CHARACTERIZATION OF PARTICULATE MATTER EMISSION FROM OPEN BURNING OF RICE STRAW

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Abstract

Emission from field burning of crop residue, a common practice in many parts of the world today, has potential effects on air quality, atmosphere and climate. This study provides a comprehensive size and compositional characterization of particulate matter (PM) emission from rice straw (RS) burning using both *in situ* experiments (11 spread field burning) and laboratory hood experiments (3 pile and 6 spread burning) that were conducted during 2003–2006 in Thailand. The carbon balance and emission ratio method was used to determine PM emission factors (EF) in the field experiments. The obtained EFs varied from field to hood experiments reflecting multiple factors affecting combustion and emission. In the hood experiments, EFs were found to be depending on the burning types (spread or pile), moisture content and the combustion efficiency. In addition, in the field experiments, burning rate and EF were also influenced by weather conditions, i.e. wind. Hood pile burning produced significantly higher EF (20 ± 8 g kg^{-1} RS) than hood spread burning (4.7 ± 2.2 g kg^{-1} RS). The majority of PM emitted from the field burning was $PM_{2.5}$ with EF of 5.1 ± 0.7 g m^{-2} or 8.3 ± 2.7 g kg^{-1} RS burned. The coarse PM fraction ($PM_{10-2.5}$) was mainly generated by fire attention activities and was relatively small, hence the resulting EF of PM_{10} (9.4 ± 3.5 g kg^{-1} RS) was not significantly higher than $PM_{2.5}$. PM size distribution was measured across 8 size ranges (from <0.4 μm to >9.0 μm). The largest fractions of PM, EC and OC were associated with $PM_{1.1}$. The most significant components in $PM_{2.5}$ and PM_{10} include OC, water soluble ions and levoglucosan. Relative abundance of some methoxyphenols (e.g., acetylsyringone), PAHs (e.g., fluoranthene and pyrene), organochlorine pesticides and PCBs may also serve as additional signatures for the PM emission. Presence of these toxic compounds in PM of burning smoke increases the potential toxic effects of the emission. For illustration, an estimation of the annual RS field burning in Thailand was made using the obtained *in situ* field burning EFs and preliminary burning activity data.

Keywords

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1. Introduction

Rice is cultivated globally and is by far the most popular crop in Asia (Kadam et al., 2000) where the annual production is rapidly increasing to meet the domestic and export demand. With improved living conditions in rural areas, farmers tend to rely more on commercial fuel and less on crop residue for domestic cooking, which leads to even more field burning of rice straw (RS). This inexpensive method of crop residue disposal is practiced in many parts of the world to clear the surface biomass from land for faster crop rotation; to control undesirable weeds, pests and diseases; and to return some nutrients to the soil. This activity emits a large amount of toxic air pollutants (particles, and inorganic and organic gases) and greenhouse gases (Andreae and Merlet, 2001; Reid et al, 2004). Agricultural field burning activities are linked to elevated air pollution levels in USA (Jiminez et al., 2007), Europe (Viana et al., 2008), and Asia, e.g. Taiwan (Yang et al., 2006) and Thailand (Tipayarom and Kim Oanh, 2007). In Asia, intensive open burning activities commonly take place during the dry season when stagnant atmospheric conditions are normally observed, hence can lead to high air pollution build-up in adjacent urban areas (Tipayarom and Kim Oanh, 2007). Overall, emissions from field burning activities deteriorate local air quality and have been reported to cause high personal exposure (Wu et al., 2006) and result in adverse health effects (Torigoe et al., 2000). Crop residue field burning is an important type of open biomass burning in Asia that is a leading cause of regional atmospheric phenomena with strong climate implications such as Atmospheric Brown Clouds (UNEP & C4, 2002; UNEP, 2008). Fine particles, one of the major pollutants emitted from the field burning of RS, are a major cause of concern due to their harmful effects on human health (Pope et al., 2009) and the earth's climate (Bond et al., 2004). Atmospheric particulate matter (PM) is itself a complex mixture and its potential environmental and health effects depend on particle size and composition. PM also carry signatures of contributing emission sources that can be used to indirectly quantify the source contribution using receptor models (Gordon, 1988). These models are especially applicable when the emission inventory data are not available. This is even more important for the crop residue field burning, as the direct method of quantification based upon emission inventories is complex because of the distributed nature and short time spans of burning events.

Despite its potential high contribution to air pollution in Asian cities (Kim Oanh et al., 2006), this important field burning emission source is often overlooked in air quality management practices, mainly due to the lack of reliable information on the magnitude and composition of the emissions. A few RS burning experiments have been conducted for the purposes of emission characterization, but most were from outside of Asia. A number of these studies compared levels of atmospheric species measured in ambient air during burning episodes and non-burning (Viana et al. 2008; Yang et al., 2006; Lee et al., 2008) and have indicated enrichment of several air pollution species in RS burning smoke that can serve as useful markers for this source. These studies, however, have not reported emission factors (EF) which are required for the emission inventory purpose. EF have mainly been derived from laboratory experiments which simulated burning conditions, such as a large enclosure (Hays et al. 2005), a wind tunnel (Jenkins et al., 1996), or burning RS fuel in a wood stove (Sheesley et al., 2003). Recently, EF of selected air pollutants (particle number and gaseous pollutants) from RS burning in a stove were reported for China (Zhang et al. 2008). Nevertheless, EF and PM emission characterization for *in situ* field RS burning in Asia have not been found in the literature.

Understandably, the random nature of combustion and many other factors may cause variations in pollutant EF and source emission profiles of RS burning. These include moisture content of RS, moisture content of field surface soil, biomass loading (which varies between rice species and cultivation practices), spreading or pile burning, fertilizers and

pesticide treatments, burning time-of-day (drier in the afternoon) and weather conditions. It is expected that a wide range of EF and emission characteristics may be observed in both *in situ* field burning and controlled laboratory experiments. To reduce the uncertainty and to recommend appropriate ranges of pollutant EF and emission profiles for Asia, more experimental studies should be conducted under conditions representative to the common practices in the region.

The present study carried out a series of *in situ* RS paddy field burning experiments and simulated burning in a laboratory fume hood. PM EF, physical and chemical characterization were accomplished for *in situ* field burning, hood spread burning and hood pile burning, and are described herein.

2. Experimental design

Experiments were conducted during the RS burning seasons (December to April next year) in the period of 2003–2006 with 11 field (*in situ* burning of harvested paddies in Pathumthani of Thailand) and 9 hood experiments (laboratory experiments for spread and pile burning) at the Asian Institute of Technology (AIT). Detailed information for both field and hood experiments are presented in Table A1, supplementary information (SI).

