Laboratory measurements of emission factors of nonmethane volatile organic compounds from burning of Chinese crop residues

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Key Points

- EFs of VOCs from Chinese crop residue burning were measured in laboratory experiments
- EFs from the burning of both dry and wet samples were determined
- Residual moisture in crop residues suppressed VOC emissions from the burning

Abstract

The emission factors (EFs) of non-methane volatile organic compounds (NMVOCs) emitted during the burning of Chinese crop residue were investigated as a function of modified combustion efficiency (MCE) in laboratory experiments. NMVOCs, including acetonitrile, aldehydes/ketones, furan, and aromatic hydrocarbons, were monitored by proton-transfer-reaction mass spectrometry (PTR–MS). Rape plant was burned in dry conditions and wheat straw was burned in both wet and dry conditions to simulate the possible burning of damp crop residue in regions of high temperature and humidity. We compared the present data to field data reported by *Kudo et al.* [2014]. Good agreement between field and laboratory data was obtained for aromatics under relatively more smoldering combustion of dry samples, but laboratory data were slightly overestimated compared to field data for oxygenated VOC (OVOC). When EFs from the burning of wet samples were investigated, the consistency between the field and laboratory data for OVOCs was stronger than for dry samples. This may be caused by residual moisture in crop residue that has been stockpiled in humid regions. Comparison of the wet laboratory data with field data suggests that *Kudo et al.* [2014] observed the biomass burning plumes under relatively more smoldering conditions in which approximately a few tens of percentages of burned fuel materials were wet.

Introduction

Biomass Burning (BB)

- ✓ The largest source of primary carbonaceous particles
  - *… affecting visibility, global climate, and human health*
- ✓ The second largest source of trace gases
  - NMVOCs ➡ *photochemical O_3, SOA formation*

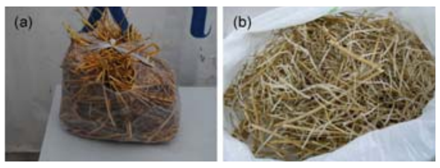
Central East China (CEC)

- ✓ Highly polluted area in Asia
- ✓ Large-scale burning of crop residues
  - Wheat straw burning in May/June
  - Rice straw burning in October

Field Measurement of NMVOCs

- **Location:** Rudong town
  - *…rural site, 100 km north of Shanghai*
- **Period:** June 2010
- BB plumes were often measured
  - *…grey areas in Figure 2*
- Typical crop residues:

Wheat Straw | Rape Plant



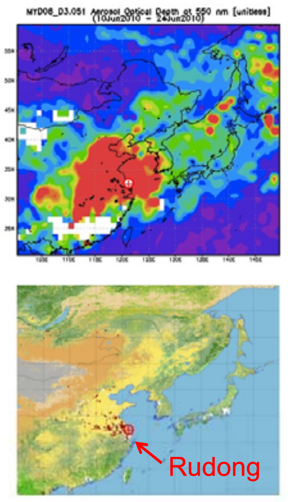


Figure 1. (Upper panel) Image of aerosol optical depth by MODIS/Aqua during the campaign; (Lower panel) Land cover type map associated with fire spots (red dots) detected by MODIS/Aqua and Terra on 16 June 2010.

Kudo et al., [2014]

