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Atmospheric Chemistry and Physics Discussions

Multi-pollutants emissions from the burning of major agricultural residues in China and the related health-economic effect assessment

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Abstract. Multi-pollutants in smoke particulate matter (SPM) were identified and quantified for biomass burning of five major agricultural residues such as wheat, rice, corn, cotton, and soybean straws in China by aerosol chamber system combining with various measurement techniques. The primary emission factors (EFs) for $PM_{1.0}$ and $PM_{2.5}$ are 3.04-12.64 and 3.25-15.16 g kg^{-1}. Organic carbon (OC), elemental carbon (EC), char-EC, soot-EC, water-soluble inorganics (WSI), water-soluble organic acids (WSOA), water-soluble amine salts (WSA), trace mineral elements (THM), polycyclic aromatic hydrocarbons (PAHs), and phenols in smoke $PM_{1.0}/PM_{2.5}$ are, 1.34-6.04/1.54-7.42, 0.58-2.08/0.61-2.18, 0.51-1.67/0.56-1.76, 0.05-0.41/0.05-0.42, 0.51-3.52/0.52-3.81, 0.13-0.64/0.14-0.77, (4.39-85.72/4.51-104.79)×10^{-3}, (11.8-51.1/14.0-131.6)×10^{-3}, (1.1-4.0/1.8-8.3)×10^{-3}, and (7.7-23.5/9.7-41.5)×10^{-3} g kg^{-1}, respectively. EC and soot-EC mainly exist in

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Atmospheric Chemistry and Physics Discussions

$PM_{1.0}$, which are confirmed by morphology analysis. Heavy metal-bearing particles favor to reside in the range of smoke $PM_{1.0-2.5}$.

With respect to five scenarios of burning activities or straw field burning rates, the total emissions of SPM from agricultural open burning in China in 2012 were estimated for $PM_{2.5}$, $PM_{1.0}$, OC, EC, char-EC, soot-EC, WSI, WSOA, WSA, THM, PAHs, and phenols to be 0.74-1.24, 0.66-1.11, 0.32-0.53, 0.10-0.16, 0.08-0.14, 0.02-0.03, 0.18-0.30, 0.019-0.031, 4.23-7.19×10^{-3}, 6.36-10.64×10^{-3}, 0.35-0.59×10^{-3}, and 2.02-3.40×10^{-3} Tg, respectively. The emissions were further temporal-spatially characterized using geographic information system (GIS) at different regions in summer and autumn post-harvest periods. It is found less than 25 % of the total emissions were released during summer harvest period that was mainly contributed by the North Plain and the Central of China, especially Henan, Shandong, and Anhui, leading the top three provinces of smoke particle emissions.

Flux concentrations of primarily emitted smoke $PM_{2.5}$ that were calculated using box-model method based on five versions of emission inventories all exceed the carcinogenic risk permissible exposure limits (PEL). The health impacts and health-related economic losses from the smoke $PM_{2.5}$ short-term exposure were assessed. The results show that China suffered from 7836 (95 % confidence interval (CI): 3232, 12362) premature mortality and 7267237 (95 % CI: 2961487, 1130784) chronic bronchitis in 2012, which led to 8822.4 (95 % CI: 3574.4, 13034.2) million US$, or 0.1 % of the total GDP losses. We suggest that percentage of open burnt crop straws at post-harvest period should be cut down by over 97 % to ensure risk aversion from carcinogenicity, especially the North Plain and the Northeast, where the emissions should decease at least by 94% to meet the PEL. Under such emission control, over 92 % of the mortality and morbidity attributed to agricultural fire smoke $PM_{2.5}$ can be avoided in China.

Key words: agricultural straw burning, aerosol chamber, smoke particle, emission factor, emission inventory, health effect, emission control policy

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Atmospheric Chemistry and Physics Discussions

1 Introduction

Biomass burning (BB) is a significant source of particulate- and gaseous- pollutants (Andreae et al., 2001; Clarke et al., 2007; Ram et al., 2011; Saikawa et al., 2009; Tian et al., 2008). It was estimated that open burning of biomass contributed approximately 40% of the globally averaged annual submicron black carbon (BC) aerosol emissions and 65 % of primary OC emissions (Bond et al., 2013). China is the major contributor that bears over 24 % of global emissions of carbonaceous aerosols, especially from agricultural field burning, about 0.04~0.5 Tg EC and 0.4~2.1 Tg OC are released annually (Bond, 2004; Cao et al., 2006; Qin et al., 2012; Saikawa et al., 2009), resulting in great radiative forcing, air quality deterioration, visibility reduction, premature mortality, and economic loss regionally and globally (Bølling et al., 2009; Bond et al., 2013; Huang et al., 2014; Janssen et al., 2011; Rosenfeld, 2006; Saikawa et al., 2009; Shindell et al., 2012).

BB also represents one of the most uncertainties in the emission, climate effect, and public health assessments, which finally relies on the uncertainties in detailed chemical emission factors or related properties and burning activities like strength or percentage of biomass fuel burned (Tian et al., 2008; Andreae et al., 2001; Levin et al., 2010). For example, studies have focused on OC and EC emissions due to their specific optical properties (Bond et al., 2013; Cao et al., 2006; Qin et al., 2012; Ram et al., 2011). OC like sulfate and nitrate can cool the atmosphere by increasing the Earth's reflectivity, however, smoke OC on the other hands together with brown carbon have been found to be a significant source of light absorption (Chen et al., 2015; Ackerman, 2000; Chakrabarty et al., 2010; Christopher et al., 2000). The coated or internal mixed sulfate or nitrate can act as lens to enhance the light absorption activity of BC (Zhang et al., 2008b), probably also the activity of brown carbon (Chen et al., 2015). However, primary emissions for OC, EC, and alkali components are confused and have a wide range (Sen et al., 2014; Cao et al., 2006; Hayashi et al., 2014), and some study still took OC with negative forcing activity (Saikawa et al., 2009; Shindell et al., 2012). Besides, smoke EC is consisting of soot

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Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

and char, and soot-EC has a higher light-absorption potential compared to char-EC (Arora et al., 2015; Reid et al., 2005a). Division and quantification of char- and soot-EC emissions for biomass burning are understudied (Arora et al., 2015; Han et al., 2009). However, other components like organic acids, amines, phenols, and mineral elements that enable CCN activity or endow health hazard of smoke aerosol are also deficient, variable, or outdated, which may hinder our overall understanding of biomass burning contributions and also atmospheric process of smoke particles (Li et al., 2015; Akagi et al., 2011; Chan et al., 2005; Dhammapala et al., 2007; Ge et al., 2011; Reid et al., 2005b).

Studies using carbon mass-balance method (CMB) and pollutant concentration-chamber volume quantification method are the two common methods to derive the emission factors for biomass burning aerosols (Akagi et al., 2011; Li et al., 2007; Zhang et al., 2008a). Carbonaceous and inorganics components of smoke particles not only vary with biomass issues (fuel types, water content, or burning strength), but also relate to burning condition and environment (flaming or smoldering, field burning or laboratory simulation), extent of aging, sampling methods and measurement technologies (Grieshop et al., 2009; Hayashi et al., 2014; Reid et al., 2005b). Comparing to field observations that are closer to the actual burning (Li et al., 2007; Akagi et al., 2011; Rose et al., 2011; Saffari et al., 2013), laboratory studies have a definite advantage over field burning research in emission analysis (Zhang et al., 2008a; Sun et al., 2016; Jayarathne et al., 2014). For example, the environment, amount of fuel, and burning conditions can be precisely controlled, the contamination from ambient atmosphere to the emissions can be excluded, and chemical compositions at different aging extent can be quantified using aerosol chamber system (Li et al., 2015, 2016; Aurell et al., 2015; Dhammapala et al., 2007).

The activity rates of biomass burning (burning rate of biomass fuels) are also response to the great uncertainties in the emission estimates (Zhang et al., 2008a; Sun et al., 2016). Seldom study ever focused on the burning rates, and the limited data were treated as simplex constant or dynamic values in many studies of emission estimation in a certain year or for annual variations with a long time scales, thus,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
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Atmospheric Chemistry and Physics Discussions

significant difference among the results were founded (Zhang et al., 2011; Qin et al., 2012; Qin et al., 2011; Zhao et al., 2012). For instance, Cao et al. (2006; 2011) estimated primary smoke carbonaceous materials emissions for 2000 and 2007 in China with same field burning rates, the results were almost the same for the two year with 103-104 Gg yr^{-1} BC and 425.9-433.3 Gg yr^{-1} OC emitted. He et al. (2011b) found the declining trends in biomass burning emissions in the Pearl River Delta for the period 2003-2007 based on constant activity data of burning rates. Lu et al. (2011) developed primary carbonaceous aerosol emissions in China for 1996-2010 with time-dependent activity rates extrapolated from 2008 to 2010 based on national fast-track statistic, rapid increase of OC and EC emissions were reported, and OC increased from 1.5 to 2.3 Tg yr^{-1}, BC increased from 418 to 619 Gg yr^{-1}. Qin et al. (2012) estimated BC emission from crop straw open burning for 1980-2009 with variable burning rates based on peasants' income development, the increasing trend in BC emission was also confirmed, and BC emission increased from 4.3 to 116.6 Gg yr^{-1}.

As most anthropogenic pollutants are concentrated in submicron particulate matters ($PM_{1.0}$) (Ripoll et al., 2015), more pronounced relationship of ambient $PM_{1.0}$ to haze formation and adverse health effect has been reported (Huang et al., 2003; Roemer et al., 2001; Shi et al., 2014). Nevertheless, associated chemical characterization of $PM_{1.0}$ is still undefined (Li et al., 2015; Safai et al., 2013; Cheng et al., 2006). The study of source-specific $PM_{1.0}$ chemical compositions and emissions are necessary to replenish database for contribution assessment and model application in atmospheric chemistry, climate changes, and public health evaluation.

The emission inventories and forecasting in the emissions of atmospheric pollutants have been widely studied, and the incurred mortality, climatic effect, and economic loss have also been estimated (Ostro et al., 1998; Saikawa et al., 2009; Shindell et al., 2012), based on which the emission control policies were proposed. Shindell et al. (2012) considered ~400 control measures in tropospheric BC and O_3 emissions for the benefit of global or regional human health and food security, and 14 optimal measures targeting CH_4 and BC emissions were identified. Saikawa et al.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
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Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

(2009) compared different scenarios of OC, EC, and sulfate emissions in China in 2030, concluding that maximum feasible reduction may avoid over 480000 premature deaths in China and decrease the radiative force from -97 to -15 mW m^{-2} globally. Wang et al. (2008) reported field burning restriction may save about 5 billion dollars losses from biological resource and air pollution. However, the generalized strategies in emission reduction were inadequate and lack actual practicality (Streets, 2007; Lin et al., 2010).

In this study, burning experiments with five major agricultural straws were conducted using a combustion stove in combination with an aerosol chamber system. Accurate compositions and emission factors for SPM in $PM_{1.0}$ and $PM_{2.5}$ were characterized and established. Afterwards, up-to-date emissions for agricultural open burning aerosol in 2012 were developed, health and health-related economic impacts from smoke $PM_{2.5}$ exposure were also assessed. Finally, emission reduction strategy that was implemented in field burning rate control for the carcinogenic risk concern was proposed, which should help establish the policy and provide an idea for the emission control.

2 Methodology

An overview of the research procedures including emission factors acquirement and emission inventory calculation is shown in Fig. 1. Tabulation of emission factors is self-established in our laboratory using a combustion stove to simulate open burning and an aerosol chamber to quantify the emissions. Then, we use a bottom-up approach to calculate the emission inventory of agricultural field burning over China mainland based on crop production data in 2012. Emissions for each species are estimated as:

$$E_{k,j} = \sum_i A_{k,i} \times EF_{i,j} \quad (1)$$

where E_j is emission, $A_{k,i}$ is effective biofuel consumption, and $EF_{i,j}$ is emission factor. k, i, and j indicates region, agricultural residue type, and particulate chemical species.

State-of-the art chemical transport and box models were commonly applied to

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
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Published: 30 August 2016

reproduce or simulate the ambient aerosol concentrations (Ram et al., 2011; Reddy et al., 2000; Saikawa et al., 2009). In this study, spatio-temporal dynamic box model is used to calculate the emission flux concentration. Regional crop straws are premised to be combusted proportionally only in the fire occurrence days. Dismissing interaction of emitted pollutants in space and time, pollutants will distribute uniformly in a space covering an area of specific region with mixing height of 0.5 km (atmospheric boundary layer). The flux concentration of agricultural burning smoke can be calculated by Eq. (2):

$$C_{k,j} = \frac{E_{k,j}}{S_k \times h \times T_k} \quad (2)$$

in Eq. (2), $C_{k,j}$ is flux concentration of smoke aerosol, S_k is regional area, h is boundary layer height, T_k is agricultural field fire duration time.

2.1 Aerosol chamber work and emission factors

2.1.1 Crop straws

Five kinds of representative crop residues were used for the burning experiments, i.e., wheat, rice, corn, cotton, and soybean straws. The straws were collected based on regional features of agricultural planting, winter wheat straws were collected from Anhui province, late rice straws from Shanghai, corn straws from Henan province, cotton and soybean residues from Xinjiang. All straws were stored under dark, airy, and cooling condition. Prior to the burning experiment, the dirt and weeds were removed, then straws were dehydrated (at 100 ^{o}C for 24 h) to minimize effect of the water content on the burning and pollutant emissions, as study found pollutants emissions and combustion efficiencies (CE) are response to water content, increased moisture content enhances the emissions but also alter the chemical compositions of smoke aerosols (Reid et al., 2005b; Aurell et al., 2015; Hayashi et al., 2014). Although straws in the field are not well dried and moisture contents vary with weather, ventilation, and storing times, for the convenience of practical application and comparison of burnings and emissions, water contents of the straws were controlled within 2 %. The dry straws were then cut to a length of approximately 10

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

cm and weighted 10.0 g per serving.

2.1.2 Burning experiments

The experiments were conducted using an aerosol chamber system (Fig. S1 in supplement information, SI), which was loaded in a temperature-controlled room (18-22 ^{o}C, 40%-60% RH). A stainless combustion stove was self-deigned to simulate typical field burning of crop straws, automatic ignition with LPG (Liquid petroleum gas) in particular, albeit on a small scale (ignition time less than 0.1 s). 10.0 g conditioned residues were sealed in the 0.227 m^3 combustion stove in advance, once ignited, the force-ventilation and HEPA filtrated particle-free air were supplied (300 L min^{-1}). The emissions were immediately injected into a clean, evacuated aerosol chamber. The burning last about 1 min and over 1 m^3 particle-free air flushed the stove to ensure all the emissions were transferred into the chamber.

The chamber was costume-built to quantify the emissions and characterize the physiochemical properties of smoke aerosols, detailed description of the chamber can be found elsewhere (Zhang et al., 2008a; Zhang et al., 2011; Li et al., 2015, 2016). Briefly, the chamber has a volume of 4.5 m^3 with 0.3 mm Teflon coating on the inner side, a magnetic fan fixed on the bottom to stir the aerosol uniformly, and a hygroclip monitor (Rotronic, Model IM-4) equipped inside to measure the temperature and relative humidity. Before experiment, the chamber was flushed with particle-free air for 6 h, oxidized by high concentration ozone (~3 ppm) for 12 h, then flushed again, filled with pure dry air to 80 KPa, and connected to the stove finally. The emissions from straw burning were aspirated into the chamber till room pressure, afterwards, size measurement and chemical samplings were conducted from the chamber. For each type of straw, four burning experiments were conducted. The unburned residues were weighted and deducted from 10.0 g after each test.

Modified combustion efficiency (MCE) for each burning was monitored. A gas-chromatograph (GC, model 930, Shanghai, Hai Xin Gas Chromatograph Co., LTD) equipped with a flame ionization detector, an Ni-H convertor, and a stainless steel column (2 m long) packed with 15% DNP was used to measure CO and CO_2

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

concentrations in the chamber. And MCE were 0.89-0.96 for all the experiments, indicating flaming combustion dominated, which were comparable to that in the field burning (Li et al., 2003; Li et al., 2007).

2.1.3 Size and morphology of smoke aerosol

Size distribution (10 nm-10 μm) of smoke particles was measured using Wide-range Particle Spectrometer (WPS, Model 1000XP, TSI, USA), which has been described by Zhang et al (2011). Briefly, WPS integrates the function of scan mobility particle sizer (SMPS) and laser particle sizer (LPS), 0.3 L min^{-1} flow is introduced to SMPS part to classify mobility size from 10 nm to 500 nm, and 0.7 L min^{-1} flow is introduced to LPS part to measure aerodynamic diameter from 350 nm to 10 μm. Particle density and refractive index are set as 1.0 g cm^{-3} and 1.45. A diffusion dryer tube filled with descant-silica gel is set prior to the inlet of WPS. Before experiment, WPS was calibrated with certified polystyrene latex spheres (PSL, 40, 80, and 220 nm, Duke Scientific).