2.1 Field burning and smoke sampling

Field experiments took place directly in harvested paddies and followed the local RS burning practices, in order to provide a representative source emission characterization. The experimental fields were harvested by combine harvesters which cut the upper part of RS and spread it in windrows while leaving the lower part virtually untouched (standing part). Fire was started at the upwind edge of a selected paddy, i.e. following the head burning method. We observed that spread RS was burned properly when fire swept over the paddy, but the standing part in many cases were only partially burned - especially when RS moisture was high. Our survey of 110 local farmer households of 7 districts in Pathumthani shows that RS from the major crop (harvested in Nov-Dec) and secondary crop (harvested mainly in March-April) is always burned in field. The burning takes place 2–7 days following the harvest of a paddy and generally in the afternoon, between 11:00–17:00 (Tipayarom and Kim Oanh, 2007).

Rice paddies selected for the experiments were located in the middle of large agricultural fields and far away from local roads and houses. Each field experiment was conducted on one selected paddy of a size up to a few thousand m^2 (Table 1A, SI), and both background (BG) sampling and burning smoke air sampling were collected. The BG sampling was conducted prior to burning and lasted 2–4 hours. After the completion of BG sampling the fire was started in the experimental paddy. RS burning smoke sampling commenced immediately after the fire became stable and continued until the fire stopped. The smoke sampling period varied between experiments and lasted from about 30 minutes to 1 hour. Both samplings were conducted on the same day, BG sampling started at about 9:00–10:00 am and the smoke sampling ended around 17:00. The difference between pollutant concentrations in the smoke and BG samples collected in a field experiment was considered as the net contribution from the RS burning smoke. All sampling equipment was placed at a fixed downwind site in each experimental paddy, about 5 m away from the downwind edge of the paddy, to avoid damage from the flame and heat. All sampling inlets were positioned at 1.5 m above ground. A Hi-Vol TSP sampler (collecting TSP and semi-VOC) and 2 dichot samplers (collecting $PM_{2.5}$ and $PM_{10-2.5}$) were located at about 1–1.5 m from each other (almost in a triangle arrangement). At this distance, the samplers were considered to be close enough to catch the same part of a smoke plume and far away enough to minimize the inlet flow disturbance. Continuous field measurements were recorded for wind (Mechanical wind

recorder), temperature and humidity (Thermo-Hydrometer, Delta TRAK®), and CO and CO_2 (IAQ-CALC™, model 8760/876). The equipment and an 8-stage cascade impactor (TISCH) were located close to the middle of the triangle so that they were also measuring the same part of the smoke plume as the PM samplers. Continuous data recorded (every 5 seconds) from the CO/CO_2 meter was used for EF estimation using emission ratio. Another CO/CO_2 meter was used to measure the gas concentrations near the fire, and these data were mainly used to determine the combustion efficiency. The second CO/CO_2 meter was hung on a tip of a 2m-long stick and kept near the flame at all times. A summary of the equipment and analytical methods used is presented in Table A2, SI. All equipment was calibrated before use.

2.2 Hood burning and stack sampling

Hood experiments were conducted to study emission from both spread burning (6 experiments) and pile burning (3 experiments). Isokinetic smoke samples were collected using a semi-volatile sampling train (Auto 5™, AST® Sampler) following US EPA modified Method 5. The hood and the source sampling method used for these experiments were similar to that previously reported by Kim Oanh et al. (2002). The sampling period covered the whole burning cycle from the moment of stable firing to the end of the burning process. A 20 liter Tedlar bag connected to a calibrated personal pump was used to collect the bulk flue gas for subsequent measurements of gaseous pollutants (CO and CO_2 were used for estimation of combustion efficiency reported in this paper, Table 3).

RS samples used for the hood experiments were collected together with a surface soil layer of about 10 cm thickness. Three 1-m^2 plots of representative unburned paddy were collected from each experimental field and were used for the hood burning. For spread burning hood experiments, first the RS in a sampled part (of a paddy) was evenly distributed, then the samples (1-m^2 plots) were randomly taken from within this part. These samples contained both spreading RS and standing RS. In 3 pile burning experiments, RS samples were mostly taken from windrows with a biomass density of about 1.5–2 times higher than the evenly spreading RS fields. Each 1-m^2 sampled plot was kept in a separate air tight plastic bag (to minimize moisture loss) and transported to AIT where the hood experiment was done on the following day. For burning in the hood, the RS paddy sample plot was further segregated into 25×25 cm^2 sub-plots. Each sub-plot was placed in a 30×30 cm^2 tray and the trays were continuously fed, one after another, into the chamber in a conveyer-like set up. RS sample in each tray was ignited and burned with free air supply (from the open bottom of the hood). The set-up was made with the intention to imitate as closely as possible the *in situ* field burning. However, there were many variables that may affect the smoke emission from both field and hood experiments hence differences are expected. Specifically, meteorological conditions in the field may affect the emission results as discussed later.

2.3 Sample analysis

PM samples—For the field burning experiments, fine ($PM_{2.5}$) and coarse particles ($PM_{10-2.5}$) were collected by two dichot samplers (Anderson series 214) on mixed cellulose (plus some Teflon) and pre-baked quartz filters. PM samples collected on pre-baked quartz filters on 8 cascade impactor stages (ranging from <0.4 μm to >9 μm) were used for further size distribution analysis. PM filters (pre-baked glass fiber filter, GFF) collected with the Andersen Hi-Vol sampler (225 L min^{-1}) were used for analyses of the particulate phase of semi-volatile organic compounds (semi-VOC). The latter included polycyclic aromatic hydrocarbons (PAH), organochlorine pesticides (OCP) and polychlorinated biphenyls (PCBs). During transportation between the field locations and the AIT laboratory the sampling materials (filters and XAD-2, PUF) were properly wrapped and placed in an ice box. Each filter was put in a separate Petri dish that was kept in an airtight plastic bag both

during transportation and refrigeration in the laboratory. Field blanks were treated in the same way and used for correction of concentration results.

The stack samples collected in hood experiments included suspended particle samples on pre-baked GFF, without size segregation (SPM), and the gaseous phase compounds (semi-VOC) collected on XAD-2. The isokinetic rates of the stack sampling were 90±10% which enabled capture of representative SPM samples.

All PM samples were analyzed for mass, water soluble ions (IC) and elements (PIXE or ICP-OES) following the methods described in Kim Oanh *et al.* (2006). Coarse and fine PM collected on pre-baked quartz filters were analyzed for EC/OC (Sunset analyzer, TOT, NIOSH 5040) at the University of Illinois at Urbana-Champaign.

