Kudo et al., JGR-Atmos.

Emissions of NMVOCs from open crop residue burning in the Yangtze River Delta region, China

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Background & Focus

NMVOCs: Non-Methane Volatile Organic Compounds

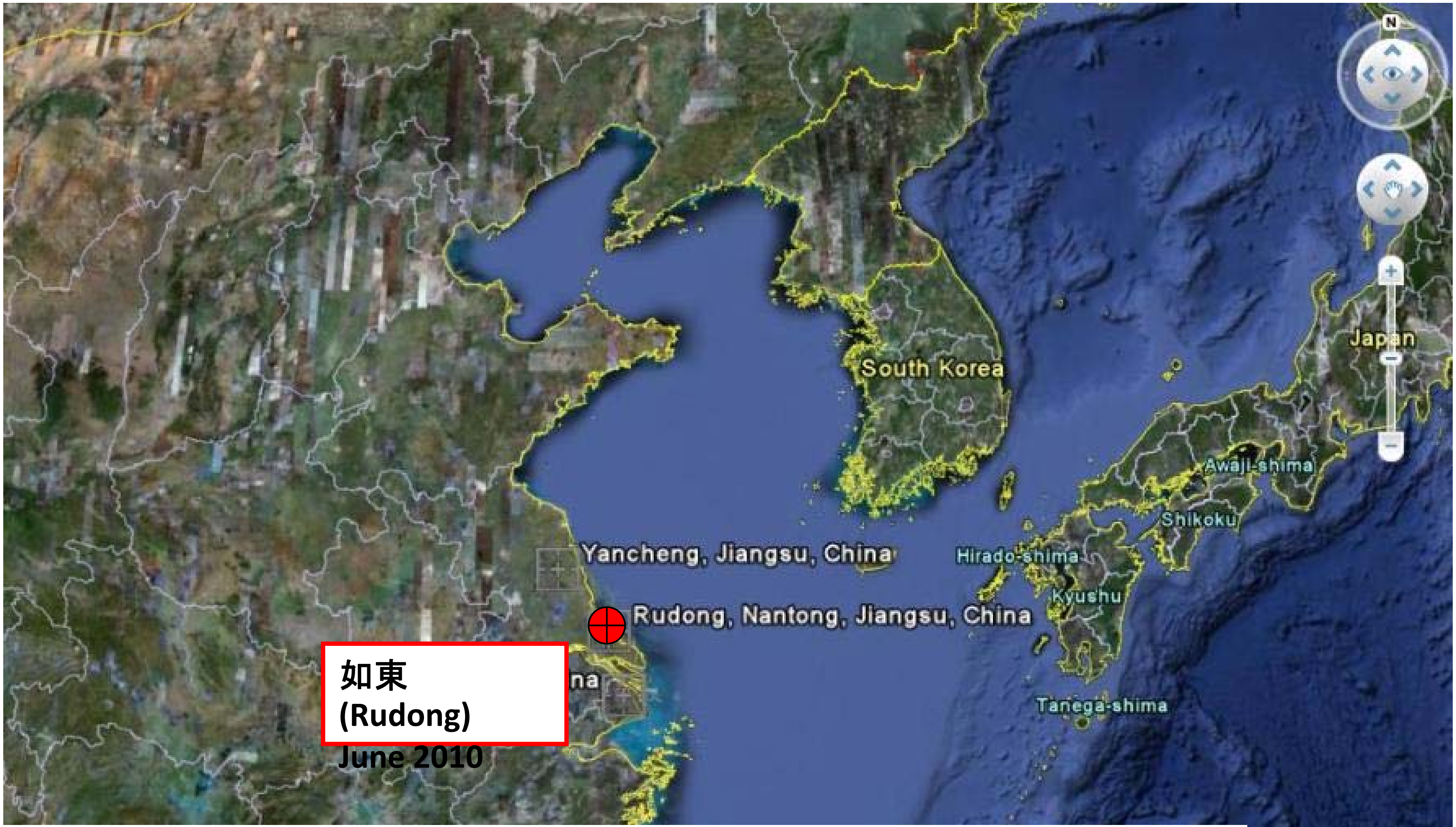
- Although NMVOCs play an important role in the formation of ozone and SOA, our understanding of the sources for individual NMVOC species is still poor, particularly in rapidly growing regions (e.g., Asia)

- Large uncertainty exists in "bottom-up" estimates of VOC emissions
  - Inventory is tougher to be built due to many speciation of VOCs
- "Top-down" approaches using satellite and/or in situ observations can help better constrain locations, speciation, and sectors of VOC emissions
  - Satellite data is limited to CO, NO_2, HCHO; observations near sources are needed

- Biomass Burning (BB) emissions occupied 23% of the total VOC emissions, and open burnings accounted for 24% of the total BB emissions in China in 2005 (Bo et al., 2008)

- We use field observations of NMVOCs near emission source regions as "top-down" constraints to derive emission factors (EFs), and thereby to estimate biome-specific emissions from open crop residue burning in China

Field campaign at Rudong, China



如東
(Rudong)
June 2010

- A rural site in Central East China, 100 km north of Shanghai
- May 14 – June 24, 2010
- Co-lead: Yugo Kanaya (JAMSTEC) & Zifa Wang (IAP)

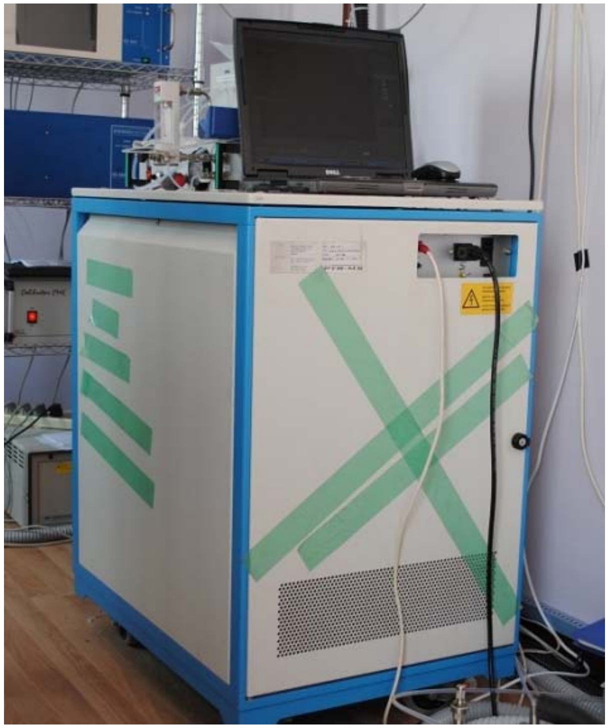
Comprehensive NMVOC measurements

1. GC/MS/FID (canister sampling & in situ)
   - high-precision, high selectivity for NMHCs
   - pre-concentration, poor time-resolution (hour)
2. PTR-MS
   - high time-resolution (min)
   - oxygenated-VOCs detectable

