Evaluation of VOCs emission inventory by ambient measurements

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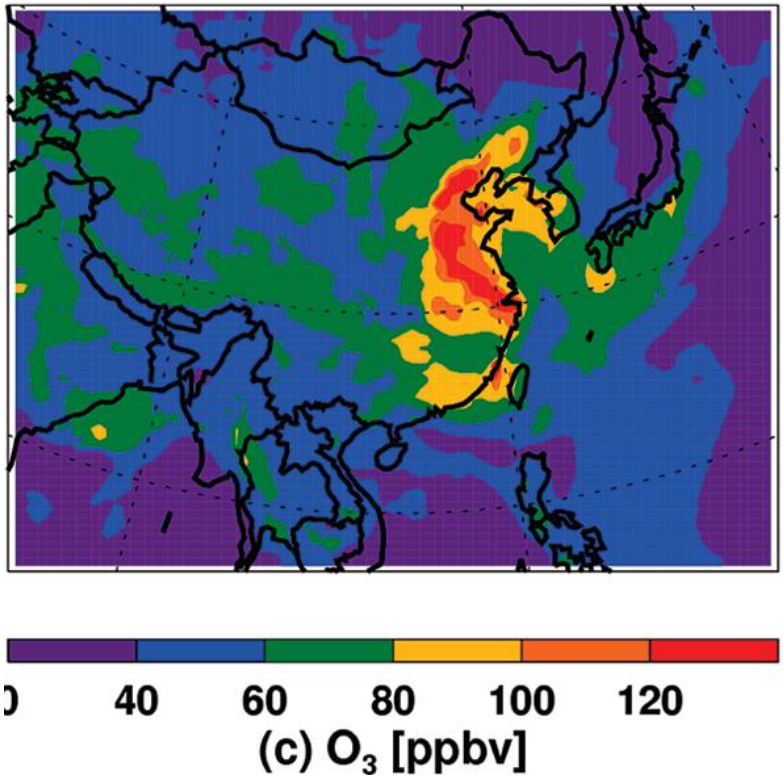
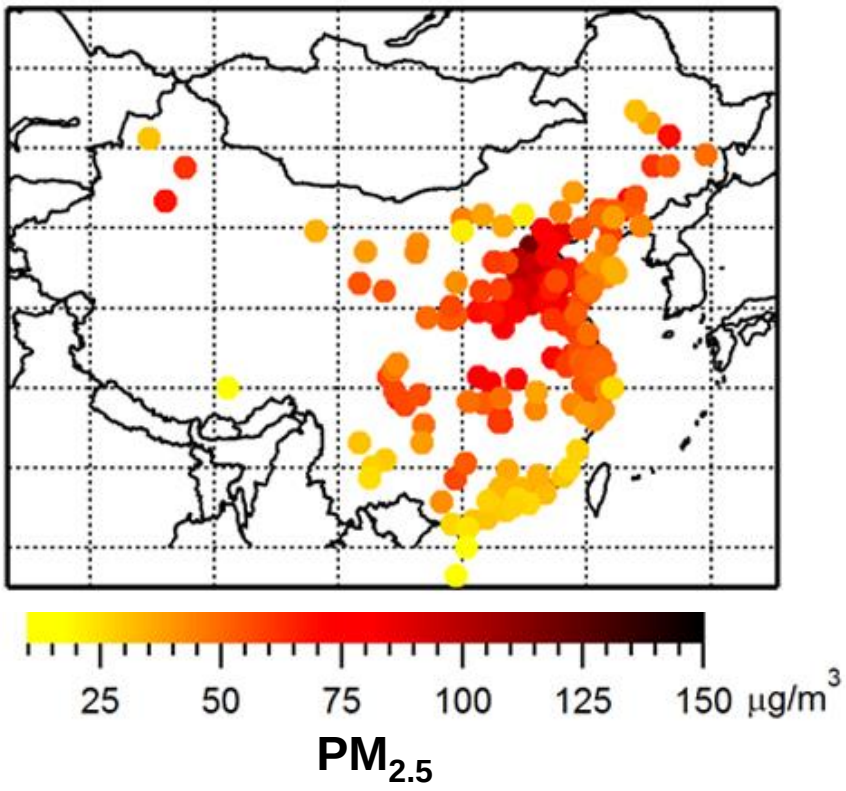
2015-12

1. **Emission inventories**
2. **Emission ratios**
3. **Trend analysis**

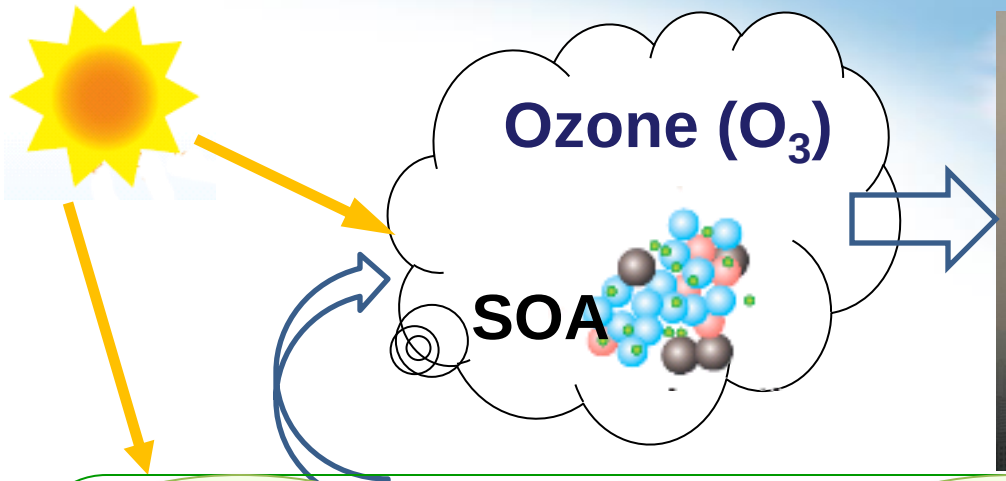
The regional pollution of O_3 and $PM_{2.5}$ in Eastern China

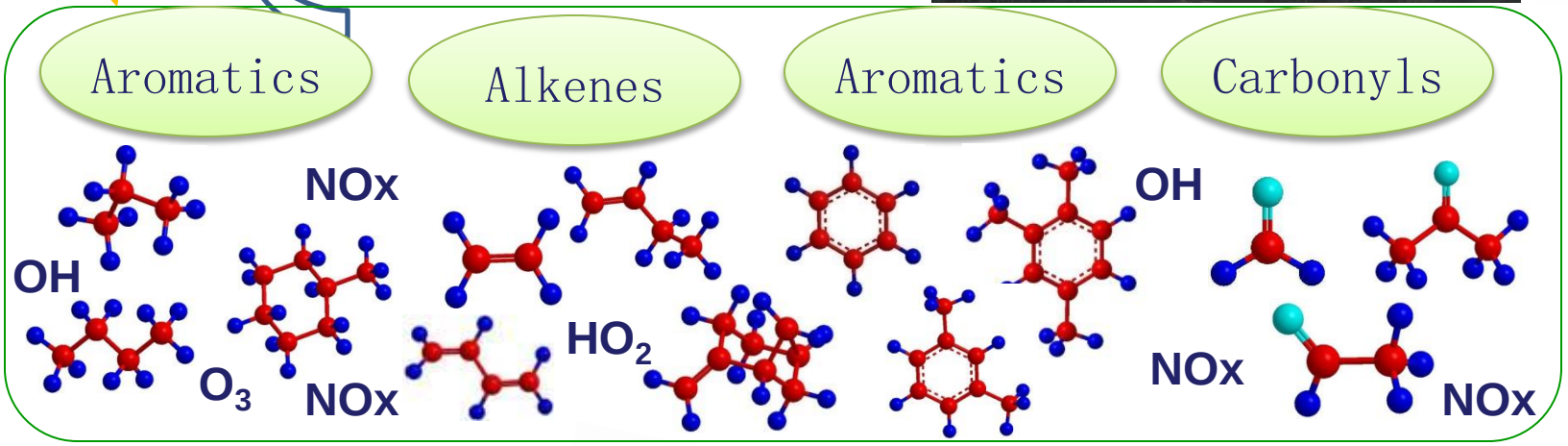




Zhao et al., 2009；
Zhang et al., 2015

VOCs played an important role in atmospheric chemistry





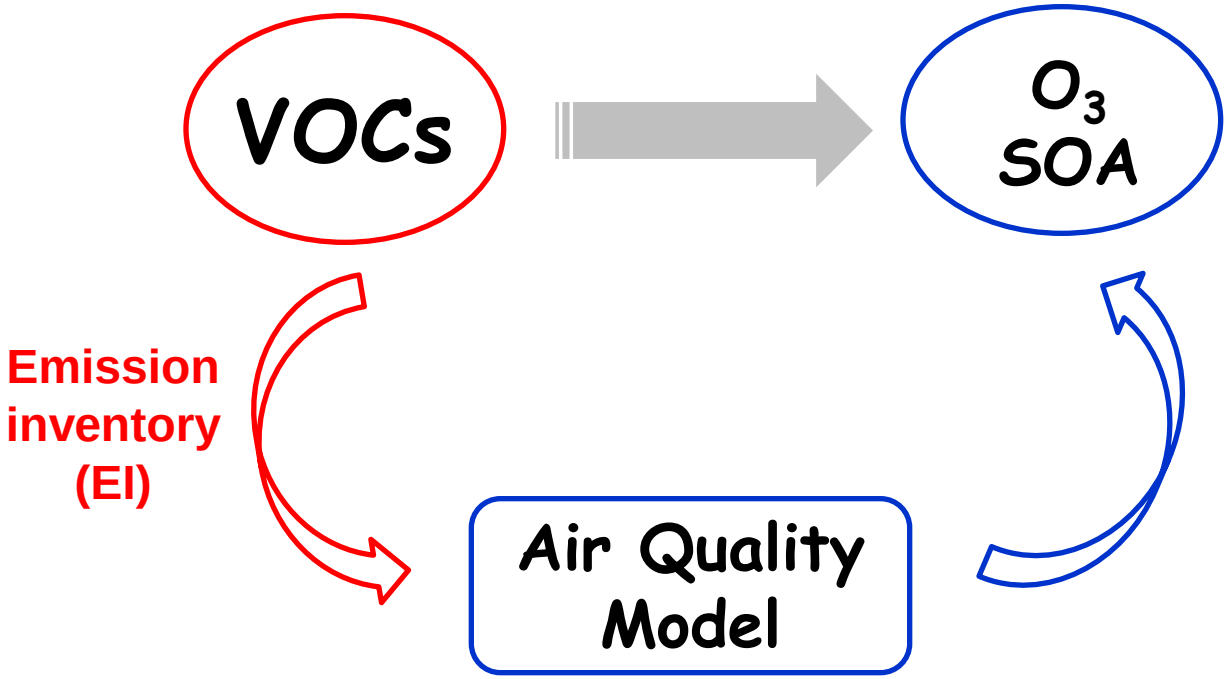
reactive species


Vehicular exhaust


Gasoline evaporation


Biogenic

The importance of VOCs emission inventory



- VOC play an important role in O_3 and SOA formation;
- The VOC emission inventory is an necessary input for air quality model to simulate secondary pollutants and investigate their formation mechanisms.