Field Hi-Vol TSP samples were segregated into 2 halves. One half was analyzed for 16 US EPA priority PAHs, following Method TO13A (US EPA, 1999a) with the detail presented in Kim Oanh *et al.* (2002). The analyzed PAHs included naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fth), pyrene (Pyr), benz(*a*)anthracene (BaA), chrysene (Chry), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(*a,h*)anthracene (DahA), benz(*g,h,i*)perylene (BghiP) and ideno(*1,2,3-c,d*)pyrene (IcdP). The other half of each TSP filter was Soxhlet extracted, using a solvent mixture of 90% hexane and 10% diethyl ether, and subsequently analyzed for PCBs and organochlorine pesticides (OCPs) using a GC/ECD, following Method TO-4A (US EPA, 1999b), as described by Pentamwa and Kim Oanh (2008). In total, 14 PCBs (PCB 18, PCB 31, PCB 28, PCB 52, PCB 44, PCB 101, PCB118, PCB138, PCB149, PCB 153, PCB 180, PCB 170, PCB 194 and PCB 209), and 16 OCPs (α-BHC, β-BHC, γ-BHC, δ-BHC, heptachlor, aldrin, heptachlor epoxide, endosulfan I, DDT, DDE, DDD, dieldrin, endrin, endrin aldehyde, endosulfan II, and endosulfan sulfate) were quantified.

For hood SPM GFF samples, one half of each filter was analyzed for PAHs (no PCBs and OCPs) and the other half was analyzed for ions and elements. One set of field experiment $PM_{2.5}$ and $PM_{10-2.5}$ samples collected on Teflon filters was analyzed for levoglucosan and methoxyphenols at the University of Washington in Seattle, following the method described previously (Simpson et al., 2004; 2005). The 21 methoxyphenols analyzed include guaiacol (GU), ethyl-guaiacol (ETGU), syringol (SY), eugenol (EUG), propyl-guaiacol (PRGU), vanillin (VAN), cis-isoeugenol (CISOEU), methyl-syringol (MESY), trans-isoeugenol (TISOEU), aceto-vanillone (ACETV), ethyl-syringol (ETSY), guaiacyl-acetone (GUACE), allyl-syringol (ALLSY), propyl-syringol (PRSY), syring-aldehyde (SYALD), acetylsyringone (ACETSY), coniferyl-aldehyde (CONIF), propionyl-syringone (PRSYON), butyryl-syringone (BUSYON), sinapyl-aldehyde (SINAP). Samples for levoglucosan and other semi-VOC were transported in ice boxes and stored in refrigerators for a maximum period of 1 month before the analyses.

Sampling and analysis for biomass density and C content—Prior to field burning, a composite above ground RS sample was collected from each experimental paddy for subsequent analyses of biomass density and RS moisture content (oven drying). The carbon content (C) was also analyzed for the last 4 field experiments. This composite sample was formed by 4 randomly selected 25×25 cm^2 paddy plots (making a total sampled area of 1 m^2). Similarly, after burning a leftover above ground biomass sample on a 1-m^2 composite paddy sample was also collected for analysis of unburned C in the last 4 field experiments. Prior to a pile burning hood experiment, a sub-sample was taken from the collected paddy sample for determination of the actual biomass density of the pile.

Composite surface soil samples were collected from the paddy before and after burning for analysis of soil carbon content. A composite soil sample was prepared from 5 subsamples that were randomly collected using a core sampler. Each subsample was of 5 cm diameter and 10 cm depth. The soil samples taken after burning also contained ash. Carbon in soil was analyzed using a CS – 200 Carbon/Sulfur Analyzer while C in RS was determined using a Leco ® CHN – 1000 analyzer at the Ministry of Science and Technology of Thailand following the ASTM standard D5373-02 method (ASTM, 2008).

2.4 Emission Factor Determination

Emission factors (EF) are presented as g m^{-2} of paddy burned and g kg^{-1} of dry RS burned for the field (*in situ*) and hood spread burning, which are convertible using the actual dry RS biomass density (kg m^{-2} paddy). For hood pile burning, the area based EF is not applicable hence only the EF in g kg^{-1} of dry RS is reported.

EF for the hood experiments was directly determined based on the measurements of flue gas volume and pollutant mass concentration using Equation 1.

$$EF = Conc\,(mg\,m^{-3}) * Flowrate\,(m^3\,h^{-1}) * Sampling\,time\,(h)/RS\,burned\,(kg)$$

(Equation 1)

Concentration of SPM was first determined using the blank-corrected mass of SPM collected and total sampled volume (provided by Auto 5™ sampler). Other data (flowrate and sampling time) were also automatically recorded by the sampler. For the spread hood burning, the area burned was 3 m^2. Thus the EF was expressed in g SPM per m^2 paddy and then converted to g SPM per kg RS. For the pile burning experiments, the "RS burned" was the mass of RS available for burning (kg) in the collected pile samples and obtained EF were directly expressed in g SPM per kg RS.

EF for the field experiments was determined using method involving the carbon balance and emission ratio, that is commonly used in biomass open burning studies (Zarate et al., 2000; Dhammapala et al. 2007; Li et al, 2008; and references therein). This method calculates the carbon emitted with carbon containing species, i.e. CO_2, CO, CH_4, NMHC and particulate C, based on the difference in C measured before and after burning (Li et al., 2008). The EF of other species are then determined using the concentration ratio of the interested species to a reference species, either CO_2 or CO, measured simultaneously in the emission plume. Reid et al. (2004) recommends to use CO_2 as the reference species if the modified combustion efficiency (MCE=CO_2/(CO+CO_2) for the flaming combustion phase is above 0.9.

In our study, the C analysis results for the above ground biomass and paddy soil samples, taken before burning and after burning, were available for field experiments 8–11. There was no significant difference in soil C before burning (3.2%) and after burning (3.1%), as seen in Table 3A (SI). Therefore, the difference in C content in the above ground biomass samples alone was used to estimate the amount of C oxidized (and released in the emission) using Equation 2.

$$C_{oxidized} = C_{BeforeBurnt} - C_{AfterBurnt}$$

(Equation 2)

Where,

$C_{oxidized}$: amount of C released

$C_{BeforeBurnt}$: amount of C available in above ground biomass sample before burning

$C_{AfterBurnt}$: amount of C remained in above ground biomass after burning

Other carbon containing species (than CO_2 and CO) were not measured in this study therefore we followed the suggestion by Reid et al. (2004) to assume that 90% of C released was in the forms of CO_2 and CO (Equation 3).

$$C_{CO2} + C_{CO} = 12/44\,CO_2 + 12/28\,CO = 0.9\,C_{oxidized} \qquad \text{(Equation 3)}$$

This study estimated $C_{oxidized}$ based on 1 m^2 of the rice paddy hence CO_2 and CO in Eq. 3 are the EF_{CO2} and EF_{CO}, respectively, on 1 m^2 of paddy basis. These can further be converted to the EF on 1 kg of RS basis using the biomass loading, kg m^{-2}, determined in each experiment. To solve Eq. 3, the ratios of net CO to CO_2 measured near fire were used to close the system. These were the average ratios (Table 3A, SI) calculated for each experiment using the net CO ($CO_{near\ fire} - CO_{background}$) and net CO_2, both in mg m^{-3}, obtained every 5 seconds.