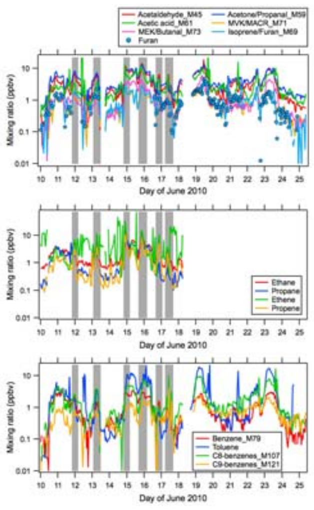
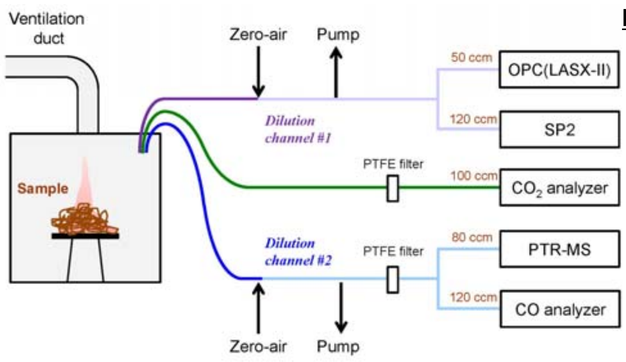


Figure 2. Temporal variations of OVOCs (isoprene/furan, acetaldehyde, acetone/propanal, acetic acid, MVK/MACR, and MEK/butanal) (upper panel), alkanes (ethane and propane) and alkenes (ethene and propene) (middle panel), and aromatics (benzene, toluene, C_8-benzenes, and C_9-benzenes) (lower panel) in Rudong in June 2010. The gray areas denote seven events heavily impacted by BB emissions.

Objectives

- Determination of EFs of NMVOCs from the BB of Chinese crop residues in **Laboratory Experiments**
- Comparison of EFs: **Laboratory Experiments** vs. Field Measurements

Experimental Setup



Modified Combustion Efficiency (MCE)

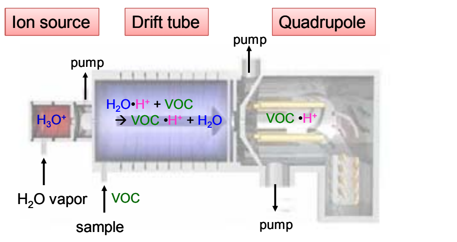
$$= \Delta CO_2/(\Delta CO_2 + \Delta CO)$$

MCE ≥ 0.99 (Pure Flaming)

MCE ~ 0.65–0.85 (Smoldering)

m/z	Compounds	MID-setting a	MID-setting A	MID-setting B	DL (ppbv)
21	Primary ($H_3{}^{18}O^+$)	0.2	0.2	0.2	
30	Primary (NO^+)	0.05	0.05	0.05	
31	Formaldehyde	0.1	0.1	0.1	0.89
32	Primary (O_2^+)	0.05	0.05	0.05	
33	Methanol	0.05	0.05	0.05	1.9
37	Primary ($H^+(H_2O)_2$)	0.05	0.05	0.05	
42	Acetonitrile	0.1	0.1	-	0.66
45	Acetaldehyde	0.1	0.1	-	0.40
47	Formic acid	-	0.1	-	1.7
59	C_3 saturated aldehyde/ketone (Propanal/Acetone)	0.1	0.1	-	0.29
61	Acetic acid/Glycolaldehyde	0.1	0.1	-	0.58
69	Furan/Isoprene	0.1	0.1	-	0.25
71	C_4 unsaturated aldehyde/ketone (MACR/MVK)	0.1	0.1	-	0.23
73	C_4 saturated aldehyde/ketone (Butanal/MEK)	0.1	0.1	-	0.22
75	Propionic acid	0.1	0.1	-	0.17
79	Benzene	0.1	0.1	-	0.14
83	Methylfuran	-	-	0.1	0.25
85	C_5 unsaturated aldehyde/ketone	0.1	0.1	-	0.13
87	C_5 saturated aldehyde/ketone	0.1	0.1	-	0.14
93	Toluene	-	-	0.1	0.28
97	Dimethylfuran	0.1	0.1	-	0.15
99	C_6 unsaturated aldehyde/ketone	-	-	0.1	0.13
101	C_6 saturated aldehyde/ketone	-	-	0.1	0.12
107	C_8-benzenes	-	-	0.1	0.26
113	C_7 unsaturated aldehyde/ketone	-	-	0.1	0.13
115	C_7 saturated aldehyde/ketone	-	-	0.1	0.13
121	C_9-benzenes	-	-	0.1	0.37
127	C_8 unsaturated aldehyde/ketone	-	-	0.1	0.13
129	Naphthalene/C_8 saturated aldehyde/ketone	0.1	0.1	-	0.10
135	C_{10}-benzenes	-	-	0.1	0.08
179	Anthracene	0.1	-	0.2	0.06
203	Pyrene	-	-	0.2	0.02
	Sum (s)	1.9	1.9	1.9	

