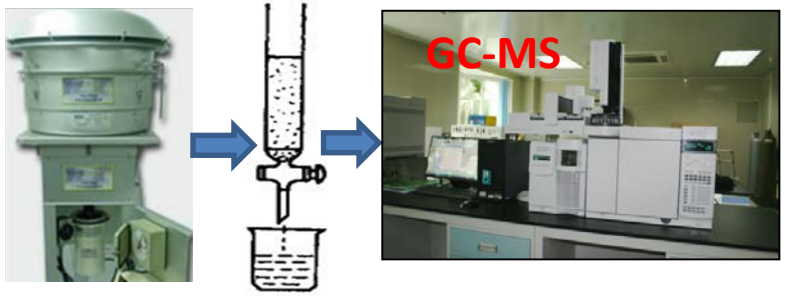
field observation in China

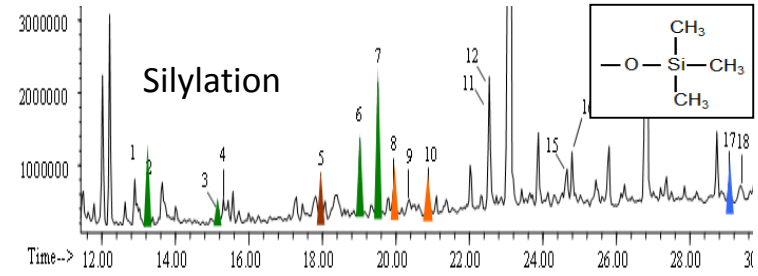


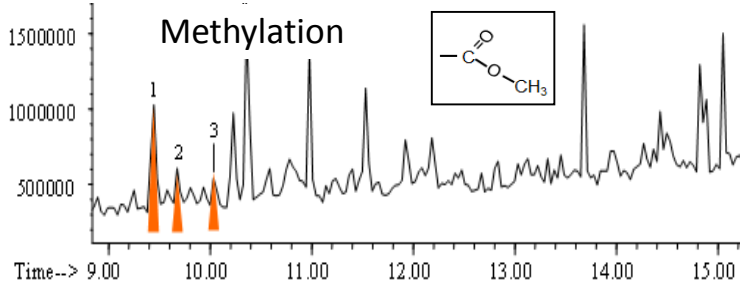
- One year concurrent observation (2012-2013) 48-h Sampling, biweekly

(Ding et al., *JGR* 2014, 2016; *ACP* 2015; *SR* 2016; *ES&T*, 2017)

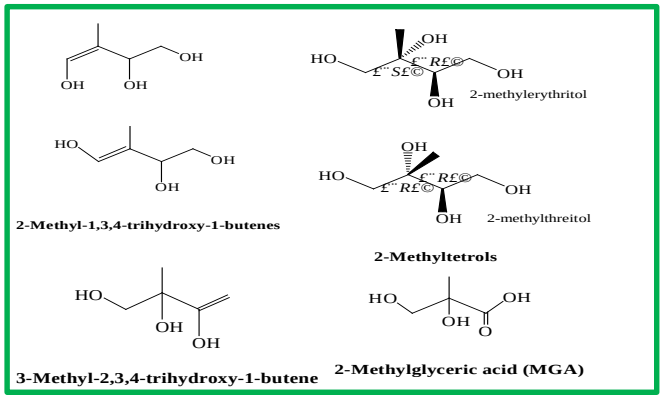
SOA tracers analysis



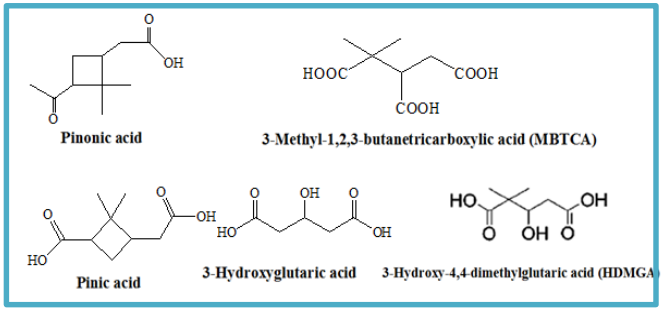




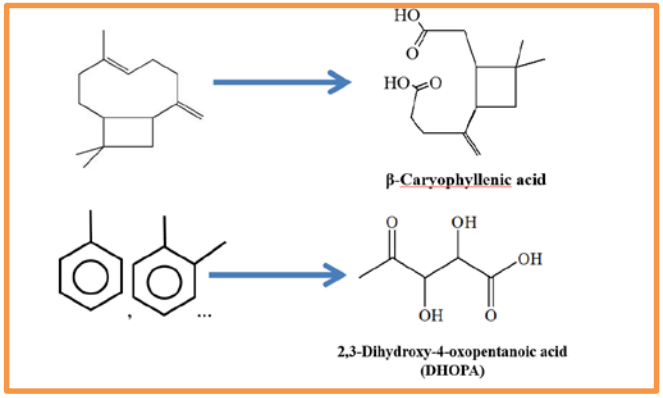
- 13 SOA tracers



Isoprene

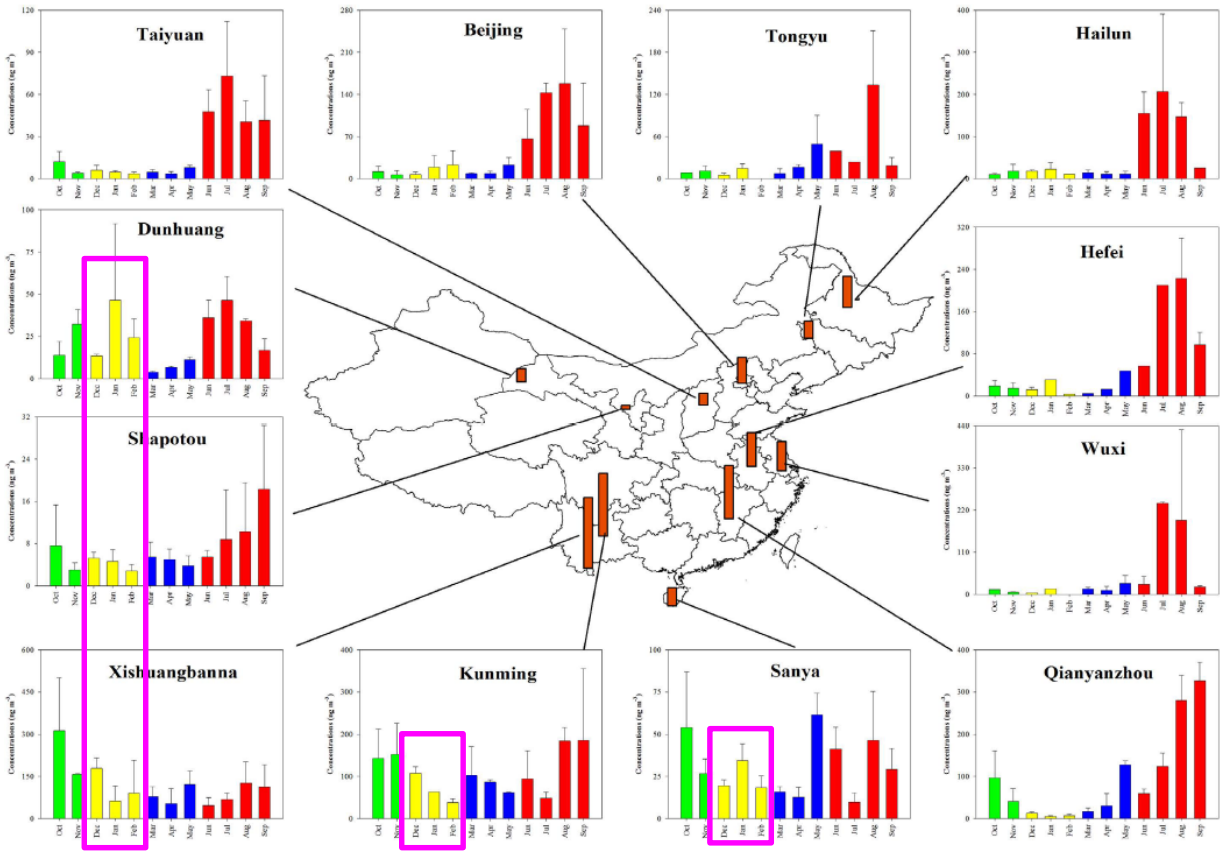


Monoterpenes



β-Caryophyllene
&
Aromatic hydros.