Subsequently, the PM EF was determined using the emission ratio method. In our field experiments the values of MCE, estimated from the measurements made near the fire, were all above 0.92 (0.93±0.01, see Table 1) which justifies the use of CO_2 as the reference species (Reid et al., 2004). Thus, the PM EF is determined using Equation 4.

$$EF_{PM} = ER_{PM/CO_2} \times EF_{CO_2} \qquad \text{(Equation 4)}$$

Where, EF_{CO2} is emission factor of CO_2 (g m^{-2} paddy or g kg^{-1} RS). The emission ratio between PM and CO_2 ($ER_{PM/CO2}$) is calculated using Equation 5.

$$ER_{PM/CO_2} = \frac{\Delta PM}{\Delta CO_2} \qquad \text{(Equation 5)}$$

Where, ΔPM and ΔCO_2 are the net contribution from the burning smoke. The delta was the difference between the concentration in the smoke plume (PM_P, $CO_{2,P}$) and that of background sampling (PM_B, $CO_{2,B}$), namely:

$\Delta PM = PM_P - PM_B$:net aerosol (in concentration units) from burning
$\Delta CO_2 = CO_{2,P} - CO_{2,B}$:net CO_2 (in concentration units) from burning

Note that the ΔCO_2 here was estimated using the CO_2 concentrations recorded at the downwind site ($CO_{2,P}$) where the PM samplers were located.

3. Results and discussion

3.1 Carbon oxidation efficiency and CO_2 EF

Average carbon content in bone dry RS in this study was 49.0±2.7% by weight which appears to be similar to that of general biomass of around 50% (Reid et al., 2004) but higher than the reported value for California RS of 38% (Jenkins et al., 1996). Carbon content was determined for 4 field experiments (8, 9, and combined 10 & 11). The oxidation efficiency

(percent $C_{oxidized}$ per total available carbon) varied between the experiments. The average carbon oxidation of >90% was obtained for field 8 and 9 when standing RS was also mostly burned, but was only 69% for field 10 and 11 (Table 3A, SI) when the standing RS stem was mostly unburned. This variation reflects the actual field burning practices observed. The obtained CO_2 EF was in the range of 1.15±0.17 kg per kg RS (available/subjected to) burning (Table 1). This is lower than the expected theoretical value because of the unburned C discussed above. Our results for CO_2 EF are higher than the reported value of around 0.8 kg per kg RS in a laboratory study in China (Zhang et al. 2008). Similarly, our CO EF results (97±8 g kg^{-1} RS) are also higher than the value of around 64 g kg^{-1} RS by Zhang et al. (2008). Note that the average RS dry biomass density in this study for all field and hood experiments was (0.58±0.14) kg m^{-2} that is comparable with the reported value for USA rice of 0.7 kg m^{-2} (Hays et al. 2005).

3.2 PM EF from field experiments

PM concentration—Levels measured at the fixed downwind sites of the burning paddies were highly fluctuating (Table 2). This was mainly caused by the varying wind directions observed during the field experiments that deflected the plume away from the equipment from time to time. Thus, average dilution factors of the smoke plume that reached the measurement equipment changed from one experiment to another. In fact, 2 field experiments failed to catch the burning plume due to abrupt changes of wind direction; hence they were excluded from further data analysis. In total, only 11 successful experiments are reported in this paper. For the purpose of this study, the ratios between pollutants (e.g. PM and CO_2) and the PM composition are more important than the measured absolute pollutant concentrations. High observed ratios of $PM_{2.5}/PM_{10}$ in the smoke, above 0.9 (Table 2), suggest the dominance of fine particles in the emission. The coarse particles ($PM_{10-2.5}$) contributed only a minor fraction of PM_{10} and the contribution was higher in those experiments when there were intensive fire suppression activities performed to prevent the fire from spreading to surrounding paddies. These activities, which included beating at the edge of the fire with green tree branches, obviously stirred up and suspended coarse ash and soil particles.

PM emission factor—PM EF values obtained from *in situ* field burning experiments using the emission ratio are presented in Table 1 only for the last 4 experiments (8 to 11) due to the absence of the C data in the first experiments. The fluctuations in the measured EF between experiments reflects the variations in burning conditions and other parameters including RS moisture, surface soil moisture, biomass density and weather conditions. Field 9, for example, was conducted in rather higher wind conditions (~3m s^{-1}) making combustion more efficient which may be a reason for the lower PM EF. Field 9 was also the experimental paddy with the highest biomass density, and yielded the highest CO_2 EF. Lower combustion efficiency in field experiments 10 and 11 plus intensive fire suppression activities may be a reason for the high PM EF in these 2 experiments. Overall, a larger data set is still required to show clear associations between EF, fuel moisture, fuel loading or meteorological conditions.

PM size distribution—The EF results (Table 1, based on dichot samples) show that majority of PM_{10} was $PM_{2.5}$. The $PM_{2.5}$ EF in g m^{-2}, averaged 5.1±0.7, was less variable than the EF in g kg^{-1} RS, 8.3±2.7. Larger variations in the latter were most probably caused by the fluctuations in biomass density, which is a function of not only rice species but also farming practices. The ratio between $PM_{2.5}$ EF and PM_{10} EF, estimated based on the dichot sampling results, is 0.90±0.10.

PM EF of different size ranges based on the cascade impactor samples are presented Figure 1. Small particles of the size 0.4–1.1 μm contributed the largest mass fraction of PM, EC and OC. The contribution from $PM_{1.1}$ and $PM_{2.1}$ was estimated at 44% and 56% of the SPM mass, respectively. $PM_{1.1}$ thus contributed about 78% to $PM_{2.1}$. The estimated EF of the $PM_{2.1}$ fraction was 6.0 ± 2.6 g m^{-2} and 9.4 ± 5.1 g kg^{-1} RS, which is comparable with the $PM_{2.5}$ EF shown in Table 1 (more detail of EF of different size ranges is given in Table 4A, SI). EF results based on the cascade impactor samples were more variable with higher values for coarse fraction compared to EFs based on the dichot samples. We did not use a pre-separator, therefore PM larger than 10 μm should also be present in the first stage of the cascade impactor. In fact, a high mass of coarse PM was observed on the first stage of the cascade impactor, especially for those samples when intensive fire suppression activities took place.

3.3 PM EF from hood experiments

Effects of moisture and MCE—EF fluctuated considerably among 9 hood experiments and, in general, higher values were obtained for the pile burning. Overall, PM EF correlated with the flue gas moisture content (Figure 2). The latter was observed to reflect not only the moisture content of RS but also that of the surface paddy soil. The linear relationship between water content in the flue gas (y) and PM EF, g kg^{-1} dry RS (x), was y = 1.98x + 12.03 with $R^2 = 0.59$. The high moisture content of RS of Hood 5 (Table 3) is a distinct feature that linked to the high EF for this experiment, even for the spread burning type. An increased period between crop harvest and RS field sampling (7 days) in Hood 2 yielded a lower moisture content in the RS, resulting in more efficient combustion and lower EF.