Proton Transfer Reaction Mass Spectrometry



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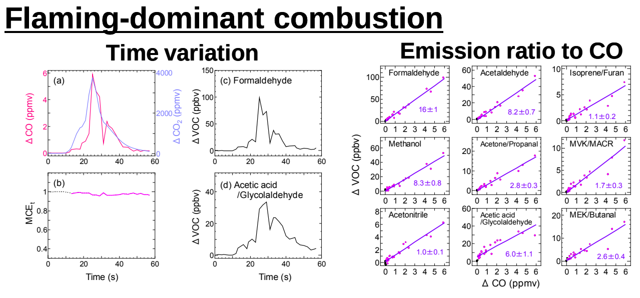
Results and Discussion

Flaming-dominant combustion



Relatively smoldering combustion

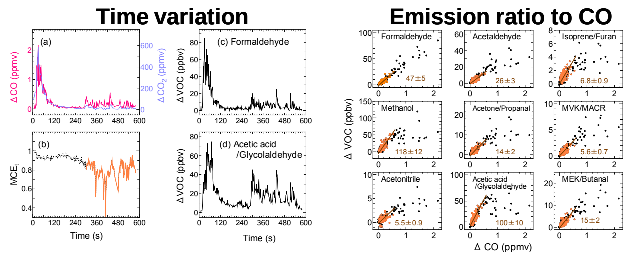


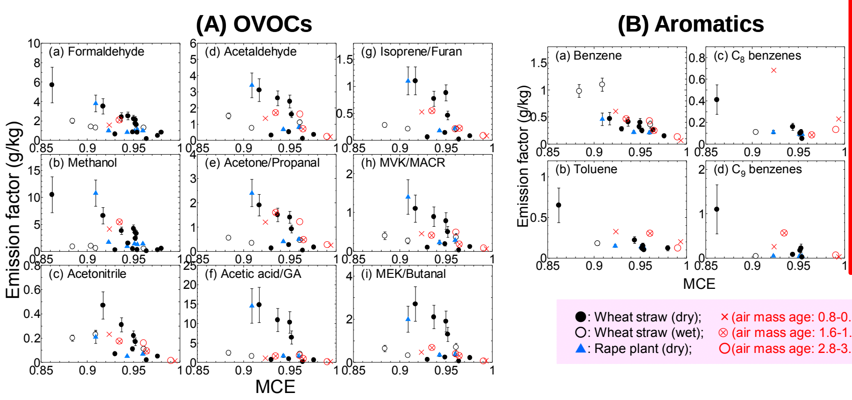
Table 1. Emission factors (g/kg) of NMVOCs from crop residue burning[a]