1. **Emission inventories: a big challenge**
2. **Emission ratios**
3. **Trend analysis**

VOCs emission inventory: a big challenge

VOCs EI

Bottom-Up

$$E = \sum EF_i \times A_i$$

***E*: emission**

EF_i : emission factor

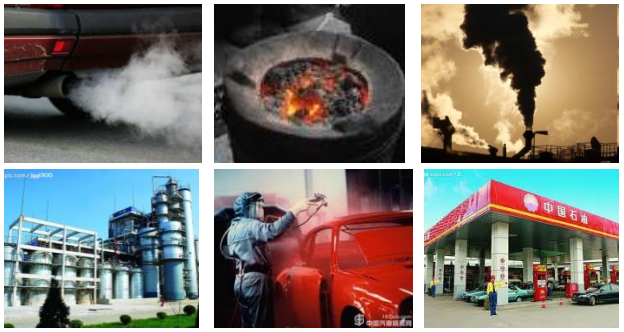
A_i : activity

Biomass burning

Song *et al.., ERL*, 2010
Yuan *et al.,* EST, 2010

Anthropogenic Sources

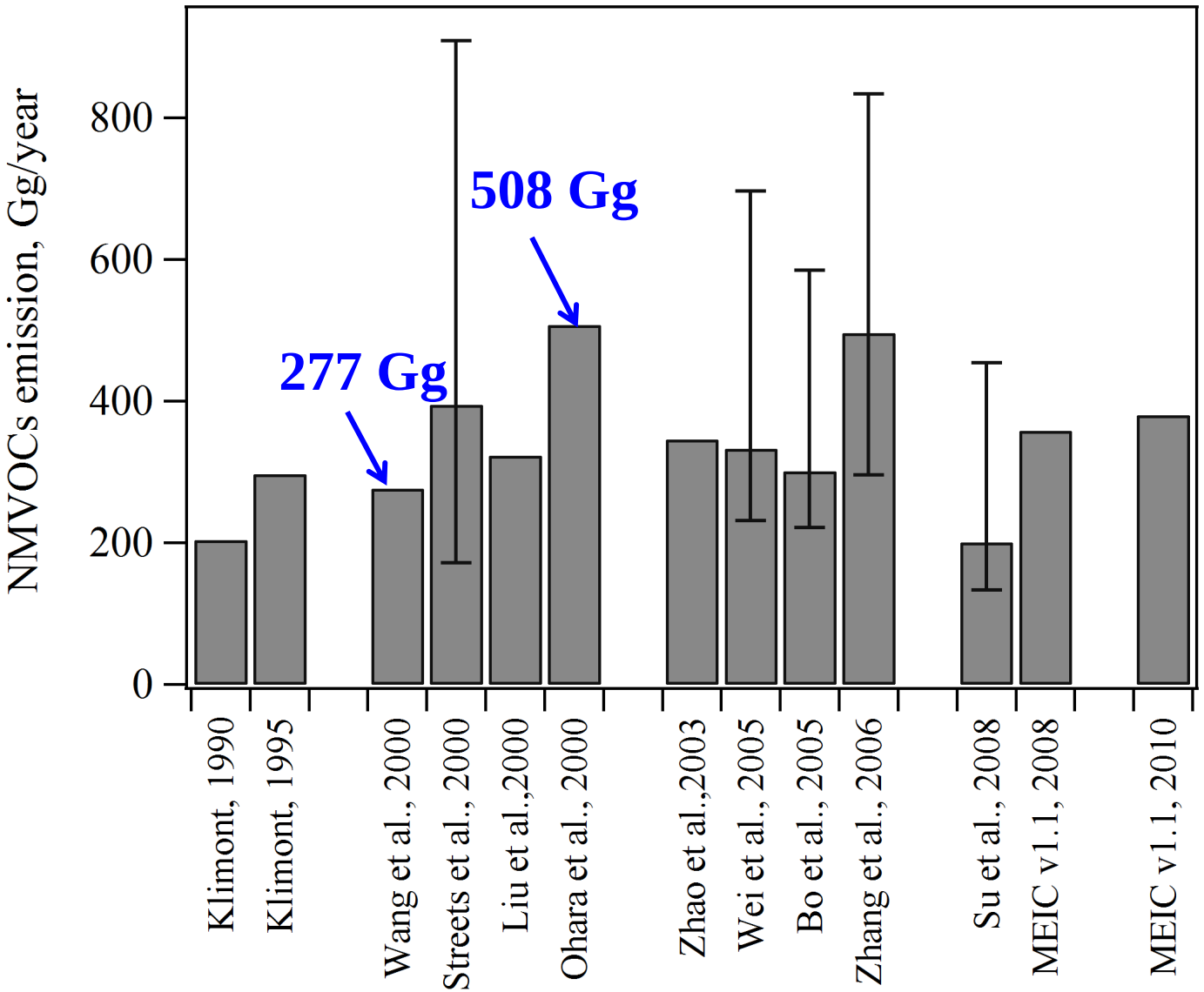
Streets *et al.,* JGR, 2003
Zhang *et al., ACP*, 2009



Biogenic emission

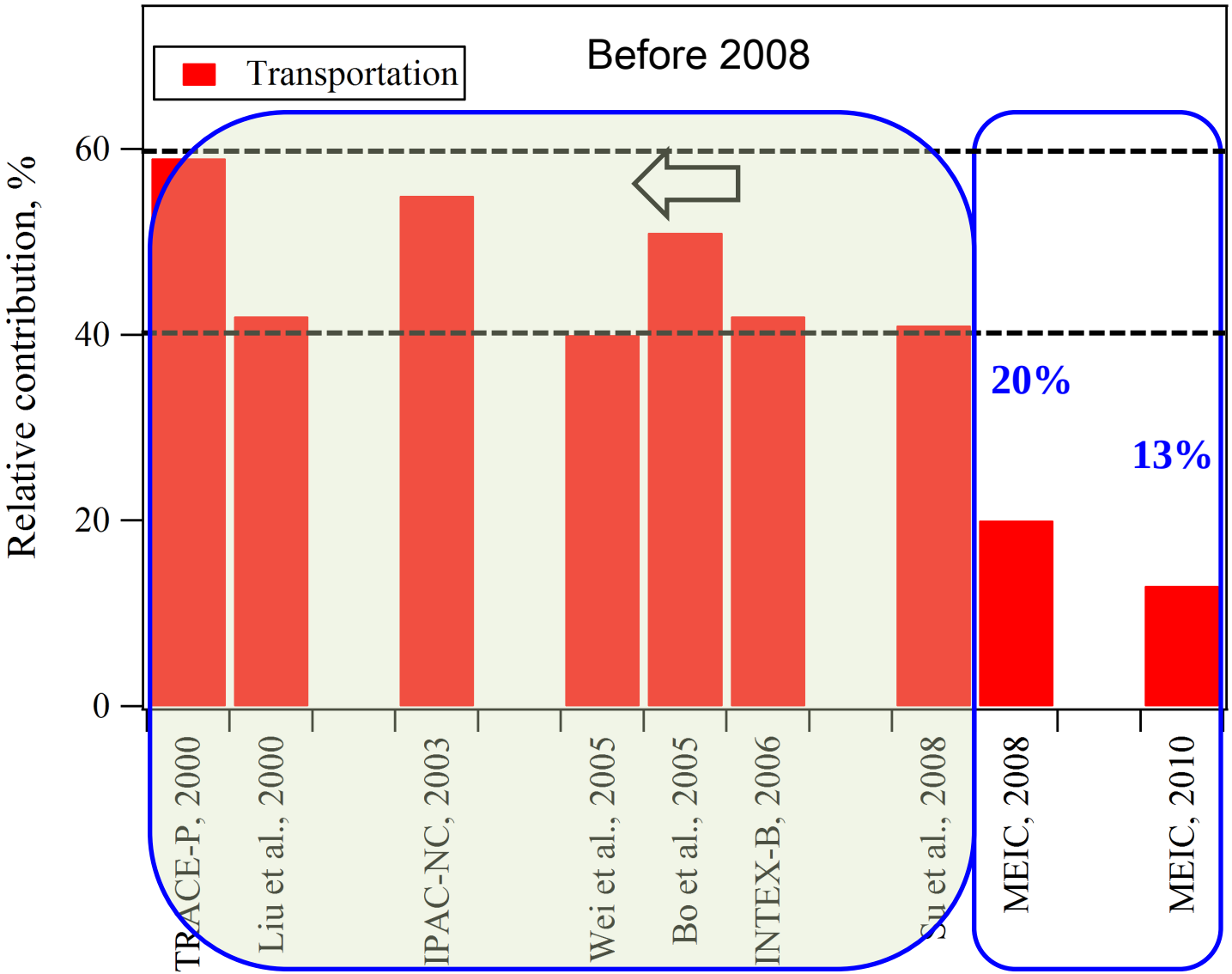
Guenther *et al.,* AE, 2000
Guenther *et al.,* ACP, 2006

Comparison of VOC emissions in Beijing



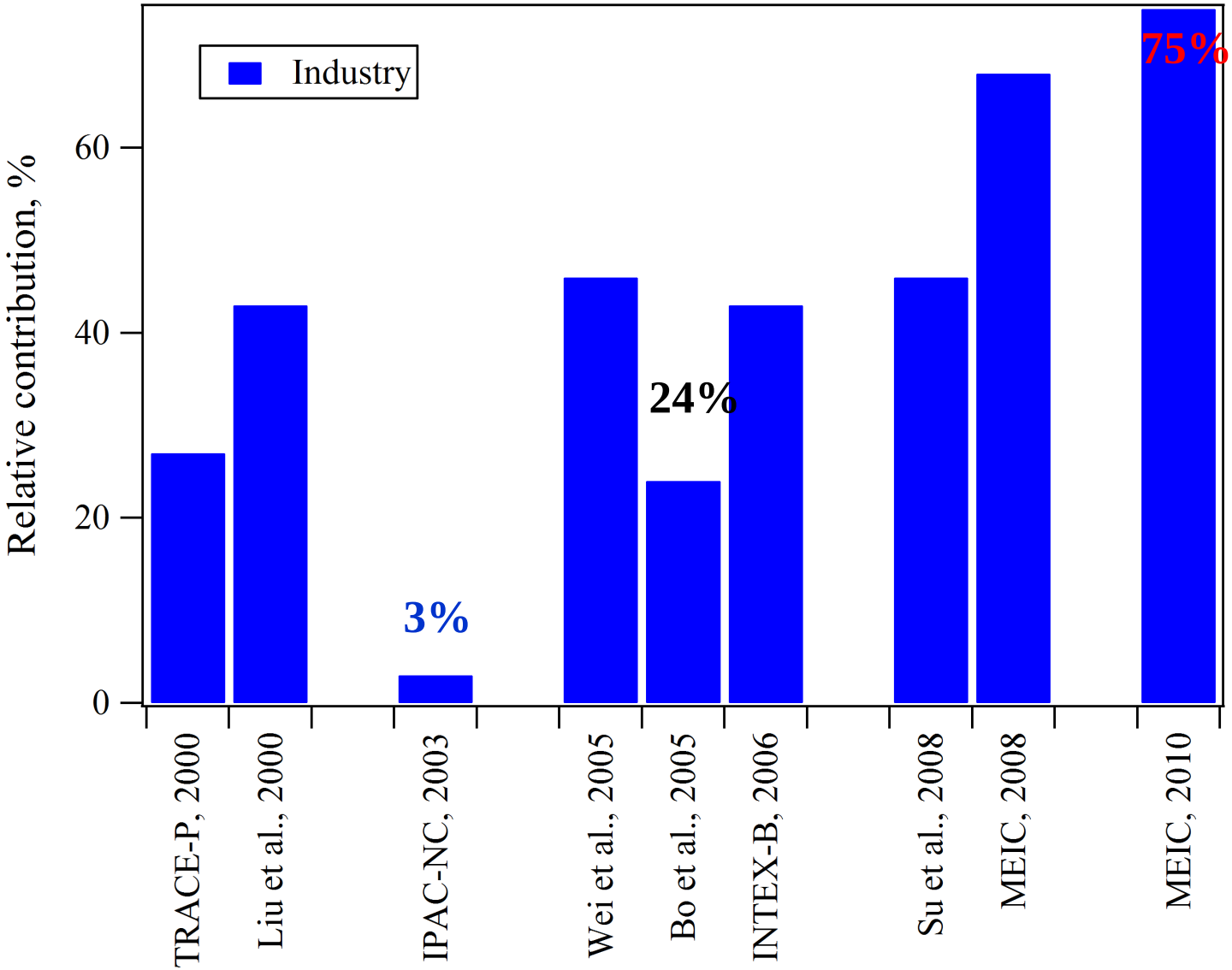
Comparison of VOC sources in Beijing:

Contributions of transportation-related emission



Comparison of VOC sources in Beijing:

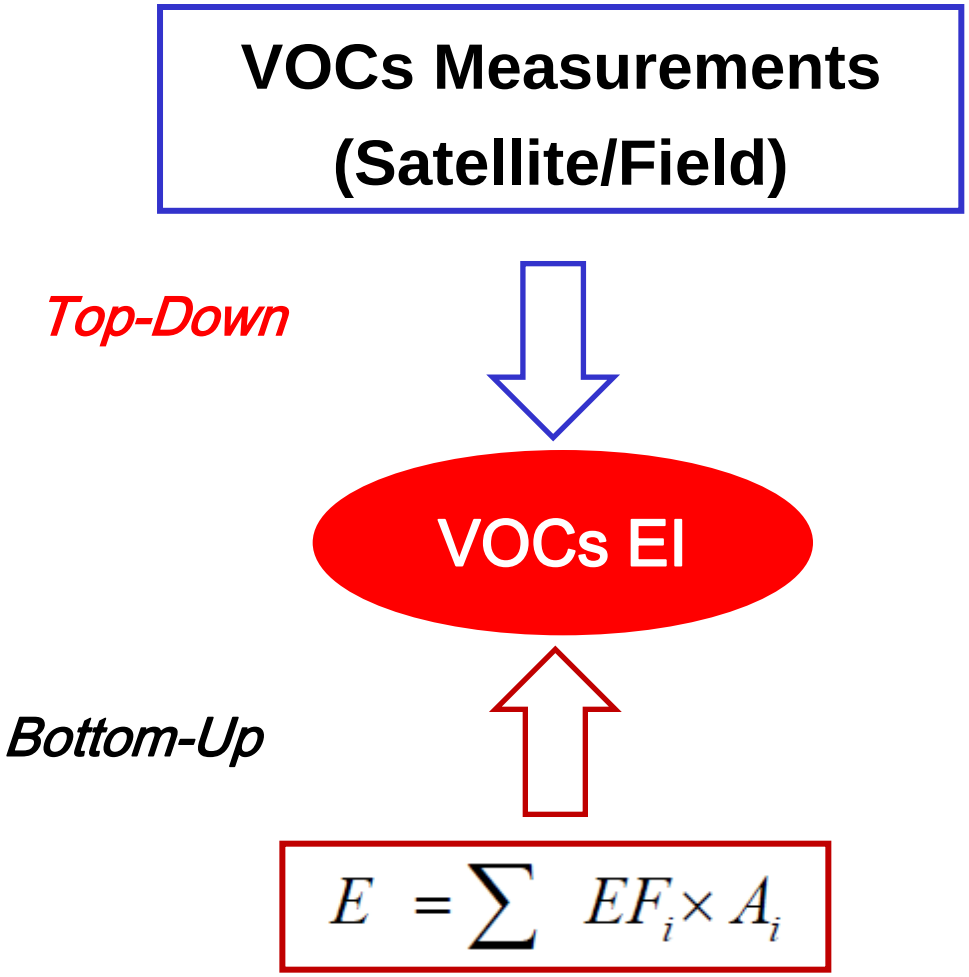
Contributions of industrial emissions



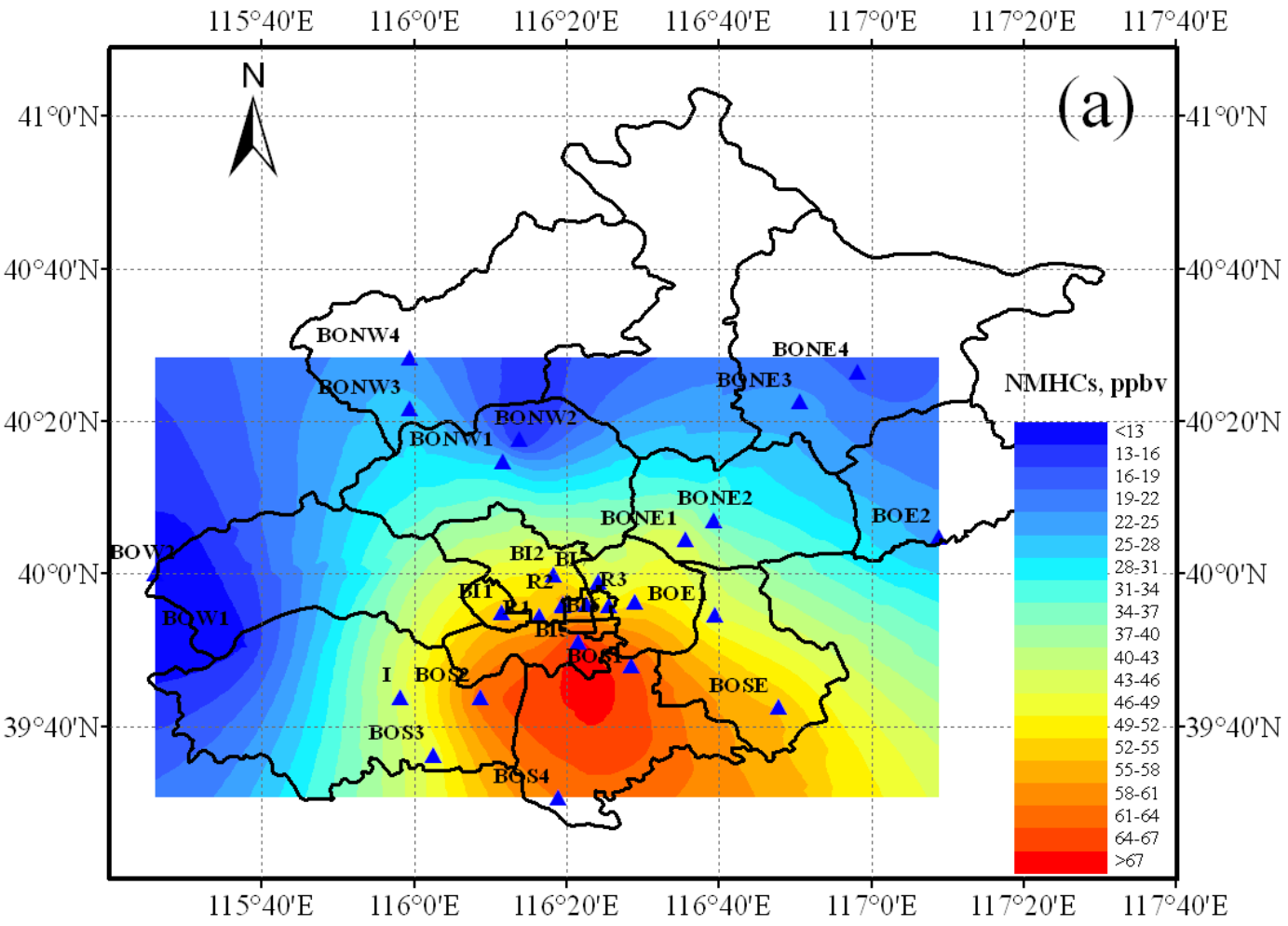
Summary

- These comparisons among different emission inventories revealed the large uncertainty of VOC emissions and sources in Beijing.
- However, these comparisons could not quantify this uncertainty, and could not identify which emission inventory is more accurate.

Evaluation of VOCs EI based on measurements



Field measurements of ambient VOCs in Beijing



16 months regional measurements (July 2009-Jan.2011) at 27 sites in Beijing.

Online VOCs measurements at the PKU site

Year	Instruments	Observation period (time resolution)	Reference
2002	Online GC-FID (PKU)	September 8–30 (30 min);	--
2004	Canister-offline GC-MS/FID [a]	August 11–20	(Lu et al., 2007)
2005	Online GC-MS/FID (ESRL)	August 1–27 (30 min)	(Liu et al., 2009a)
2006	Online GC-FID (RCEC)	August 15–24 (1 h)	(Xie et al., 2008)
2007	Online GC-FID/PID	August 7–31 (30 min)	(Zhang et al., 2014)
2008	Online GC-MS/FID (RCEC)	July 27–August 30 (1 h)	(Wang et al., 2010a)
2009	Online GC-FID/PID	August 8–31 (30 min)	(Zhang et al., 2014)
2010	Online GC-MS/FID (PKU)	August 12–31 (1 h)	(Yuan et al., 2012)
2011	Online GC-MS/FID (PKU)	August 3–September 13 (1 h)	(Wang et al., 2014a)
2012	Online GC-MS/FID (PKU)	August 1–31 (1 h)	--
2013	Online GC-MS/FID (PKU)	August 7–25 (1 h)	--

65 VOC species were quantified under QA/QC

Alkanes(28)		Alkenes (12)	Aromatics (14)	OVOC (11)
Ethane*	n-Heptane	Ethene*	Benzene	Methanol
Propane*	2-Methylhexane	Propene*	Toluene	Formaldehyde
n-Butane*	3-Methylhexane	1-Butene*	Ethylbenzene	Acetaldehyde
i-Butane	2,4-Dimethylpentane	1,3-Butadiene	m/p-Xylene	Propanal
n-Pentane	2,3-DimethylPentane	trans-2-Butene	o-Xylene	n-Butanal
i-Pentane	Methylcyclohexane	cis-2-Butene	Styrene	n-Pentanal
Cyclopentane	n-Octane	1-Pentene	i-Propylbenzene	n-Hexanal
n-Hexane	2-Methylheptane	Isoprene	n-Propylbenzene	Acetone
2-Methylpentane	3-Methylheptane	trans-2-Pentene	m-Ethyltoluene	MEK
3-Methylpentane	2,2,4-Trimethylpentane	cis-2-Pentene	p-Ethyltoluene	MACR
2,2-Dimethylbutane	2,3,4-Trimethylpentane	1-Hexene	o-Ethyltoluene	MVK
2,3-Dimethylbutane	n-Nonane	Ethyne	1,3,5-Trimethylbenzene	
Cyclohexane	n-Decane		1,2,4-Trimethylbenzene	
Methylcyclopentane	n-Undecane		1,2,3-Trimethylbenzene	

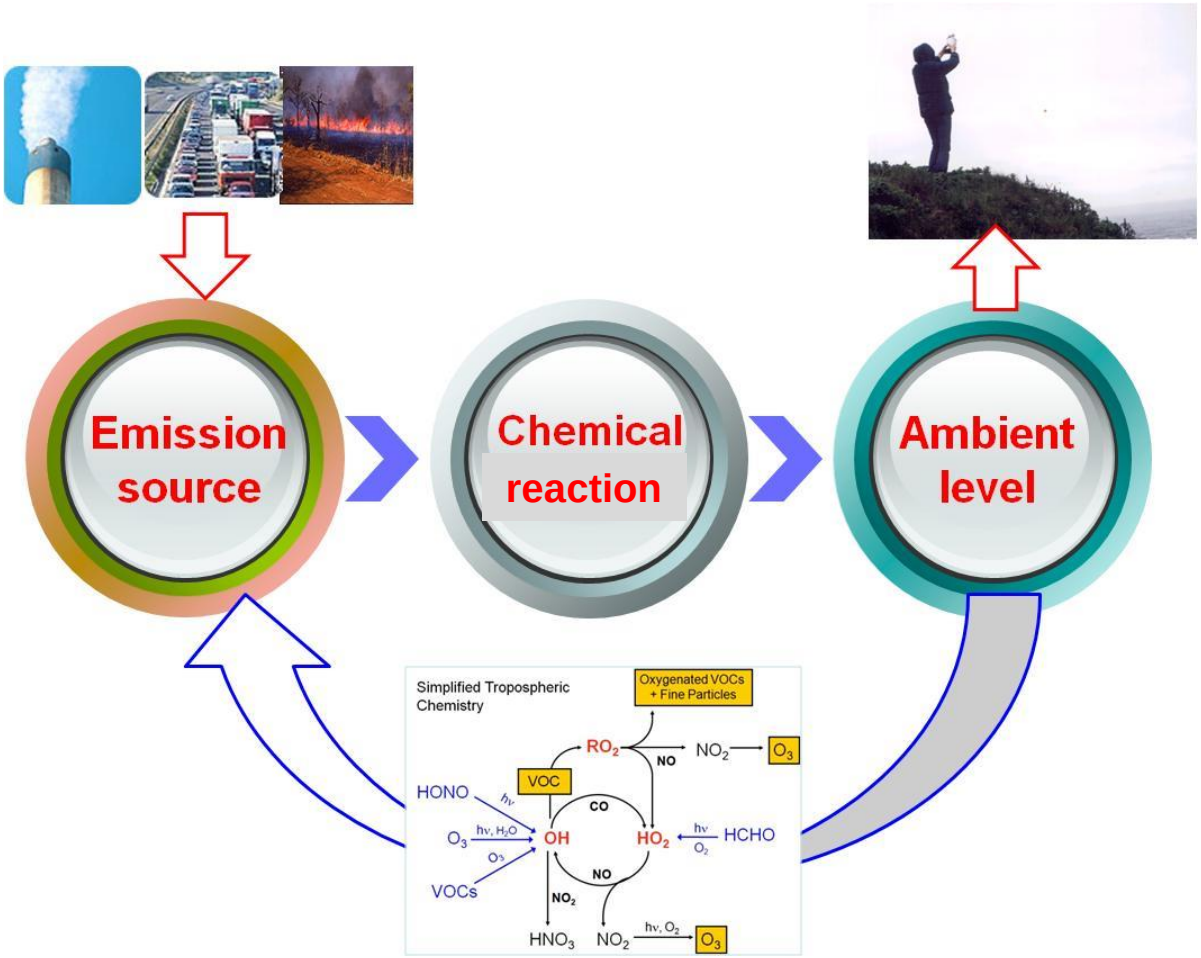
Top-down approaches to evaluating VOCs EI