C2-C11 NMHCs: GC/FID (IAP)

C2-C9 NMHCs: GC/MS/FID

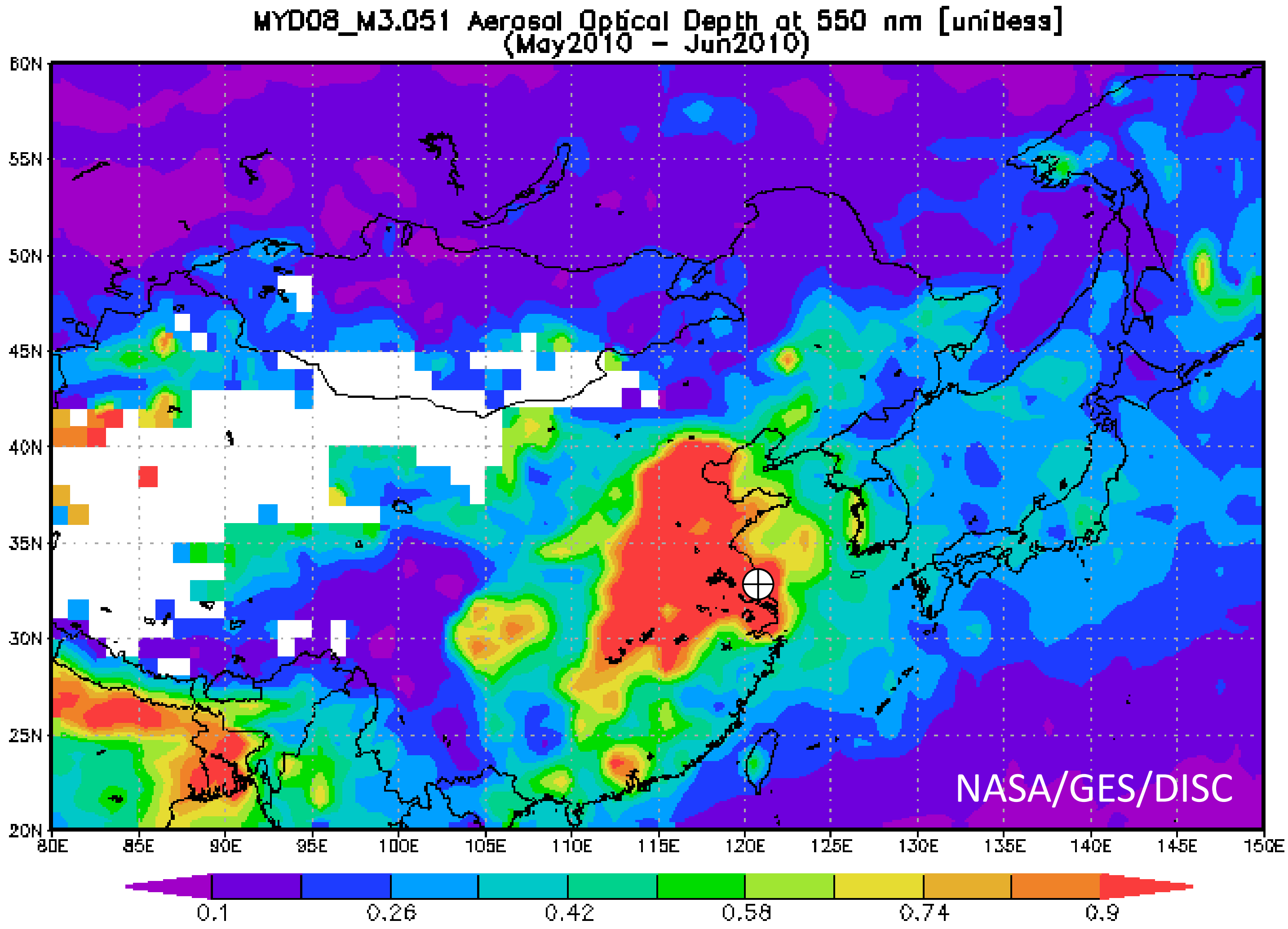
OVOCs: PTR-MS



Other measurements

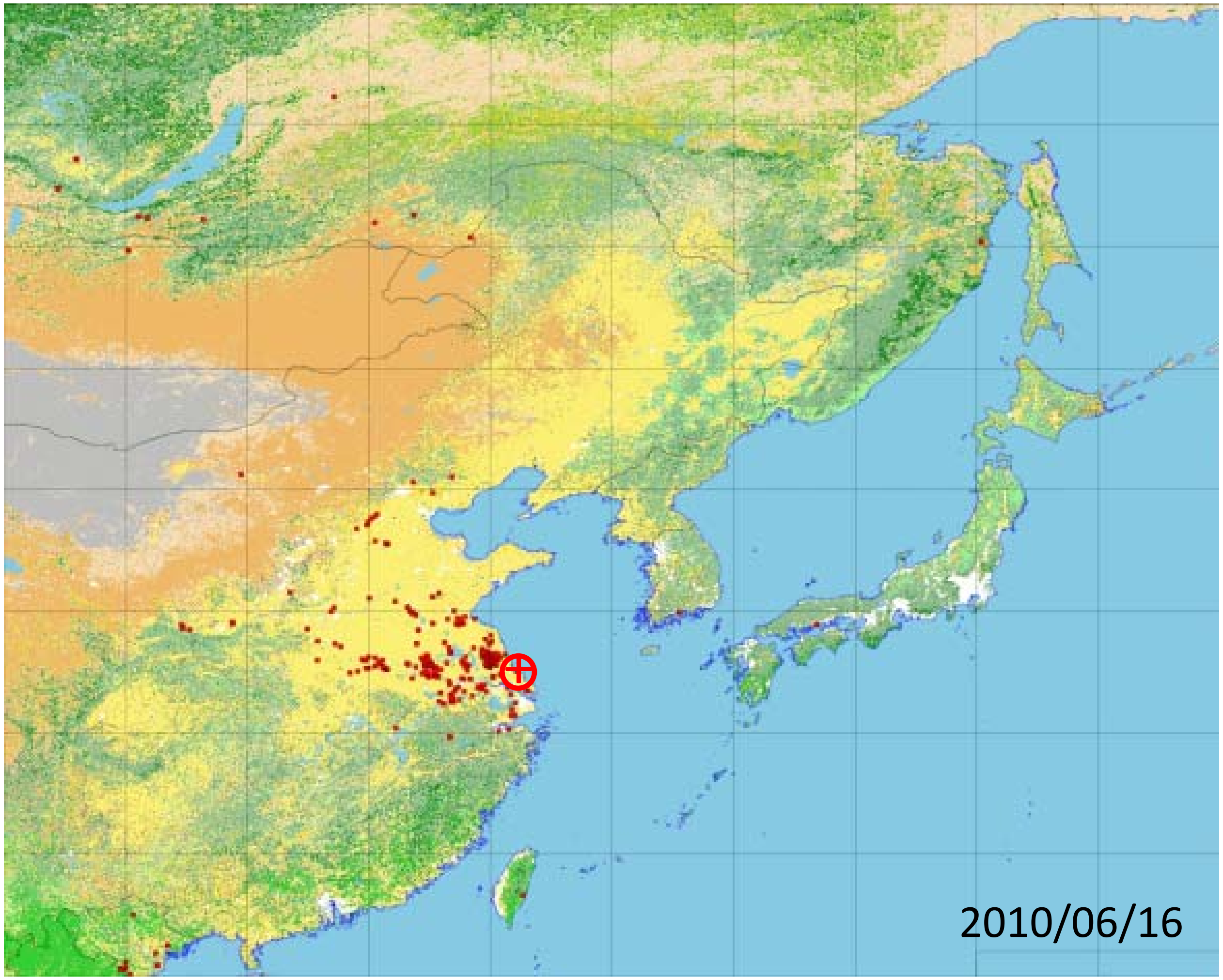
Observed Parameters	**Organization**	**Instrument**
Ozone	JAMSTEC	Thermo 49C
CO	JAMSTEC	Thermo 48C
NO/NO2/NOy	NIES	Thermo 42CTL mod + BLC/Mo converters
VOC, OVOCs	NIES	PTR-MS
NMHCs (fast)	IAP	GC/FID/PID
NMHCs (slow but accurate)	NIES	GC/MS/FID
J values	JAMSTEC	spectroradiometer
CH4, CO2	NIES	Picarro G1301 analyzer
SO2	IAP	Thermo 43C/ 43i
PM2.5 mass conc.	JAMSTEC	Thermo SHARP5030
PM2.5 mass conc.	IAP	TEOM
BC	NIES	Kanomax BCM (COSMOS)
BC	IAP/JAMSTEC	Thermo MAAP5012
ECOC	JAMSTEC	Sunset semi-continuous ECOC analyzer
SO4, NO3, Cl, NH4, Na, Ca, metals, organics, reactivity	JAMSTEC	High vol air sampler/ion chromatograph/ICP-AES
Major ions etc.	IAP	Low vol samplers, PM2.5/PM10