	Laboratory experiment[b]					Field measurement		Literature[d]	Literature[e]	Literature[f]	Literature[g]
	Wheat straw			Rape plant		Rudong, China[c]		Wheat straw	Rice straw	Crop residue	Rice straw
	dry	dry	wet	dry	dry	June 2010					
	Flaming-dominant	Relatively more smoldering	Relatively more smoldering	Flaming -dominant	Relatively more smoldering	Flaming	Relatively more smoldering				
MCE	0.97(0.01)	0.93(0.07)	0.91(0.05)	>0.92	0.94(0.03)	0.992	0.930	-	0.93[j]	0.925	0.942
Formaldehyde	0.6(0.5)	2.7(3.0)	1.5(0.5)	0.9(0.1)	1.7(2.1)	-	1.07[i]	-	0.0031(0.0002)	1.93(1.32)	-
Methanol	0.3(0.3)	4.5(6.0)	0.7(0.3)	1.3(0.4)	3.7(7.1)	-	2.94[i]	-	-	1.87(1.53)	-
Acetonitrile	0.06(0.05)	0.29(0.18)	0.18(0.07)	{0.05}	0.14(0.07)	0.01(0.00)	0.20(0.03)	-	-	0.225(0.173)	-
Acetaldehyde	0.3(0.2)	2.4(0.8)	1.1(0.4)	{0.67}	2.1(1.3)	{0.19}	1.02[i]	-	0.0067(0.0023)	2.68(2.42)	-
Acetone /Propanal	0.2(0.1)	1.4(0.5)	0.5(0.1)	{0.41}	1.5(1.0)	{0.24}	0.83[i]	-	0.0074(0.0032) /0.0025(0.0009)	0.884(0.611) /-	0.11(0.02) /0.013(0.006)
Acetic acid /Glycolaldehyde	0.6(0.4)	10.6(4.2)	2.1(0.5)	{1.7}	8.1(6.4)	{0.11}[h]	0.54[h,i]	-	-	3.88(3.64) /2.29(3.04)	- /-
Isoprene /Furan	0.08(0.07)	0.8(0.3)	0.23(0.05)	{0.18}	0.7(0.4)	{0.08}	0.52(0.01)	-	0.28(0.02)[k] /-	0.220(0.170) /0.355(0.445)	0.088(0.018) /0.085(0.017)
MVK /MACR	0.11(0.08)	0.8(0.3)	0.34(0.07)	{0.23}	0.9(0.6)	{0.06}	0.43(0.02)	-	- /0.0021(0.0013)	0.607(0.515)	0.13(0.03) /0.043(0.021)
MEK /Butanal	0.16(0.10)	2.0(0.7)	0.6(0.2)	{0.34}	1.2(0.8)	{0.05}	0.28[i]	-	0.0014(0.0004) /0.0008(0.0002)	0.290(0.243) /-	0.068(0.014) /0.016(0.003)
Benzene	0.25(0.10)	0.4(0.1)	0.8(0.5)	{0.22}	0.3(0.1)	0.09(0.02)	0.53(0.07)	0.31(0.08)	0.42(0.05)[k]	0.301(0.177)	0.14(0.03)
Toluene	0.11(0.01)	0.3(0.3)	{0.18}	{0.15}	0.14(0.01)	0.16(0.04)	{0.32}	0.14(0.06)	0.73(0.06)[k]	0.296(0.228)	0.14(0.03)
C_8-benzenes	{0.05}	0.2(0.2)	{0.11}	{0.11}	0.09(0.00)	0.18(0.05)	{0.68}	0.09(0.05)	0.44(0.11)[k]	0.107(0.088)	0.069(0.014)
C_9-benzenes	{0.02}	0.4(0.7)	{0.04}	{0.05}	0.04(0.00)	0.03(0.02)	0.40(0.15)	0.06(0.04)	0.18(0.06)[k]	0.066(0.061)	0.026(0.006)

[a]The values in parentheses represent the ranges of the data (+/– errors). The values in curly brackets are based on single data. [b]This work. [c]*Kudo et al.* [2014]. [d]*Li et al.* [2009]. [e]*Zhang et al.* [2013]. [f]*Stockwell et al.* [2015]. [g]*Hatch et al.* [2015]. [h]The EFs may be underestimated due to the condensation of water vapor in the sampling tube. [i]The EFs are determined by extrapolation from the measured normalized excess mixing ratios (NEMRs) and photochemical ages to the values at an air mass age of 0. [j]The MCE was estimated from the reported EFs of CO_2 and CO. It was reported that the burning cycles were dominated by the flaming pattern. [k]The value was derived from the EF of total NMHCs and the fraction of each compound.