Tracers of isoprene SOA



- High levels in summer (red) and southern China
- Unexpected increase in winter (yellow)

Ding et al., SR 2016

MEGAN: $E_I = EF_I \times C_L \times C_T$

light Temp

(Guenther 1993, 1995, 1998, 2006, 2014)

Model of Emissions of Gases and Aerosols from Nature

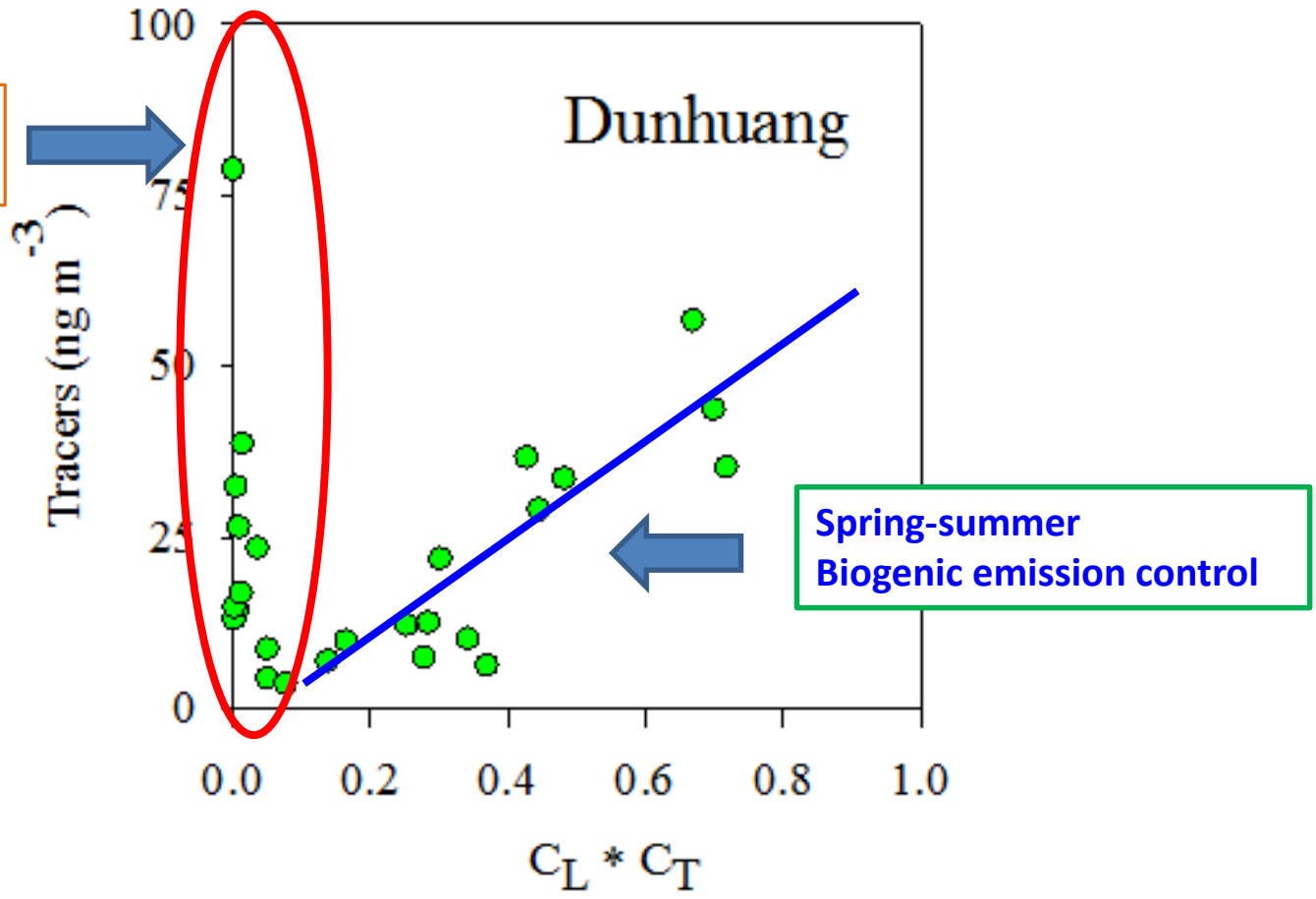
MEGAN

MEGAN Model

Model of Emissions of Gases and Aerosols from Nature

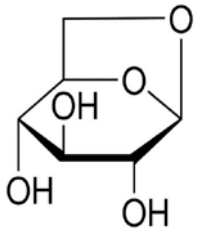
Contact: Alex Guenther (aguenther@wsu.edu)

Fall-winter
Non-biogenic control



Spring-summer
Biogenic emission control

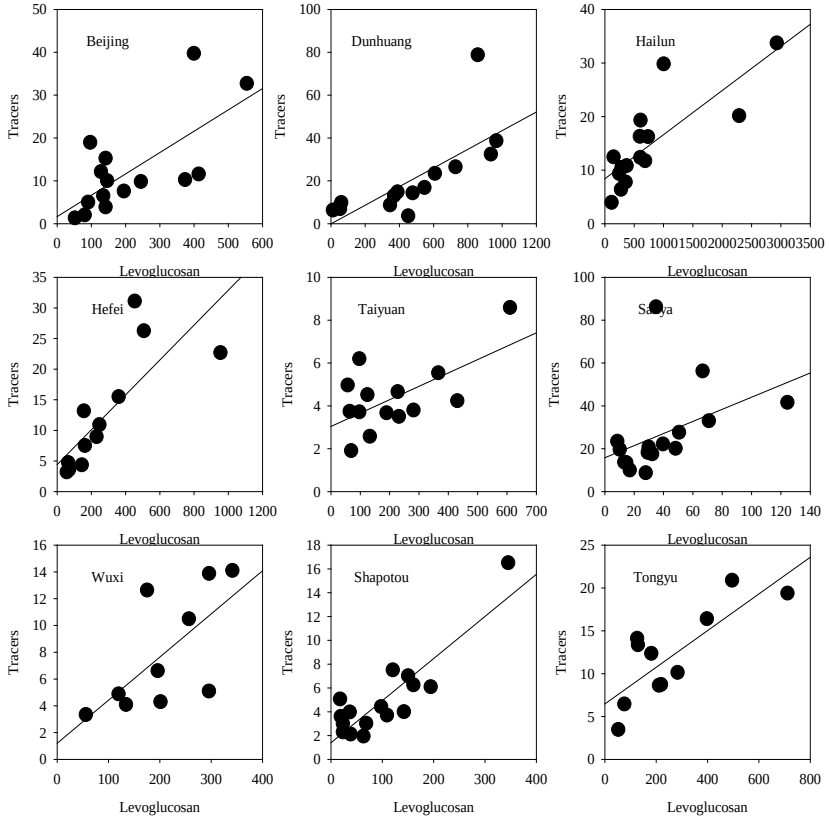
Biomass Burning affects seasonal trend of isoprene SOA