SPM from the 5 types crop straws burning were sampled onto copper grids coated with carbon film (carbon type-B, 300-mesh copper, Tianld Co., China) using a single-stage cascade impactor with a 0.5 mm diameter jet nozzle at a flow rate of 1.0 L min^{-1}. The sampler has a collection efficiency of 100 % at 0.5 μm aerodynamic diameter. More information can be found elsewhere (Fu et al., 2012; Hu et al., 2015). Then, a JEOL-2010F field emission high-resolution transmission electron microscope (FE-HRTEM) coupled with an oxford energy-dispersive X-ray spectrum (EDX) was applied to investigate the morphology, composition, and mixing state of individual particles.

2.1.4 Chemical sampling and analysis

$PM_{1.0}$ and $PM_{2.5}$ samples for each burning were collected on 90 mm quartz filter (Tissuquartz, Pall Corp., USA) from the chamber using a high-volume Particle Sampler (HY-100, Qingdao Hengyuan S.T. Development Co., Ltd) operating at 100 L min^{-1}. Each filter sampling duration time is 5 min, and total 44 samples (including

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

4 blank samples) were gathered for the experiments. The quartz microfiber filters were prebaked for 8 h at 450 ^{o}C to eliminate contamination. Before and after the sampling, the filters were weighted using a balance (Sartorius BP211D) with an accuracy of 10 μg, and the balance was treated in an electronic desiccator (40 % RH, 22 ^{o}C) for 24 h before its use. After weighting, the loaded filters were stored at -20 ^{o}C in a refrigerator for further analysis.

Water soluble species including general inorganic ions (ions: F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}), organic acids (CH_3COOH, HCOOH, $C_2H_2O_4$, CH_3SO_3H), and seven protonated amines ($MeOH^+$, $TeOH^+$, $MMAH^+$, $DMAH^+$, $TMAH^+$, $MEAH^+$, and $DEAH^+$ for short, corresponding to monoethanolaminium, triethanolaminium, monomethylaminium, dimethylaminium, triethylaminium, monoethylaminium, and diethylaminium) were measured from 1/4 of each filter with ion chromatography (IC, Model 850 Professional IC, Metrohm, USA) consists of a separation column (Metrosep A Supp 7 250/4.0 for anion and organic acids, Metrosep C-4 150/4.0 for cation, and Metrosep C4-250/4.0 for water soluble aminiums).

1/4 of each filter was acid dissolved to measure the selected elements (As, Pb, Cr, Cd, Ni, V, Zn, Al), of which As, Zn, Pb, Cr, Cd, and Ni are USEPA priority controlled pollutants (Wu et al., 2011). The smashed filters were digested at 170 ℃ for 4 h in high-pressure Teflon digestion vessel with 3 mL concentrated HNO_3, 1 mL concentrated $HClO_4$, and 1 mL concentrated HF. Afterwards, the almost dry solution was diluted and characterized using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Atom Scan 2000, JarroU-Ash, USA).

Another 1/4 of each filter was ultrasonically extracted with CH_2Cl_2. The extracts were then condensed with rotary evaporator. 16 targeted PAHs (2-ring, naphthalene (Nap); 3-ring, acenaphthylene (Ac), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant); 4-ring, fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr); 5-ring, benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBA); and 6-ring: indeno[1,2,3-cd] pyrene (IP), benzo[ghi]perylene (BghiP)) and 5 selected phenols

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

(phenol, 2-methoxyphenol, 4-ethylphenol, 4-ethyl-2-methoxyphenol, 2,6-dimethoxyphenol) were measured from those concentrated extracts using gas chromatography-mass spectrometer (GC-MS, Agilent 6890-5973N) equipped with column DB-5ms (Agilent 123-5532).

Organic carbon (OC) and elemental carbon (EC) were measured with the rest quartz filters using a carbon analyzer (Sunset laboratory Inc., Forest Grove, OR) based on the thermal-optical transmittance (TOT) method with a modified NIOSH-5040 (National Institute of Occupational Safety and Health) protocol. Four organic fractions (OC1, OC2, OC3, and OC4 at 150, 250, 450, and 550 ^{o}C, respectively), PC fraction (a pyrolyzed carbonaceous component determined when transmitted laser returned to its original intensity after the sample was exposed to oxygen), and three EC fractions (EC1, EC2, and EC3 at 550, 700, and 800 ^{o}C, respectively) are produced. And OC is technically defined as OC1 + OC2 + OC3 + OC4 + PC, while EC is defined as EC1 + EC2 + EC3 - PC (Seinfeld et al., 2012). Han et al (2007; 2009) furtherly differentiated char-EC and soot-EC from EC measurement as EC2 + EC3 equals to soot-EC, and the rest is char-EC.

The quality of the data above was guaranteed by standard materials calibration, recovery rate, and operational blank correction.

2.1.5 Calculation of emission factors

The emission quantities derived from the experiment were converted into quantities per unit weight of initial residues as emission factor (EF, unit: g kg-1), which can be calculated from effective filter sampling weight, chamber volume, and amount of crop straw consumed (Dhammapala et al., 2007; Zhang et al., 2008a). To be more accurate, wall loss and makeup air dilution of smoke particles in the chamber during sampling should be corrected, and details see in SI.

2.2 Emission inventory calculation

2.2.1 Agricultural field fire survey

Fire sites over China from 2011 to 2013 were statistically analyzed, and the data was

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

collected from the Ministry of Environmental Protection of China that obtained by NASA's Terra and Aqua satellites remote sensing (http://www.mep.gov.cn/). Agricultural fire sites were screened out from MODIS daily fire products (1 km × 1 km resolution level 3 hotspot) using a high resolution real time land use based on geography information system (GIS). Spatial and temporal distributions of fire sites were displayed in Fig. S2 (SI), over 5000 fire sites were allocated into two prominent filed burning periods corresponding to summer (May to July) and autumn (September to November) harvests, and filed burning lasts 54 days and 60 days on statistical average during the two harvests. In the North of China, open burning occurred primarily in autumn, while temporal-character of field fires was not significant in the North Plain and the Center of China.

2.2.2 Crop straw production

Corp straw production was generally derived from annul or monthly crop production by multiplying crop-specific ratios of production-to-residue (He et al., 2011b; Cao et al., 2011; Zhao et al., 2012). In this study, crop productions were furtherly classified into summer harvest and autumn harvest productions according to field fire sites analysis and traditional seasonal planting and harvesting. The amount of straw produced was calculated by Eq. (3):

$$M_{t,k,i} = P_{t,k,i} \times r_i \times H_{t,k,i} \times D_i \quad (3)$$

in which M is mass of crop straws produced; P is annual crop-specific amount of crop production; r is the production-to-residue ratio; D is the dry matter content; $H_{t,k,i}$ is production ratio of crop i at region k during summer or autumn harvest period t.

Province-level crop production data of wheat, rice, corn, cotton, and soybean were taken directly from the China Yearbook 2013 (National Bureau of Statistics of China, NBSC, 2013). Crop-specific production-to-residue ratios were cited from Chinese Association of Rural Energy Industry (CAREI, 2000; Wang et al., 2008; data available at http://www.carei.org.cn/index.php, in Chinese). Dry matter contents of crop straws were referred to He et al. (2011b) and Greenhouse Gas Inventory

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
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Published: 30 August 2016

Reference Manual (IPCC, 2007). The parameters of production-to-residue ratios and dry matter contents were summarized in Table S1 (SI). The regional crop production ratios in summer and autumn harvests were listed in Table S2 (SI).

2.2.3 Field burning rate

Uncertainty of emission estimations mostly relies on intangibility of straw open burning rate (Zhao et al., 2012; He et al., 2011b). However, regional or national percentage of straw open burned was seldom studied, and the limited data were outdated and variable. The available studies indicate national filed burning rate of crop straws range from 15.2% to 27.2% in China (Daize, 2000; Wei et al., 2004; Zhang et al., 2008a), and more detailed studies indicate about 31.9% of the crop burned in the Pearl River Delta from 2003 to 2007 (He et al., 2011b), while the corresponding figures were almost 100% for the Huabei region in 2003 (Zhao et al., 2012). Two versions of province-level field burning rates that commonly used were reported by Cao et al. and Wang et al. Cao et al. (2006; 2011; 2005; Chen et al., 2001) deduced the rates based on regional economic level, the proposal of the rates to be proportional to peasants' income was confirmed later, and the rates was first used to calculate the open burning emission in 2000. Wang and Zhang (2008) obtained provincial percentage of residue open burnt via filed survey in 2006. Herein, the two versions were both applied directly into the emission estimation of 2012 and named as business-as-usual scenarios (BAU, BAU-I from Cao et al. and BAU-II from Wang and Zhang in specific).

In fact, the burning rates should be dynamic parameters that been influenced by industrial structure, government policy orientation, or public awareness. With crop yields increasing and energy consumption structure changes in rural areas, more straws will be discarded and burned in the field. Nonetheless, rigorous agricultural fire policy may still suppress the condition worsen as it worked during 2008 for Beijing Olympics and 2010 for Shanghai Expo (Huang et al., 2013; Cermak et al., 2009; Wang et al., 2010). Qin et al. (2012; 2011) ever deduced year specific open burning rates in different zone for the period of 1980-2009 according to their

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

respective peasant income changes in a certain year on the basis of peasant income and filed burning rates in 2006. However, the simple linear relationship should be doubted, as great increase in per capita income after 2006 will surely overestimate the burning rates. We supposed that the values were inverse proportional to peasants' agricultural income proportion (AIP), without considering the policy or potential gain or loss related to agricultural residue treatment. Thus the burning rates established in 2000 and 2006 from Cao et al. (2005) and Wang and Zhang (2008) can be converted into that of 2012 based on economic data from equation below:

$$R_{k,2012} = \frac{I_{k,2012}}{AI_{k,2012}} \times \frac{AI_{k,y}}{I_{k,y}} \times R_{k,y} \quad (4)$$

where R is agricultural straw filed burnt rate, $I_{k,y}$ is peasants' annual income, $AI_{k,y}$ is peasants' annual agricultural income. y indicates reference year (2000 for BAU-I, and 2006 for BAU-II). $I_{k,y}$ and $AI_{k,y}$ can be found or calculated from China Yearbook and China Rural Statistic Yearbook (NBSC, 2004-2013).

The versions of converted rates based on primary industry level were called Economic Models I and II (EM -I and EM-II in short) corresponding to BAU-I and BAU-II. Besides, in 2013, the National Development and Reform Commission of China published the Chinese agricultural straw treatment report of 2012 (NDRC, [2014] No.516, data available at http://www.sdpc.gov.cn/, in Chinese) for the first time. The percentages of crop residues discarded in the report were applied in our estimation, which was called NDRC version.

2.2.4 Emission and flux concentration

From above study, emission of SPM pollutants can be calculated by recount of Eq. (1), as Eq. (5) showed below:

$$E_{t,k,j} = \sum_i M_{t,k,i} \times R_k \times f_i \times EF_{i,j} \quad (5)$$

where $E_{t,k,j}$ is emission amount of chemical species j at region k during harvest period t; f_i is burning efficiency, the crop specific values were cited as 0.68 for soybean residue and 0.93 for the rest four straws (Zhang et al., 2011; Wang and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Zhang, 2008; Zhang et al., 2008a; Koopmans et al., 1997). Thus, flux concentration of corresponded pollutants can be also assessed from box model as mentioned in front.

2.3 Estimating health impacts and health-related economic losses

2.3.1 Carcinogenic risk of Smoke Particulate Matter (CRSPM)

Apart from the enormous climatic effects due to optical properties of smoke particle from IPCC, new epidemiological and toxicological evidence have also linked carbonaceous aerosol to cardiovascular and respiratory health effects according to the World Health Organization (Bruce et al., 1987; IPCC, 2007). Here, we present the fuel-specific carcinogenic risk of SPM (CRSPM, unit: per μg m^{-3}) to assess health hazard from agricultural straw burning particles and help source-specific air quality control. The cancer risk attributed to inhalation exposures of smoke $PM_{2.5}$ from crop straw i burning was calculated as:

$$CR_i = \sum_j f_j \times UnitRisk_j \quad (6)$$

where f_j is mass fraction of individual species j in smoke $PM_{2.5}$, $UnitRisk_j$ is corresponded unit carcinogenic risk value of species j extracted from database provided by the Integrated Risk Information System (IRIS), California Environmental Protection Agency (CEPA), and related documents (Bruce et al., 1987; Burkart et al., 2013; Tsai et al., 2001; Wu et al., 2011; Wu et al., 2009).

CR_i is estimated based on dose addition model of selected hazardous air pollutants (HAPs) including USEPA priority pollutants of PAHs and heavy metals. And UnitRisk values of the selected HAPs presented in Table S3 (SI). Synergistic interactions among pollutants are dismissed, albeit possible. The cancer risk of chromium is adjusted by multiplying a factor of 0.2, assuming that only 20% Cr measured is in the toxic hexavalent form (Bell et al., 1997). Benzo[a]pyrene (BaP) is used as an indicator compound of carcinogenicity, legally binding threshold of BaP in most countries ranges from 0.7 to 1.3 ng m^{-3}, corresponded carcinogenic risk of BaP is about 1.1×10^{-6} per ng m^{-3} (Bruce et al., 1987; Burkart et al., 2013). Thus, one

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

in million level of carcinogenic potential is frequently used to identify risks of concern in public health and environmental decision making, and permissible exposure limits (PEL, unit: μg m^{-3}) of crop straw burning particles can be estimated as:

$$PEL_i = \frac{10^{-6}}{CR_i} \quad (7)$$

2.3.2 Human exposure and health impacts

Robust relationship between surface $PM_{2.5}$ and health effects has been revealed and confirmed by many studies (Pope et al., 2004; Wong et al., 2008). $PM_{2.5}$-related health endpoints are composed of a range of elements from sub-clinical effects to the onset of diseases and the final death (Davidson et al., 2005). In this study, incidence of commonly studied endpoints like premature mortality, respiratory and cardiovascular hospital admissions, and chronic bronchitis from primary emitted smoke $PM_{2.5}$ short-term exposure were assessed using the Poisson regression model, shown as below (Guttikunda et al., 2014):

$$\Delta E = \Delta Pop \times IR \times \left(1 - \frac{1}{e^{\beta \times \Delta C}}\right) \quad (8)$$

where ΔE represents the number of estimated cases of mortality and morbidity, ΔC is the incremental concentration of particulate matter or flux concentration; ΔPop is the population exposed to the incremental particulate concentration of ΔC; IR is short for incidence rate of the mortality and morbidity endpoints, and β is the coefficient of exposure-response function, defined as the change in number case per unit change in concentration per capita.

Concentration-response function and incidence rate of each health endpoint are important in health impacts evaluation and they have variation for different population and regions (Yang et al., 2012; Wong et al., 2008). Here, the variance for sex and ages were neglected. Region-specific exposure-response coefficients for individual mortality were summarized from previous studies, as presented in Table S4 (SI). The coefficients for individual respiratory and cardiovascular hospital admission, and chronic bronchitis were cited as 1.2 %, 0.7 %, and 4.4 % (per 10 μg

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

459 m^{-3}, 95% CI) from Aunan and Pan's work (Aunan et al., 2004). This is the case
460 because seldom studies ever confirmed these topics in China. Region-specific
461 mortality and hospitalization IRs were taken from statistical reports authorized by
462 National Health and Family Planning Commission of the People's Republic of China
463 (NHFPC, 2013), and morbidity of chronic bronchitis were defined as 13.8 ‰ based
464 on the forth national health survey, which was released by the Chinese Ministry of
465 Health in 2008 (CMH, 2009).

466 **2.3.3 Economic valuation of the health impacts**

467 The economic losses of the health impacts associated with smoke $PM_{2.5}$ exposure in
468 2012 were further evaluated. The amended human capital (AHC) approach was
469 employed to calculate the unit economic cost of premature mortality. The commonly
470 applied AHC method uses per capita GDP to measure the value of a statistical year
471 of life (IBRD and SEPA, 2007) based on Eq. (9). It can be used as a social statement
472 of the value of avoiding premature mortality and estimates human capital (HC) from
473 the perspective of entire society, neglecting individual differences (Hou et al., 2012).

474 $$HC_k = \frac{GDP_k}{POP_k} \times \sum_{i=1}^{\tau} \frac{(1+\alpha)^i}{(1+\gamma)^i} \quad (9)$$

475 GDP_k and POP_k are gross domestic production and population of target region k
476 that were reported in the statistical yearbook in 2012; α and γ are economic
477 parameters referring to national GDP growth rate and social discount rate, which
478 were 7.7 % and 8.0 % in 2012 from National Bureau of Statistics of China (NBSC,
479 2013, data available at http://www.stats.gov.cn/tjsj/ndsj/, in Chinese).τ is the
480 life-expectancy lost due to aerosol pollution, and 18 year of life was widely applied
481 (Hou et al., 2012). The annual exchange rate of US dollar to RMB was 6.31 in 2012.
482 One can deduce the HC values of the provinces, municipalities, and autonomous
483 regions in the country, and the calculated regional HC values were listed in Table S5
484 (SI). In this paper, the cost of respiratory, cardiovascular hospital admissions, and
485 chronic bronchitis were 632.2, 1223.4, and 948.6 US$ per case in 2012, which were
486 derived from the national health statistical reports (NHFPC, 2013).