Approaches		Emission	Source	Spatial distribution	Temporal variation
Receptor-oriented	Flux measurements, box model etc.	√			
	Emission ratio	√			
	Trend analysis	√			√
	Receptor model		√		
	Regional measurements			√	
Model-based	Air quality model (Forward, inverse)	√	√	√	√

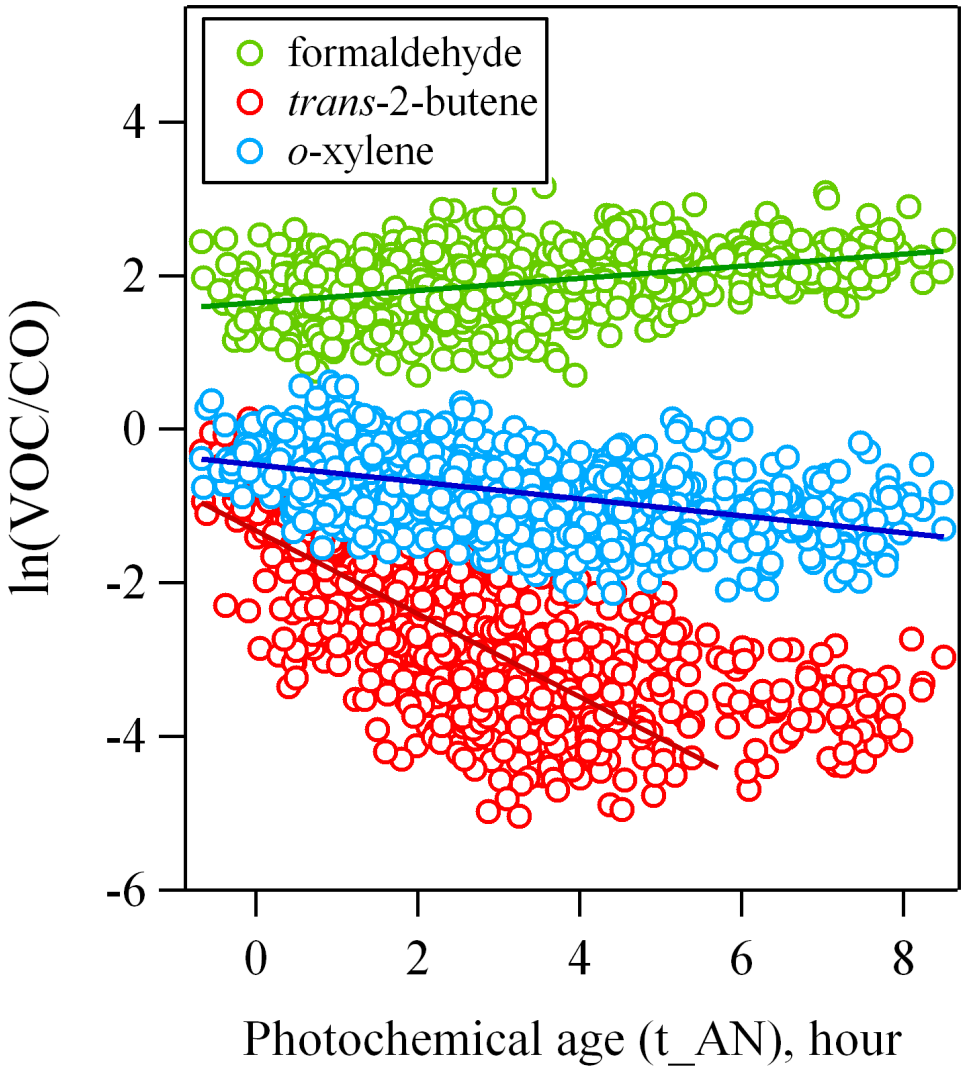
1. Emission inventories
2. Emission ratios: estimate VOC emissions
3. Trend analysis

Emission ratio (ER) of VOC:

the ratio of VOC to reference compound (e.g. CO) in fresh emissions



Photochemical evolution of measured ratios of VOC/CO



Calculation of photochemical age:

$$[\mathrm{OH}]\Delta t = \frac{1}{k_{\mathrm{HC}_1} - k_{\mathrm{HC}_2}} \times \left(\ln\left(\frac{[\mathrm{HC}_1]_0}{[\mathrm{HC}_2]_0}\right) - \ln\left(\frac{[\mathrm{HC}_1]}{[\mathrm{HC}_2]}\right)\right)$$

$$[\mathrm{OH}]\Delta t = \frac{[\mathrm{OH}]}{k_\mathrm{A} - k_\mathrm{B}} \times \left(\ln\left(\frac{[\mathrm{RONO}_2]}{[\mathrm{RH}]} - \frac{\beta k_\mathrm{A}}{k_\mathrm{B} - k_\mathrm{A}}\right) - \ln\left(\frac{[\mathrm{RONO}_2]_0}{[\mathrm{RH}]_0} - \frac{\beta k_\mathrm{A}}{k_\mathrm{B} - k_\mathrm{A}}\right)\right),$$

Determination of VOC ER from measured ratios

HC: reaction with OH radical

$$\frac{[HC]_{t_M}}{[CO]_{t_M}} = ER_{HC} \times \exp\left(-\left(k_{HC} - k_{CO}\right)[OH]\Delta t\right)$$

ER: Emission Ratio
Δt: Photochemical age

OVOC: production as well as chemical loss

$$[OVOC]_{t_M} = ER_{OVOC} \times [CO]_{t_M} \times \exp\left(-\left(k_{OVOC} - k_{CO}\right)[OH]\Delta t\right)$$

Anthropogenic emissions

$$+ER_{precursor} \times [CO]_{t_M} \times \frac{k_{precursors}}{k_{OVOC} - k_{precursors}} \times \frac{\exp\left(-k_{precursors}[OH]\Delta t\right) - \exp\left(-k_{OVOC}[OH]\Delta t\right)}{\exp\left(k_{CO}[OH]\Delta t\right)}$$

$$+[biogenic]+[background)$$

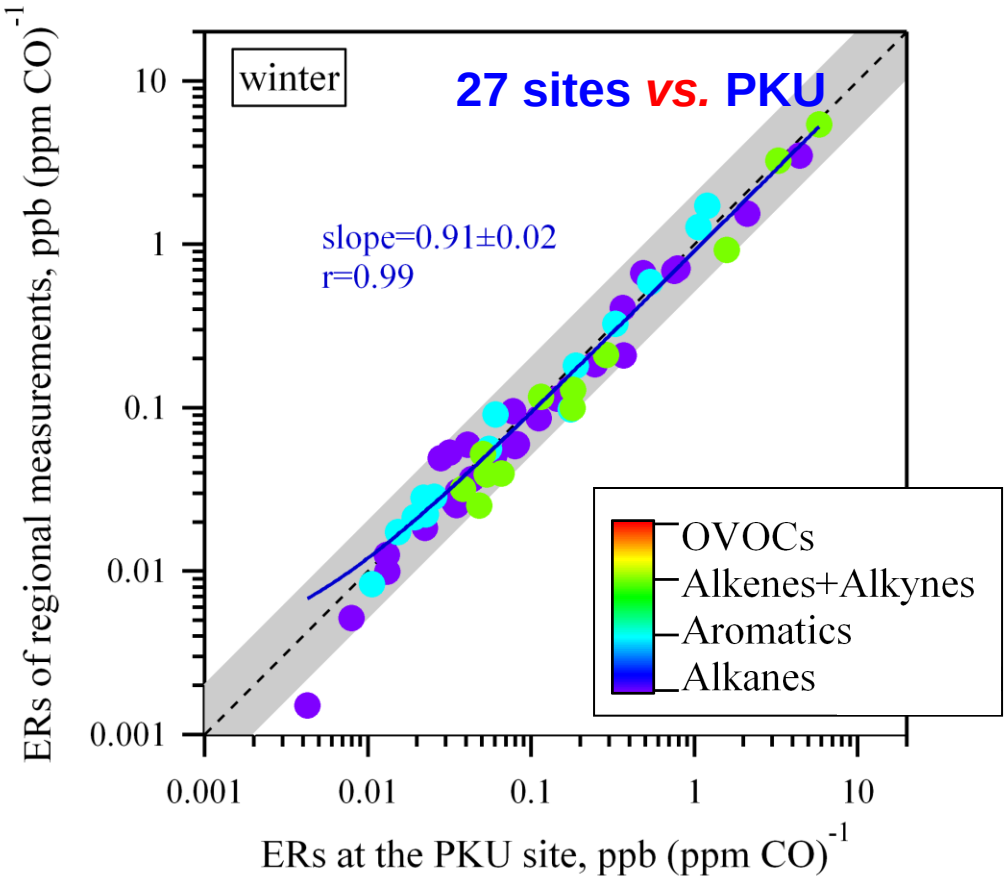
Secondary production

de Gouw et al., JGR, 2005; Warneke et al., JGR, 2007

Four datasets for VOC ERs

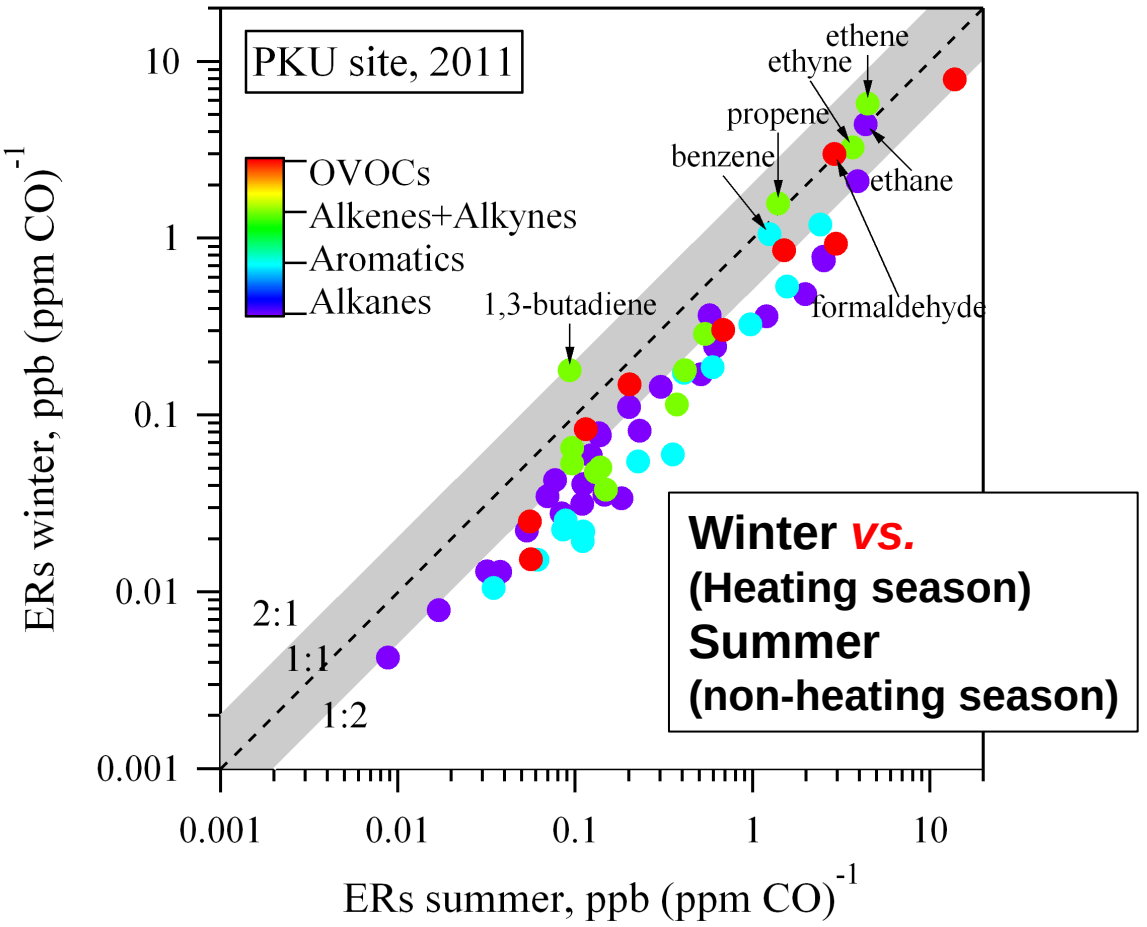
- **Regional VOC measurements at 27 sites in Beijing:**
  - VOC ERs during summer
  - VOC ERs during winter
- **Online VOC measurements at the PKU site:**
  - VOC ERs during summer
  - VOC ERs during winter

Similarity of VOC ERs at different sites



- The VOC ERs obtained at the PKU site showed good agreements with those for regional sites in Beijing.
- The VOC ERs at the PKU site can represent the chemical composition of VOC emissions in Beijing.