- Spring-summer： determined by biogenic emissions
- Fall-winter： highly associated with BB enhancement

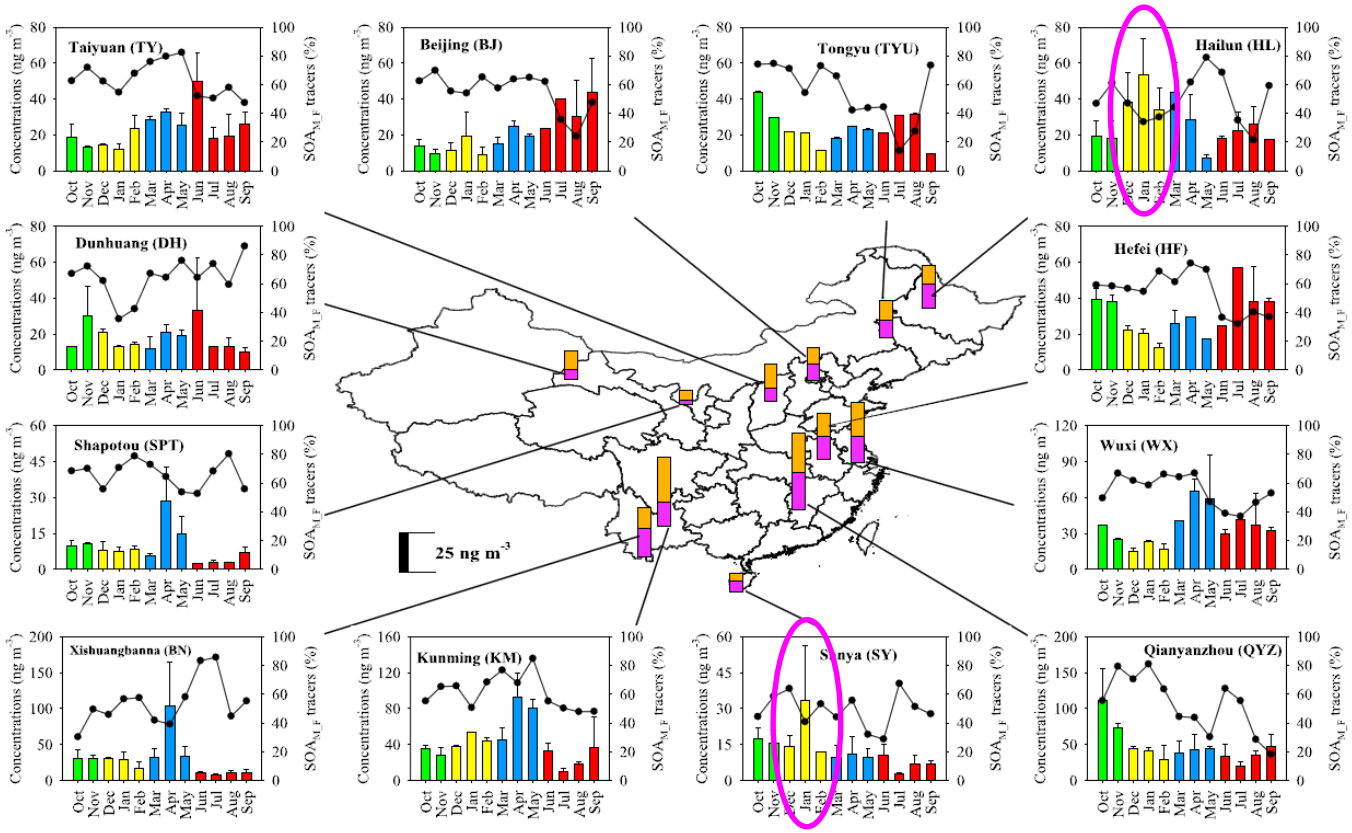
Region	Site	Warm period (May-September)		Cold period (October-April)	
		$C_L \times C_T$	Levo	$C_L \times C_T$	Levo
Northeast China	HL	**0.803**[a]	-0.351	-0.213	**0.799**
	TYU	**0.921**	-0.379	0.217	**0.799**
North China	BJ	**0.796**	-0.032	-0.003	**0.694**
	TY	**0.603**	0.347	0.101	**0.621**
Northwest China	DH	**0.827**	0.154	-0.423	**0.734**
	SPT	**0.844**	0.499	0.207	**0.874**
East China	HF	**0.973**	-0.612	-0.002	**0.780**
	WX	**0.888**	-0.384	0.458	**0.668**
	QYZ	**0.638**	0.526	**0.663**	-0.202
Southwest China	KM	0.005	0.586	0.159	0.169
	BN	0.391	0.561	0.287	-0.017
South China	SY	**0.768**	0.364	0.100	0.421

Temperature<10 °C



Tracers of monoterpene SOA

- High levels in spring-summer (blue & red) and southern China
- Unexpected increase in winter (yellow) at some sites