487 The regional and national health-related economic loss from smoke $PM_{2.5}$

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

exposure can be calculated based on the excess mortality and morbidity multiplied by the corresponding unit economic values.

3 Result

3.1 Particulate chemical compositions and emission factors

3.1.1 Organic carbon and elemental carbon

An overview of particulate chemical compositions for smoke $PM_{2.5}$ and $PM_{1.0}$ is pie-graphically profiled in Fig. 2, and the corresponded emission factors are given in Table 1-4. Significant differences of chemical compositions in size range and fuel types can be observed, implying the non-uniform mixing and distribution of particulate pollutants from biomass burning. Emission factors of particulate species from this study are comparable with that from literature as summarized in Table 5. EFs of smoke $PM_{2.5}$ and $PM_{1.0}$ were 8.99 ± 5.55 and 7.91 ± 4.67 g kg^{-1} for the five kinds of crop straws, and over 70 wt.% of SPM was organic components (OM and EC), with average of 73.4 wt.% in $PM_{2.5}$ and 71.3 wt.% in $PM_{1.0}$. Organic matter (OM) was converted from OC by multiplying a factor of 1.3 to account for noncarbon materials (Li et al., 2007). Due to the technical limitation and ambiguous artificial boundary, carbon contents of biomass burning particles have vast variability and uncertainty (Lavanchy et al., 1999; Levin et al., 2010). EFs of EC and OC from this work agree well with previous study, average EFs of OC were 4.21 and 3.58 g kg^{-1} in smoke $PM_{2.5}$ and $PM_{1.0}$, and the values for EC were 1.09 and 1.01 g kg^{-1}. Mass ratio of OC/EC is an important parameter to indicate the primary organic aerosol (OA) emission and secondary organic aerosol (SOA) production. The ratio is response to burning conditions, source, aging extent, and particle size (Engelhart et al., 2012; Grieshop et al., 2009). Smoke emitted from smoldering fires is OC-dominated while flaming combustion produces more EC, and the discrepancy of OC/EC ratio can be an order of magnitude (Grieshop et al., 2009). SOA production upon photo-oxidation will increase the OC/EC ratio, and positive relation between oxidation level of OA and OC/EC ratio was reported (Grieshop et al., 2009). Here,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

516 OC/EC ratio in primary emissions varied from 2.4 to 6.2 under flaming condition,
517 similar to previous studies (Lewis et al. 2009; Dhammapala et al. 2007; Hayashi et al.
518 2014; Arora et al. 2015). The ratios were larger in $PM_{2.5}$ with average value of 3.8,
519 while it was 3.6 in $PM_{1.0}$, indicating more EC resides in $PM_{1.0}$.

520 EC in smoke particle can be further classified as char-EC and soot-EC based on
521 the distinct different physiochemical properties and formation mechanisms of soot
522 and char (Arora et al., 2015; Lin et al., 2011; Reid et al., 2005a; Richter et al., 2000).
523 Both char- and soot-EC represent the major light-absorbing fraction of PM; however,
524 light-absorption potential of soot-EC exceeds char-EC (Arora et al., 2015). Char-EC
525 can be distinguished as brown carbon, as carbonaceous materials that are optically
526 between the strongly absorbing soot and non-absorbing organics are operationally
527 defined as brown carbon (Yang et al., 2009; Andreae et al., 2006). Char-EC is
528 formed from solid residues during relative low-temperature combustion, while
529 generation of soot-EC takes place under high-temperature conditions from
530 recondensation and dihydrogen-carbonization of gaseous materials (Han et al., 2009;
531 Han et al., 2007). Average EFs of char- and soot-EC in smoke $PM_{2.5}$ were 0.93 ±
532 0.50 and 0.15 ± 0.15 g kg^{-1} in this study. Mass ratio of char-EC/soot-EC is a more
533 effective indicator for source identification and apportionment than OC/EC (Han et
534 al., 2009; Han et al., 2007). The ratios of char-EC/soot-EC also varied with fuel
535 types and PM fraction. Similar to OC/EC, char-EC/soot-EC was larger in $PM_{2.5}$ with
536 average ratio of 7.28, and the ratio was 6.29 in $PM_{1.0}$, the result indicates that
537 char-EC dominates the EC fraction in SPM and char particle has a larger size than
538 soot, as soot particle is mainly within several hundred nanometers, while char is
539 reported primarily to be supermicron particle (Arora et al., 2015; China et al., 2014;
540 Lin et al., 2011; Wornat et al., 2007). Besides, correlation among the multi-pollutants
541 was analyzed by relevance matrix as shown in Table S6 (SI), the strong positive
542 linear relationship (R^2>0.99, p<0.05) between EC and char-EC also confirms the
543 reliable source of biomass burning to produce char-EC (Lin et al., 2011; Arora et al.,
544 2015).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

3.1.2 Water soluble organic acids

Smoke particles comprise a considerable amount of water soluble organic acids (WSOA), it was 3.35 wt.% in $PM_{2.5}$ and 3.17 wt.% in $PM_{1.0}$ on average, which was in line with previous work that organic acids measured represented less than 5 wt.% of the total smoke aerosol mass load (Falkovich et al., 2005; Gao et al., 2003). Acetic acid followed by methysulfonic acid contributes the most of the measured low molecule weight acids. The sums of EFs of these organic acids ranged from 46.7 to 770.0 mg kg^{-1}, and the WSOA were highly correlated with emissions of OC and PM in Table S6 (SI). Study has shown organic acids contribute a significant fraction of both oxygenated volatile organic compounds (OVOCs) in gaseous phase and SOA in particulate phase, the direct emission of particulate organic acids from biomass burning also represents a significant source of precursors for SOA formation, as the low molecular organic acids will evaporate into gas phase or involve in the heterogeneous reaction directly (Takegawa et al., 2007; Veres et al., 2010; Yokelson et al., 2007; Carlton et al., 2006). Moreover, as the significant fraction of water soluble organic carbon, organic acids plays major response to CCN activity of smoke particles, and organic acids coating or mixing can amplify hygroscopic growth of inorganic salts by decreasing the deliquescence RH, enable the particle to be CCN at relative low degree of supersaturation (Falkovich et al., 2005; Ghorai et al., 2014). In the ambient environment, organic acids can enhance atmospheric new particle formation by impairing nucleation barrier (Zhang et al., 2004), besides, particulate organic acids can also mobilize the solubility of mineral species, like iron, altering the chemical process of particles (Cwiertny et al., 2008). And prominent optical properties of organic acids like humic/fulvic substance make them as potential contributors to the global warming (Yang et al., 2009; Andreae et al., 2006).

3.1.3 Water soluble aminiums

Interest has been focused on the vital role of amines in particle nucleation-growth process and acidity regulating due to their strong base (Tao et al., 2016; Bzdek et al., 2011; Bzdek et al., 2010). Though ultratrace gaseous amines and particulate

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

aminiums were on the order of pptv and ng m^{-3}, aminium salts exhibit potential climatic and health effect due to their significant different properties in hygroscopic, optical and also toxicological (Qiu et al., 2012; Qiu et al., 2011; Samy et al., 2013; Zheng et al., 2015; Ho et al., 2015; Tao et al., 2016). It ever proposed that biomass burning is an important emission source of gaseous amines, especially from smoldering burning, and particulate alkyl amides can be served as biomarkers (Ge et al., 2011; Ho et al., 2015; Lee et al., 2013; Lobert et al., 1990; Simoneit et al., 2003). However, seldom study ever quantitatively explored the particulate water soluble amine salts (WSA) in primary smoke particle emissions (Schade et al., 1995; Ge et al., 2011). From this study, WSA contributed 4.81 wt.‰ of smoke $PM_{2.5}$ and 4.69 wt.‰ of $PM_{1.0}$ on average, implicating aminium favored to be abundant in fine-mode smoke particles, especially in $PM_{2.5-1.0}$. $DEAH^+$, $TMAH^+$, $TEOH^+$ and $DMAH^+$ made up over 80 wt. % of the measured WSA. Fuel-dependence of WSA distribution and emission were obvious. EFs of WSA ranged from 4.5 to104.8 mg kg^{-1} in smoke $PM_{2.5}$, the least was from burning of soybean straw and the largest from cotton and rice straws. We used mass ratio of WSA to NH_4^+ to denote the enrichment of aminium in particulate phase. WSA/NH_4^+ in smoke $PM_{1.0}$ and in $PM_{2.5}$ was 0.16 ± 0.03 and 0.18 ± 0.06.

3.1.4 PAHs and Phenols

Atmospheric PAHs are primarily the byproduct of incomplete combustion of biomass and fossil fuels (Simcik et al., 1999; Galarneau, 2008). Due to their high degree of bioaccumulation and carcinogenic or mutagenic effect, the sources and environmental fate of the ubiquitous PAHs have been the subjects of extensive studies (Santodonato, 1997; Kim et al., 2013). PAHs can involve in photochemical reaction to form SOA, the process is influenced by gas-to-particle partition and meteorological conditions. Oxidation may increase the toxicity of PAHs (Arey et al., 2003; Wang et al., 2011). Biomass burning is one of the main sources of gaseous and particulate PAHs, which even contributes to about half of total PAHs emissions in the atmosphere in China (Xu et al., 2006; Zhang et al., 2011). Burning conditions

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

603 can significantly influence the emission of PAHs, under the flaming phase in this
604 study, PAHs contributed 0.46 wt.‰ of smoke $PM_{2.5}$ and 0.28 wt.‰ of $PM_{1.0}$, over 60%
605 of the total PAHs were associated to respiratory submicron particles. Emission
606 factors of 16 PAHs in smoke $PM_{2.5}$ ranged from 1.81 to 8.30 mg kg^{-1}, which were
607 consistent with the values from literature (Dhammapala et al., 2007; Lee et al., 2005;
608 Zhang et al., 2011). Dhammapala et al. also found laboratory simulated burnings
609 might overestimate the emission factors of PAHs compared with field burnings
610 (Dhammapala et al., 2007). The distribution of particulate PAHs emission factors
611 was presented in Fig. 3a. Of the particle bound PAHs, 3~4-rings components were
612 the primary ones, including Pyr, Ant, Ace, Flu, Phe, and Chr. Concentration ratios of
613 selected PAHs, namely diagnostic ratios, were usually used to trace the source and
614 make apportionment of specific pollutions (Yunker et al., 2002; Simcik et al., 1999).
615 In this work, average Ant/(Ant+Phe), Flu/(Flu+Pyr), BaA/(BaA+Chr), and
616 IP/(IP+BghiP) ratios of 5 types agricultural residue burning smokes were 0.72, 0.36,
617 0.47, and 0.58, respectively. There was no significant difference of the ratios in
618 $PM_{1.0}$ and $PM_{2.5}$. According to previous work, Ant/(Ant+Phe) above 0.1 and
619 BaA/(BaA+Chr) above 0.35 indicate the dominance of combustion and pyrolytic
620 sources, Flu/(Flu+Pyr) and IP/(IP+BghiP) ratios greater than 0.50 suggest coal or
621 biomass burnings dominate (Simcik et al., 1999; Yunker et al., 2002). However,
622 validation of source apportionment using specific diagnostic ratios should have its
623 constraints, because of variations in source strengths and atmospheric processing of
624 PAHs (Arey et al., 2003; Galarneau, 2008).

625 From Table S6 (SI), The PAHs in smoke particles were highly correlated with EC
626 and OC contents. PAHs primarily originate from pyrolysis of organic materials
627 during combustion, and formation mechanisms of PAHs and soot are closely
628 intertwined in flames. High-molecular-weight PAHs (>500 atomic mass unit) act as
629 precursors of soot particles (Lima et al., 2005; Richter et al., 2000). Thus, PAHs with
630 3, 4, and 5 rings accumulate and dominate in the emissions of biomass burning, as
631 larger molecular weight PAHs tend to incorporate into soot particles. PAHs
632 expulsion-accumulation in OC and EC fractions were analyzed by linear fitting of

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

PAHs mass fractions and EC mass fractions in carbonaceous materials (EC+OC) in Fig. 3b. The partitions can be parameterized as Eq. (10):

$$f_{PAHs} = \frac{m_{PAHs}}{m_{OC}+m_{EC}} = \beta_{EC} \times \frac{m_{EC}}{m_{OC}+m_{EC}} + \beta_{OC} \times \frac{m_{OC}}{m_{OC}+m_{EC}} = \beta_{EC} \times f_{EC} + \beta_{OC} \times f_{OC} \quad (10)$$

where f_{EC} and f_{OC} are the mass fraction of OC and EC in carbonaceous materials (EC+OC). β_{EC} and β_{OC} are expulsion-accumulation coefficients of PAHs in OC and BC. The coefficient of β_{EC} is 1.1×10^{-3} in smoke $PM_{1.0}$ and 1.9×10^{-3} in $PM_{2.5}$; the corresponded β_{OC} is 0.3×10^{-3} and 0.5×10^{-3}.

Phenols are the most common SOA precursor/product and organic pollutants in the atmosphere (Berndt et al., 2006; Schauer et al., 2001). Hydroxyl functional group and aromatic benzene ring make phenols a paradigm in heterogeneous reaction upon photo oxidation research and aqueous phase reaction research. Phenols are also ROS precursors that present health hazard (Bruce et al., 1987). Phenol and substituted phenols are thermal products of lignin pyrolysis during biomass burning (Dhammapala et al., 2007), and the five measured phenols contributed 2.98 wt. ‰ and 2.47 wt. ‰ of $PM_{2.5}$ and $PM_{1.0}$. 2, 6-dimethoxyphenol was the major one of the measured phenols. Mass fraction of phenols was about 7~9 time of PAHs in smoke aerosols.

3.1.5 Inorganic components

From Fig. 2, smoke particles consisted of approximately 24 wt.% water soluble inorganics (WSI), and the inorganic salts resided more in $PM_{1.0}$. K^+, NH_4^+, Cl^-, and SO_4^{2-} were the major inorganic ions in WSI. Particulate enriched K^+ together with levoglucose are treated as tracer of pyrogenic source (Andreae et al., 1998). And specific mass ratio of K^+/OC or K^+/EC will help make source apportionment of particulate pollutants with PMF (Positive Matrix Factorization) and PFA (Principle Balance Analysis) models (Lee et al., 2015). K^+/OC in smoke particles ranged from 0.11 to 0.25 with average value of 0.17 in $PM_{1.0}$ and 0.14 in $PM_{2.5}$, which were similar to those reported for the Savannah burning and agricultural waste burning emissions in India and China (Echalar et al., 1995; Ram and Sarin, 2011). However, OC represents large uncertainty arise from degree of oxidization and burning

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

condition, K^+/EC is more practical parameter to distinguish the pyrogenic pollutants in ambient study. To smoke particle emitted from flaming fires, K+/EC was 0.58 ± 0.24 in $PM_{1.0}$ and 0.53 ± 0.18 in $PM_{2.5}$. Cl^- was the main anion to balance the charge of WSI in smoke particles. Mean charge ratio of Cl^- : K^+ was 1.46 and 1.49 in $PM_{1.0}$ and $PM_{2.5}$, with atmospheric aging, the ratio will decrease as chloride be replaced by secondary sulfate and nitrate (Li et al., 2015; Li et al., 2003). Equivalent charge ratio of primary cations (NH_4^+ + K^+) to primary anions (SO_4^{2-} + Cl^-) was 1.05 in $PM_{1.0}$ and 1.01 in $PM_{2.5}$ on average, and charge ratios of total cations to anions ($R_{C/A}$) was 1.09 and 1.07 in $PM_{1.0}$ and $PM_{2.5}$. $R_{C/A}$ was used to indicate the neutralizing level of particulate matters in many studies. $R_{C/A} \geq 1$ indicates most of the acids can be neutralized, while $R_{C/A} < 1$ means atmospheric ammonia is deficient and the aerosol is acidic (Adams et al., 1999; He et al., 2011a; Kong et al., 2014). In ambient environment, acidic aerosol was prevailing urban pollutants in many cities from field investigation (He et al., 2011a; Kong et al., 2014). Acidic aerosols can increase the risks to human health and affect the atmospheric chemistry by activating hazardous materials and promoting the solubility of particulate iron and phosphorus (Amdur et al., 1989; Meskhidze, 2005). The emission and transport of biomass burning particles may neutralize the acidity of ambient particles. However, only limited WSI were brought into in the analytical system, considering the existence of massive organic acids and ammniums, it is not really to tell the acidity or base of smoke particles.