Differences of VOC ERs between winter and summer



The wintertime emission ratios for most VOC species were significantly lower than the summertime values, with the exception of acetylene, alkenes, benzene, ethane, and formaldehyde.

Estimation of VOC emissions in Beijing

Summer (non-heating season) **Winter (Heating season)**

$$E_{VOC,A} = \left(ER_{VOC,S} \times E_{CO,S} + ER_{VOC,W} \times E_{CO,W} \right) \times MW_{VOC} / MW_{CO}$$

$E_{VOC,A}$: annual emission of VOC (Gg/year);

$ER_{VOC,S}$: VOC emission ratio during summer (ppbv/ppmv);

$ER_{VOC,W}$: VOC emission ratio during winter (ppbv/ppmv);

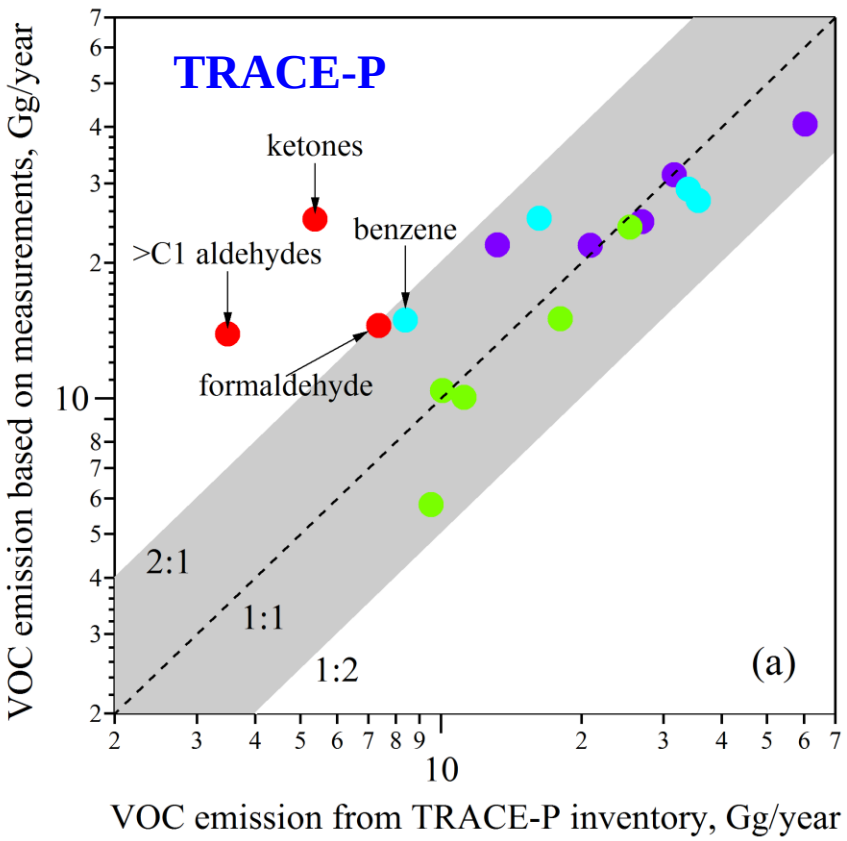
$E_{CO,S}$: CO emission during summer (Tg/year);

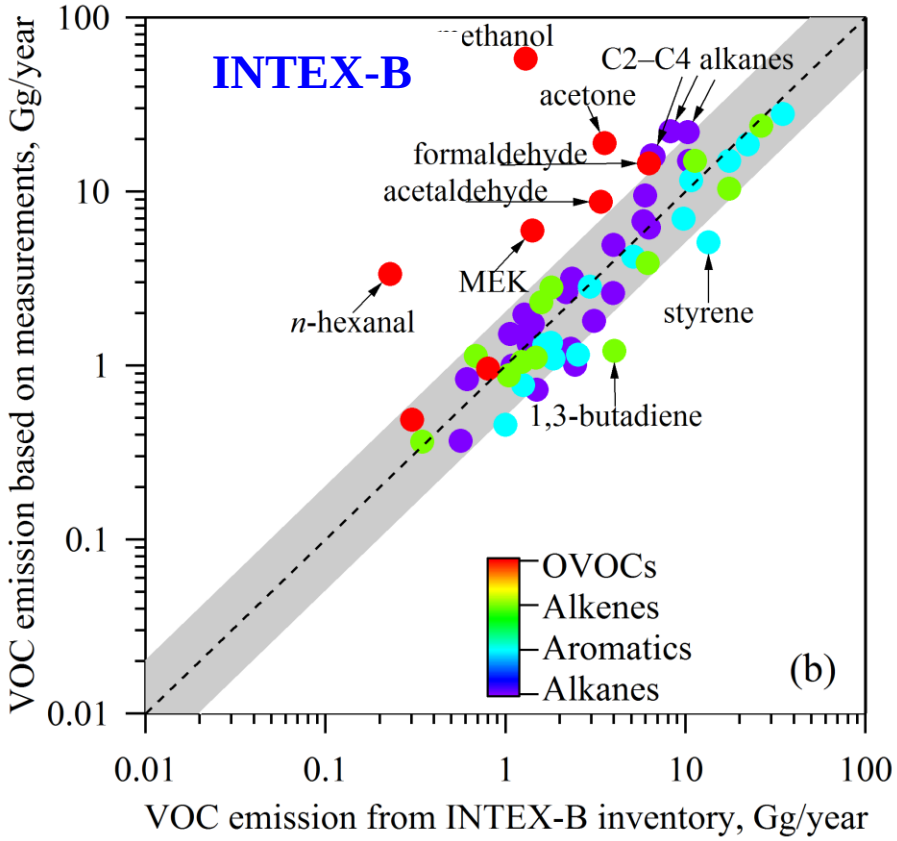
$E_{CO,W}$: CO emission during winter (Tg/year);

MW_{VOC}: molecular weight of VOC (g/mol);

MW_{CO}: molecular weight of CO (g/mol).

Comparison of VOCs emissions derived from measurements with current inventories





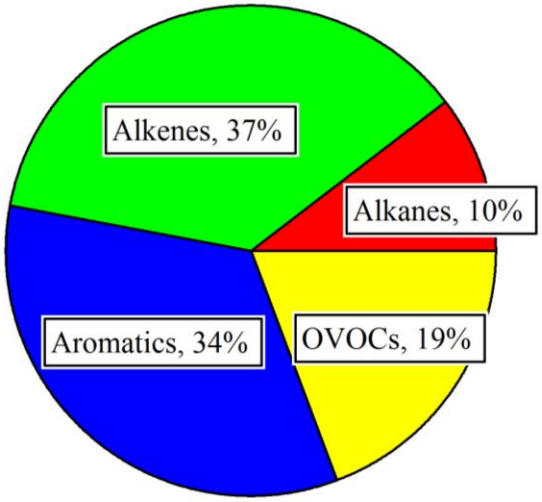
1. OVOCs emissions estimated based on ambient measurements were higher than those reported by the current inventories;
2. The emissions of light alkanes derived from measurements were also higher than those reported by the INTEX-B inventory;
3. Styrene and 1,3-butadiene emissions were higher in the INTEX-B inventory.

Ozone formation potential (OFPs)

$$OFPs = \sum MIR \times E_{VOC}$$

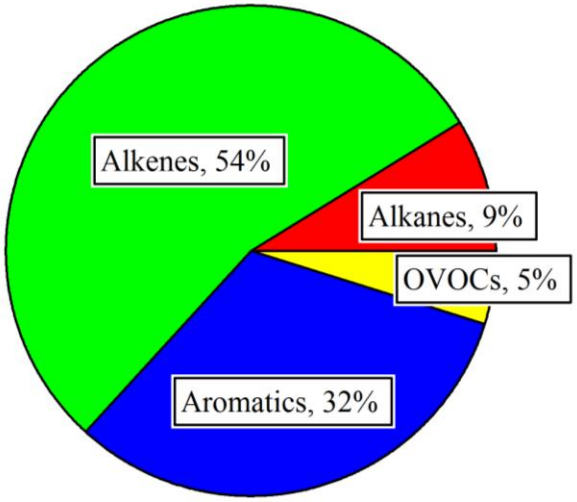
E_{VOC}: emissions of VOCs ;
MIR: Maximun incremental reactivity (gO_3/gVOC).