Ding et al., JGR 2016

Large amounts of VOCs and NOx from Biomass Burning

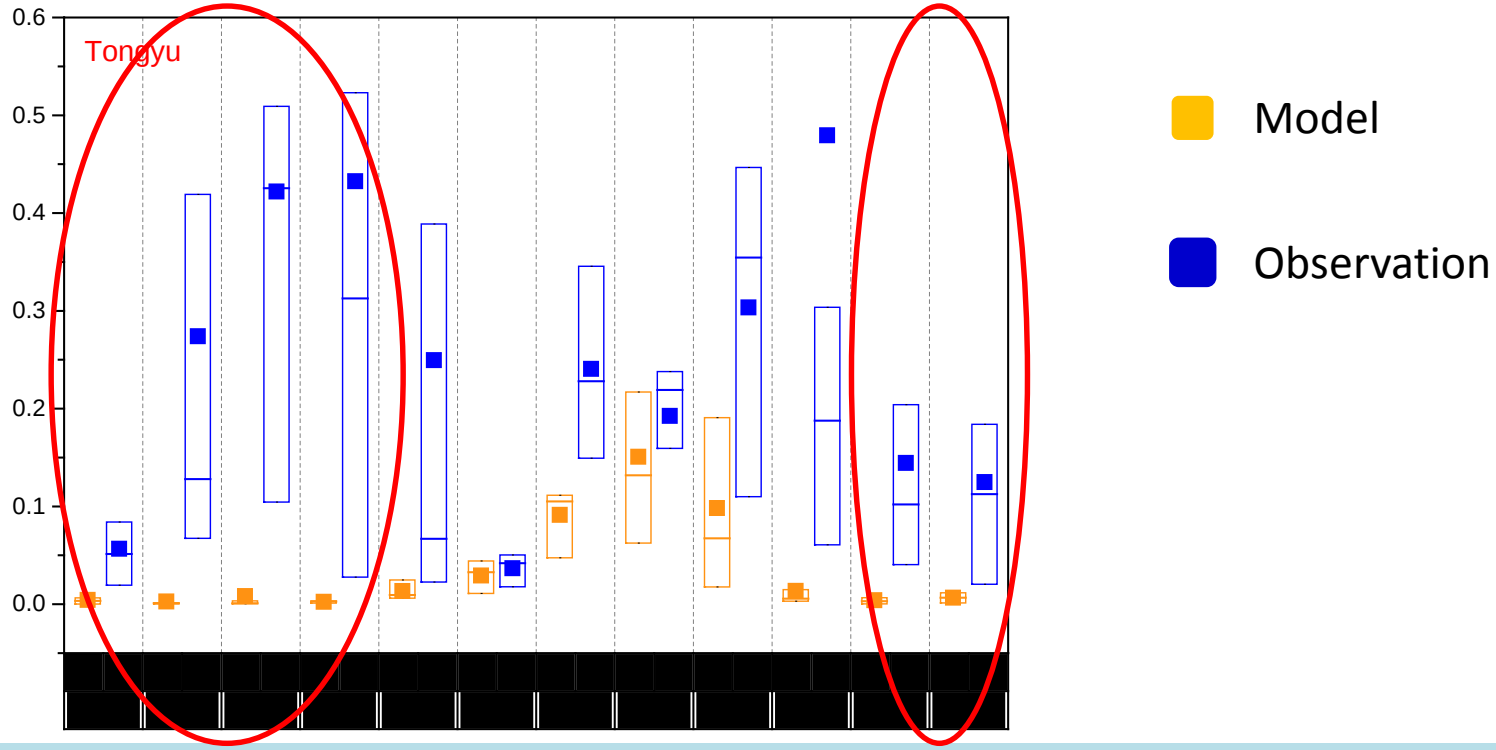
Isoprene
Monoterpenes

Aromatics
NOx

	Tropical Forest	Savanna	Crop Residue	Pasture Maintenance	Boreal Forest	Temperate Forest	Extratropical Forest[b]
Carbon Dioxide (CO_2)	1643 (58)	1686 (38)	1585 (100)	1548 (142)	1489 (121)	1637 (71)	1509 (98)
Carbon Monoxide (CO)	93 (27)	63 (17)	102 (33)	135 (38)	127 (45)	89 (32)	122 (44)
Methane (CH_4)	5.07 (1.98)	1.94 (0.85)	5.82 (3.56)	8.71 (4.97)	5.96 (3.14)	3.92 (2.39)	5.68 (3.24)
Acetylene (C_2H_2)	0.44 (0.35)	0.24 (0.10)	0.27 (0.08)	0.21 (0.29)	0.18 (0.10)	0.29 (0.10)	0.19 (0.090)
Ethylene (C_2H_4)	1.06 (0.37)	0.82 (0.35)	1.46 (0.59)	1.28 (0.71)	1.42 (0.43)	1.12 (0.35)	1.38 (0.42)
Ethane (C_2H_6)	0.71 (0.28)	0.66 (0.41)	0.91 (0.49)	0.95 (0.43)	1.79 (1.14)	1.12 (0.67)	1.70 (1.05)
Propadiene (C_3H_4)	0.016 (0.0066)	0.012 (0.005)	–	0.020 (0.009)	–	–	–
Propylene (C_3H_6)	0.64 (0.43)	0.79 (0.56)	0.68 (0.37)	0.85 (0.66)	1.13 (0.60)	0.95 (0.54)	1.11 (0.61)
Propyne (C_3H_4)	–	–	–	–	0.059	–	0.059
Propane (C_3H_8)	0.126 (0.060)	0.10 (0.067)	0.28 (0.15)	0.22 (0.10)	0.44	0.26 (0.11)	0.42 (0.18)
n-Butane (C_4H_{10})	0.038 (0.023)	0.016 (0.013)	0.072 (0.036)	0.040 (0.018)	0.12	0.083 (0.10)	0.12 (0.14)
i-Butane (C_4H_{10})	0.011 (0.009)	0.0043 (0.0027)	0.025 (0.013)	0.014 (0.0063)	0.042	–	0.042
1-Butene (C_4H_8)	0.079 (0.024)	0.043 (0.022)	0.134 (0.060)	0.17 (0.077)	0.16	–	0.16
i-Butene (C_4H_8)	0.11 (0.051)	0.024 (0.0051)	0.117 (0.060)	0.11 (0.05)	0.11	–	0.11
1,3-Butadiene (C_4H_6)	0.039	0.052 (0.028)	0.151 (0.072)	–	0.14	–	0.14
trans-2-Butene (C_4H_8)	0.029 (0.013)	0.011 (0.0055)	0.057 (0.030)	0.050 (0.023)	0.040	–	0.040
cis-2-Butene (C_4H_8)	0.024 (0.010)	0.0084 (0.0043)	0.043 (0.023)	0.040 (0.018)	0.030	–	0.030
n-Pentane (C_5H_{12})	8.03×10^{-3} (8.03×10^{-3})	0.0032 (0.0032)	0.025 (0.012)	0.0056 (0.0025)	0.085	–	0.085
i-Pentane (C_5H_{12})	0.010 (0.010)	0.0022 (0.0032)	0.020 (0.012)	0.0074 (0.0033)	0.038	–	0.038
trans-2-Pentene (C_5H_{10})	3.30×10^{-3}	0.0045 (0.0028)	–	–	–	–	–
cis-2-Pentene (C_5H_{10})	1.90×10^{-3}	0.0025 (0.0018)	–	–	–	–	–
3-Methyl-1-Butene (C_5H_{10})	3.80×10^{-3}	0.0051 (0.0034)	–	–	–	–	–
2-Methyl-2-Butene (C_5H_{10})	4.00×10^{-3}	0.0048 (0.0035)	–	–	–	–	–
2-Methyl-1-Butene (C_5H_{10})	4.40×10^{-3}	0.0059 (0.0037)	–	–	–	–	–
Isoprene (C_5H_8)	0.13 (0.056)	0.039 (0.027)	0.38 (0.16)	0.12 (0.055)	0.15	–	0.15
Cyclopentane (C_5H_{10})	–	–	0.0019 (0.0012)	–	–	–	–
2+3-Methylpentane (C_6H_{14})	–	–	–	–	0.036	–	0.036
2-Methyl-1-Pentene (C_6H_{12})	2.80×10^{-3}	0.0035 (0.0021)	–	–	–	–	–
n-Hexane (C_6H_{14})	0.010	0.013 (0.0074)	–	–	0.055	–	0.055
Heptane (C_7H_{16})	5.60×10^{-3}	0.0070 (0.0072)	–	–	0.048	–	0.048
Benzene (C_6H_6)	0.39 (0.16)	0.20 (0.084)	0.15 (0.04)	0.70 (0.32)	1.11	–	1.11
Toluene ($C_6H_5CH_3$)	0.26 (0.13)	0.080 (0.058)	0.19 (0.06)	0.34 (0.15)	0.48	–	0.48
Xylenes (C_8H_{10})	0.11 (0.082)	0.014 (0.024)	–	0.11 (0.050)	0.18	–	0.18
Ethylbenzene (C_8H_{10})	0.050 (0.036)	0.006 (0.010)	–	0.067 (0.030)	0.051	–	0.051
n-Propylbenzene (C_9H_{12})	–	–	–	–	0.018	–	0.018
α-Pinene ($C_{10}H_{16}$)	–	–	–	–	1.64	–	1.64
β-Pinene ($C_{10}H_{16}$)	–	–	–	–	1.45	–	1.45
Ethanol (CH_3CH_2OH)	–	–	–	–	0.055	–	0.055
Sulfur Dioxide (SO_2)	0.40 (0.19)	0.48 (0.27)	–	0.32 (0.14)	–	–	–
Nitrous Acid (HONO)	1.18	0.20	–	0.16 (0.07)	–	0.52 (0.15)	0.52 (0.15)
Nitrogen Oxides (NO_x as NO)	2.55 (1.40)	3.9 (0.80)	3.11 (1.57)	0.75 (0.59)	0.90 (0.69)	2.51 (1.02)	1.12 (0.69)
Nitrous Oxide (N_2O)	–	–	–	–	0.41	0.16 (0.21)	0.38 (0.35)