Trace mineral elements attracted great attention for the role as catalyst in atmospheric heterogeneous reaction and health cares (Davidson et al., 2005; Dentener et al., 1996). Wet/dry deposition of particles during long range transport will affect the ecological balance by releasing mineral elements (Jickells et al., 2005). Dust storm, weathering, and industrial process are the main sources of particulate metals, and incineration can also produce a lot of mineral elements (Moreno et al., 2013). However, the emissions of trace metals from biomass burning are highly uncertain (Li et al., 2007), the great influence from local soil environment and soil heavy metal pollution will certainly affect the metal content in biomass fuel and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

692 smoke particle. In this study, THM resided more in $PM_{2.5}$ than in $PM_{1.0}$. Smoke
693 $PM_{2.5}$ consisted of 6.7 wt.‰ THM on average, $PM_{1.0}$ comprised 4.1 wt.‰ THM. EFs
694 of THM in $PM_{2.5}$ and $PM_{1.0}$ were 0.056 g kg^{-1} and 0.028 g kg^{-1} for all the five straws
695 burning aerosol. Al contributed over 90% of total THM, and As was the second most
696 element. Smoke particles from wheat, rice, and corn straws contained more mineral
697 elements than that from cotton and soybean residues combustion. Regardless the
698 difference in biomass fuels, the result can imply that soil heavy metal pollution is
699 heaver in the East China than that in Xinjiang in the West North of China (Wei et al.,
700 2010).

701 **3.2 Size, morphology, and mixing state of smoke particles**

702 Fresh smoke particles exhibited unimodal size distribution within 500 nm (Fig. S3,
703 SI), and previous chamber study has also confirmed that agricultural fire produces
704 large amount of ultrafine particles, implying more profound threat to human health
705 (Araujo et al., 2008; Delfino et al., 2005; Zhang et al., 2011). However, the role of
706 particles in the atmospheric process and health hazard depends not only size, but also
707 morphology and chemical mixing states (Dusek et al., 2006; Kennedy, 2007;
708 Mikhailov et al., 2006; Schlesinger, 1985). From TEM images in Fig. 4, agricultural
709 straw burning aerosols comprised a broad class of morphological and chemically
710 heterogeneous particles. Non-uniformly internal mixing of the agglomerates was
711 noticeable, including the major carbonaceous particles and a considerable amount of
712 inorganic salt particles, which was consistent with particulate chemical compositions
713 analysis. KCl particles containing minor sulfate or nitrate were the primary inorganic
714 particles, which presented crystal or amorphous state from X-ray diffraction analysis
715 (Fig. 4 a, b, c). And potassium-bearing particles have been used as a tracer of
716 ambient biomass burning pollutants. Fly ash particles were arresting due to visible
717 morphology difference and mineral chemical composition (Fig. 4 d, e, f). Fly ash
718 particles were more compact and rich in mineral elements like Ca, Si, Fe, Al, Mn,
719 and Cr. Besides, these particles had larger size, statistical average diameter of fly ash
720 particles obtained from bulk analysis was 2.2 ± 1.6 μm. The result also proved heavy

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

721 metals resided more in $PM_{2.5}$ than $PM_{1.0}$. Fly ashes are by products of incineration
722 process (Buha et al., 2014), including coagulation of fuel issue debris, condensation
723 of evaporated mineral metal from biomass fuels or adhered dirt at different burning
724 phase. These fly ashes coated by or agglomerated with carbonaceous materials were
725 like mash of mineral without clear lattice. Tar ball as a specific form of brown
726 carbon and soot were representative particles of biomass burning aerosol (Wilson et
727 al., 2013; Chakrabarty et al., 2010; Tóth et al., 2014). From Fig. 4 g, chain-like soot
728 particles were coagulated with tar ball. Soot particles were agglomerates of small
729 roughly spherical elementary carbonaceous particles, these chemical consistent
730 particles were within 20~30 nm, and high-resolution TEM showed the soot spheres
731 consisted of concentrically wrapped graphitic layers, while monomeric tar balls
732 possessed disordered microstructure. Tar balls and soot corresponded to different
733 stages in the aging of organic particles; tar balls abundant in fresh or slightly aged
734 biomass smoke are formed by gas-to-particle conversion of high-molecular weight
735 organic species or from aged primary tar droplets upon biomass burning. Soot
736 represents further aged carbon-bearing particles, formed from the pyrolysis of lignin,
737 cellulose, or tar balls (Pósfai, 2004; Tóth et al., 2014). The botryoid aggregates in
738 Fig. 4 g can be viewed as transformation of tar ball to soot. Tar ball and soot were
739 also internal mixed with inorganic salt including sulfate and nitrate (Fig. 4 g, h, i),
740 which made the physiochemical properties of BC even complicated, as study has
741 confirmed inorganic sulfate mixing will enhance light absorption and hygroscopicity
742 of BC (Zhang et al., 2008b). Dark-ring like shell of tar ball (Fig. 4 g, h) and spot-like
743 particles adhered to the surface of tar ball (Fig. 4 i) were K-rich materials. And size
744 of soot particles was mainly within 200 nm, while tar ball and other carbonaceous
745 particles can be over one micrometer.

746 **3.3 Open burning emissions**

747 **3.3.1 Crop straw production**

748 The agricultural straw productions were calculated and geographically displayed in
749 Fig. 5 a-c. Totally 647.3 Tg agricultural straws were produced in 2012 and dispersed

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

mainly in the North and Northeast of China. The distributions of the straws clearly correspond to the distinct planting regions that are divided by Qinling Mountain-Huaihe River line and the Yangtze River. Rice is primarily planted in the south of Qinling Mountain-Huaihe River line, only 10 % rice (single cropping rice dominate) is planted in Heilongjiang, Jilin, and Liaoning province, while wheat and corn are grew mostly in the north of the Yangtze River. Over 90 % of the wheat planted in China is winter wheat that gets ripe in summer, and more than 80 % rice including middle and late rice grows mature in autumn. Summer harvest contributed about 25 % of the agricultural straw production, which solely consists of rice and wheat straws in this period and distributes in the central and east of China. 493.9 Tg crop straws were produced mainly from corn and rice harvesting in autumn. Soybean and cotton straws account for about 8.6 % of autumn straw production that were primarily produced in Heilongjiang and Xinjiang province.

3.3.2 Open burning rate

The five scenarios of field burning rates and regional AIP ($\frac{I_{k,y}}{AI_{k,y}}$) in the year of 2000, 2006, and 2012 were listed in Table 6 and statistically analyzed in Fig. 6. A significant difference of regional burning rates among the versions was observed, and the rates from NDRC report were generally higher. For convenience, six zones were classified by geographic divisions and economic areas in China, including the North Plain (Anhui, Shandong, Hebei, Shanxi, Tianjin, Beijing), the Central of China (Hunan, Henan, Hubei), the Yangtze River Delta (Zhejiang, Jiangsu, Shanghai), the Northeast of China (Heilongjiang, Liaoning, Jilin), the Pan-Pearl River Delta (Hainan, Guangdong, Fujian, Guangxi, Guizhou, Sichuan, Yunnan, Jiangxi), the West of China (Shannxi, Chongqing, Xinjiang, Qinghai, Ningxia, Tibet, Inner Mongolia, Gansu). And the bulk-weighted burning rates that averaged from BAU, EM, and NDRC versions for the six zones were 22.3 % ± 3.1 %, 21.1 % ± 3.3 %, 28.4 % ± 6.2 %, 23.3 % ± 9.2 % 21.4 % ± 6.5 %, and 14.2 % ± 8.0 %, respectively. It was obvious that condition of agricultural field burning was most serious in the Yangtze River Delta, especially in the Zhejiang province. The

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

779 nationwide filed burning rate was 21.4 %, 16.3 %, 26.0 %, 14.9 %, and 26.8 % for
780 BAU-I, BAU-II, EM-I, EM-II, and NDRC, respectively, which were comparable
781 with the document values (Daize, 2000; Wei et al., 2004; Zhang et al., 2008a).

782 **3.3.3 Agricultural open burning emissions**

783 $PM_{2.5}$ emissions from agricultural field burnings based on BAU, EM, and NDRC
784 versions were calculated and geographically presented in Fig. 7 (emissions of
785 detailed chemical species in SI). A similar spatial character of regional emission
786 distribution was observed for BAU, EM, and NDRC versions, most emissions were
787 allocated in the North Plain and the Central of China where the primary agricultural
788 regions locate, echoing the agricultural fire sites in Fig. S2 (SI). Although filed
789 burning rates were higher in the Yangtze River Delta, the crop residue productions of
790 this zone were much less, which only contributed 4.3 % of the national straw
791 productions. Take NDRC as the basis, BAU and EM scenarios all underestimated the
792 emissions in the Northeast of China, especially in Heilongjiang.

793 The temporal distributions of field burning emissions also echoed the crop residue
794 productions and the agricultural fire sites in summer and autumn harvest. Apart from
795 Henan and Tibet where the main crop straws were produced in summer period, more
796 pollutants were emitted in autumn harvest period to the rest place, which has been
797 confirmed by many studies (He et al., 2011b; Wang and Zhang, 2008). And the large
798 scale filed burning emissions in autumn exhibited great influence on the haze
799 formation and visibility degradation in the North and East of China (Leng et al.,
800 2014; Shi et al., 2014). In summertime, filed burnings concentrated in the North
801 Plain, the Central, and the South regions. While in autumn, filed burning emissions
802 became more ubiquitous and serious in the Northeast of China.

803 Nationwide emission inventories and flux concentrations were graphically
804 displayed in Fig. 8 and tabular presented in Table 7. The total $PM_{2.5}$ emission from
805 agricultural field burnings was 0.74-1.24 Tg in 2012, of which $PM_{1.0}$ was 0.66-1.11
806 Tg, OC was 0.32-0.53 Tg, and EC was 0.09-0.16 Tg, and the results were
807 comparable with the precious studies (Cao et al., 2006; Cao et al., 2011; Wang et al.,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

2012). Allocated the emissions into the six zones to get the contribution of the North Plain (21 %) ≥ the Northeast (20 %) > Pan-Pearl River Delta (19 %) ≥ the Central (19 %) > the West (16 %) >the Yangtze River Delta (5 %). Summertime field burnings accounted for 20-25 % of national emissions. 24.60 Gg char-EC, 3.79 Gg soot-EC, 6.82 Gg WSOA, 1.00 Gg WSA, 0.11 Gg PAHs, 0.86 Gg phenol and substituted phenols, and 2.07 Gg THM on average were released in summer harvest from agricultural field burning. The corresponded values for autumn harvest were 88.77, 17.21, 18.36, 4.82, 0.37, 1.86, and 6.62 Gg, respectively. Zhang et al. (2011) estimated particulate PAHs emissions form three types of crop residues to be 0.46 Gg in 2003. Xu et al. (2006) counted PAHs from all straws without considering burning rates to get 5-10 Gg emissions in 2003.

The nationwide flux concentration of smoke $PM_{2.5}$ was 0.7-1.0 μg m^{-3} d^{-1} in summer harvest and 1.4-3.5 μg m^{-3} d^{-1} in autumn harvest, while average annual flux concentrations for OC and EC were 0.80 and 0.25 μg m^{-3} d^{-1}. Saikawa et al. (2009) assessed the annual concentrations of OC and BC from biomass burning primary emission in China using global models of chemical transport (MOZART-2) to be 1.8 and 0.35μg m^{-3}. The most polluted areas were Anhui, Henan, Shandong, Jiangsu, Liaoning, and Hunan.

3.3.4 Uncertainties of the emissions

The fuzziness and uncertainties of major pollutants emissions from fuel combustion in China came from the uncertainties in specific-source emission factors and effective consumption of bio- or fossil fuel. Frey et al. analyzed uncertainties in emission factors and emissions of air toxic pollutants and technology dependent coal-fire power plants via bootstrap simulation method (Frey et al., 2004; Frey et al., 2002). Zhao et al. estimated uncertainties in national anthropogenic pollutants emissions based on Monte Carlo simulation, and they believed activity rates (e.g. fuel consumption) are not the main source of emissions uncertainties at the national level (Zhao et al., 2012; Zhao et al., 2011). The uncertainties can also be estimated by comparing the specific emissions from different studies. With this method, the

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

uncertainties represent the bias among different copies of emission inventory.

In this study, the bias in smoke $PM_{2.5}$ emissions among BAU, EM, and NDRC versions was investigated and presented in Table 8. The average national smoke $PM_{2.5}$ emissions had 19% relative error. More variability of the emissions was in the West of China (51.4 %), followed by the Northeast (39.8 %), Pan-Pearl River Delta (25.9 %), and Yangtze River Delta (21.5 %). Although uncertainty was largest in the West, the contribution of the emissions was much less.

3.4 Health and health-related economic impacts

3.4.1 Carcinogenic risk

Calculated CR_{SPM} for smoke $PM_{2.5}$ from wheat, corn, rice, cotton, and soybean straw burning were 5.3×10^{-6}, 3.8×10^{-6}, 2.6×10^{-6}, 0.7×10^{-6}, and 1.3×10^{-6} per μg m^{-3}, respectively. And the corresponded one in million PEL was 0.2, 0.3, 0.4, 1.4, and 0.8 μg m^{-3}. Wu et al. (2009) ever assessed unit risk of wood and fuel burning particles using metals merely, the results were 3.2×10^{-6} and 1.5×10^{-6} per μg m^{-3}, which were close to that in our study. In actual application, PEL of smoke particles should be bulk mass concentration of mixed aerosols.

It was noticeable that apart from Tibet and Qinghai, the flux concentration of smoke $PM_{2.5}$ among all the five emission versions in other regions far surpassed the PEL, especially the North Plain and the Central of China, exhibiting great potential inhalable cancer risk. For the health care, emission flux concentration should be constrained within the PEL of crop straw burning aerosol. Thus the critical filed burning rates can be derived to ensure risk aversion following Eq. (11):

$$R_k \leq \frac{10^{-6}\times S_k\times h\times T_k}{\sum_j\sum_i P_{t,k,i}\times r_i\times H_{t,k,i}\times D_i\times f_i\times EF_{i,j}\times CRF_i} \quad (11)$$

The conservative values of regional field burning rates from Eq. (11) were named as Carcinogenic Risk Control scenarios (CRC) and listed in Table S7 (SI), which would be instructive in emission control. Under CRC, national crop straw field burning rate was less than 3%, emissions of $PM_{2.5}$ were geographically presented in Fig. S4 (SI), and 146.3 Gg yr^{-1} smoke $PM_{2.5}$ should be released at largest in China,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

the corresponded annual flux concentration of $PM_{2.5}$ was within 0.3 μg m^{-3} d^{-1} (see in SI).

3.4.2 Health impacts

Health impacts from acute exposure of agricultural residue burning aerosol were assessed using daily flux concentrations of smoke $PM_{2.5}$, the result was tabulated in Table S8 (SI). The impacts from smoke $PM_{2.5}$ exposure were severest in Jiangsu, Shandong, and Henan province, where annual premature mortality was over one thousand. On average, China suffered from 7836 (95% CI: 3232, 12362) premature death, 31181 (95% CI: 21145, 40881) respiratory hospital admissions, 29520 (95% CI: 12873, 45602) cardiovascular hospital admissions, and 7267237 (95% CI: 2961487, 1130784) chronic bronchitis related to agricultural fire smoke in 2012 from Table 9. According to national health statistical reports (NHFPC, 2013), the hospital admission due to respiratory and cardiovascular disease was 5071523 in China in 2012, and smoke $PM_{2.5}$ exposure might contribute ~1.2% of the hospital admissions from this study. Saikawa et al. (2009) ever reported 70000 premature deaths in China and an additional 30000 deaths globally due to OC, EC, and sulfate exposure that were primarily emitted from biofuel combustion in China in 2000, however, the results should be overestimated not only in the exaggerated pollutant emissions but also in the iterative operations of respective species induced mortality, besides, the exposure-response coefficient β and incidence rate he applied from Pope et al. (2002) and WHO (2000) were higher than the practical values from local research (Cao et al., 2012; Chen et al., 2011; Hou et al., 2012). From Table 9, under CRC version, over 92 % mortality and morbidity can be avoided.

3.4.3 Health-related economic losses

Health-related total economic losses from straw open burning smoke $PM_{2.5}$ exposure were assessed to be 8822.4 (95% CI: 3574.4, 13034.2) million US$ on average from Table 10, accounting for 0.1 % of the total GDP in 2012, and detailed regional economic losses were listed in Table S9. Economic losses from premature death

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

contributed about 17% of total losses, and loss from chronic bronchitis dominated. Hou et al. (2012) ever estimated 106.5 billion US$ lost due to ambient PM_{10} exposure in China in 2009; even a severe haze episode ($PM_{2.5}$ be focused on) in January 2013 may cause 690 premature death and 253.8 million US$ loss in Beijing, and source-specification analysis stressed the emission from biomass burning (Yang et al., 2015; Gao et al., 2015). It was obvious that smoke $PM_{2.5}$ contributed a noticeable damage to public health and social welfare. According to CRC version estimation, the carcinogenic risk control policy can save over 92 % of the economic loss.