VOCs emission from measurements



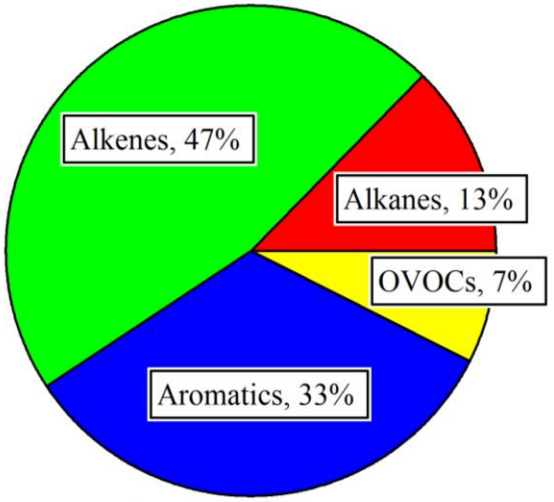
OFPs of total VOCs=1433 Gg O_3

INTEX-B inventory



OFPs of total VOCs=1169 Gg O_3

TRACE-P inventory

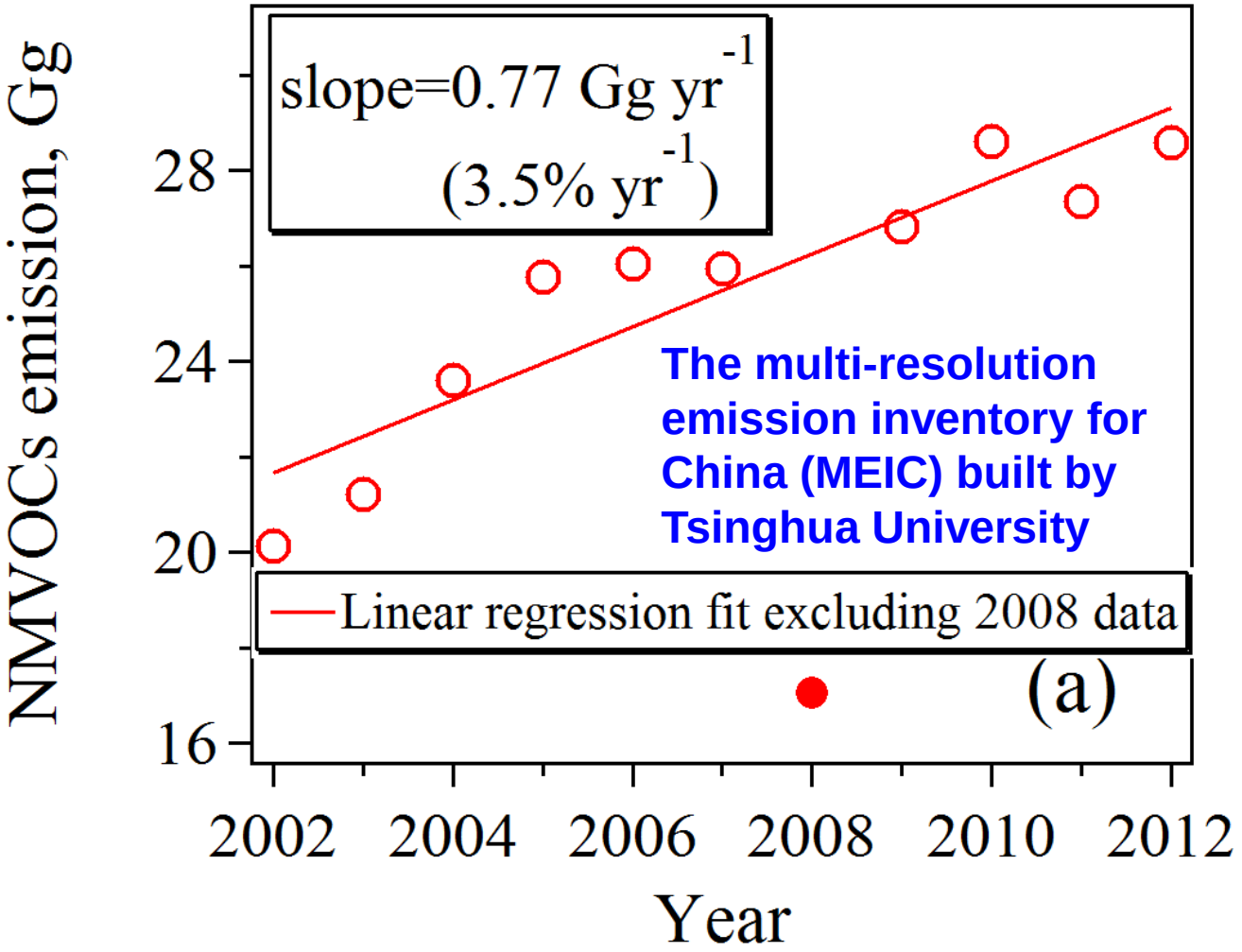


OFPs of total VOCs=1346 Gg O_3

- The total OFPs derived from measurements agreed relatively well with those calculated based on current inventories;
- However, the relative contributions of different VOC groups to the total OFPs showed significant differences. The relative contributions of OVOC were significantly lower in current emission inventories, whereas alkenes contributions were higher.

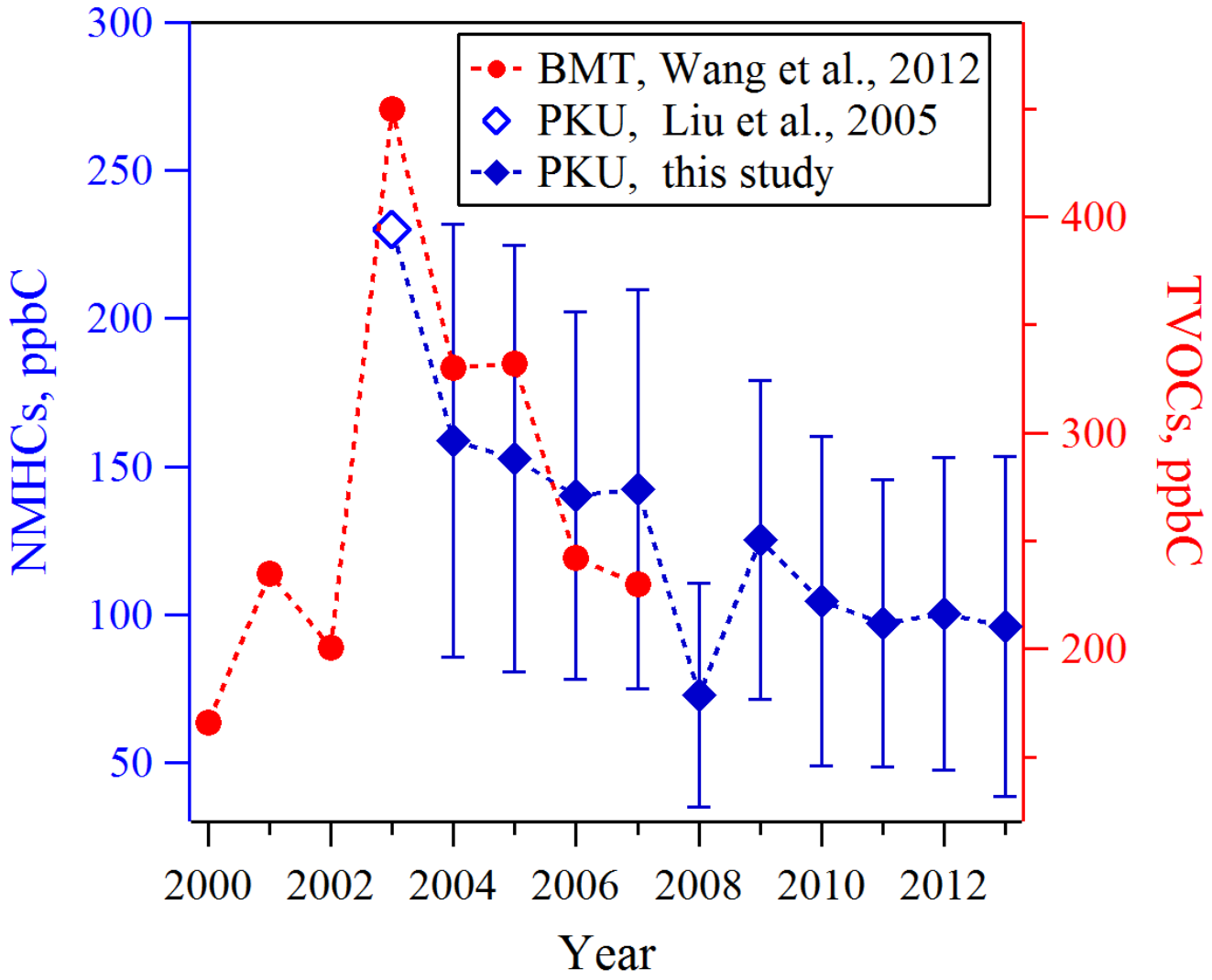
1. **Emission inventories**
2. **Emission ratios**
3. **Trend analysis: evaluate emission trends**

Anthropogenic VOCs emission in Beijing during 2002–2012



- **Anthropogenic VOCs emissions during August in Beijing increased by 35% between 2002 and 2012.**

However, the measured VOCs mixing ratios during August at urban sites of Beijing exhibited a decreasing trend from 2003.



- **This discrepancy of VOC temporal changes between measurements and the MEIC inventory suggests the possible uncertainties of VOC emission trends for one or more sources in this inventory.**

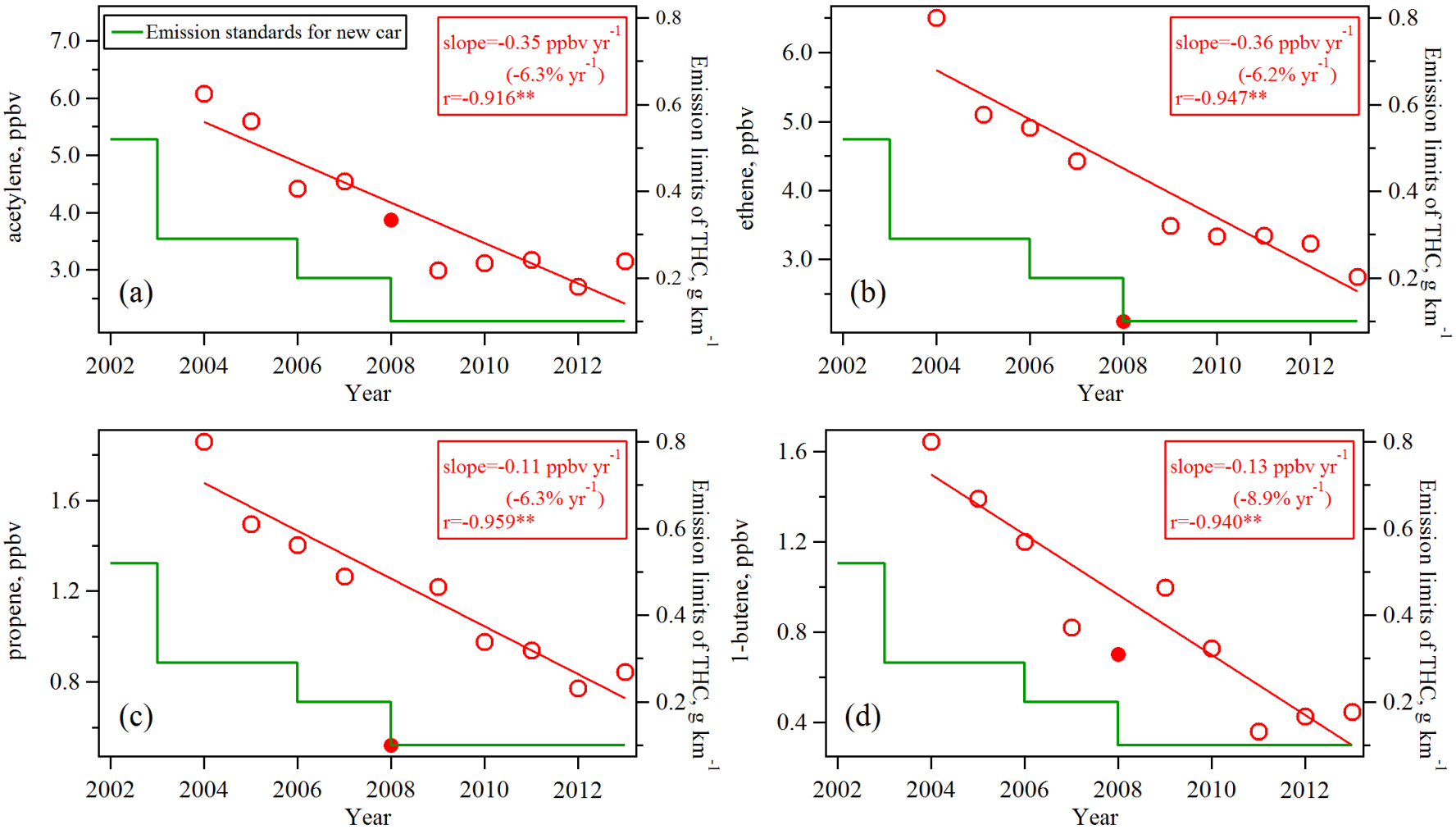
Major VOCs sources in Beijing

- Vehicle exhaust: alkenes and acetylene
- Gasoline evaporation: i-pentane
- Paint and Solvent use: BTEX
- Natural gas and liquefied petroleum gas use: ethane and propane

(Liu et al., 2005; Song et al., 2007; Wang et al., 2010; Shao et al., 2011; Yuan et al., 2012; Chen et al., 2014; Wang et al., 2014)