Aerosol size distribution	JAMSTEC	RION KR12A (0.3,0.5,0.7,1,2,5um)
Aerosol size distribution	CRAES	TSI EEPS3090 (5.6nm~560nm)
Aerosol size distribution	CRAES	TSI APS3321 (0.5~20 µm)
Scattering coefficient and its RH dependence	JAMSTEC	Radiance Research, Integrating nephelometer, M903
NO2, aerosol, and other gases (HCHO, etc.)	JAMSTEC	MAX-DOAS
Positive/negative ions	JAMSTEC	
T, RH, P, wind	IAP	

MODIS Aerosol Optical Depth in May-June 2010



- Mixed influence from anthropogenic & biomass burning sources
- PMF was applied to get better estimates of BB contribution

Land-cover type & fire spots



2010/06/16

IIS, Univ. Tokyo

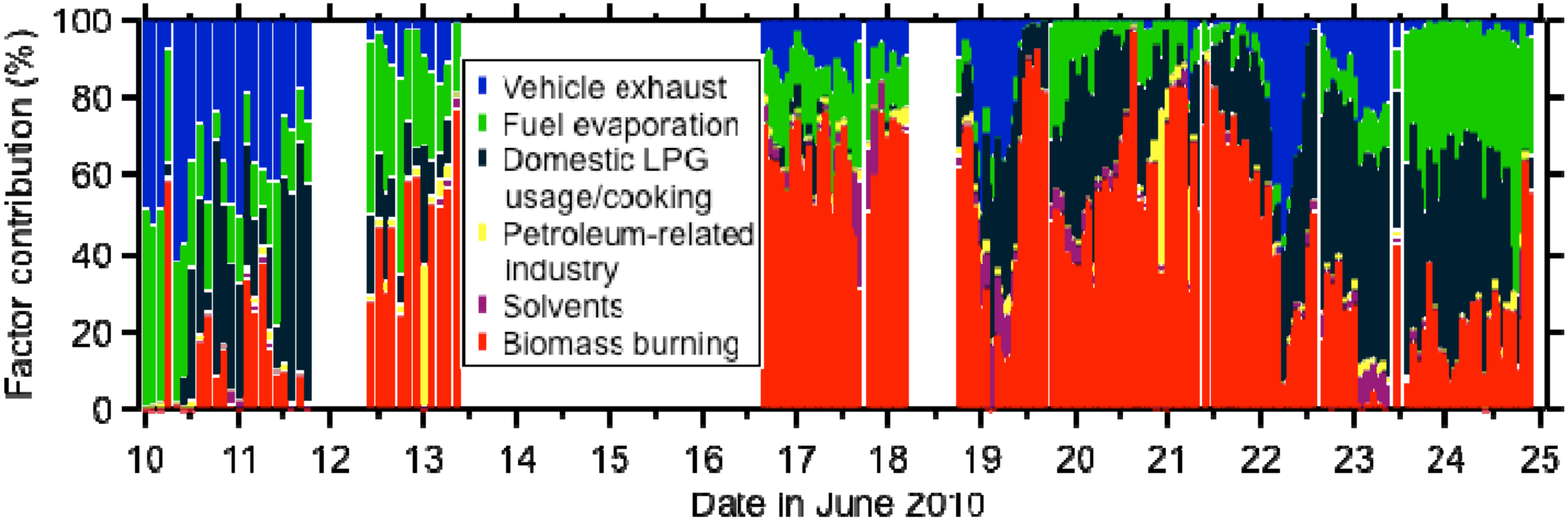
- The site is in croplands of the YRD region
- Approx. 300 fire counts/day were detected by MODIS

Are “all” crop burnings seen from space?