4 Conclusion

Detailed chemical compositions of smoke aerosol from five major agricultural straws burning were characterized using an aerosol chamber system. And corresponded emission factors for particulate OC-EC, char-/soot-EC, WSI, WSOA, WSA, PAHs, Phenols, and THM in smoke $PM_{2.5}$ and $PM_{1.0}$ were established.

Permissible exposure limits (PEL) of the smoke particles were assessed for carcinogenic risk concern based on selected hazard pollutants including PAHs and THM in smoke $PM_{2.5}$. Daily exposure concentration should be constrained within 0.2, 0.3, 0.4, 1.4, and 0.8 μg m^{-3} for wheat, corn, rice, cotton, and soybean straw, respectively.

Emission inventories of primary particulate pollutants from agricultural field burning in 2012 were estimated based on BAU-I, BAU-II, EM-I, EM-II, and NDRC scenarios, which were further allocated into different regions at summer and autumn open burning periods. The estimated total emissions were 0.74-1.24 Tg $PM_{2.5}$, 0.66-1.11 Tg $PM_{1.0}$, 0.32-0.53 Tg OC, 0.09-0.16 Tg EC, 0.08-0.14 Tg char-EC, 0.02-0.03 Tg soot-EC, 18.77-30.82 Gg WSOA, 4.23-7.19 Gg WSA, 0.35-0.59 Gg PAHs, 2.02-3.40 Gg Phenols, and 6.36-10.64 Gg THM, respectively. The spatial and temporal distributions of the five versions have similar characters that echo to the agricultural fires sites from satellite remote sensing. Less than 25 % of the emissions were released from summer field burnings that were mainly contributed by the North

Plain and the Central of China. Large uncertainties of the emissions were found in the West and the Northeast of China (59.4% and 39.8% relative error). Flux concentrations of annual smoke $PM_{2.5}$ that were calculated using box-model method based on five versions all exceed the PEL. From assessment of health impacts and health-related economic losses due to smoke $PM_{2.5}$ short-term exposure, China suffered from 7836 (95%CI: 3232, 12362) premature mortality and 7267237 (95% CI: 2961487, 1130784) chronic bronchitis in 2012, which led to 8822.4 (95%CI: 3574.4, 13034.2) million US$, or 0.1 % of the total GDP losses.

Percentage of open burned crop straws at post-harvest period should cut down to less than 3% to ensure risk aversion from carcinogenicity, especially the North Plain and the Northeast, where the emissions should decease at least by 94% to meet the PEL. And by applying such emission control policy, over 92% of the mortality and morbidity attributed to agricultural fire smoke $PM_{2.5}$ can be avoided in China.

Supplementary material related to this article is available online at:

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Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

Tables and figure captions

Table 1. Emission factors of particulate chemical species in smoke $PM_{2.5}$ from agricultural residue burning.

Table 2. Emission factors of particulate chemical species in smoke $PM_{1.0}$ from agricultural residue burning.

Table 3. Emission factors of particulate THM, PAHs, and Phenols in smoke $PM_{2.5}$ from agricultural residue burning.

Table 4. Emission factors of particulate THM, PAHs, and Phenols in smoke $PM_{1.0}$ from agricultural residue burning.

Table 5. Comparison of emission factors with literature (specific chemical materials in form of $PM_{2.5}$)

Table 6. Summary of field burning rates and economic data in China

Table 7. National agricultural field burning emissions of BAU, EM, NDRC, and CRC scenarios in China, 2012.

Table 8. Uncertainties in emission estimates**.**

Table 9. Estimated number of cases (95% CI) attributable to agricultural fire smoke $PM_{2.5}$ exposure in China, 2012

Table 10. Health-related economic loss (95% CI) from agricultural fire smoke $PM_{2.5}$ exposure in China, 2012

Figure 1. Schematic methodology for developing emission estimations

Figure 2. Chemical profiles of smoke $PM_{2.5}$ and $PM_{1.0}$ from 5 types agricultural residue burnings. OM (organic matter = 1.3×OC). OWSI, other water soluble ions including F^-, NO_2^-, Na^+, Ca^{2+}, Mg^{2+}. THM, trace heavy metals. WSA, water-soluble amine salts. WSOA, water-soluble organic acids.

Figure 3. a) Emission factors of 16 USEPA priority PAHs in smoke $PM_{2.5}$ and $PM_{1.0}$; b) expulsion-accumulation of PAHs in OC-EC of smoke $PM_{2.5}$ and $PM_{1.0}$

Figure 4. Transmission electron microscope (TEM) images and EDX analysis of fresh agricultural residue burning particles. (a)-(c) Crystal and amorphous KCl particles internally mixed with sulfate, nitrate, and carbonaceous materials. (d)-(f) Heavy metal-bearing fractal-like fly ash particles. (e)-(g) Chain-like soot particles and tar ball.

Figure 5. Annual agricultural residue production of five major crops and allocated

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

into two harvest (summer and autumn harvest) based on agricultural yield in China, 2012.

Figure 6. Statistical analysis of field burning rates from BAU, EM, and NDRC versions

Figure 7. Spatial and temporal distribution of smoke $PM_{2.5}$ emissions and flux concentrations from agricultural field burning over China, 2012

Figure 8. Nationwide $PM_{2.5}$ emissions and flux concentrations based on different burning versions. The inset pie-graphs are chemical compositions of integrated $PM_{2.5}$ from five major agricultural residue burning.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
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Atmospheric Chemistry and Physics Discussions

1511 **Table 1.** Emission factors of particulate chemical species in smoke $PM_{2.5}$ from
1512 agricultural residue burning.

Chemical Species (g kg^{-1})	wheat straw	corn straw	rice straw	cotton residue	soybean residue
$PM_{2.5}$	5.803 ±0.363	5.988 ±0.723	14.732 ±2.417	15.162 ±2.053	3.249 ±0.350
OC	2.813 ±0.147	2.393 ±0.351	6.882 ±0.689	7.415 ±0.547	1.539 ±0.253
EC	0.676 ±0.027	0.778 ±0.152	2.182 ±0.278	1.192 ±0.171	0.614 ±0.190
Char-EC	0.606 ±0.024	0.667 ±0.132	1.761 ±0.166	1.072 ±0.154	0.564 ±0.177
Soot-EC	0.069 ±0.007	0.110 ±0.043	0.421 ±0.061	0.120 ±0.034	0.051 ±0.031
Inorganic ions (g kg^{-1})	**1.273 ±0.072**	**1.810 ±0.030**	**3.086 ±0.266**	**3.810 ±0.246**	**0.523 ±0.149**
SO_4^{2-}	0.084 ±0.028	0.217 ±0.041	0.409 ±0.127	0.701 ±0.081	0.073 ±0.014
Cl^-	0.576 ±0.038	0.709 ±0.034	1.158 ±0.232	1.351 ±0.114	0.178 ±0.030
F^-	0.023 ±0.061	0.061 ±0.005	0.073 ±0.024	0.265 ±0.012	0.009 ±0.004
NO_3^-	0.023 ±0.000	0.032 ±0.002	0.051 ±0.025	0.072 ±0.004	0.009 ±0.004
NO_2^-	0.006 ±0.001	0.016 ±0.002	0.018 ±0.002	0.036 ±0.001	0.004 ±0.003
Ca^{2+}	0.030 ±0.011	0.036 ±0.003	0.046 ±0.007	0.060 ±0.003	0.010 ±0.002
Na^+	0.005 ±0.001	0.012 ±0.001	0.028 ±0.004	0.050 ±0.004	0.005 ±0.001
NH_4^+	0.152 ±0.005	0.197 ±0.010	0.542 ±0.107	0.347 ±0.008	0.029 ±0.004
Mg^{2+}	0.005 ±0.000	0.017 ±0.002	0.023 ±0.004	0.032 ±0.002	0.005 ±0.001
K^+	0.368 ±0.041	0.514 ±0.009	0.739 ±0.049	0.947 ±0.070	0.200 ±0.023
Organic Acids (mg kg^{-1})	**156.680 ±81.830**	**46.670 ±9.000**	**557.130 ±269.380**	**769.990 ±317.550**	**143.310 ±39.770**
CH_3COOH	148.900 ±79.290	36.640 ±8.210	417.930 ±186.140	743.320 ±159.600	135.500 ±62.320
MSA	7.170 ±2.110	10.030 ±30.000	136.990 ±81.700	12.980 ±1.530	3.200 ±1.530
$H_2C_2O_4$	2.610 ±0.430	ND	2.210 ±1.560	4.760 ±2.640	2.170 ±2.380
HCOOH	ND	ND	ND	8.930 ±2.630	2.440 ±1.450
Amine salts (mg kg^{-1})	**19.246 ±9.368**	**32.877 ±19.141**	**104.787 ±15.635**	**102.409 ±13.379**	**4.514 ±1.776**
$MeOH^+ + MMAH^+$	1.322 ±0.086	5.735 ±0.102	17.226 ±1.454	19.888 ±0.351	0.456 ±0.196
$MEAH^+$	0.201 ±0.055	0.675 ±0.135	4.175 ±0.920	3.690 ±1.959	ND
$TEOH^+$	2.562 ±0.962	4.118 ±0.741	25.129 ±0.343	14.376 ±8.688	0.672 ±0.558
$DEAH^+ + TMAH^+$	13.728 ±7.512	18.973 ±0.466	46.148 ±12.185	28.568 ±5.321	2.012 ±0.878
$DMAH^+$	1.434 ±0.925	3.376 ±0.674	12.110 ±6.166	35.887 ±2.940	1.374 ±0.144
Elemental Species (mg kg^{-1})	**53.813 ±18.860**	**53.546 ±9.070**	**131.612 ±5.920**	**27.577 ±3.700**	**14.003 ±8.710**
Phenols (mg kg^{-1})	**26.785 ±8.582**	**16.390 ±2.652**	**27.238 ±4.861**	**41.481 ±5.517**	**9.673 ±2.272**
PAHs (mg kg^{-1})	**1.814 ±0.348**	**2.706 ±0.798**	**7.267 ±1.722**	**8.302 ±2.856**	**1.832 ±0.353**

1513 *ND means not detected*

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Atmospheric Chemistry and Physics Discussions

1514 **Table 2.** Emission factors of particulate chemical species in smoke $PM_{1.0}$ from
1515 agricultural residue burning.

Chemical Species (g kg^{-1})	wheat straw	corn straw	rice straw	cotton residue	soybean residue
$PM_{1.0}$	5.298 ±0.295	5.360 ±0.551	13.200 ±1.440	12.635 ±1.243	3.036 ±0.257
OC	2.419 ±0.126	2.063 ±0.340	6.024 ±0.602	6.036 ±0.360	1.338 ±0.128
EC	0.650 ±0.037	0.728 ±0.122	2.083 ±0.413	1.023 ±0.205	0.575 ±0.260
Char-EC	0.567 ±0.033	0.580 ±0.098	1.671 ±0.331	0.916 ±0.184	0.511 ±0.233
Soot-EC	0.083 ±0.014	0.148 ±0.057	0.411 ±0.073	0.107 ±0.048	0.063 ±0.057
Inorganic ions (g kg^{-1})	**1.215 ±0.040**	**1.768 ±0.010**	**2.940 ±0.249**	**3.516 ±0.145**	**0.510 ±0.156**
SO_4^{2-}	0.078 ±0.011	0.199 ±0.032	0.333 ±0.107	0.581 ±0.054	0.073 ±0.056
Cl^-	0.544 ±0.033	0.712 ±0.027	1.145 ±0.118	1.243 ±0.067	0.175 ±0.031
F^-	0.022 ±0.007	0.041 ±0.004	0.078 ±0.030	0.151 ±0.011	0.001 ±0.001
NO_3^-	0.021 ±0.005	0.027 ±0.002	0.043 ±0.016	0.061 ±0.003	0.009 ±0.002
NO_2^-	0.006 ±0.001	0.010 ±0.003	0.013 ±0.004	0.019 ±0.002	0.004 ±0.003
Ca^{2+}	0.027 ±0.013	0.028 ±0.002	0.045 ±0.008	0.067 ±0.005	0.010 ±0.002
Na^+	0.004 ±0.000	0.012 ±0.000	0.027 ±0.003	0.056 ±0.006	0.005 ±0.002
NH_4^+	0.147 ±0.005	0.191 ±0.009	0.511 ±0.067	0.401 ±0.004	0.031 ±0.005
Mg^{2+}	0.005 ±0.001	0.035 ±0.001	0.024 ±0.006	0.033 ±0.002	0.005 ±0.001
K^+	0.359 ±0.040	0.513 ±0.015	0.721 ±0.073	0.994 ±0.067	0.197 ±0.035
Organic Acids (mg kg^{-1})	**124.310 ±25.170**	**47.830 ±10.610**	**427.400 ±221.270**	**639.820 ±244.960**	**130.760 ±59.310**
CH_3COOH	115.790 ±21.940	38.960 ±9.610	383.360 ±179.050	615.790 ±232.860	124.310 ±69.000
MSA	6.830 ±2.030	8.870 ±2.730	41.380 ±38.480	11.380 ±2.360	3.200 ±1.730
$H_2C_2O_4$	1.690 ±1.200	ND	2.660 ±1.760	3.620 ±1.250	1.560 ±1.670
HCOOH	ND	ND	ND	9.030 ±7.710	1.690 ±1.390
Amine salts (mg kg^{-1})	**18.191 ±5.351**	**29.891 ±13.480**	**81.726 ±11.455**	**85.720 ±21.337**	**4.385 ±1.445**
$MeOH^+ + MMAH^+$	1.300 ±0.282	5.647 ±0.342	16.627 ±0.104	18.834 ±1.991	0.464 ±0.265
$MEAH^+$	0.157 ±0.037	0.787 ±0.211	3.581 ±0.602	2.771 ±1.304	ND
$TEOH^+$	1.719 ±0.283	5.115 ±0.732	17.575 ±0.844	11.441 ±3.229	0.529 ±0.304
$DEAH^+ + TMAH^+$	13.716 ±9.047	15.921 ±1.620	33.565 ±6.795	29.057 ±3.793	2.278 ±0.533
$DMAH^+$	1.300 ±0.702	2.420 ±0.575	10.377 ±4.521	23.617 ±20.086	1.115 ±0.343
Elemental Species (mg kg^{-1})	**31.586 ±10.630**	**29.265 ±4.240**	**51.062 ±5.920**	**16.738 ±3.480**	**11.817 ±6.650**
Phenols (mg kg^{-1})	**20.774 ±4.972**	**13.193 ±2.181**	**20.480 ±1.403**	**23.521 ±8.521**	**7.689 ±1.356**
PAHs (mg kg^{-1})	**1.257 ±0.398**	**1.420 ±0.232**	**3.967 ±0.970**	**4.359 ±1.373**	**1.123 ±0.205**

1516 *ND means not detected*

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Atmospheric Chemistry and Physics Discussions

1517 **Table 3.** Emission factors of particulate THM, PAHs, and Phenols in smoke $PM_{2.5}$
1518 from agricultural residue burning.