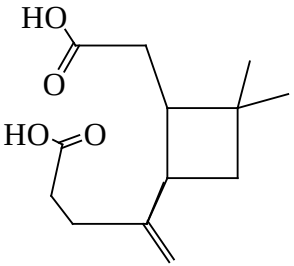
(Akagi et al., ACP 2011)

Unexpected high levels of isoprene during non-growing seasons

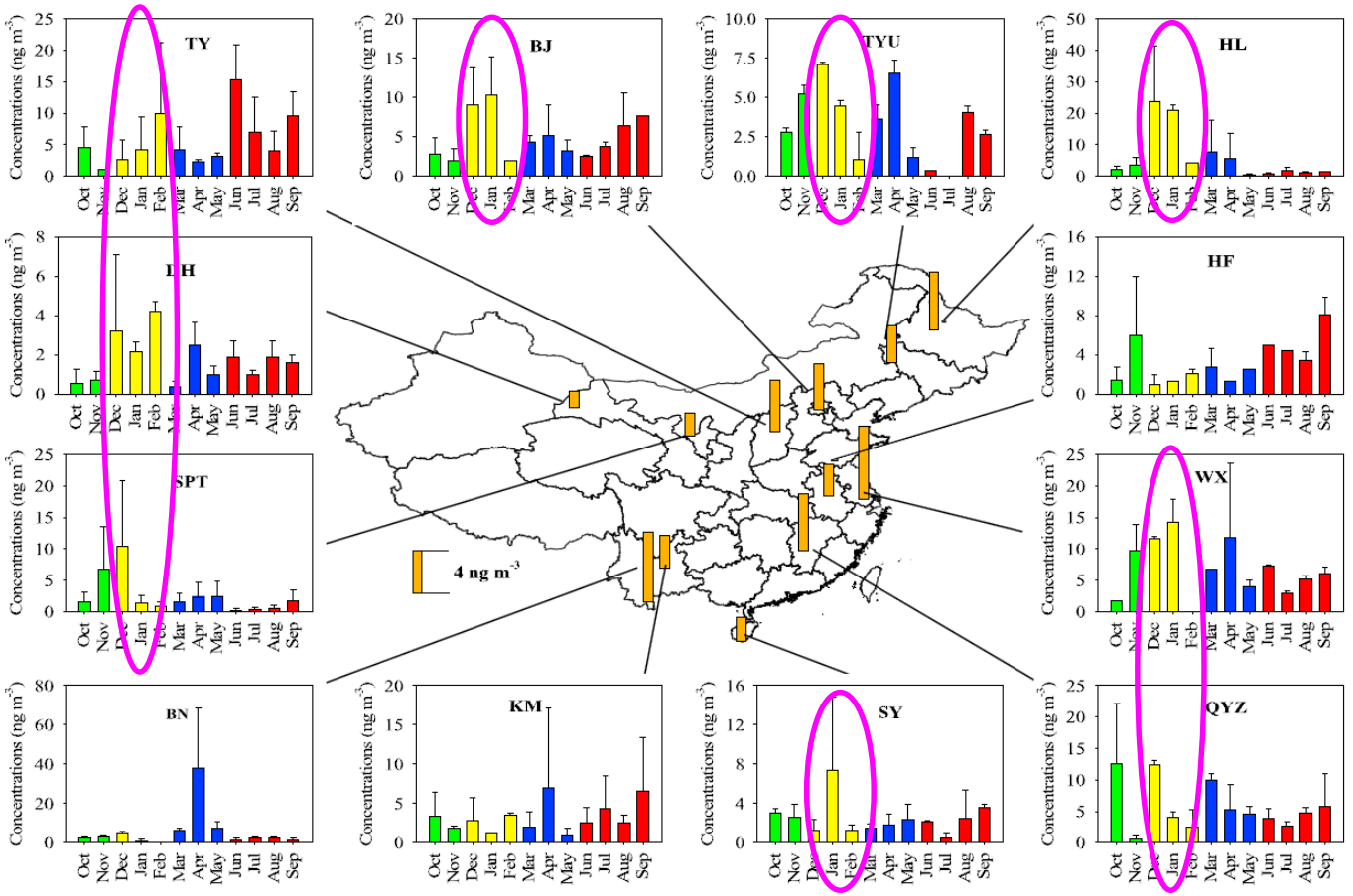


- Significantly high mixing ratios of isoprene were observed during non-growing seasons from ambient observation results.
- Biomass/biofuel/coal burning might be the potential sources?

Tracer of β-Caryophyllene SOA (SOA_C)



- Unexpected high levels in winter (yellow) at many sites in China



(Ding et al., JGR, 2016)

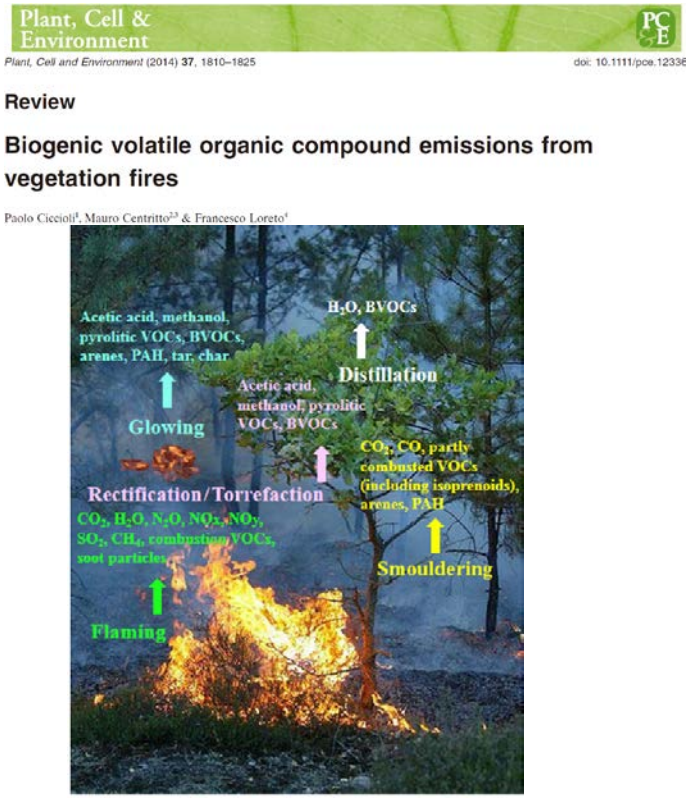
High levels of SOA_C tracer during winter in South China