Both moisture content and burning types (pile or spread) affect the combustion efficiency. Averaged MCE for Hood 5 was the lowest 0.88, i.e. smoldering phase (Reid et al., 2004), that resulted in higher PM EF, as mentioned above. A linear relationship between the MCE (y) and PM EF (x) was obtained (y = −0.0023x + 0.9462; $R^2 = 0.76$ for hood experiments alone; and y = −0.0022x + 0.9504; $R^2 = 0.66$ for all hood and field experiments). The negative slopes in these equations confirm that more complete combustion with higher MCE would result in lower PM emission.

Pile, spread vs. field burning—With biomass loads of around 1.0–1.3 kg m^{-2}, i.e. 1.5–2.0 times the biomass load for the spread hood burning experiments, the pile burning (Hood 1, 8 and 9) produced higher PM EF (than the spread burning) even when the RS moisture content was in the same range (Table 3). PM EF in g kg^{-1} RS for hood experiments were estimated assuming an oxidation efficiency of 90%, which is the average carbon oxidation efficiency when standing RS was also partially burned, i.e. similar to Field 8 and 9 (Table 3A, SI). The average EF of hood pile burning was 20 ± 8 g kg^{-1} RS. It was observed that pile burning SPM samples may also contain coarse fraction (ash) carried up with a high flame. The hood spread burning with typical RS moisture content of that in paddies, i.e. of 22–35% (except for Hood 2 and Hood 5) yielded PM EF of 4.7 ± 2.2 g kg^{-1} RS or 2.4 ± 1.5 g m^{-2} which are lower than the EF of $PM_{2.5}$ obtained in the field experiments (8.3 ± 2.7 g kg^{-1}). The burning in the hood spread experiments was with a low flame and no large ash particles were seen in the collected SPM samples. The PM size range in the hood spread burning experiments is therefore likely to be comparable with the $PM_{2.5}$ in field experiments, assuming that all PM generated from agricultural biomass open burning would be in the submicron size (Hays et al. 2005). However, the PM EF from the hood spread experiments were unlikely to have been influenced by the coarse particles generated by fire suppression activities that influenced the PM EF for some of the field experiments. Furthermore, the evenly spread RS paddy samples used in these hood experiments would have biomass density less than the RS windrows but higher than the RS standing rows present in the field

burning samples. Overall, the RS in the paddy samples prepared for hood spread burning experiments may have been more evenly distributed compared to the experimental fields, and may have burned more efficiently and yielded lower EF. These, together with other factors including the random nature of combustion, may be the causes of the differences observed for the hood spread burning experiments compared to the field spread burning experiments.

A few EF values extending over a wide range have been previously reported in the literature. Overall, our $PM_{2.5}$ EF for field experiments (8.3 ± 2.7 g kg^{-1}) and SPM EF for hood spread burning (4.7 ± 2.2 g kg^{-1} are lower than the EF obtained for simulated field burning conditions in an enclosure of 13 ± 0.3 g kg^{-1} (Hays et al., 2005), whereas our values are higher than the value reported for RS burning in a wind tunnel of 3.9 g kg^{-1} (Jenkins et al., 1996). The EF obtained for a domestic woodstove burning RS fuel of 6.2 ± 1.0 g kg^{-1} (Sheesley et al., 2003) is in between our field and hood spread burning values.

Air pollution EF from field burning activities depend upon many variables, hence caution should be taken when applying a specific range of values for the purpose of developing emission inventory. The PM EF obtained in this study for the field experiments would be more relevant to the places where combine harvesters are used (e.g. Thailand), whereas those obtained for hood pile burning may be applicable for places where the manual harvesting technique is common (e.g. many regions of Vietnam or Indonesia, where RS after harvest is piled up at a paddy corner and burned largely under smoldering conditions). However, these real piles would have higher biomass loads than the piles in our hood experiments. If fire is started at the pile base the combustion is even more smoldering hence resulting in larger EF than those obtained in our hood pile experiments.

3.4 PM composition

PM composition is presented for field ($PM_{2.5}$, PM_{10}) and hood pile burning (SPM) emissions (Table 4). Due to the predominant presence of the analytes in $PM_{2.5}$, and also that the coarse fraction ($PM_{10-2.5}$) contributed only a minor fraction (<10%) of the PM_{10} mass, the fractional compositions of $PM_{2.5}$ and PM_{10} of field burning smoke are quite similar, except for some elements. The compositional characterization was more complete for the field experiments compared to hood experiments, hence, in this section we focus the discussion on the field experiment results. Hood samples were analyzed for ions, elements and PAHs in SPM, with no size segregation, therefore the obtained profiles may not be fully comparable with $PM_{2.5}$ and PM_{10} profiles obtained from the field experiments.

Carbon speciation, ions and elements—The largest contribution comes from OC, (average 330 mg g^{-1} PM), followed by EC (57 mg g^{-1} PM) and levoglucosan (56–57 mg g^{-1} PM). The ratio of EC to TC (total carbon) of 0.15 obtained for PM emitted from RS burning was much lower than the value of above 0.70 obtained for PM emitted from diesel vehicles (Kim Oanh et al. 2010) which is a remarkable feature to distinguish between these two source categories.

The majority of EC was found in fine particles. In fact, the cascade impactor samples show that all EC was associated with $PM_{3.3}$. $PM_{1.1}$ contained 68% of total EC and 52% of total OC in SPM (Figure 1). The sum of water soluble ionic species for $PM_{2.5}$ and PM_{10} were about 160 mg g^{-1} of PM mass. The relatively high concentrations of these ionic markers are similar to those reported in literature (Hays et al. 2005). However our results for Cl$^-$, K$^+$, SO_4^{2-} and NH_4^+ are higher than Hays et al., which may be linked to the application of fertilizers (Potash and urea-based) to the paddy fields by local farmers. Elements typically associated with soil minerals, such as Ca, Al, Mg, Cr and Fe, were higher in PM_{10} than in $PM_{2.5}$. For other elements the fractional compositions in $PM_{2.5}$ and PM_{10} were mostly

similar. The sum of analyzed elements contribute 2.1±0.2 mg g^{-1} for PM$_{2.5}$ and 4.9±0.5 mg g^{-1} for PM$_{10}$.