Chemical Species (mg kg^{-1})	wheat straw	corn straw	rice straw	cotton residue	soybean residue
Elemental Species	**53.813 ±18.860**	**53.546 ±9.070**	**131.612 ±5.920**	**27.577 ±3.700**	**14.003 ±8.710**
As	6.433 ±1.424	4.684 ±0.879	6.724 ±0.737	2.082 ±1.078	0.777 ±0.525
Zn	0.868 ±0.180	0.358 ±0.624	0.275 ±0.177	0.229 ±0.264	0.053 ±0.046
Pb	ND	ND	0.467 ±0.313	0.063 ±0.053	0.059 ±0.047
Cd	ND	ND	0.053 ±0.000	ND	ND
Ni	0.726 ±0.074	0.695 ±0.138	1.100 ±0.113	0.372 ±0.170	0.193 ±0.092
Cr	1.026 ±0.335	0.746 ±0.299	3.324 ±0.257	0.543 ±0.055	0.266 ±0.127
V	0.159 ±0.006	0.104 ±0.061	0.560 ±0.022	0.110 ±0.011	0.051 ±0.044
Al	44.602 ±5.269	46.957 ±10.471	119.108 ±4.636	24.178 ±2.331	12.603 ±6.709
PAHs	**2.407±0.348**	**2.706 ±0.798**	**7.267 ±1.722**	**6.017±2.856**	**1.832 ±0.353**
naphthalene	0.417±0.116	0.087 ±0.077	0.780 ±0.128	0.116±0.086	0.093 ±0.041
acenaphthylene	0.032±0.023	0.028 ±0.013	0.701 ±0.269	0.201±0.277	0.004 ±0.006
acenaphthene	0.107±0.034	0.285 ±0.143	1.713 ±0.542	0.502±0.667	0.073 ±0.173
flourene	0.021±0.010	0.003 ±0.002	0.069 ±0.005	0.017±0.024	0.001 ±0.001
anthracene	0.343±0.121	0.384 ±0.111	0.656 ±0.003	1.177±0.536	0.245 ±0.127
phenathrene	0.179±0.090	0.112 ±0.030	0.202 ±0.007	0.547±0.239	0.105 ±0.011
flouranthene	0.368±0.071	0.561 ±0.217	0.926 ±0.029	0.930±0.250	0.306 ±0.042
pyrene	0.628±0.107	0.853 ±0.240	1.460 ±0.039	1.818±0.598	0.586 ±0.178
benz[a]anthracene	0.057±0.019	0.056 ±0.023	0.118 ±0.016	0.158±0.056	0.058 ±0.026
chrysene	0.058±0.008	0.088 ±0.033	0.119 ±0.010	0.166±0.057	0.063 ±0.010
benzo[a]pyrene	0.148±0.025	0.113 ±0.044	0.398 ±0.083	0.148±0.076	0.131 ±0.072
benzo[b]flouranthene	0.017±0.012	0.051 ±0.049	0.026 ±0.008	0.086±0.011	0.047 ±0.007
benzo[k]flouranthene	0.021±0.008	0.014 ±0.011	0.022 ±0.009	0.036±0.006	0.020 ±0.013
benzo[g,h,i]pyrene	0.006±0.003	0.024 ±0.024	0.011 ±0.004	0.046±0.011	0.033 ±0.046
indeno[1,2,3-cd]pyrene	0.005±0.001	0.086 ±0.011	ND	0.022±0.012	ND
dibenz[a,h]anthracene	0.002±0.001	0.038 ±0.051	0.068 ±0.027	0.066±0.003	0.067 ±0.047
Phenols	**26.785 ±8.582**	**16.390 ±2.652**	**27.238 ±4.861**	**41.481 ±5.517**	**9.673 ±2.272**
phenol	2.357 ±0.797	3.974 ±0.759	10.737 ±6.373	3.992 ±0.128	2.834 ±2.944
2-methoxyphenol	0.567 ±0.061	0.531 ±0.015	2.545 ±0.200	0.371 ±0.083	0.363 ±0.712
4-ethylphenol	2.239 ±0.323	1.417 ±0.536	1.624 ±0.740	5.105 ±0.707	0.475 ±0.358
4-ethyl-2-methoxyphenol	0.671 ±0.318	0.290 ±0.070	0.383 ±0.116	1.588 ±0.244	0.187 ±0.375
2,6-dimethoxyphenol	20.952 ±8.677	10.178 ±2.334	11.949 ±0.456	30.424 ±4.662	5.815 ±2.117

1519 *ND means not detected*

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Atmospheric Chemistry and Physics Discussions

1520 **Table 4.** Emission factors of particulate THM, PAHs, and Phenols in smoke $PM_{1.0}$
1521 from agricultural residue burning.

Chemical Species (mg kg^{-1})	wheat straw	corn straw	rice straw	cotton residue	soybean residue
Elemental Species	**31.586 ±10.630**	**29.265 ±4.240**	**51.062 ±5.920**	**16.738 ±3.480**	**11.817 ±6.650**
As	2.781 ±1.159	2.984 ±0.617	4.861 ±0.737	1.751 ±1.529	0.342 ±0.750
Zn	0.607 ±0.514	0.137 ±0.091	0.293 ±0.489	0.112 ±0.059	0.040 ±0.035
Pb	ND	ND	ND	0.007 ±0.004	0.013 ±0.006
Cd	ND	ND	0.043 ±0.000	ND	ND
Ni	0.435 ±0.057	0.365 ±0.042	0.654 ±0.113	0.218 ±0.033	0.171 ±0.098
Cr	0.556 ±0.024	0.487 ±0.000	0.923 ±0.257	0.292 ±0.030	0.233 ±0.092
V	0.101 ±0.005	0.118 ±0.044	0.188 ±0.022	0.065 ±0.010	0.049 ±0.023
Al	27.106 ±3.566	25.115 ±3.497	44.037 ±4.636	14.293 ±1.834	10.968 ±5.592
PAHs	**1.257 ±0.398**	**1.420 ±0.232**	**3.967 ±0.970**	**3.159 ±1.373**	**1.123 ±0.205**
naphthalene	0.118 ±0.031	0.112 ±0.131	0.360 ±0.106	0.043 ±0.011	0.082 ±0.130
acenaphthylene	0.023 ±0.018	0.028 ±0.021	0.339 ±0.333	0.074 ±0.102	0.008 ±0.008
acenaphthene	0.034 ±0.014	0.173 ±0.055	0.828 ±0.783	0.269 ±0.354	0.068 ±0.025
flourene	0.009 ±0.007	0.003 ±0.001	0.033 ±0.005	0.006 ±0.006	0.002 ±0.000
anthracene	0.210 ±0.107	0.209 ±0.052	0.178 ±0.166	0.600 ±0.251	0.197 ±0.051
phenathrene	0.097 ±0.030	0.084 ±0.016	0.055 ±0.045	0.259 ±0.048	0.077 ±0.149
flouranthene	0.212 ±0.086	0.219 ±0.077	0.636 ±0.048	0.475 ±0.116	0.178 ±0.026
pyrene	0.391 ±0.146	0.385 ±0.142	1.160 ±0.009	1.043 ±0.714	0.298 ±0.065
benz[a]anthracene	0.031 ±0.009	0.032 ±0.016	0.097 ±0.006	0.086 ±0.010	0.033 ±0.019
chrysene	0.034 ±0.004	0.056 ±0.022	0.091 ±0.011	0.096 ±0.009	0.037 ±0.018
benzo[a]pyrene	0.071 ±0.031	0.057 ±0.038	0.129 ±0.039	0.107 ±0.010	0.055 ±0.002
benzo[b]flouranthene	0.013 ±0.005	0.018 ±0.018	0.047 ±0.033	0.043 ±0.010	0.031 ±0.005
benzo[k]flouranthene	0.009 ±0.003	0.011 ±0.008	0.014 ±0.005	0.018 ±0.001	0.012 ±0.013
benzo[g,h,i]pyrene	0.005 ±0.005	0.007 ±0.005	ND	0.005 ±0.005	0.014 ±0.057
indeno[1,2,3-cd]pyrene	ND	0.011 ±0.006	ND	0.011 ±0.012	ND
dibenz[a,h]anthracene	ND	0.014 ±0.015	ND	0.025 ±0.029	0.031 ±0.001
Phenols	**20.774 ±4.972**	**13.193 ±2.181**	**20.480 ±1.403**	**23.521 ±8.521**	**7.689 ±1.356**
phenol	3.296 ±1.962	4.389 ±0.089	8.917 ±2.588	2.824 ±0.031	1.660 ±0.293
2-methoxyphenol	0.604 ±0.003	0.682 ±0.357	1.711 ±0.155	0.353 ±0.088	0.195 ±0.034
4-ethylphenol	1.387 ±0.408	0.490 ±0.246	1.171 ±0.233	2.965 ±0.441	0.495 ±0.087
4-ethyl-2-methoxyphenol	0.438 ±0.193	0.231 ±0.004	0.222 ±0.039	0.834 ±0.180	0.137 ±0.024
2,6-dimethoxyphenol	15.050 ±6.336	7.402 ±0.478	8.459 ±0.759	16.545 ±2.113	5.202 ±0.917

1522 *ND means not detected*

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Table 5. Comparison of emission factors with literature (specific chemical materials in form of $PM_{2.5}$).

Species	Emission factors (g kg^{-1})		Reference
	This work	Reference value	
$PM_{2.5}$	8.99 ± 5.55	7.6~11.7(AR), 6.26~15.3 (TL), ~3.0 (AR), 2.2~15.0 (AR)	Li et al., 2007; Akagi et al., 2011; Dhammapala et al., 2007; Hayashi et al 2014
$PM_{1.0}$	7.91 ± 4.67	4.4.3~12.1 (TL)	May et al., 2014
OC	4.21 ± 2.73	2.7~3.9 (AR), 2.3~9.7(TL), ~1.9(AR) , 1.0~9.3 (AR), 0.8~5.9 (TL)	Li et al., 2007; Akagi et al., 2011; Dhammapala et al., 2007; Hayashi et al., 2014; May et al.2014
EC	1.09 ± 0.65	0.35~0.49 (AR), 0.37~0.91(TL), ~0.4(AR), 0.21~0.81(AR), 1.13~1.73 (TL)	Li et al., 2007; Akagi et al., 2011; Dhammapala et al., 2007; Hayashi et al., 2014; May et al.2014
WSOA	0.33 ± 0.31	0.039~0.109 (TL)	Akagi et al., 2011
WSA	0.05 ± 0.05	0.08~0.13 (TL), ~0.55 (TL)	Akagi et al., 2011; Andreae et al., 2001
WSI	2.10 ± 1.34	1.84~4.9 (AR),0.8~1.31(TL), 0.43~1.63 (AR)	Li et al., 2007; Akagi et al., 2011; Hayashi et al., 2014
THM	0.06 ± 0.05	0.06~0.09 (AR)	Li et al., 2007
PAHs ($\times 10^3$)	4.38 ± 3.15	~17(AR), 0.72~1.64(AR), ~9.0 (W)	Dhammapala et al., 2007; Zhang et al., 2011; Lee et al.2005
Phenols ($\times 10^3$)	24.31 ± 12.11	~35(AR), ~5 (AR), ~13 (TL)	Dhammapala et al., 2007; Hays et al., 2005; Andreae et al.2001

AR: agricultural residue; TL: total, including forest fires and straw burning; W: wood

Atmospheric Chemistry and Physics Discussions
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Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

Table 6. Summary of field burning rates and economic data in China.

Province	Burning rate from literature		Agricultural income ratio [c]			Estimated burning rate		NDRC report [d]	Average rate
	BAU-I [a]	BAU-II [b]	2000	2006	2012	EM-I	EM-II	NDRC	
Beijing	0.00	0.17	0.08	0.06	0.06	0.00	0.19	0.13	0.10 ±0.08
Tianjin	0.00	0.17	0.10	0.14	0.12	0.00	0.20	0.30	0.13 ±0.12
Hebei	0.20	0.17	0.27	0.22	0.24	0.22	0.16	0.19	0.19 ±0.02
Shanxi	0.20	0.17	0.20	0.21	0.25	0.16	0.14	0.22	0.18 ±0.03
InnerMongolia	0.00	0.12	0.44	0.49	0.66	0.00	0.09	0.27	0.10 ±0.10
Liaoning	0.20	0.12	0.30	0.29	0.39	0.16	0.09	0.34	0.18 ±0.09
Jilin	0.30	0.12	0.73	0.73	0.77	0.28	0.11	0.25	0.21 ±0.08
Heilongjiang	0.30	0.12	0.99	0.83	0.59	0.50	0.17	0.25	0.27 ±0.13
Shanghai	0.00	0.32	0.10	0.08	0.09	0.00	0.29	0.12	0.15 ±0.14
Jiangsu	0.30	0.32	0.32	0.22	0.30	0.32	0.23	0.19	0.27 ±0.05
Zhejiang	0.30	0.32	0.19	0.08	0.09	0.64	0.28	0.22	0.35 ±0.15
Anhui	0.20	0.32	0.44	0.39	0.43	0.21	0.29	0.43	0.29 ±0.08
Fujian	0.30	0.32	0.18	0.10	0.14	0.39	0.22	0.17	0.28 ±0.08
Jiangxi	0.20	0.11	0.45	0.31	0.44	0.20	0.08	0.25	0.17 ±0.06
Shandong	0.30	0.17	0.33	0.25	0.24	0.40	0.17	0.21	0.25 ±0.09
Henan	0.20	0.17	0.39	0.35	0.33	0.23	0.18	0.22	0.20 ±0.02
Hubei	0.20	0.11	0.42	0.30	0.41	0.21	0.08	0.30	0.18 ±0.08
Hunan	0.20	0.33	0.47	0.31	0.43	0.22	0.24	0.35	0.27 ±0.06
Guangdong	0.30	0.33	0.19	0.10	0.13	0.44	0.25	0.18	0.30 ±0.09
Guangxi	0.20	0.33	0.40	0.25	0.33	0.25	0.25	0.35	0.28 ±0.06
Hainan	0.30	0.33	0.35	0.16	0.21	0.51	0.25	0.56	0.39 ±0.12
Chongqing	0.20	0.11	0.35	0.23	0.30	0.24	0.08	0.45	0.22 ±0.13
Sichuan	0.20	0.11	0.37	0.22	0.28	0.26	0.09	0.30	0.19 ±0.08
Guizhou	0.20	0.11	0.38	0.23	0.25	0.31	0.10	0.43	0.23 ±0.13
Yunnan	0.20	0.11	0.36	0.26	0.31	0.24	0.09	0.28	0.18 ±0.07
Tibet	0.00	0.16	0.15	0.09	0.05	0.00	0.30	0.16	0.12 ±0.11
Shannxi	0.20	0.17	0.33	0.27	0.26	0.25	0.18	0.28	0.22 ±0.04
Gansu	0.10	0.16	0.25	0.20	0.28	0.09	0.11	0.33	0.16 ±0.09
Qinghai	0.00	0.16	0.23	0.10	0.08	0.00	0.20	0.28	0.13 ±0.11
Ningxia	0.10	0.16	0.42	0.38	0.45	0.09	0.13	0.16	0.13 ±0.03
Xinjiang	0.10	0.16	0.43	0.61	0.73	0.06	0.13	0.30	0.15 ±0.08
Nationwide	**0.21**	**0.16**	**0.34**	**0.27**	**0.31**	**0.26**	**0.15**	**0.27**	**0.21 ±0.05**

a. Zhao et al., 2012; Cao et al., 2006; Cao et al., 2011

b. Wang and Zhang., 2008

c. Calculated based on data from China Yearbook 2001~2013 (NBSC, 2001-2013), China Rural Statistic Yearbook 2001~2013, data available at http://www.grain.gov.cn/Grain/

d. *Data from the National Development and Reform Commission report ([2014]No.516) : http://www.sdpc.gov.cn/*

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Table 7. National agricultural field burning emissions of BAU, EM, NDRC, and CRC scenarios in China in 2012.

Unit: Gg	BAU-I			BAU-II			EM-1			EM-2			NDRC			Average		
	Total	Summer	Autumn	Total	Summer	Autumn	Total	Summer	Autumn	Total	Summer	Autumn	Total	Summer	Autumn	Total	Summer	Autumn
$PM_{2.5}$	1001.05	218.99	782.06	835.42	209.29	626.13	1211.92	258.58	953.34	738.36	182.34	556.02	1241.69	258.24	983.46	1007.650	226.007	781.646
$PM_{1.0}$	897.52	198.93	698.59	748.57	189.92	558.65	1087.05	234.85	852.20	661.81	165.61	496.20	1111.90	234.44	877.46	903.125	205.217	697.911
OC	429.51	102.87	326.64	360.99	97.67	263.32	519.26	121.33	397.94	318.84	85.55	233.29	533.19	120.86	412.33	433.184	105.885	327.300
EC	133.61	27.37	106.24	111.40	26.52	84.88	162.71	32.39	130.32	98.06	22.85	75.21	164.97	32.53	132.45	134.414	28.404	106.010
char-EC	112.75	23.76	88.99	93.82	22.88	70.94	137.15	28.09	109.06	82.79	19.81	62.98	139.21	28.14	111.07	113.366	24.596	88.770
soot-EC	20.80	3.59	17.21	17.54	3.62	13.91	25.50	4.28	21.22	15.23	3.02	12.21	25.70	4.36	21.33	20.992	3.787	17.205
SO_4^{2-}	30.22	3.96	26.26	24.97	3.94	21.04	36.39	4.71	31.68	22.09	3.32	18.76	38.21	4.78	33.44	30.440	4.155	26.285
NO_3^-	4.35	0.84	3.51	3.55	0.80	2.75	5.24	0.99	4.25	3.17	0.70	2.47	5.40	0.99	4.41	4.350	0.864	3.486
NH_4^+	32.08	6.37	25.71	26.65	6.21	20.44	39.09	7.54	31.55	23.43	5.32	18.11	39.46	7.59	31.87	32.202	6.623	25.580
K^+	67.49	13.12	54.38	54.75	12.38	42.37	81.40	15.45	65.95	49.10	10.90	38.20	83.62	15.36	68.26	67.412	13.469	53.943
WSOA	24.44	6.55	17.89	21.94	6.39	15.55	29.69	7.76	21.93	18.77	5.48	13.30	30.82	7.81	23.01	25.174	6.815	18.360
WSA	5.75	0.95	4.80	4.85	0.95	3.90	6.99	1.13	5.86	4.23	0.80	3.43	7.19	1.15	6.04	5.815	1.000	4.815
PAHs	0.48	0.11	0.37	0.40	0.10	0.30	0.58	0.12	0.45	0.35	0.09	0.26	0.59	0.13	0.47	0.480	0.109	0.371
Phenols	2.71	0.85	1.87	2.25	0.78	1.47	3.25	0.99	2.26	2.02	0.70	1.323	3.40	0.98	2.36	2.721	0.861	1.861
THM	8.68	2.01	6.67	7.19	1.92	5.27	10.56	2.37	8.19	6.36	1.67	4.69	10.64	2.37	8.27	8.702	2.073	6.628
WSI	249.96	47.46	202.50	204.46	45.24	159.22	301.75	56.01	245.74	182.31	39.50	142.82	310.31	55.88	254.43	250.269	48.927	201.342

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

Table 8. Uncertainties in emission estimates.