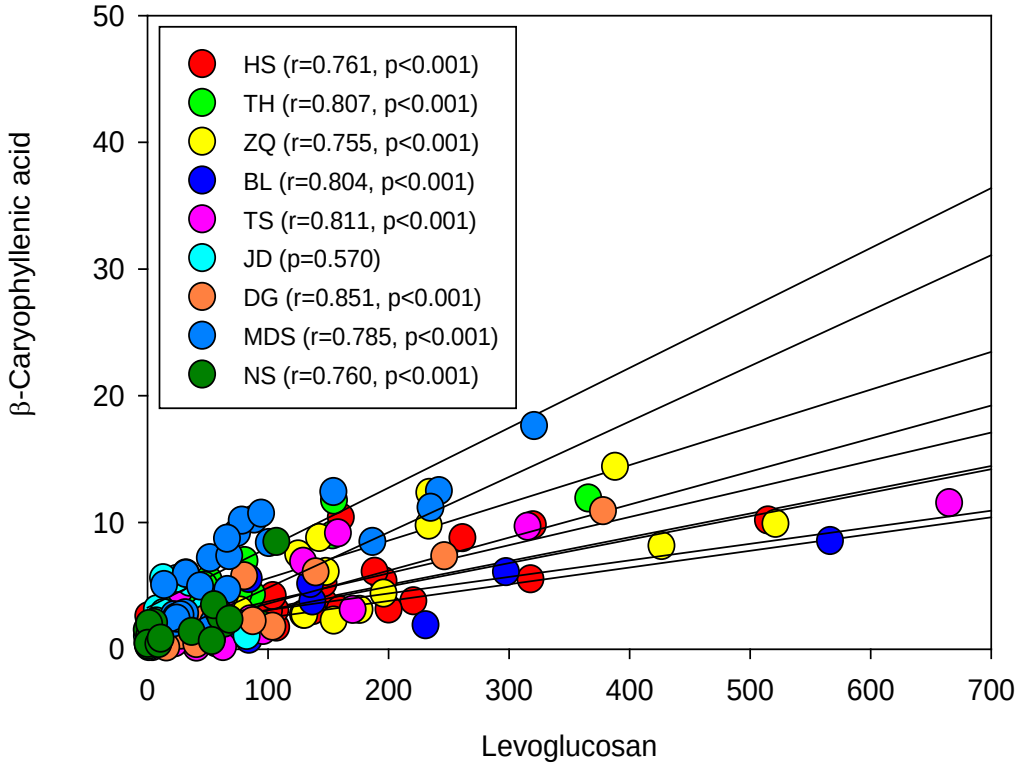
- Similar seasonal trend at 9 sites in South China
- Highest levels in winter (January)

Ding et al., in preparation)

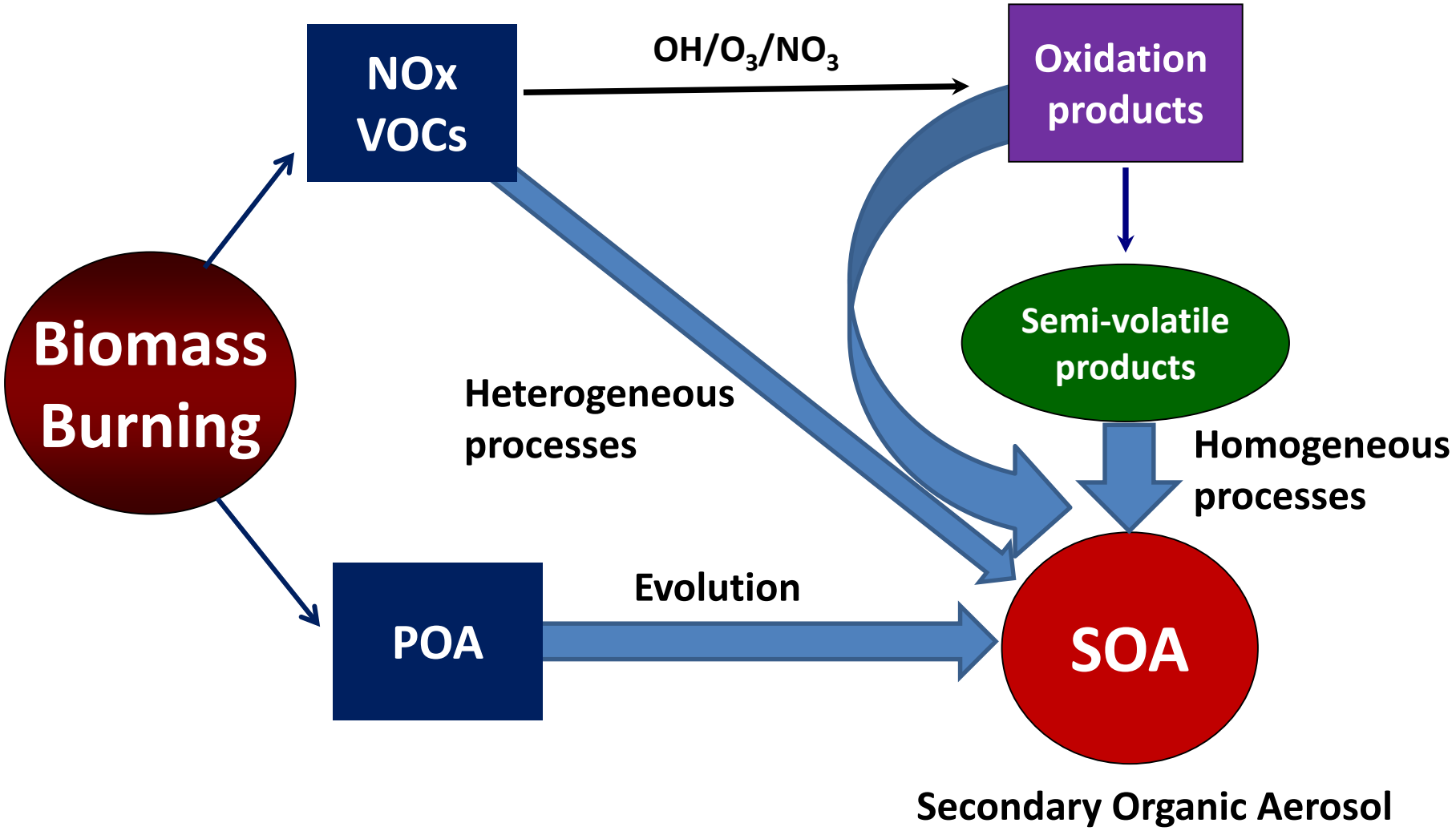
Significant impact of Biomass Burning on SOA_C

- Strong and significant correlations with the BB tracer (levoglucosan)
- BB could be an important source of SOA_C in wintertime