- Some crop burnings are too small to be detected from space
- Fire activities are likely under-sampled by MODIS, particularly under continued hazy sky conditions

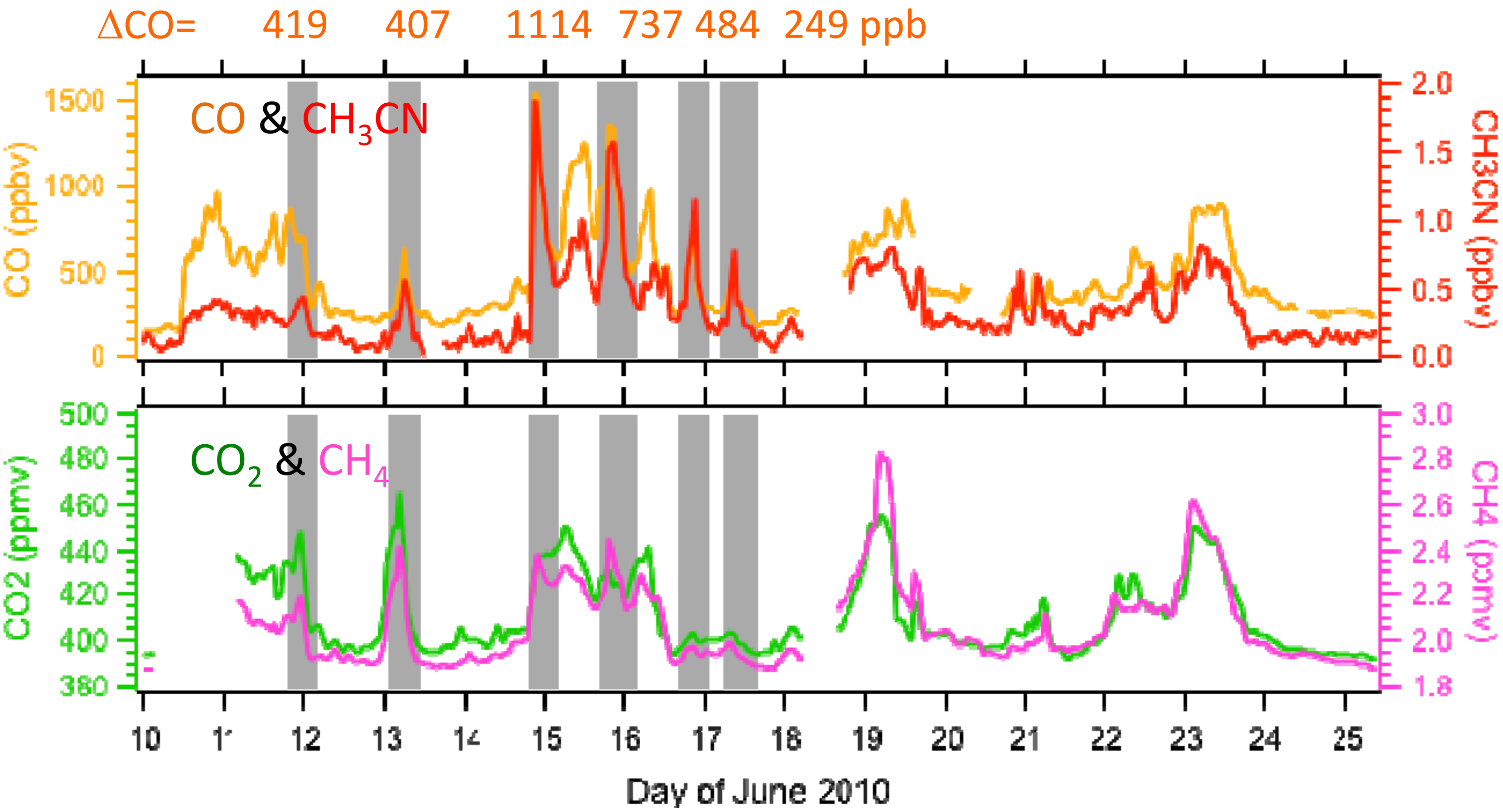
Source contributions by PMF

PMF: Positive Matrix Factorization



- Contribution from BB factor was generally dominant, 40% on average
- The contributions from domestic LPG usage/cooking (24%), fuel evaporation (17%), and vehicle exhaust (13%) were also substantial
- The BB contribution was more than 60% during 13-21th June

BB tracers & Combustion Efficiency

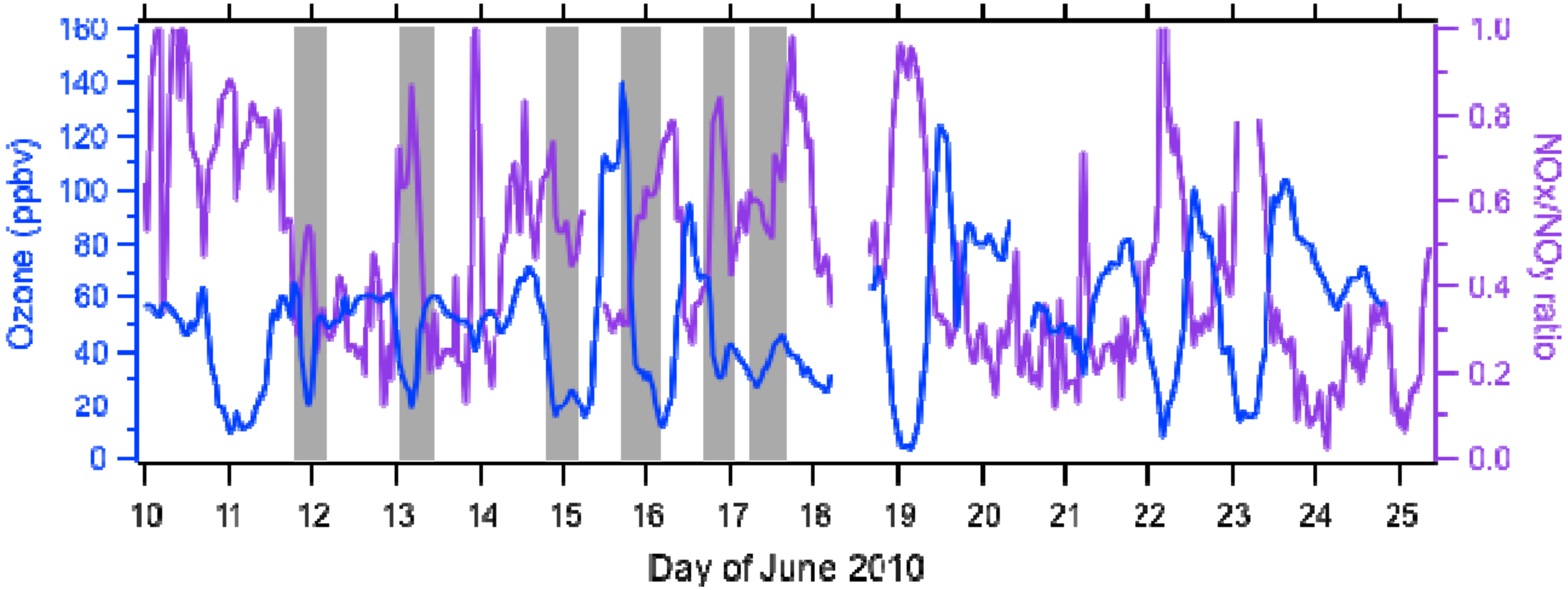


Modified Combustion Efficiency (MCE) = $\Delta CO_2/(\Delta CO_2 + \Delta CO)$

- Relative abundance of flaming & smoldering combustion
  - Flaming: >0.99
  - Smoldering: 0.65–0.85 (most often ~0.8)

How fresh were the fire plumes?