Region	2012	Region	2012
Anhui	28.9%	The North Plain	12.7%
Shandong	35.5%		
Hebei	11.4%		
Beijing	84.0%		
Tianjin	87.7%		
Shanxi	16.0%		
Hubei	43.5%	The Center of China	16.0%
Hunan	22.6%		
Henan	11.4%		
Shanghai	94.1%	The Yangtze River Delta	21.5%
Jiangsu	19.4%		
Zhejiang	42.0%		
Liaoning	48.0%	The Northeast of China	39.8%
Jilin	38.1%		
Heilongjiang	49.1%		
Guangdong	28.8%	The Pan-Pearl River Delta	25.9%
Guangxi	20.2%		
Hainan	31.3%		
Fujian	27.6%		
Sichuan	42.6%		
Guizhou	54.5%		
Yunnan	39.9%		
Jiangxi	37.5%		
Inner Mongolia	93.4%	The West of China	51.4%
Tibet	91.5%		
Shannxi	19.6%		
Gansu	56.5%		
Qinghai	87.1%		
Ningxia	22.9%		
Xinjiang	54.7%		
Chongqing	60.5%		
Nationwide	**19.8%**		

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

Table 9. Estimated number of cases (95% CI) attributable to agricultural fire smoke $PM_{2.5}$ exposure in China, 2012.

Emission version	Mortality	Respiratory hospital admission	Cardiovascular hospital admission	Chronic bronchitis
BAU-I	7864 (3154, 12489)	31123 (21114, 40788)	29454 (12849, 45481)	7577067 (2952006, 11024705)
BAU-II	7187 (3056, 11260)	28711 (19443, 37693)	27156 (11825, 42007)	7132581 (2735111, 10523803)
EM-I	9435 (3817, 14933)	36950 (25151, 48269)	35116 (15373, 54042)	8712880 (3484325, 12430411)
EM-II	6175 (2554, 9751)	25166 (17004, 33112)	23745 (10316, 36816)	6383442 (2407643, 9526727)
NDRC	8523 (3581, 13377)	33957 (23015, 44542)	32131 (14003, 49664)	8332216 (3228351, 12148274)
Average	7836 (3232, 12362)	31181 (21145, 40881)	29520 (12873, 45602)	7267237 (2961487, 1130784)
CRC	538 (227, 850)	2191 (1462, 2920)	2038 (874, 3199)	636650 (214617, 1052153)

Table 10. Health-related economic loss (95% CI) from agricultural fire smoke $PM_{2.5}$ exposure in China, 2012.

Emission version	Economic cost (million US$)				Total cost (million US$)	GDP ratio (‰)
	Mortality	Respiratory hospital admission	Cardiovascular hospital admission	Chronic bronchitis		
BAU-1	1544.5 (730.7, 2430.0)	19.6 (13.3, 25.7)	36.0 (15.7, 55.6)	7187.6 (2800.3, 10458.3)	8787.8 (3560.0, 12969.4)	1.0 (0.4 , 1.5)
BAU-2	1453.9 (719, 2252.2)	18.1 (12.2, 23.8)	33.2 (14.4, 51.3)	6766.0 (2594.5, 9982.9)	8271.2 (3340.3, 12310.3)	1.0 (0.4 , 1.4)
EM-1	1855.2 (870.3, 2913.7)	23.3 (15.9, 30.5)	42.9 (18.8, 66.1)	8265.0 (3305.2, 11791.5)	10186.5 (4210.2, 14801.8)	1.2 (0.5 , 1.7)
EM-2	1228.1 (600.6, 1917.6)	15.9 (10.7, 20.9)	29.0 (12.6, 450)	6055.3 (2283.9, 9037.1)	7328.4 (2907.9, 11020.7)	0.9 (0.3 , 1.3)
NDRC	1573.4 (759.3, 2456.2)	21.4 (14.5, 28.1)	39.3 (17.1, 60.7)	7903.9 (3062.4, 11523.9)	9538.2 (3853.4, 14069.0)	1.1 (0.4 , 1.6)
Average	1531.0 (736.0, 2393.9)	19.7 (13.3, 25.8)	36.1 (15.7, 55.7)	7235.6 (2809.3, 10558.7)	8822.4 (3574.4, 13034.2)	1.0 (0.4 , 1.5)
CRC	100.0 (48.0, 157.1)	1.3 (0.9, 1.8)	2.4 (1.0, 3.9)	603.9 (203.6, 998.1)	707.8 (253.6, 1160.9)	0.1 (0.0 , 0.1)

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

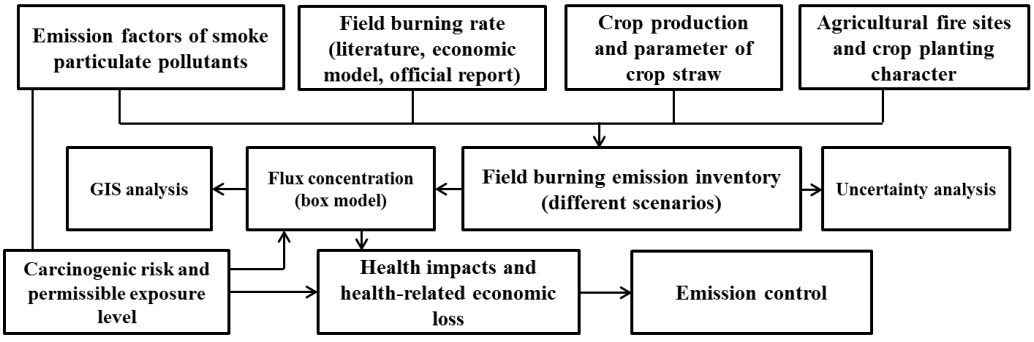

Figure 1. Schematic methodology for developing emission estimations.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

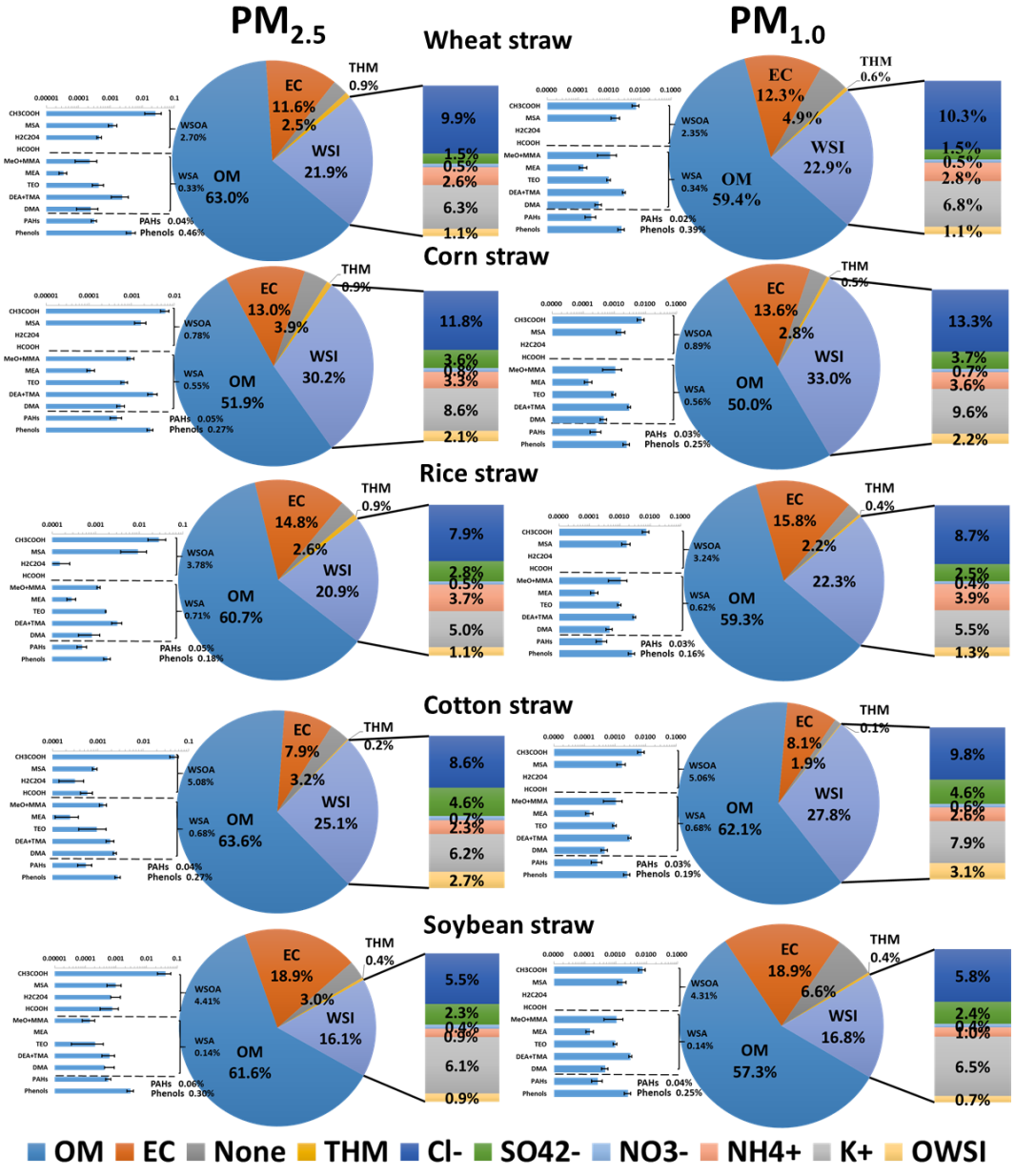

Figure 2. Chemical profiles of smoke $PM_{2.5}$ and $PM_{1.0}$ from 5 types agricultural residue burnings. OM (organic matter = 1.3×OC). OWSI, other water soluble ions including F^-, NO_2^-, Na^+, Ca^{2+}, and Mg^{2+}.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

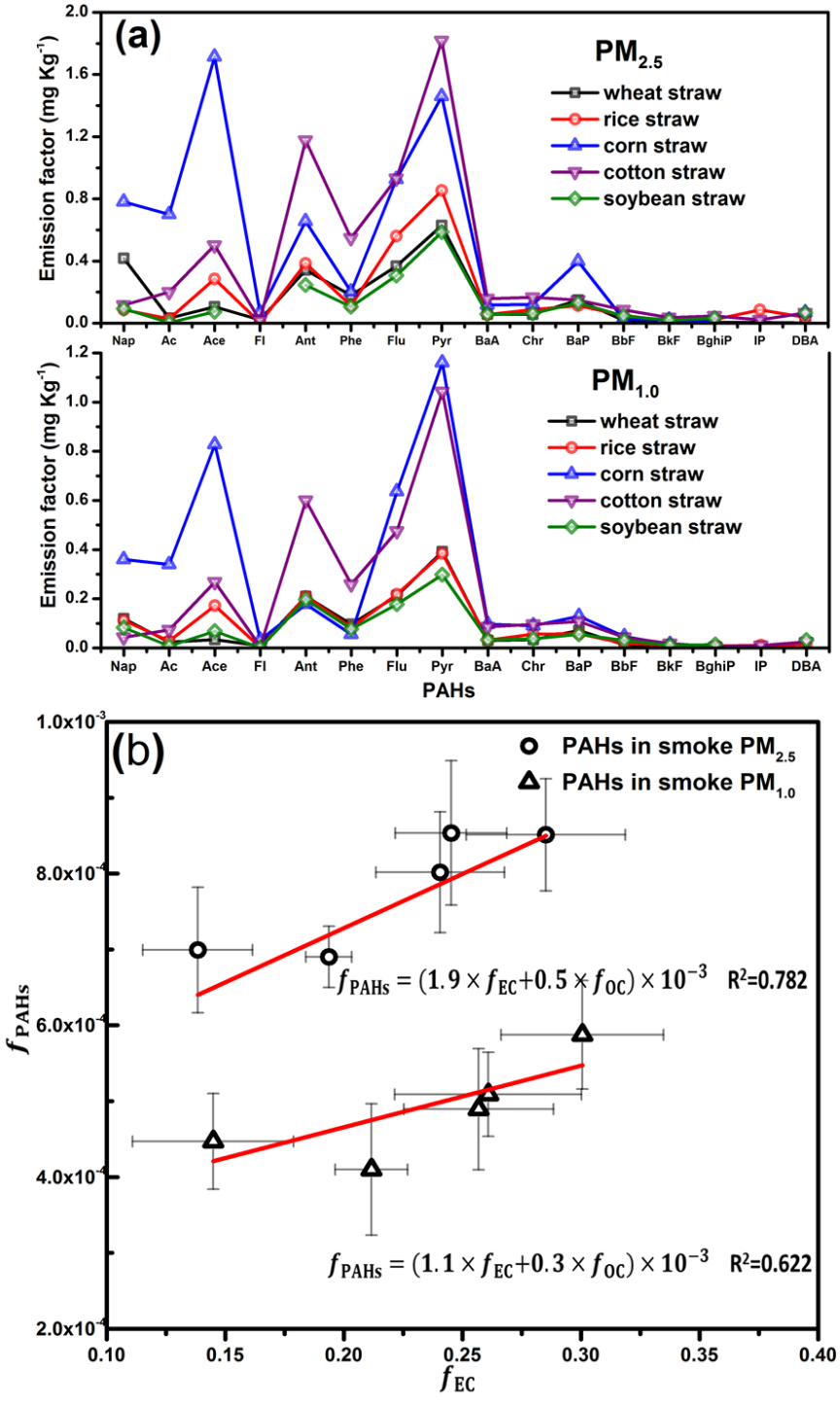

Figure 3. (a) Emission factors of 16 USEPA priority PAHs in smoke $PM_{2.5}$ and $PM_{1.0}$; (b) expulsion-accumulation of PAHs in OC-EC of smoke $PM_{2.5}$ and $PM_{1.0}$.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

Atmospheric Chemistry and Physics Discussions

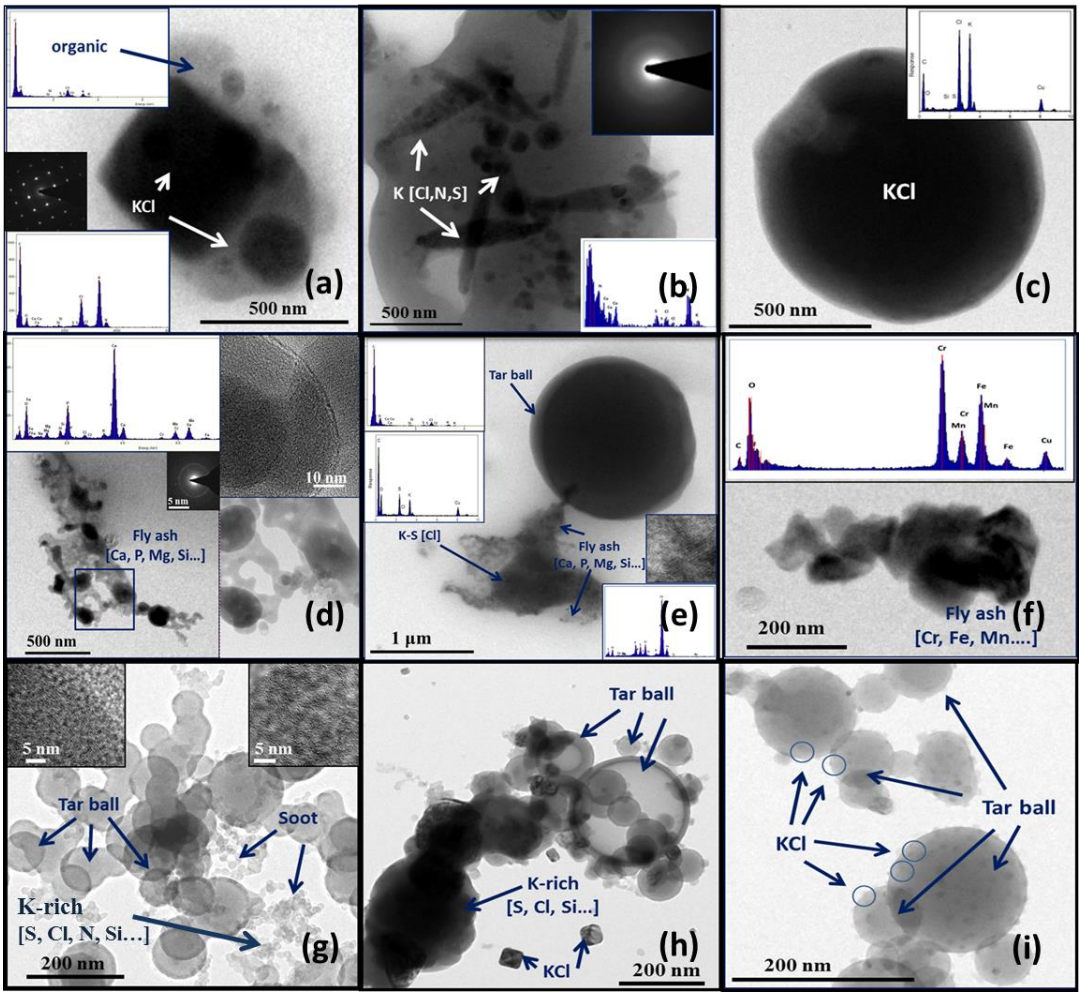

Figure 4. Transmission electron microscope (TEM) images and EDX analysis of fresh agricultural residue burning particles. (a)-(c) Crystal and amorphous KCl particles internally mixed with sulfate, nitrate, and carbonaceous materials. (d)-(f) Heavy metal-bearing fractal-like fly ash particles. (e)-(g) Chain-like soot particles and tar ball.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