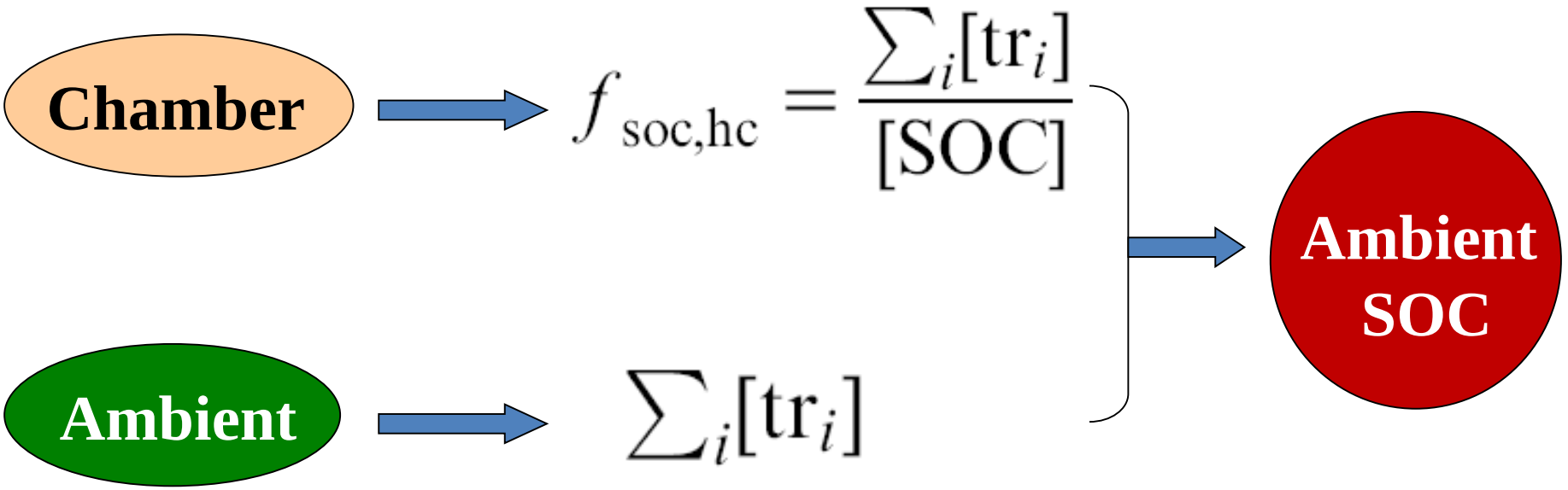




Biomass Burning could be an important source of SOA



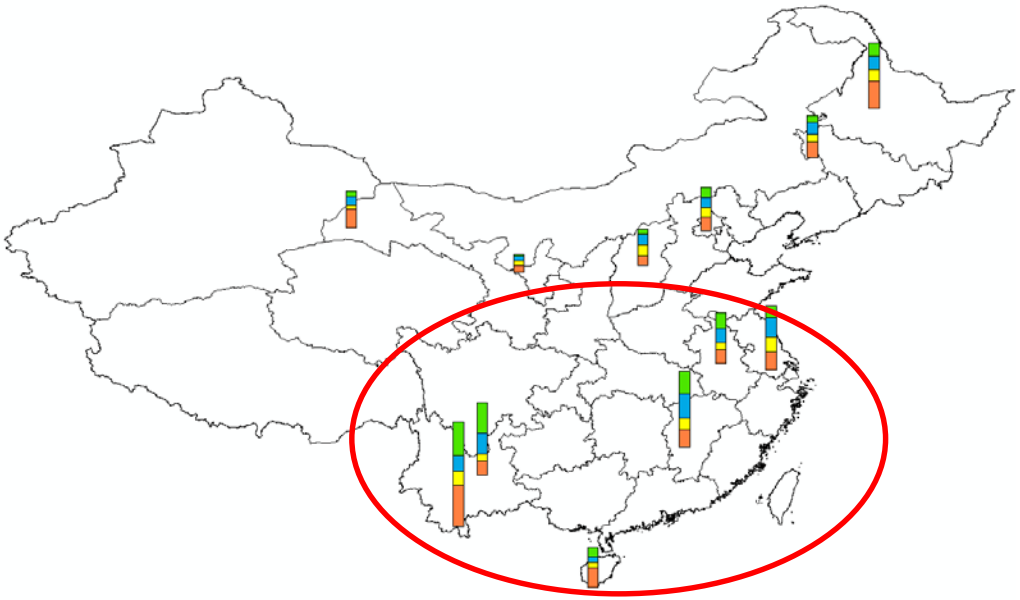
SOA estimation: Tracer method

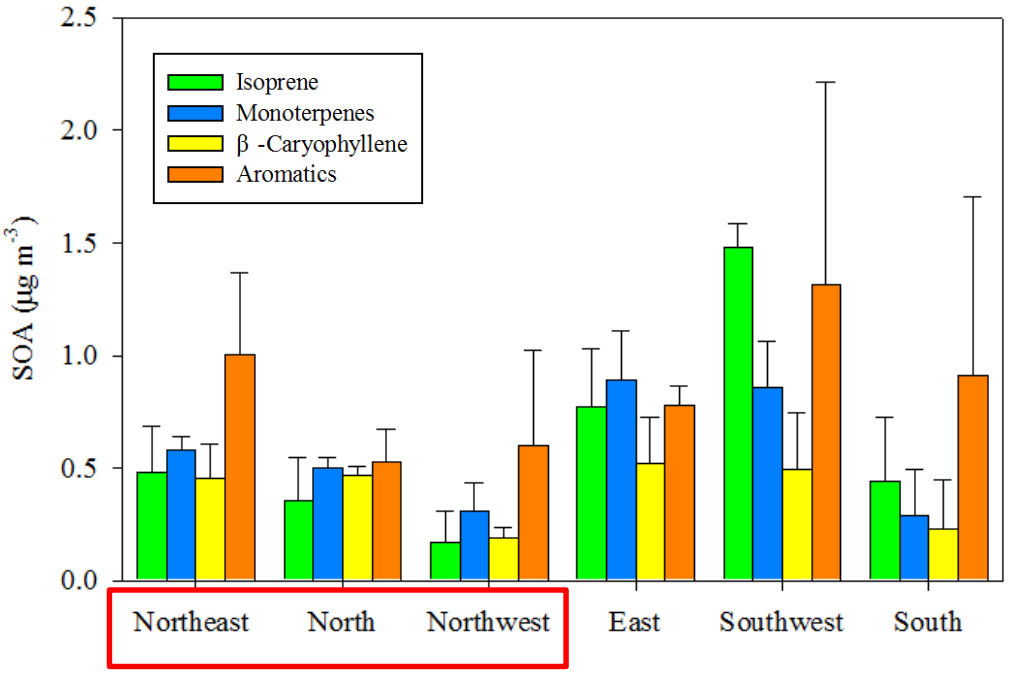


(Kleindienst et al. 2007*)*

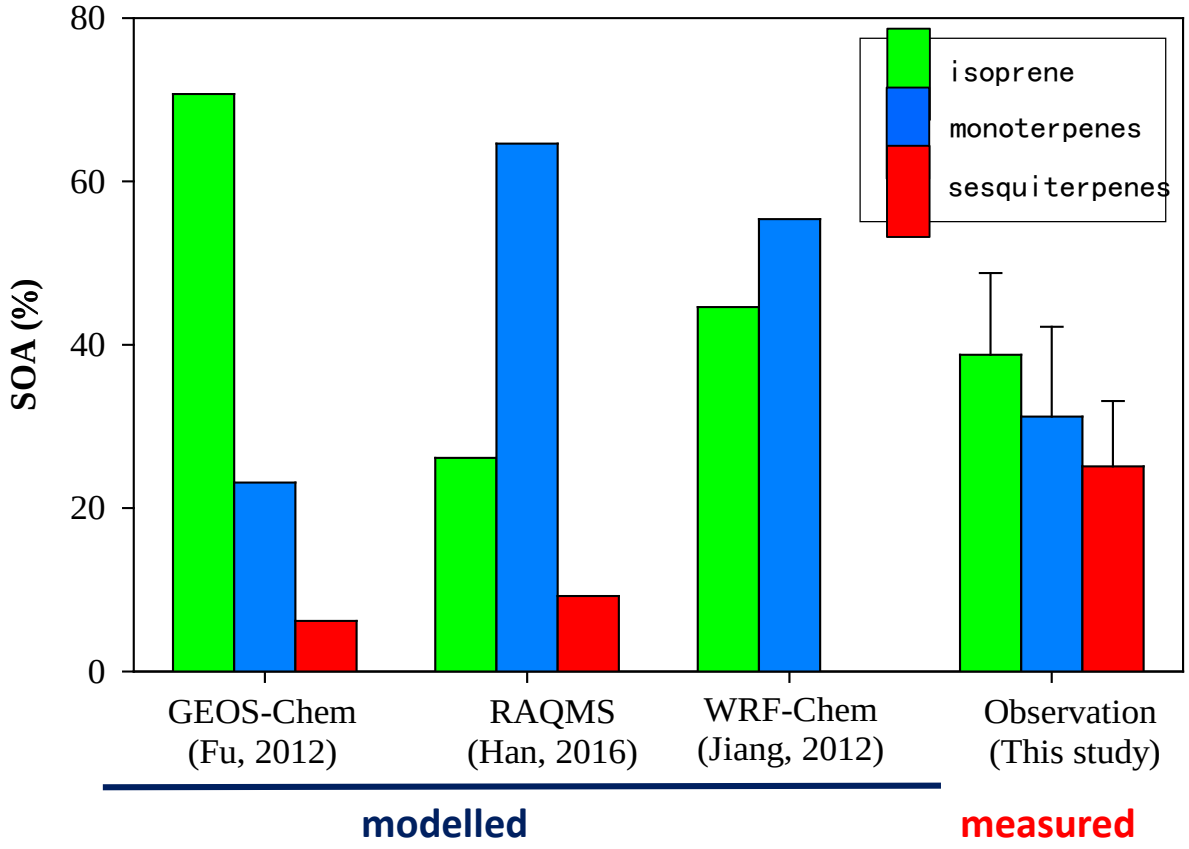
Spatial distribution of SOA

- High levels of SOA in the southern China;
- Aromatics are dominant over the biogenic VOCs in the northern China;
- The BVOCs' contributions are high in southern China.