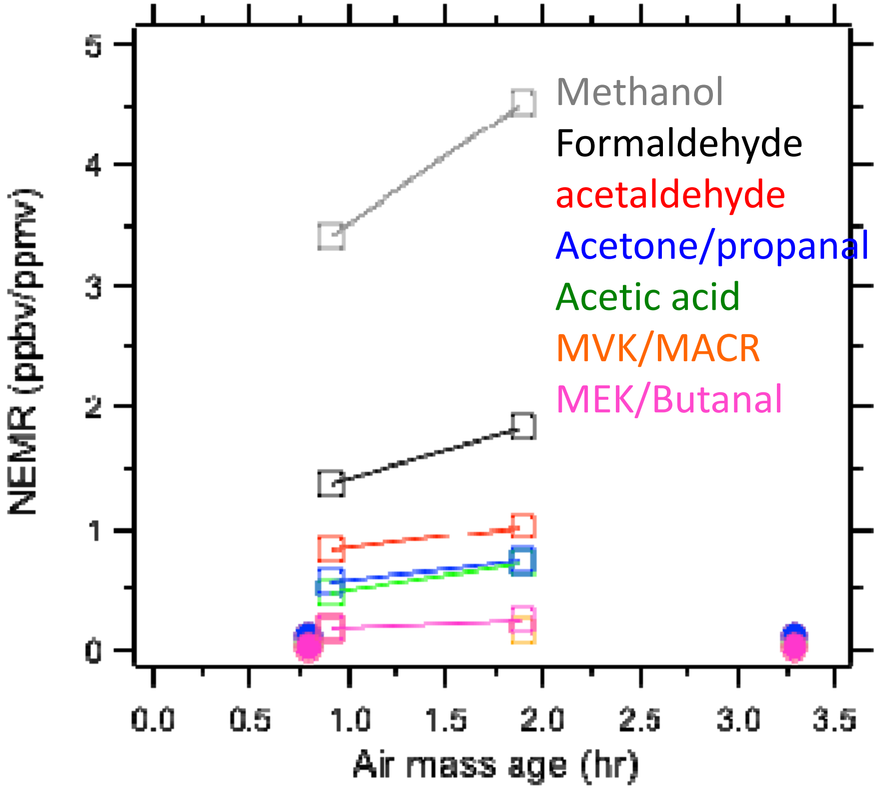
NOx/NOy= 0.54 0.87 0.74 0.70 0.84 0.59

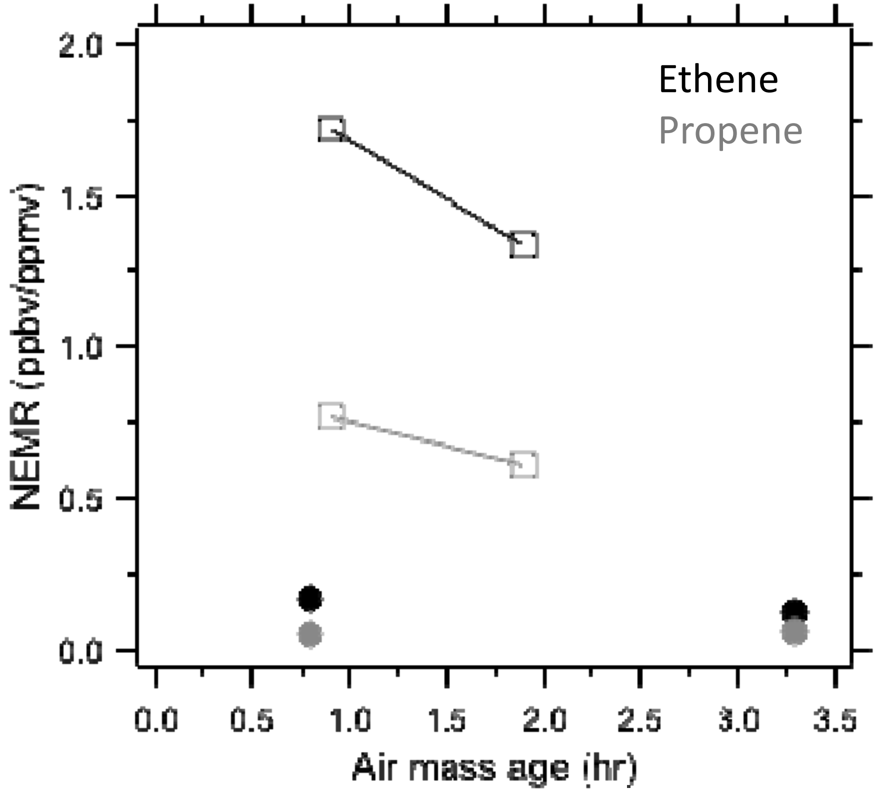


- “Freshness” is critical to obtain “accurate” EF for reactive species
- Ozone is depleted, indicating fresh plumes
- “Air mass age” is determined by NO_2+OH→HNO_3 (k=2.58 × 10^{-11}, OH=2x10^6), to be 0.8-3.3 h, which corresponds to distance of 10-20 km from sources

Smoke plume chemistry affects NMVOCs

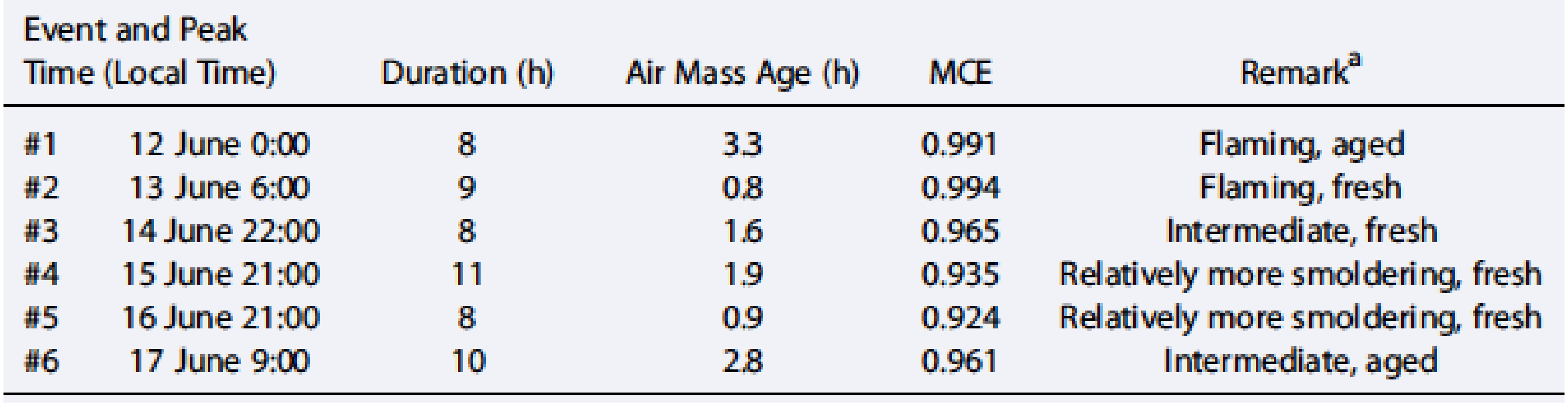
NEMR: Normalized Excess Mixing Ratio





- Enhancement shows dependence on air mass age even in fresh smoke plumes
- During plume evolution OVOCs are rapidly produced, alkenes are rapidly lost
- Intercept values (at time = 0) are taken for EF calculation