Levoglucosan and methoxyphenols—These two classes of organic compounds have been suggested as tracers for PM derived from biomass combustion (Jiminez et al., 2007; Oros and Simoneit, 1999; Kjallstrand et al., 2000; Schauer and Cass, 2000). Levoglucosan is formed via pyrolysis of the wood polymer cellulose, whereas methoxyphenols are formed via pyrolysis of the wood polymer lignan (Jiminez et al., 2007). Therefore, these chemicals can serve as unique tracers for the contribution of biomass combustion to ambient PM. The levoglucosan abundance in PM found in our study (~55 mg g^{-1} PM) is intermediate between values previously reported by Sheeslay et al. (2003) (~18 mg g^{-1} PM$_{2.5}$) and Hays et al. (2005) (~87 mg g^{-1} PM$_{2.5}$). Our results are consistent with previous studies of biomass tracers (measured in ambient PM samples impacted by residential wood combustion) which also found that levoglucosan was present almost exclusively in the fine fraction of PM (e.g. Simpson et al., 2004).

Among the 21 analyzed methoxyphenols, four compounds (GU, MEGU, PRGU, MESY) were not quantified and four (SY, CISOEU, ETSY, BUSYON) were not detected in any sample. Table 4 presents only the 13 detected compounds. Acetylsyringone was the most abundant (~0.4 mg g^{-1} PM) while others were detected at lower concentrations. In a study of RS combustion, Hays *et al.* (2005) also found that acetylsyringone was the most abundant particle-bound methoxyphenol (0.8 mg g^{-1} PM$_{2.5}$). Sheesley et al. (2003) reported much higher concentrations of acetylsyringone (1.5 mg g^{-1} PM$_{2.5}$), and other low molecular weight syringols were present in even higher concentrations (e.g. syringol, 5.5 mg g^{-1} PM$_{2.5}$). Note that the methoxyphenol measurements in the current study, and those of Hays *et al.* (*2005*) and Sheesley *et al.* (2003), were done only for the particulate phase. Previous studies have shown that methoxyphenols are semi-VOC and distributed between the gaseous and particulate phases in smoke, and low molecular weight compound such as guaiacol and syringol exist almost exclusively in the gas phase under typical ambient temperatures and particle concentrations (Hawthorne et al., 1989; Schauer et al., 2001).

Semi-VOC—Particulate phase concentrations of 16 PAHs, 14 PCBs and 16 OCPs are discussed in this paper. The source profiles of these semi-VOC compounds in the field experiments were estimated assuming that their presence was entirely in the fine fractions (PM$_{2.5}$). Thus, to estimate the profiles, the mass of a compound found in TSP samples was divided by the mass of PM$_{2.5}$ and PM$_{10}$ samples, respectively, which were collected simultaneously with TSP in each field experiment. The 16 PAHs contributed only around 2 mg g^{-1} PM$_{2.5}$ and PM$_{10}$, in the field burning and only 0.11 mg g^{-1} SPM from the hood pile burning. Beside naphthalene, the most abundant PAHs detected are fluoranthene and pyrene. Other 4 and 5-ring compounds (from BaA to BaP) were also relatively abundant while of the 6-ring compounds BghiP was detected at a low level and IcdP was not detected. The relative abundance of the light PAHs in PM found in this study is similar to other studies for RS burning (Jenkins et al., 1996; Sheesley et al., 2003) and other biomass smoke (Oros and Simoneit, 1999). The ratios of individual PAH to PM found in our study, mostly 0.1–0.2 mg g^{-1} PM for 4–5 benzene ring compounds, are also similar to those reported by Jenkins *et al.* (1996) but higher than the ratio for 5 ring PAHs reported by Sheesley *et al.* (2003) of 0.03–0.04 mg g^{-1} PM. Fluoranthene, the most abundant PAH in our study, has a higher contribution, averaging 0.5 mg g^{-1} PM, but varying significantly among the field experiments.

OCP and PCB—Out of 16 OCPs 6 were detected in the filter samples (Table 5). Although the levels found in the smoke PM samples (gas phase not included) were less than 0.5 ng m^{-3} for individual OCP, their presence certainly increases toxicity of the PM emitted from

the field burning activities. In Thailand, by about 2002 the use of all the OCPs analyzed in this study was banned (FDA, 2007). However, remaining OCPs in paddy soil from the over 40 years of past intensive applications may be re-emitted during the burning. For PCB, out of 14 analyzed compounds 9 (plus overlapped peaks of PCB149 and PCB118 with endosulfan II) were detected in particles, generally at levels less than 1 ng m^{-3}. PCBs were found to be ubiquitous in soil, water and air in the region (Iwata et al., 1994) and specifically in airborne particles in Thailand (Pentamwa and Kim Oanh, 2008). PCBs deposited in soil may also be re-emitted during the paddy burning. In addition, we cannot exclude the possibility that some of the chlorinated semi-VOC we detected may be formed during the combustion of RS.

The average reconstructed mass (sum of all analytes minus the double counted elements) is 61–62% of $PM_{2.5}$ and PM_{10} mass. There is some double counting of levoglucosan (6%), PAHs (0.3%) and methoxyphenols (0.06%) with OC. If the organic matter (OM) is estimated based on the OC value using a scaling factor of 2.0 (suggested range of 1.4–2.1 by Turpin and Lim, 2001) then the mass closure would be 85–90%. Further speciation of this primary OC may help to improve mass closure and provide additional source signatures.

Hood burning SPM profiles

No detailed composition data are available for hood spread burning experiments except for EC and OC data for Hood 2 and Hood 3 (not presented in Table 4). Higher EC (75 vs. 28 mg g^{-1} SPM) and lower OC (290 mg g^{-1} vs. 470 mg g^{-1} SPM) were obtained in Hood 2 burning (dry RS, 5% moisture) than Hood 3 burning (RS of 22% moisture). The EC/OC content in SPM of these 2 spread burning hood experiments are in the same range of those in $PM_{2.5}$ and PM_{10} of the field experiments (Table 4).

For the 3 hood pile burning experiments presented in Table 4 no EC/OC data were available. Available composition data show fractional compositions of PAHs and water soluble ions were substantially lower in SPM from hood pile burns compared to those (in $PM_{2.5}$ and PM_{10}) obtained from the field (spread burning) experiments (Table 4). Data for the elements/ions was less consistent – some elements (e.g. Si and Zn) were much more abundant in SPM from the hood pile burning, whereas other elements (e.g. Ti and V) were much less abundant in SPM from the hood pile burning. We observed (visually) that SPM in the hood burning samples contained a significant amount of ash and unburned biomass particles which would contribute a high mass fraction but little PAH and elements/ions. This could lead to the lower emission ratios we observed for PAHs, water soluble ions and several of the elements.