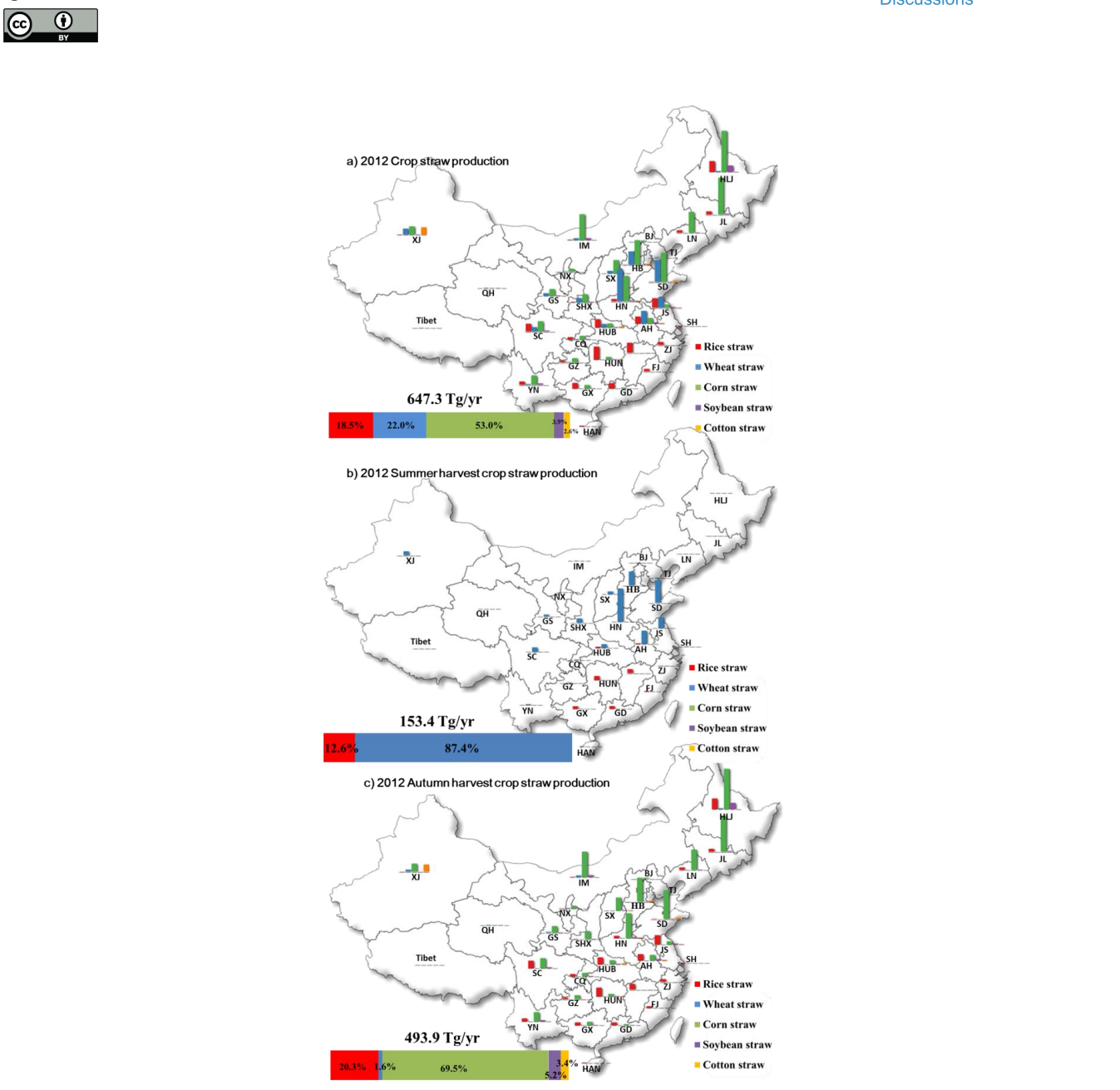

Figure 5. Annual agricultural residue production of five major crops and allocated into two harvest (summer and autumn harvest) based on agricultural yield in China, 2012. (Abbreviation, BJ: Beijing; TJ: Tianjin; HB: Hebei; SX: Shanxi; IM: Inner Mongolia; LN: Liaoning; JL: Jilin; HLJ: Heilongjiang; SH: Shanghai; JS: Jiangsu; ZJ: Zhejiang; AH: Anhui; FJ: Fujian; JX: Jiangxi; SD: Shandong; HN: Henan; HUB: Hubei; HUN: Hunan; GD: Guangdong; GX: Guangxi; HAN: Hainan; CQ: Chongqing; SC: Sichuan; GZ: Guizhou; YN: Yunnan; SHX: Shannxi; GS: Gansu; QH: Qinghai; NX: Ningxia; XJ: Xinjiang)

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 30 August 2016

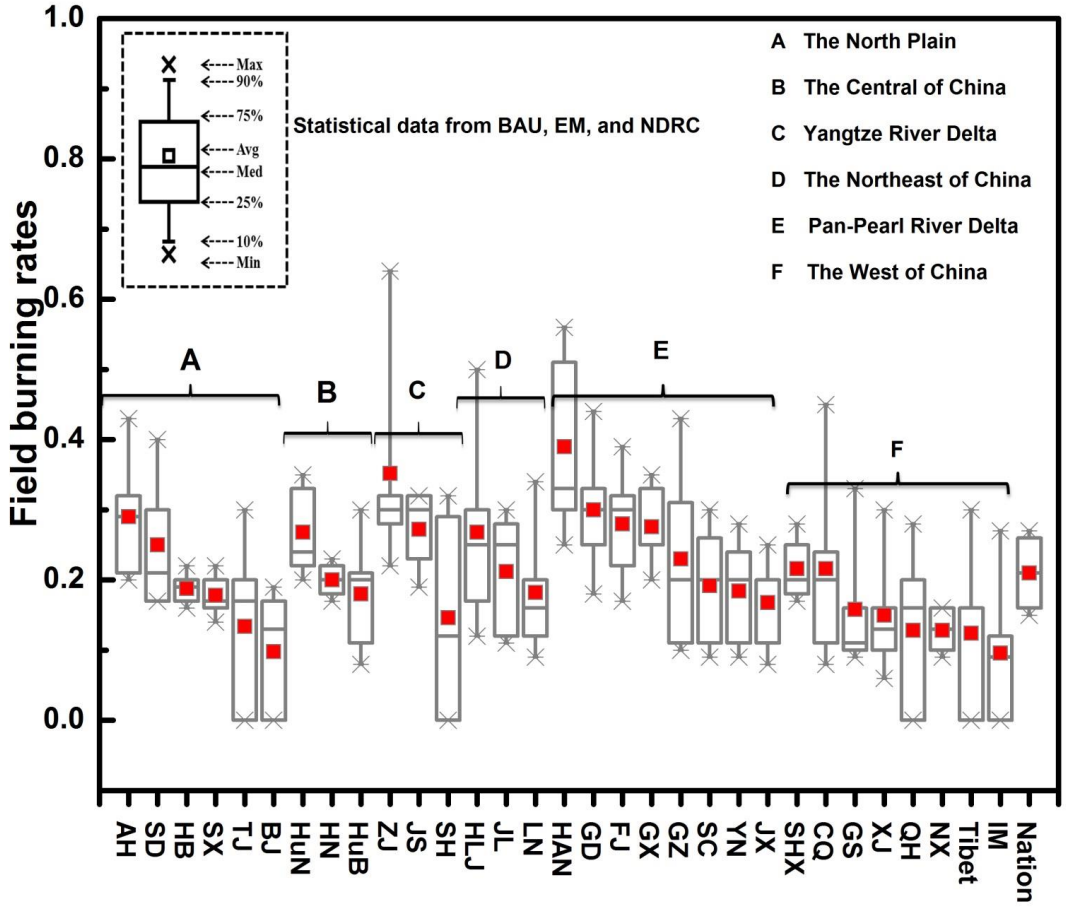

Figure 6. Statistical analysis of field burning rates from BAU, EM, and NDRC versions. The North Plain (Anhui, Shandong, Hebei, Shanxi, Tianjin, Beijing), the Central of China (Hunan, Henan, Hubei), the Yangtze River Delta (Zhejiang, Jiangsu, Shanghai), the Northeast of China (Heilongjiang, Liaoning, Jilin), the Pan-Pearl River Delta (Hainan, Guangdong, Fujian, Guangxi, Guizhou, Sichuan, Yunnan, Jiangxi), the West of China (Shannxi, Chongqing, Xinjiang, Qinghai, Ningxia, Tibet, Inner Mongolia, Gansu)

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-651, 2016
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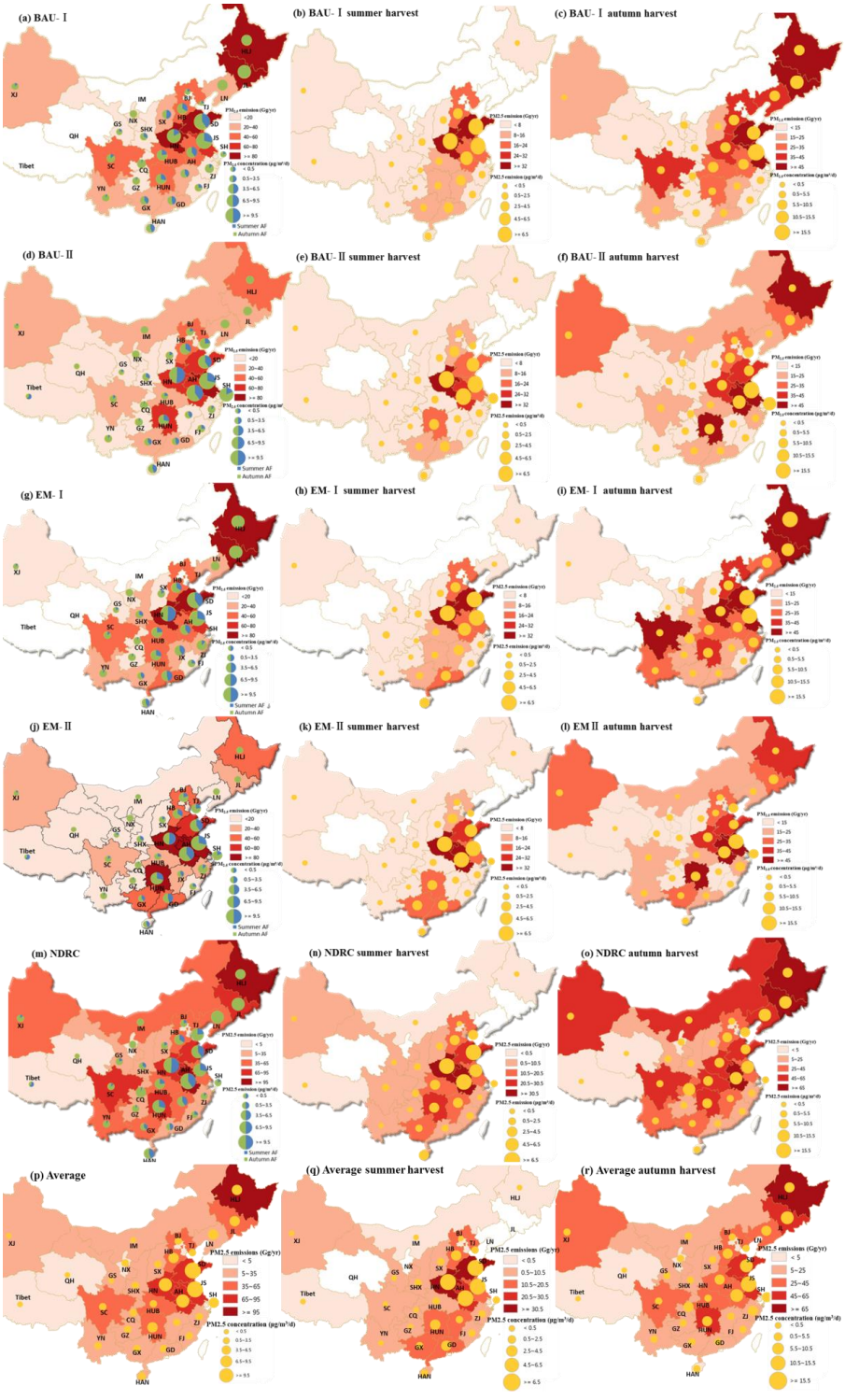

Figure 7. Spatial and temporal distribution of smoke $PM_{2.5}$ emissions and flux concentrations from agricultural field burning over China, 2012.

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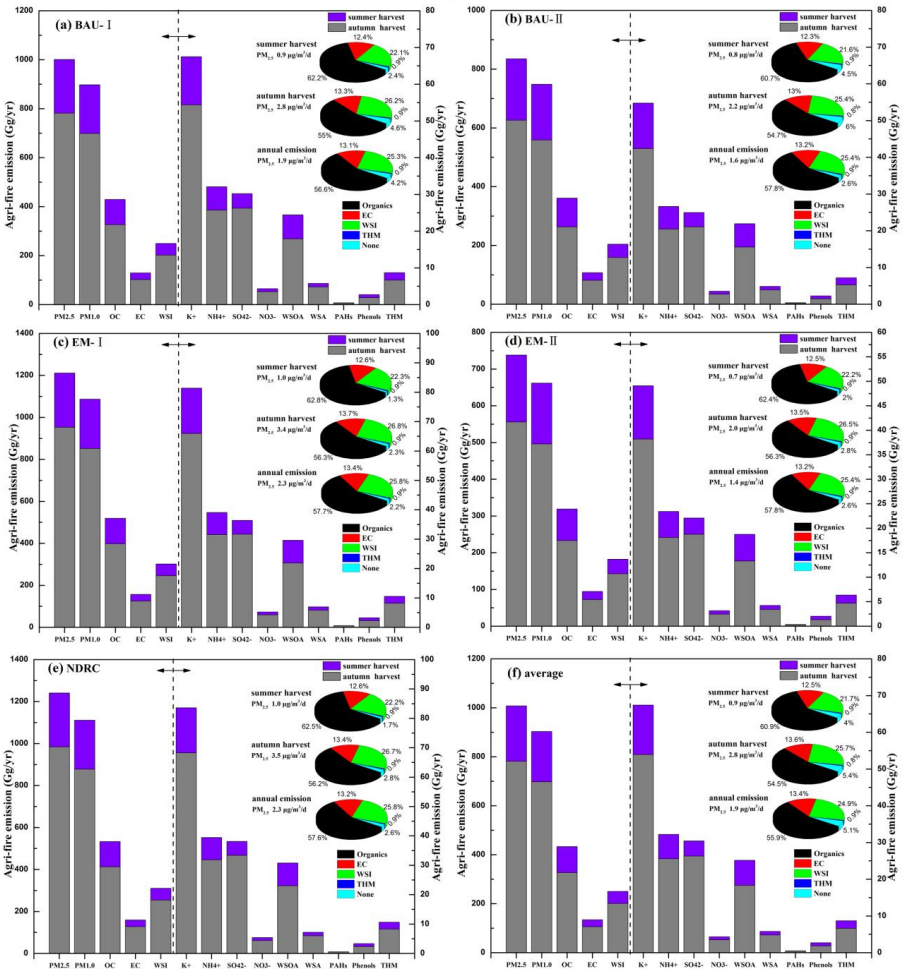

Figure 8. Nationwide $PM_{2.5}$ emissions and flux concentrations based on different burning versions. The inset pie-graphs are chemical compositions of integrated $PM_{2.5}$ from five major agricultural residue burning.