Emission factor from fresh events



Event and Peak Time (Local Time)	Duration (h)	Air Mass Age (h)	MCE	Remark[a]
#1 12 June 0:00	8	3.3	0.991	Flaming, aged
#2 13 June 6:00	9	0.8	0.994	Flaming, fresh
#3 14 June 22:00	8	1.6	0.965	Intermediate, fresh
#4 15 June 21:00	11	1.9	0.935	Relatively more smoldering, fresh
#5 16 June 21:00	8	0.9	0.924	Relatively more smoldering, fresh
#6 17 June 9:00	10	2.8	0.961	Intermediate, aged

- Plumes were observed during night for short duration
- Overall fire-integrated MCE near 0.9 suggests roughly equal amounts of biomass consumption by flaming & smoldering
- EF was calculated for “fresh (<2h)” plumes

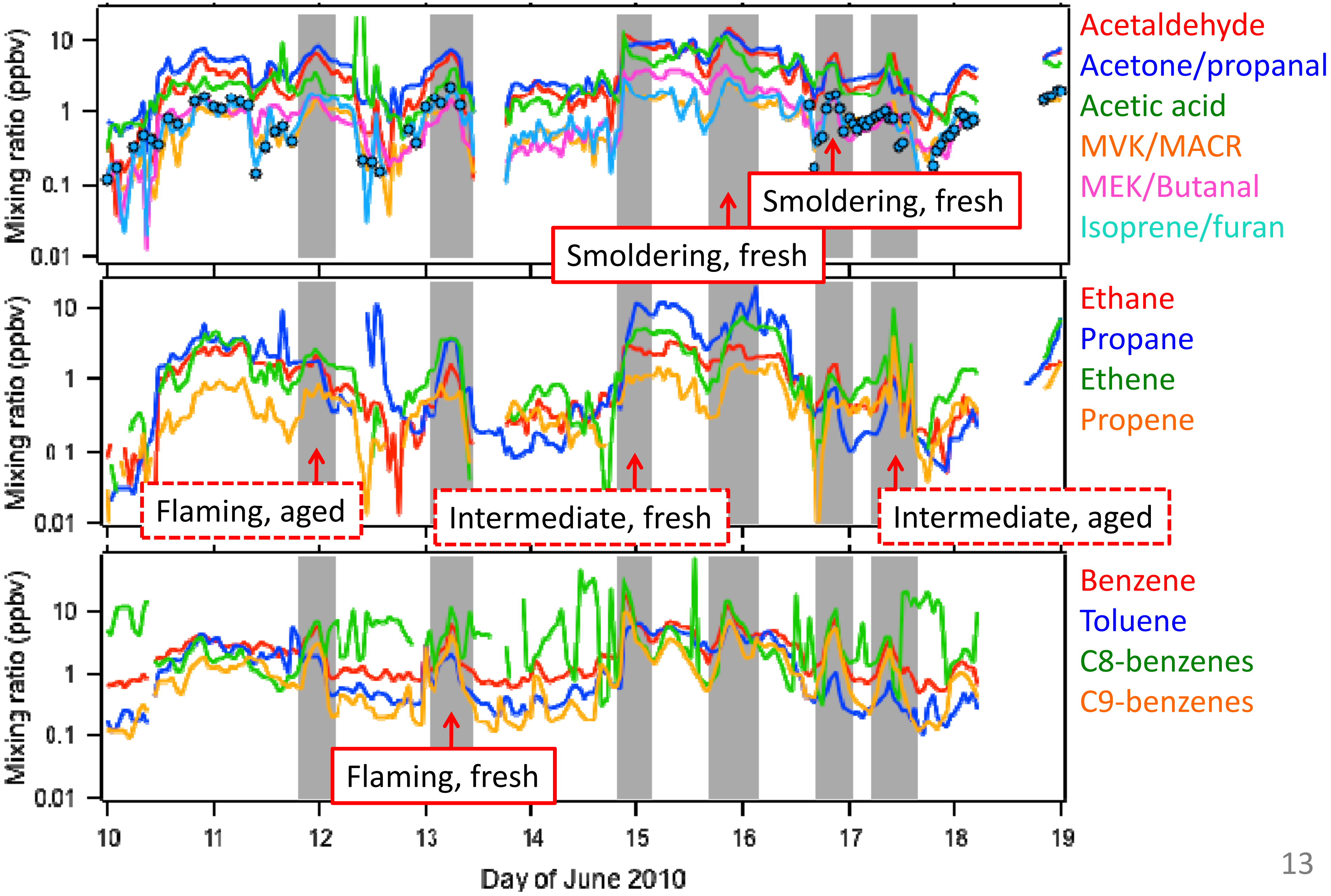
Emission Factor (EF) - based on C mass balance

Yokelson et al. 1999

$$EF_X \text{ (g/kg)} = F_C * 1000 \text{ (g/kg)} * MM_X \text{ (g)}/MM_C \text{ (g)} * C_X/C_{total}$$

$$C_X/C_{total} = \Delta C_X / \Delta CO_2 / \Sigma(nC_Y \times \Delta C_Y/\Delta CO_2)$$