3.5 Preliminary estimation of RS burning emission

We used the obtained EF from *in situ* field burning experiments to roughly estimate the emission from RS field burning in Thailand using only preliminary burning activity data available. OAE (2007) reports that the annual harvesting area of rice paddies in Thailand was 10,227,870 ha, which accounts for both the major crop and the secondary crop. There is also a third rice crop per year cultivated in some areas in the central part of Thailand, but it is harvested in the rainy season and we assumed, for simplicity, that no field burning was done for this crop. Simply assuming that all RS of these two crops are subjected to field burning and using the area based EF (g m^{-2}) for *in situ* field burning presented above, the RS field burning activity in Thailand would generate, 0.52±0.07 Tg $PM_{2.5}$, 77±27 Tg CO_2 and 6.3±1.0 Tg CO annually. The corresponding EC and OC emitted with $PM_{2.5}$ would be 0.03±0.01 and 0.18±0.05 Tg, respectively.

Note that the presented values are most likely to be the high estimates of the total RS burning emission in the country. Further investigation is required to obtain realistic burning activities, e.g. the portion of the RS burned in the field, for better emission estimation. Nevertheless, non-burning alternatives or efficient energy recovery from this crop residue would help to relieve the atmosphere from this pollution burden.

The EF obtained in this study can be used to estimate the emission from RS burning in other countries in Asia where comparable conditions exist. The use of the area based EF (g m^{-2}) much simplified the emission calculation as the plantation area is generally known. However, if biomass loadings are not in the same range presented in this study (0.58±0.14 kg RS m^{-2}) the mass based EF (g kg^{-1}) should be used instead.

4. Conclusions

PM EF from RS burning in the field and hood experiments varied considerably depending on a range of factors such as moisture content, meteorological conditions, and fire control activities, which all affected the combustion process and hence the emission. There is a clear relationship between SPM and moisture content of flue gas emitted from the hood experiments. Hood pile burning produced the highest PM EF, especially for the RS and surface soil samples with high moisture content. $PM_{2.5}$ contributed the majority (about 90%) of PM_{10} emission. Among the 8 cascade impactor size ranges, the first 2 stages or PM1.1 contributed the largest fraction of SPM mass (44%), EC (68%) and OC (52%). The most abundant components in $PM_{2.5}$ and PM_{10} were OC, water soluble ions and levoglucosan. Characteristics of PM emissions from RS burning include EC/TC ratio (~0.15) as well as the high relative abundance of K^+, NH_4^+, Cl^-, SO_4^{2-}, acetylsyringone, fluoranthene and pyrene. These features may serve as potential markers for RS PM. The presence of some OCPs and PCBs in the emitted PM may not only serve as useful signatures for RS PM in source apportionment studies but also emphasize the additional toxicity of the emission. Further investigation on the potential formation and presence of toxic compounds in RS burning smoke would provide useful information for source identification and health risk analysis. A wide range of EF obtained in our study suggests that care should be taken to select the most appropriate EF values, based on fuel properties (especially moisture) and dominant regional burn practices (spread vs. pile burning), when calculating emission inventories.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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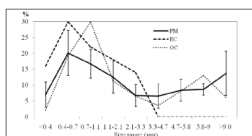
Figure 1.
Percentage size distribution based on smoke samples by Cascade impactor of PM (averaged for 4 field experiments) and EC/OC (for one experiment: Field 7, Dec 21, 2003, total EC: 40 μg m^{-3}, total OC: 243 μg m^{-3})
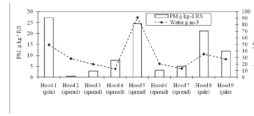
Figure 2.
SPM emission factors vs. water content in flue gas in hood experiments

Table 1

PM EF (dichot samples) of field burning based on carbon balance and emission ratios to CO_2 (n=4)

Field exp.	EF, g m^{-2} paddy				EF, g kg^{-1} of dry RS burned				RS Moist., %	MCE	Rice species	Dry mass, kg m^{-2}	Wind m s^{-1}
	PM$_{2.5}$	PM$_{10}$	CO$_2$	CO	PM$_{2.5}$	PM$_{10}$	CO$_2$	CO					
Field 8	4.85	4.93	902	62	6.66	6.77	1238	85	33	0.940	Pit 2	0.73	1.1 (N)
Field 9	4.25	4.86	1049	78	5.43	6.21	1339	100	26	0.937	Path 1	0.78	3 (SE)
Field 10	5.75	6.02	533	50	10.85	11.35	1005	102	22	0.920	Sup 90	0.53	1.2 (SW)
Field 11	5.40	7.03	533	50	10.19	13.27	1005	102	22	0.920	Sup 90	0.53	1.2 (SW)
Average	5.1±0.7	5.7±1.0	754±263	62±10	8.3±2.7	9.4±3.5	1147±169	97±8	26±5	0.93±0.01	-	0.64±0.13[a]	-

EFCO2 estimated based on carbon were available only for the last 4 field experiments (8–11)

[a] - Average dry biomass for all 11 fields is 0.58±0.14 kg m^{-2}

Pit 2: Pisanulok 2; Path1 : Pathumthani 1; Sup90: Supanburi 90

MCE: modified combustion efficiency; na: not available.

Table 2

PM concentrations ($\mu g\ m^{-3}$) in the field burning experiments (n=11)

Parameter	$PM_{2.5}$	$PM_{10-2.5}$	PM_{10}	$PM_{2.5}/PM_{10}$
Plume	1089±1477	160±143	1168±1611	0.92±0.08
Background	23±14	20±16	36±28	0.57±0.10
Net burning smoke	1067±1479	142±143	1134±1614	0.93±0.07

All concentrations are reported at 25°C, 1 atmosphere

Table 3

SPM EF and detail of hood experiments

Hood exp.	Hood 1	Hood 2	Hood 3	Hood 4	Hood 5	Hood 6	Hood 7	Hood 8	Hood 9
Burning type	pile	spread	spread	spread	spread	spread	spread	pile	pile
MCE[a]	na	na	na	na	0.88	0.93	0.93	0.92	0.92
RS moist., %	na	5	22	30	46	36	30	27	27
DAH[b]	1	7	4	2	na	5	na	3	3
EF, g kg^{-1} RS	27.3	0.5	2.9	7.7	24.4	3.2	5.1	21.1	12.0
EF, g m^{-2}	-	0.2	1.7	4.4	15.9	1.4	1.9	-	-

[a]-MCE: modified combustion efficiency; na: not available

[b] - DAH (day after harvest) is the number of days between the crop harvest and the field burn experiment, hood burning took place 1 day after field burning

na – not available; - EF in g m^{-2} is not applicable for pile burning

Table 4

PM emission factors (g kg^{-1} RS) and composition (mg g^{-1} PM)