Vehicle exhaust

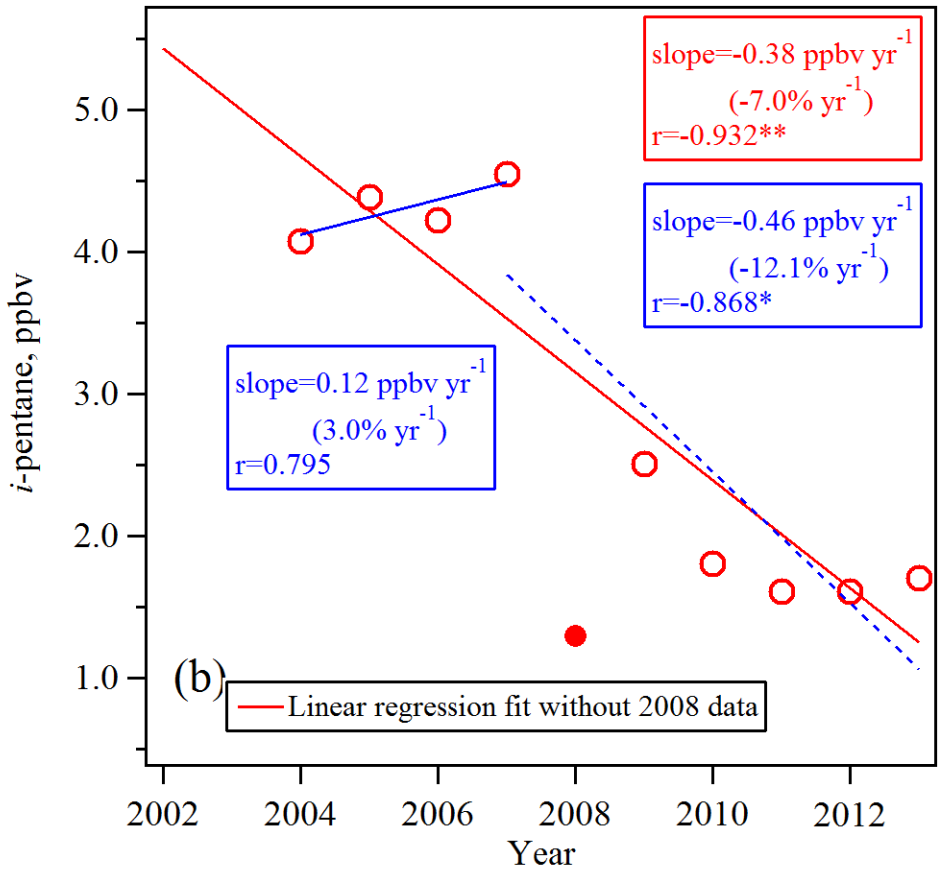
- Acetylene and alkenes are mainly emitted from vehicle exhaust (Parrish 2006; Wang et al., 2010; Shao et al., 2011)



2004-2013: acetylene, ethene, and propene decreased by ~60%

Gasoline evaporation

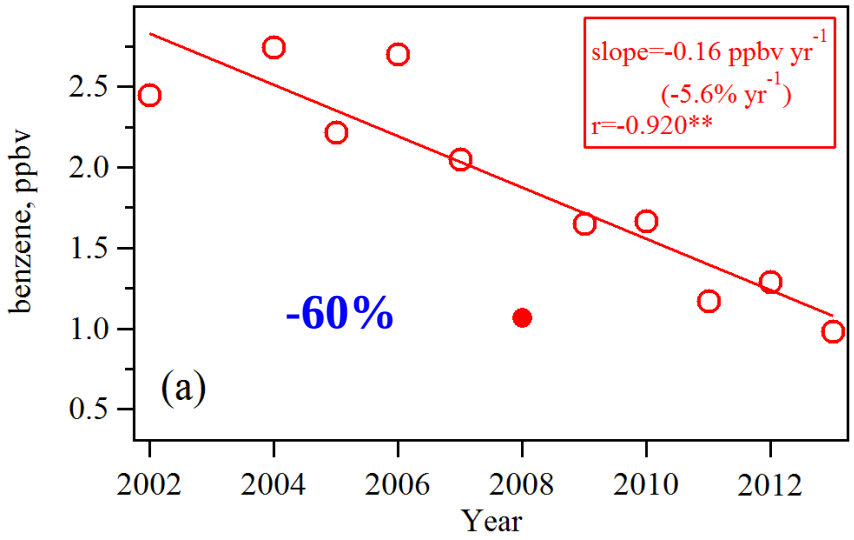
Besides vehicle exhaust, i-pentane can also be emitted from gasoline evaporation (Harely et al., 1998).

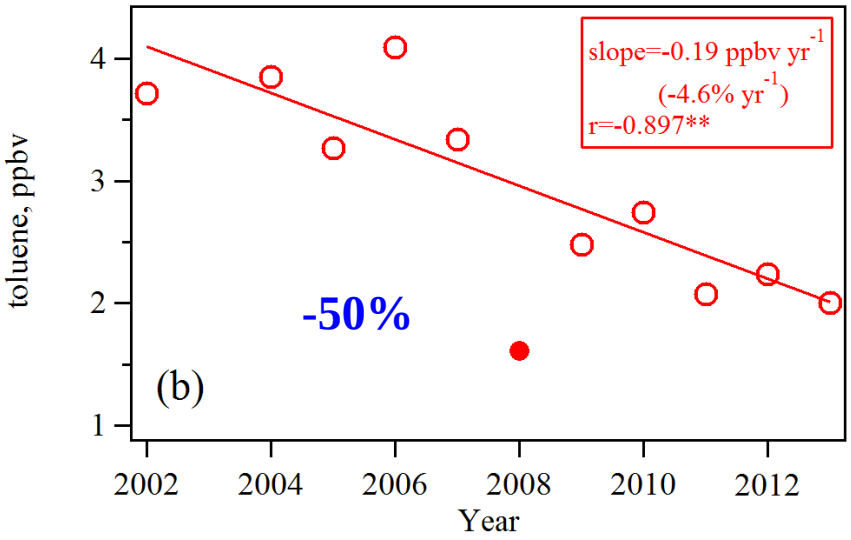


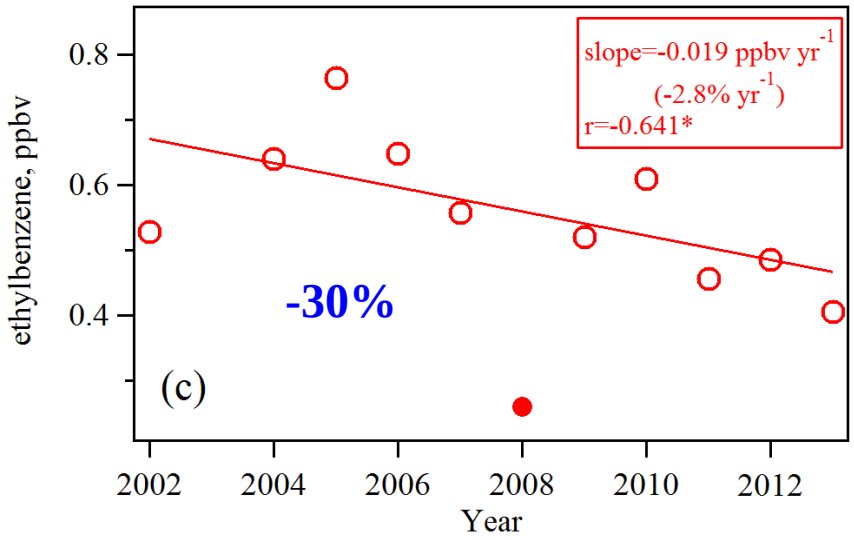
2004-2013: i-pentane decreased by ~60%

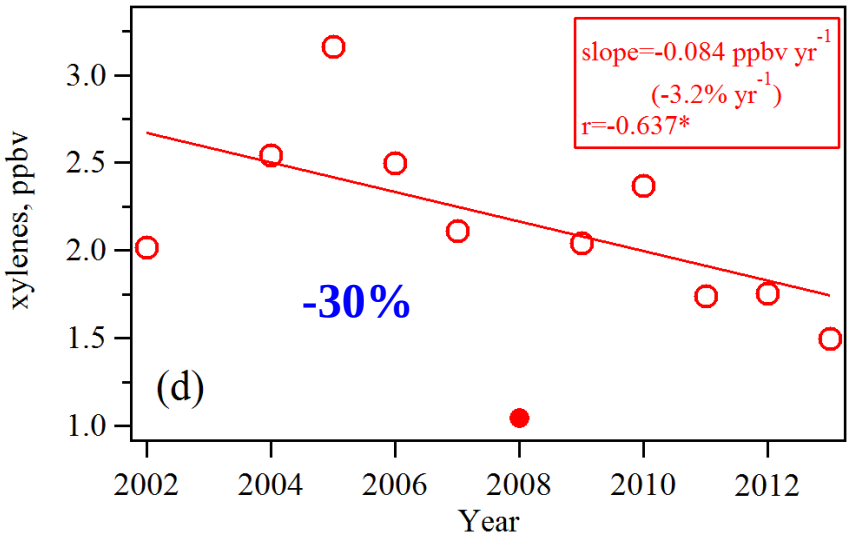
Paint & Solvent utilization

Toluene, ethylbenzene, and xylenes are important components of paint and solvent emissions (Yuan et al., 2010).