SOA from BVOC?



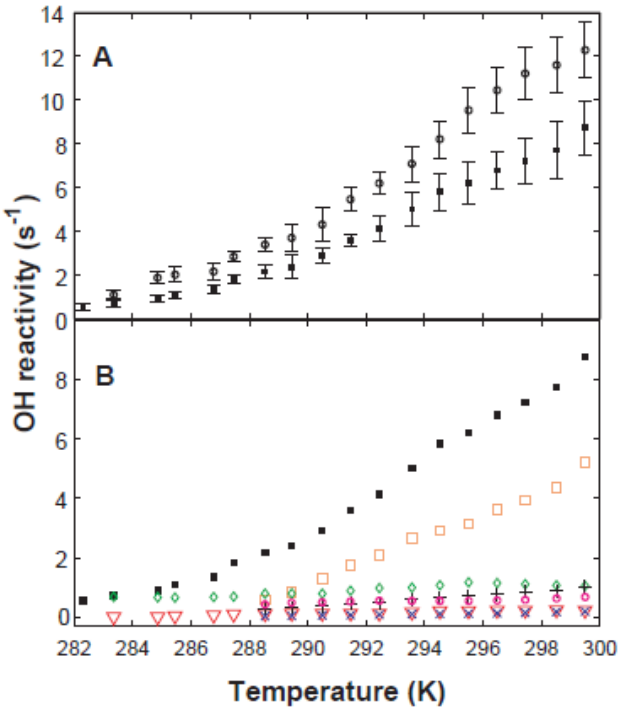
(Ding et al., JGR, 2016)

Missing OH reactivity in a forest: sesquiterpenes or higher?

Missing OH Reactivity in a Forest: Evidence for Unknown Reactive Biogenic VOCs

Piero Di Carlo,[1,2]* William H. Brune,[1] Monica Martinez,[1]†
Hartwig Harder,[1]† Robert Lesher,[1] Xinrong Ren,[1]
Troy Thornberry,[3,4]‡ Mary Anne Carroll,[3,4] Valerie Young,[5]
Paul B. Shepson,[6] Daniel Riemer,[7] Eric Apel,[8] Colleen Campbell[4]

Forest emissions of biogenic volatile organic compounds (BVOCs), such as isoprene and other terpenes, play a role in the production of tropospheric ozone and aerosols. In a northern Michigan forest, the direct measurement of total OH reactivity, which is the inverse of the OH lifetime, was significantly greater than expected. The difference between measured and expected OH reactivity, called the missing OH reactivity, increased with temperature, as did emission rates for terpenes and other BVOCs. These measurements are consistent with the hypothesis that unknown reactive BVOCs, perhaps terpenes, provide the missing OH reactivity.

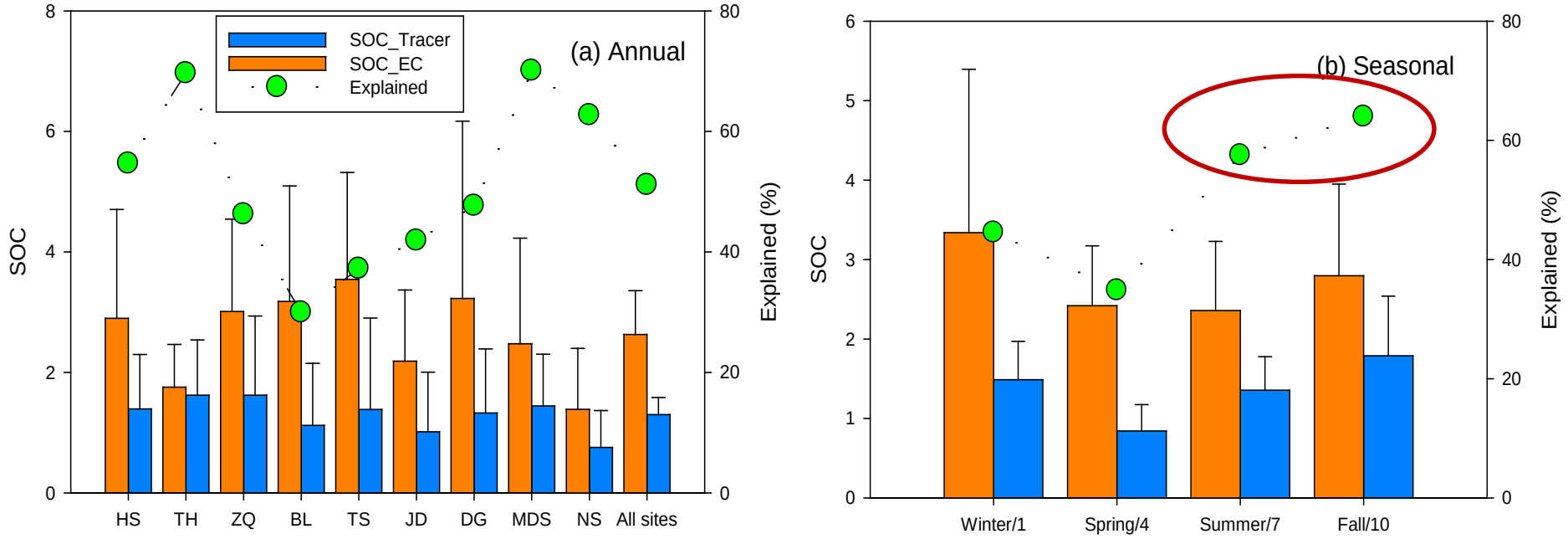


Carlo et al., 2004, Science

Unexplained SOA at 9 sites in South China

EC method: $$SOC = OC - (OC/EC)_{\mathrm{p}} \times EC$$

- SOC_{Tracer} explains 30-70% of total SOC with an average of ~50%
- SOC_{Tracer} explains more in summer and fall, less in winter and spring



Summaries

- For important emission sources, including biomass burning and vehicle exhaust, traditional VOCs can explain quite limited portions of SOA formed;
- Further source characterization of these combustion sources and biogenic emission is need with the inclusion of IVOC/OVOC/SVOC to update emission inventories and related emission standards
- Biomass burning could be an important source of traditionally biogenic VOCs and hence contributes to isoprenoid-SOA especially in wintertime.
- Improving SOA monitoring is needed.
- Field observation suggest that SOA reconstructed with SOA-tracer of traditional precursors (including sesquiterpenes) could explain ~50% of SOC estimated by EC-tracer method.

Acknowledgement

- **The Strategic Priority Research Program of the CAS.**
- **NSFC**
- **MOST**
- **Students (Bernard F; Liu TY; Mackenzie-Rae F; Deng W; Fang Z; …….)**

Thanks for your attention!