		Field, PM2.5	Field, PM10	Hood pile, SPM
EF PM, g kg^{-1} RS burned		8.3±2.7 (n=4)	9.4±3.5 (n=4)	20.1±7.7 (n=3)
PM composition, mg g^{-1} PM (part per thousand)				
		(n=9)	(n=9)	(n=3)
EC/OC	EC	57.7±27.9	56.9±25.3	
	OC	335.4±88.0	328.6±84.7	
	TC	*393.0±64.0*	*385.5±63.3*	
Ions	Na$^+$	2.56±2.77	3.53±3.48	0.12±0.24
	K$^+$	50.0±34.0	47.3±33.6	7.2±10.5
	NH$_4^+$	23.8±11.7	22.8±9.2	0.54±0.88
	Mg^{2+}	0.11±0.22	0.18±0.28	nd
	Ca^{2+}	0.15±0.41	1.08±1.06	0.75±0.90
	F$^-$	2.45±3.28	2.48±3.17	0.81±1.36
	Cl$^-$	69.3±31.6	68.6±30.7	14.6±17.8
	NO$_3^-$	2.93±3.72	2.91±3.20	0.56±0.88
	SO$_4^{2-}$	9.82±7.21	15.53±13.06	3.5±4.1
	Total	*161.2±24.5*	*164.4±24.3*	*28.1±4.9*
Element[a]	Fe	0.038±0.108	0.105±0.306	0.040±0.025
	Ni	0.036±0.068	0.047±0.070	
	Pb	0.045±0.094	0.115±0.197	0.049±0.015
	Sr	0.013±0.029	0.016±0.028	
	Ti	0.015±0.046	0.016±0.043	0.005±0.002
	V	0.091±0.130	0.140±0.191	0.004±0.002
	Zn	0.036±0.099	0.066±0.155	0.26±0.15
	Si	0.14±0.34	0.185±0.364	5.89±2.88
	Al	0.18±0.33	2.53±2.47	0.26±0.04
	Ca	0.85±1.33	2.65±3.40	0.50±0.12
	Cd	0.009±0.023	0.009±0.022	
	Cr	0.080±0.169	0.163±0.292	0.003±0.002
	Cu	0.171±0.409	0.162±0.391	
	Mg	0.906±1.710	1.739±1.783	0.065±0.012
	Mn	0.005±0.015	0.010±0.028	0.025±0.026
	S	1.174±0.404	1.24±0.24	
	As	0.003±0.003	0.003±0.004	
	Se	0.0001±0.0002	0.0005±0.0004	
	Br	0.047±0.011	0.044±0.013	
	Rb	0.036±0.013	0.035±0.013	
	Zr	4E-05±7E-05	0.0002±0.0003	
	Ag	0.004±0.005	0.005±0.005	

		Field, PM2.5	Field, PM10	Hood pile, SPM
	Sn	nd	0.002±0.003	
	Sb	nd	0.001±0.001	
	Ba	0.016±0.022	0.015±0.016	
	Bi	nd	0.001±0.001	
	Total	*2.1±0.2*	*4.9±0.5*	*6.5±1.8*
PAH[b]	Naph	0.42±0.57	0.39±0.53	0.012±0.025
	Acy	nd	nd	nd
	Ace	0.02±0.07	0.02±0.05	0.001±0.002
	Flu	nd	nd	0.005±0.011
	Phe	0.03±0.07	0.02±0.05	0.004±0.008
	Ant	0.02±0.01	0.01±0.01	0.0003±0.0007
	Fth	0.50±0.75	0.49±0.75	0.015±0.029
	Pyr	0.29±0.33	0.26±0.27	0.01±0.02
	BaA	0.12±0.18	0.11±0.14	0.012±0.024
	Chry	0.17±0.21	0.15±0.17	0.01±0.02
	BbF	0.13±0.12	0.12±0.11	0.021±0.037
	BkF	0.05±0.04	0.05±0.04	0.011±0.022
	BaP	0.13±0.15	0.11±0.13	0.013±0.025
	DahA	0.08±0.10	0.08±0.10	nd
	BghiP	0.02±0.03	0.02±0.03	nd
	Ideno	nd	nd	nd
	Total PAH	*2.0±0.2*	*1.8±0.1*	*0.11±0.01*
Levoglucosan Methoxy- phenols [c]	*LG*	*56.2*	*57.4*	
	ETGU	0.0019	0.0018	
	EUG	0.0050	0.0047	
	VAN	0.0294	0.0278	
	TISOEU	0.0034	0.0032	
	ACETV	0.0073	0.0069	
	GUACE	0.0172	0.0163	
	ALLSY	0.0037	0.0035	
	PRSY	0.0029	0.0028	
	SYALD	0.0835	0.0797	
	ACETSY	0.3880	0.3715	
	CONIF	nd	0.0058	
	PRSYON	0.0622	0.0597	
	SINAP	0.0100	0.0109	
	Total meth.	*0.62*	*0.60*	
Total all		**614±42**	**613±41**	

nd: not detected; blank cells: not analyzed (for SPM in hood experiments)

EC/OC data available for 2 hood spread burning experiments, not presented in Table 4 (see the text).

[a]- Elements analyzed by PIXE and ICP-OES: Be, Co, Li, Mo, Tl were not detected in any sample

[b] - The detection limits of the PAHs were in the order of 1 ng mL^{-1} sample extract.

[c] - only 13 detected among 21 analyzed methoxyphenols are presented in Table 4. Detection limits for the methoxyphenols were in the range of 1 – 30 ng mL^{-1} of sample extract.

Table 5

OCP and PCB in PM emitted from field burning (mg g^{-1} of PM)

Compounds	Field PM$_{2.5}$ (n=10)	Field PM$_{10}$ (n=10)
OCP		
α-BHC	0.00011±0.00013	0.00010±0.00011
γ-BHC	3.E-06 ±5.E-06	2.E-06±5.E-06
Heptachlor	0.00013±0.00025	0.00011±0.00020
Aldrin	0.00034±0.00051	0.00029±0.00039
Heptachlor epoxide	0.00056±0.00125	0.00049±0.00109
Endosulfan I	0.0001±0.0003	0.00008±0.00023
PCB		
PCB 18	0.00002±0.00004	0.00002±0.00004
PCB 31	0.0044±0.0053	0.0040±0.0049
PCB 28	0.00015±0.00020	0.00013±0.00018
PCB 52	0.00033±0.00058	0.00027±0.00046
PCB 44	0.00029±0.00035	0.00025±0.00029
PCB 101	0.00005±0.00014	0.00004±0.00011
PCB149, 118 & Endo II	0.00001±0.00004	0.00001±0.00003
PCB 153	nd	2E-06±5E-06
PCB 180	0.00021±0.00043	0.00018±0.00036
PCB 209	0.00020±0.00046	0.00020±0.00045

Detection limits (DL) of 11 analyzed PCB were in the range of 0.195–0.3 ng mL^{-1} while DL of 16 OCP was 0.06–0.35 ng mL^{-1} (total sample extract was 1.5mL). Only detected compounds are presented in Table 5.

PCB 149, 118 & Endo II: overlapped peaks of PCB149, PCB118, and Endosulfan II