Variations of NMVOCs



Smoldering, fresh

Smoldering, fresh

Flaming, aged

Intermediate, fresh

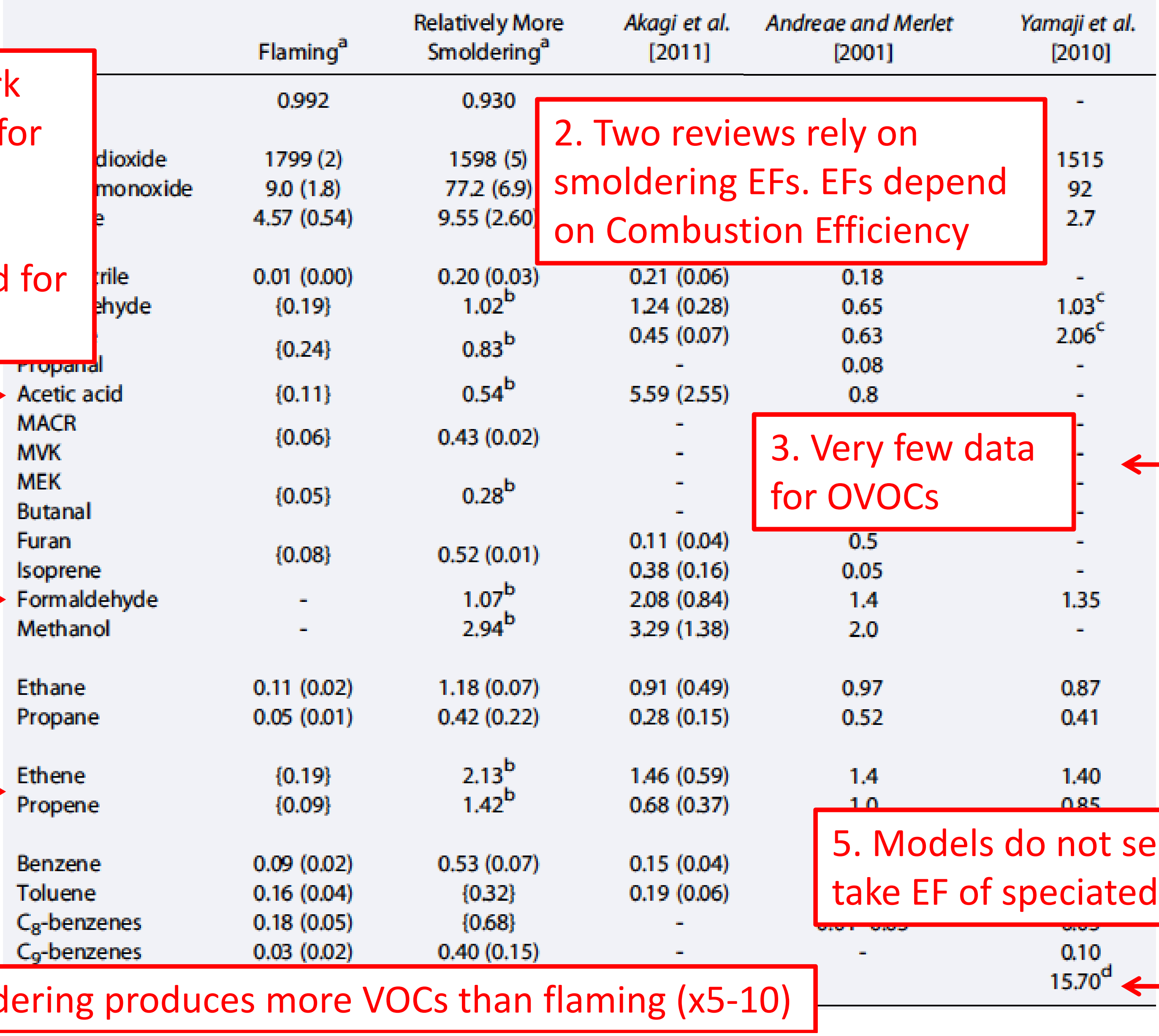
Intermediate, aged

Flaming, fresh

Emission factors of NMVOCs

This work *Reviews* *Model*

4. Previous work overestimated for acetic acid & formaldehyde, underestimated for alkenes



	Flaming[a]	Relatively More Smoldering[a]	*Akagi et al.* [2011]	*Andreae and Merlet* [2001]	*Yamaji et al.* [2010]
	0.992	0.930			-
dioxide	1799 (2)	1598 (5)			1515
monoxide	9.0 (1.8)	77.2 (6.9)			92
e	4.57 (0.54)	9.55 (2.60)			2.7
rile	0.01 (0.00)	0.20 (0.03)	0.21 (0.06)	0.18	-
ehyde	{0.19}	1.02[b]	1.24 (0.28)	0.65	1.03[c]
	{0.24}	0.83[b]	0.45 (0.07)	0.63	2.06[c]
Propanal			-	0.08	-
Acetic acid	{0.11}	0.54[b]	5.59 (2.55)	0.8	-
MACR	{0.06}	0.43 (0.02)	-		-
MVK			-		-
MEK	{0.05}	0.28[b]	-		-
Butanal			-		-
Furan	{0.08}	0.52 (0.01)	0.11 (0.04)	0.5	-
Isoprene			0.38 (0.16)	0.05	-
Formaldehyde	-	1.07[b]	2.08 (0.84)	1.4	1.35
Methanol	-	2.94[b]	3.29 (1.38)	2.0	-
Ethane	0.11 (0.02)	1.18 (0.07)	0.91 (0.49)	0.97	0.87
Propane	0.05 (0.01)	0.42 (0.22)	0.28 (0.15)	0.52	0.41
Ethene	{0.19}	2.13[b]	1.46 (0.59)	1.4	1.40
Propene	{0.09}	1.42[b]	0.68 (0.37)	1.0	0.85
Benzene	0.09 (0.02)	0.53 (0.07)	0.15 (0.04)		
Toluene	0.16 (0.04)	{0.32}	0.19 (0.06)		
C_8-benzenes	0.18 (0.05)	{0.68}	-		
C_9-benzenes	0.03 (0.02)	0.40 (0.15)	-	-	0.10
					15.70[d]