Emission factors (EFs) of NMVOCs

Yokelson *et al.*, [1999]



●: Wheat straw (dry); ○: Wheat straw (wet); ▲: Rape plant (dry); × (air mass age: 0.8-0.9h), ⊗ (air mass age: 1.6-1.9h), ○(air mass age: 2.8-3.3h): Field measurement at Rudong, China, in June 2010 (*Kudo et al.* [2014])

$$EF_X\ (g/kg) = F_C \times 1000\ (g/kg) \times MM_X\ (g)/MM_C\ (g) \times C_X/C_{Total}$$

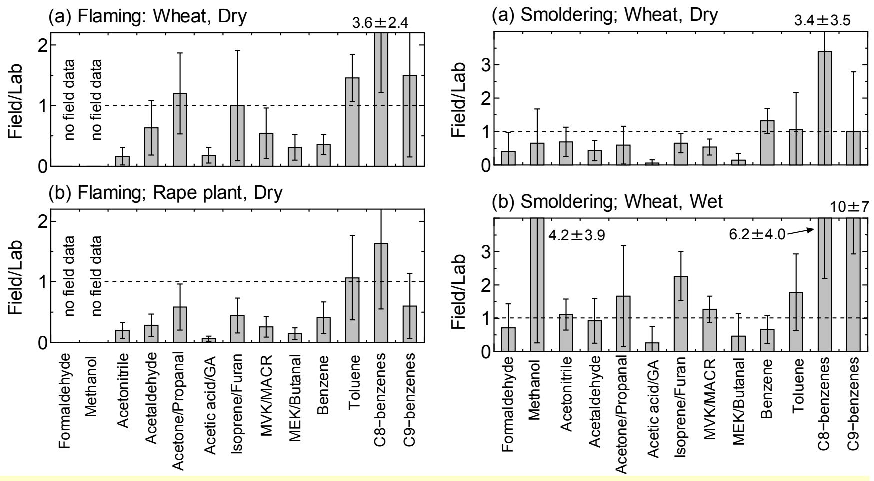
F_C: the mass fraction of carbon in the fuel (assumed to be 0.5)
MM_X: the molecular mass of compound X
MM_C: the molecular mass of carbon (12.011 g mol^{-1})
C_X/C_{Total}: the number of emitted moles of compound X divided by the total number of moles of carbon emitted.

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

$\Delta C_X/\Delta CO_2$: the fire-averaged emission ratio (ER) of species X to CO_2
nC_Y: the number of carbon atoms in compound Y
The sum is over all carbon-containing species including CO_2, CO and CH_4.

- A trend that the EFs increase as the MCE decreases was observed.
- There is no meaningful difference between the wheat straw (dry) and the rape plant (dry) samples.
- The EFs of wet wheat straw are low relative to those of dry wheat straw for OVOCs.

Laboratory Experiments vs. Field Measurements

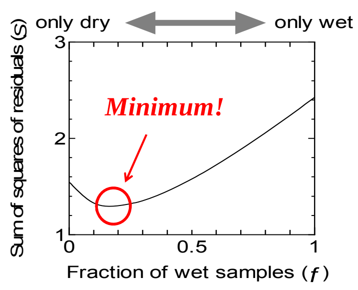


- ✓ **For flaming-dominant data,** the field data for most OVOCs were smaller than the laboratory data.
- ✓ **For relatively smoldering data,** the field data were smaller than the laboratory data for OVOCs.
- ✓ The underestimations for OVOCs were improved with wet samples.

Estimation of the fraction of wet sample in the field data

$$S = \sum_i (\log_{10} R_{F/L}(i))^2$$

$$R_{F/L}(i) = (1-f) \times R^d_{F/L}(i) + f \times R^w_{F/L}(i)$$



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