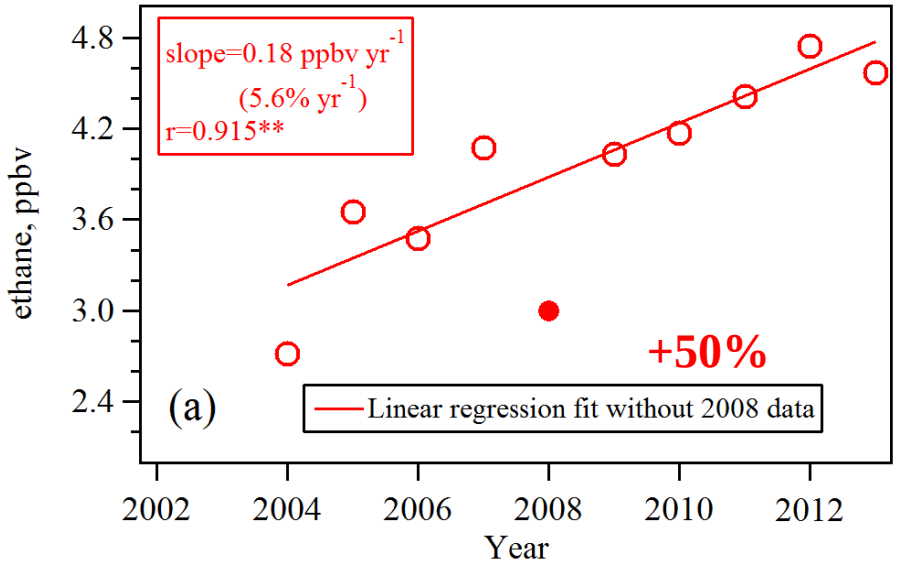


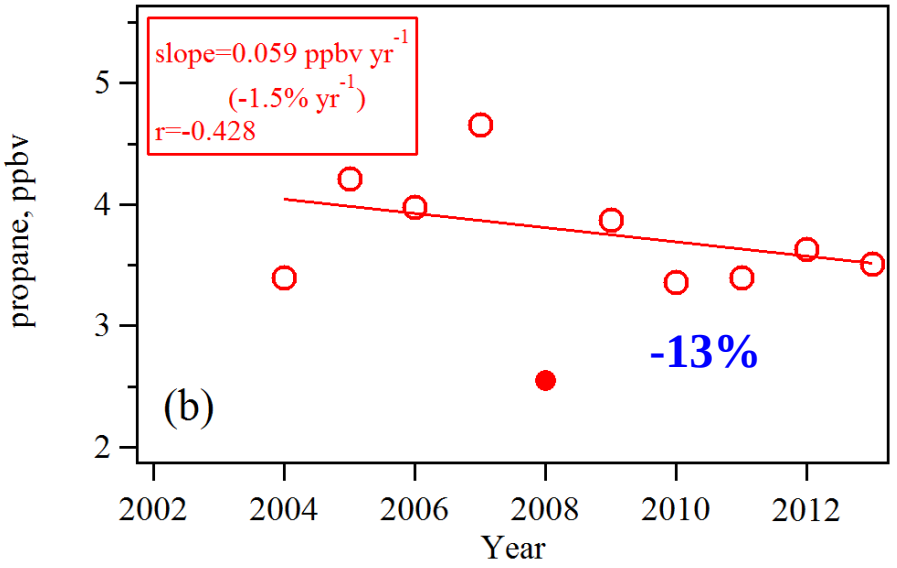






Natural Gas (NG) and Liquefied Petroleum Gasoline (LPG) usage





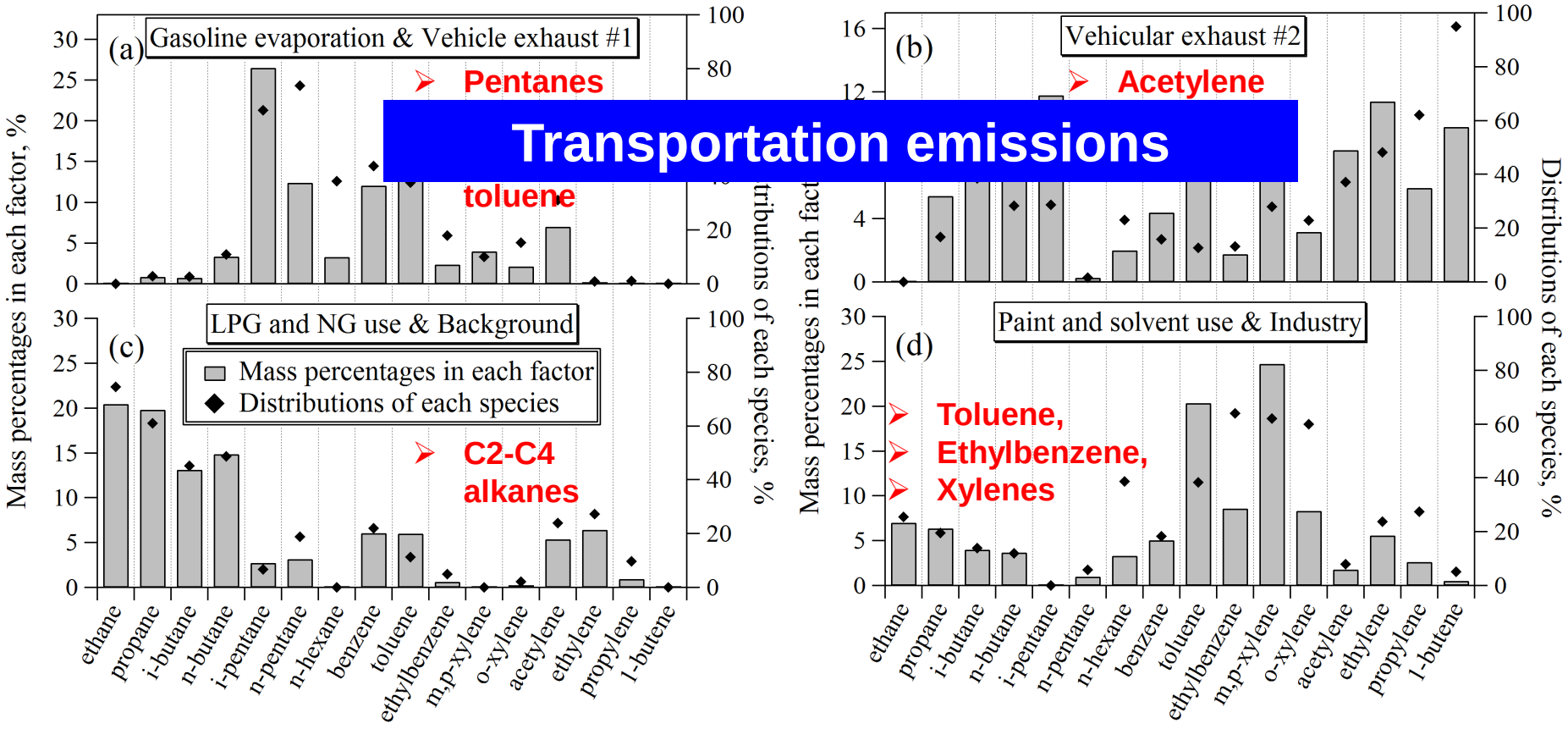
VOCs source apportionment by PMF

- EPA PMF 3.0
- 15 species

ethane	toluene
propane	*m,p*-xylene
i-butane	*o*-xylene
n-butane	acetylene
i-pentane	ethylene
n-pentane	propylene
n-hexane	1-butene
benzene	

- 4 factors
- 2004-2012 data

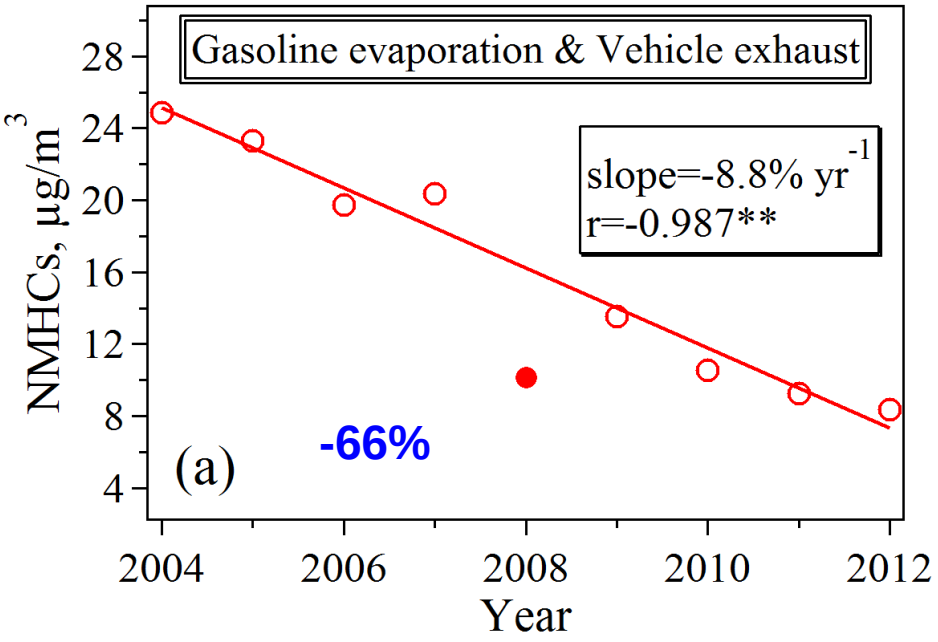
Four PMF factors were identified



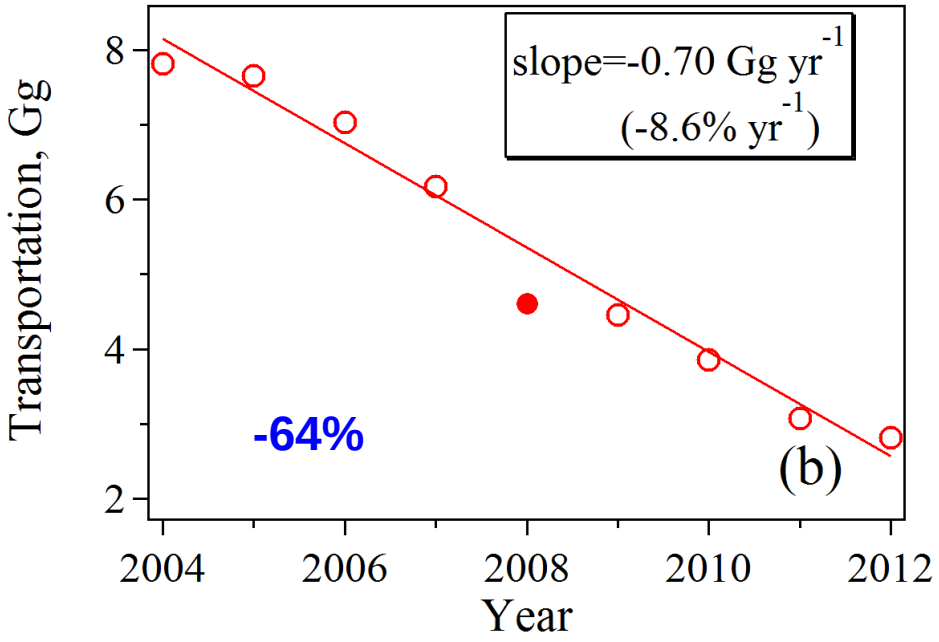
Transportation emissions

Transportation

NMHC concentrations from PMF



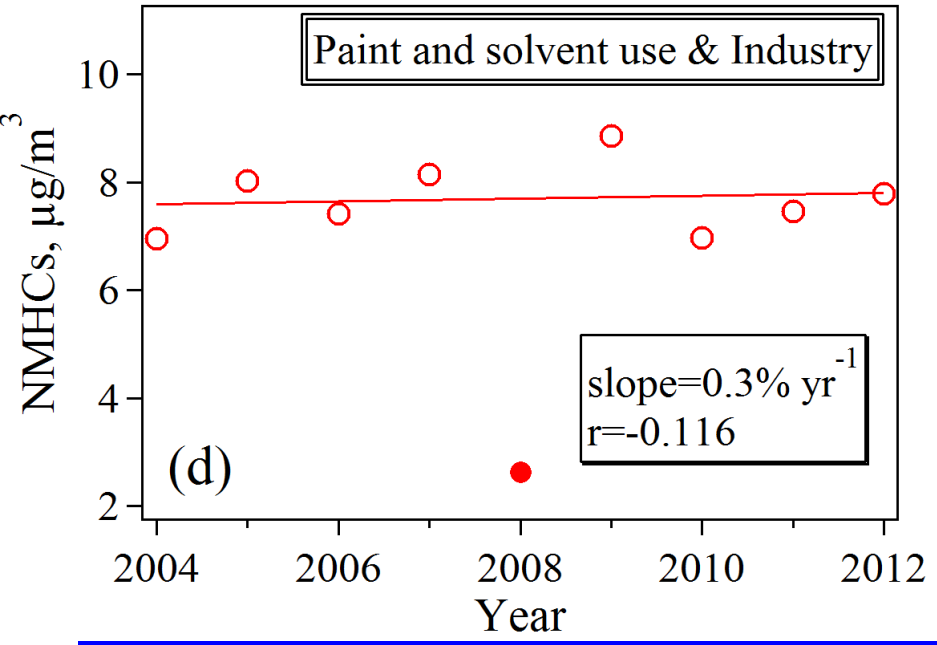
NMVOC emissions from MEIC



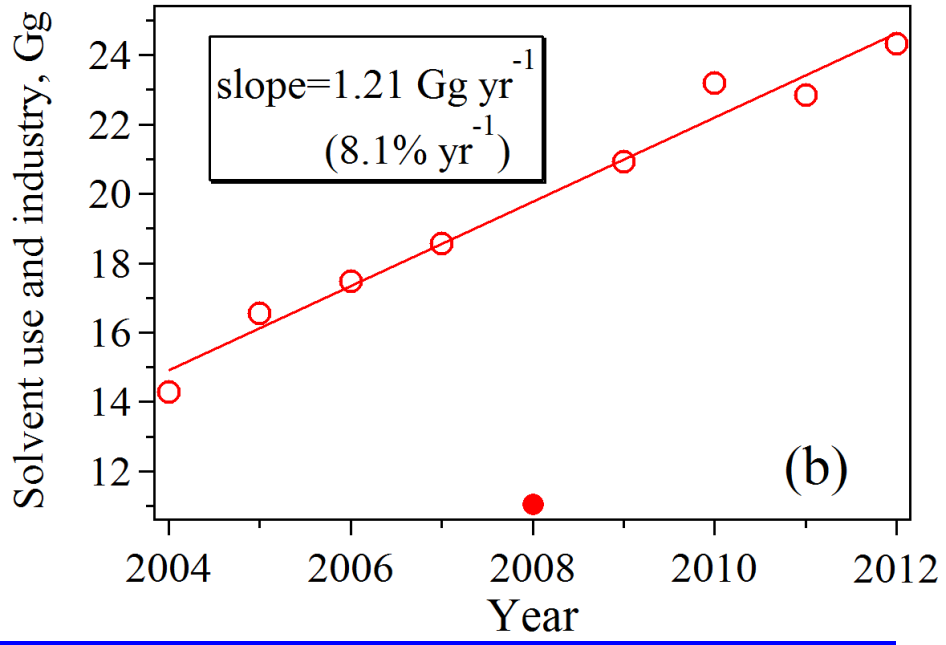
The PMF results suggested that the NMHC concentrations from transportation-related sources decreased by 66% between August 2004 and August 2012, which is close to the relative decline of 64% for transportation-related emissions during August in Beijing reported by the MEIC inventory.

Solvent and industry

NMHC concentrations from PMF



VOC emissions from MEIC



- The PMF results indicate that there were no significant temporal changes in NMHC concentrations during August from 2004 to 2012;
- However, the VOC emissions from solvent use and industry reported by the MEIC inventory increased by 65% between 2004 and 2012.

Summary and conclusions

- OVOC emissions were possibly underestimated by current inventories;
- VOC emissions form solvent use and industry showed large uncertainties;
- More studies are needed in the future to verify VOC emissions from solvent use and industry.

Atmos. Chem. Phys., 14, 5871–5891, 2014
www.atmos-chem-phys.net/14/5871/2014/
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A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China

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Trends of non-methane hydrocarbons (NMHC) emissions in Beijing during 2002–2013

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