2. Two reviews rely on smoldering EFs. EFs depend on Combustion Efficiency

3. Very few data for OVOCs

5. Models do not seriously take EF of speciated VOC

1. Smoldering produces more VOCs than flaming (x5-10)

Annual emissions of NMVOCs

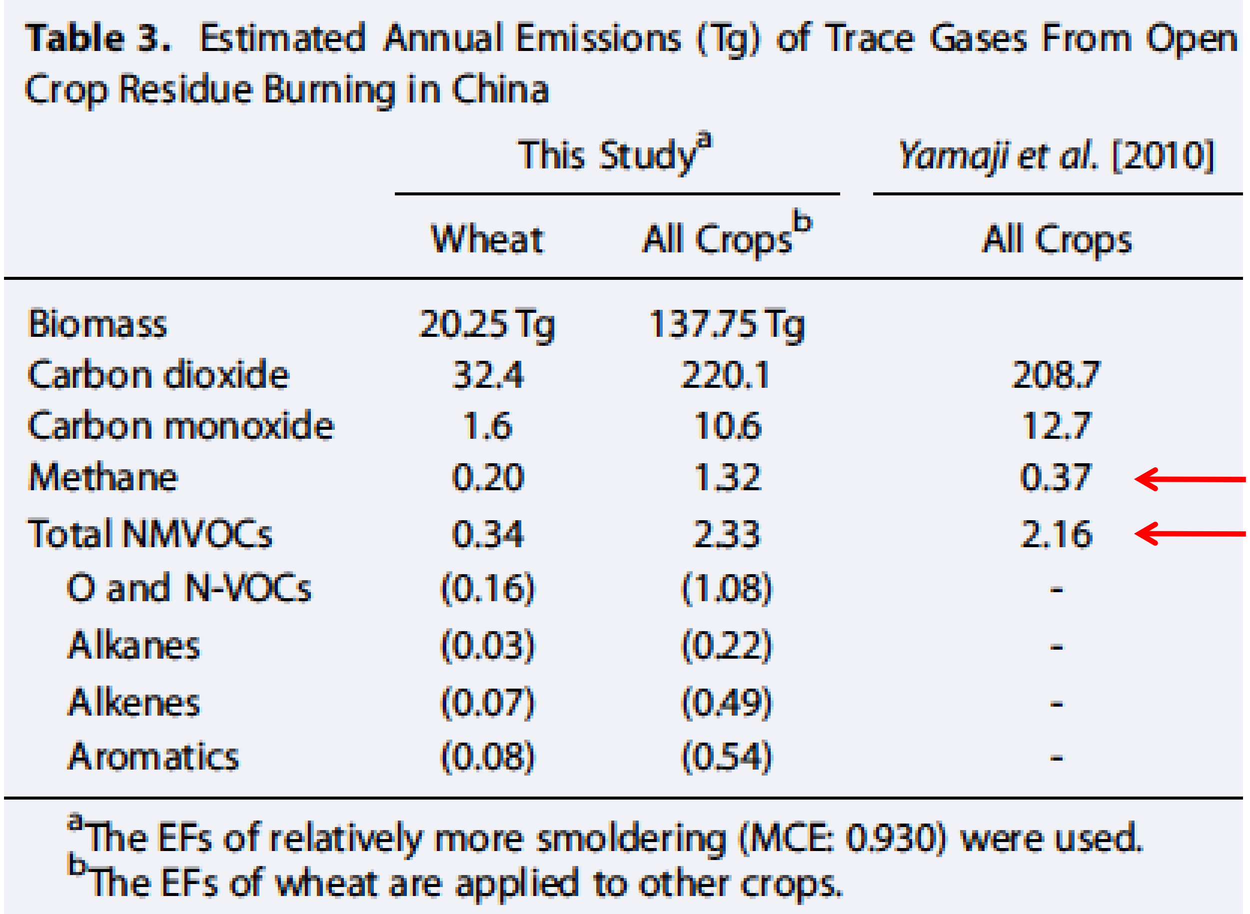


Table 3. Estimated Annual Emissions (Tg) of Trace Gases From Open Crop Residue Burning in China

	This Study[a]		*Yamaji et al.* [2010]
	Wheat	All Crops[b]	All Crops
Biomass	20.25 Tg	137.75 Tg	
Carbon dioxide	32.4	220.1	208.7
Carbon monoxide	1.6	10.6	12.7
Methane	0.20	1.32	0.37
Total NMVOCs	0.34	2.33	2.16
O and N-VOCs	(0.16)	(1.08)	-
Alkanes	(0.03)	(0.22)	-
Alkenes	(0.07)	(0.49)	-
Aromatics	(0.08)	(0.54)	-

[a] The EFs of relatively more smoldering (MCE: 0.930) were used.
[b] The EFs of wheat are applied to other crops.

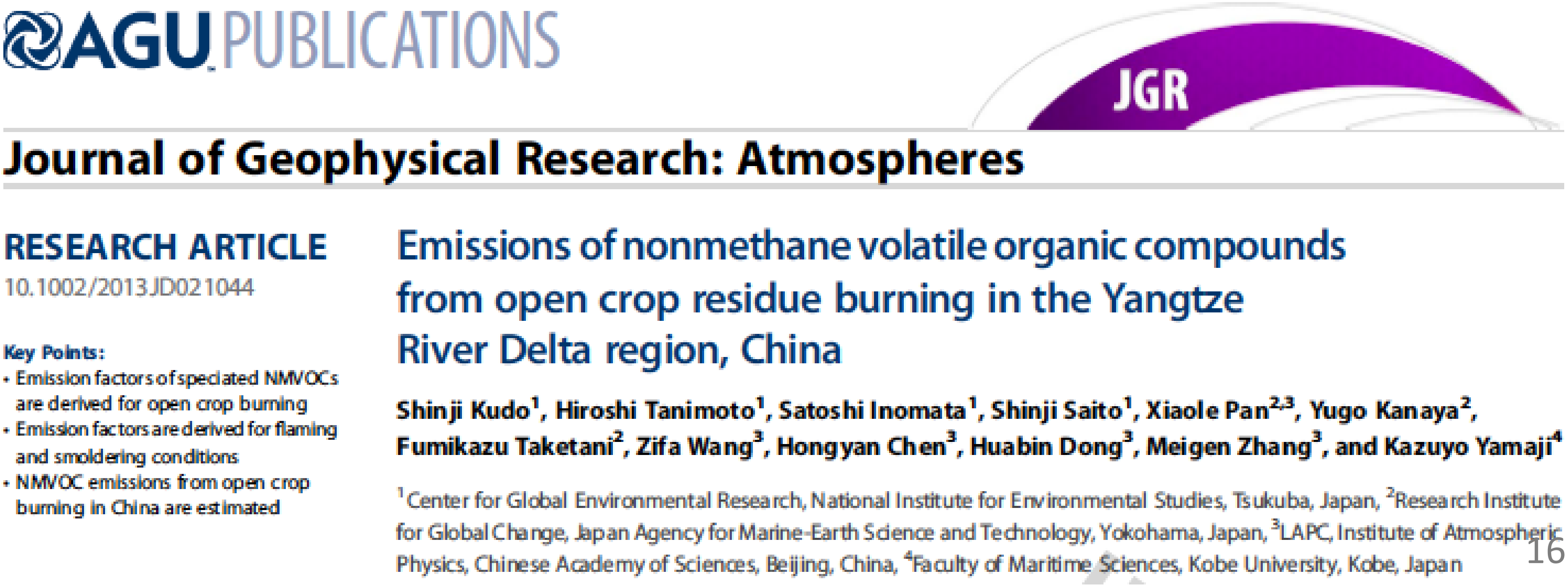
x4

comparable

- Burning of wheat residue in China releases about 0.34 Tg NMVOCs annually
- If the same EFs are applied to all crops, the annual emissions would be 2.3 Tg

Summary

- EFs of speciated NMVOCs are determined for wheat burning
- EFs are different between smoldering and flaming - MCE is a key factor
- These EFs act as additional contribution to improve the BB inventories
- Other crops need to be tested to achieve biome-specific EFs
- Time & area-averaged MCE in intensive BB regions in Asia is needed



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Key Points:

- Emission factors of speciated NMVOCs are derived for open crop burning
- Emission factors are derived for flaming and smoldering conditions
- NMVOC emissions from open crop burning in China are estimated

Emissions of nonmethane volatile organic compounds from open crop residue burning in the Yangtze River Delta region, China

Shinji Kudo[1], Hiroshi Tanimoto[1], Satoshi Inomata[1], Shinji Saito[1], Xiaole Pan[2,3], Yugo Kanaya[2], Fumikazu Taketani[2], Zifa Wang[3], Hongyan Chen[3], Huabin Dong[3], Meigen Zhang[3], and Kazuyo Yamaji[4]

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