Atmospheric Environment 119 (2015) 182–191

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Characterization of gaseous and semi-volatile organic compounds emitted from field burning of rice straw

Nguyen Thi Kim Oanh [a, *], Aungsiri Tipayarom [a], Thuy Ly Bich [a], Danutawat Tipayarom [a], Christopher D. Simpson [b], David Hardie [b], L.-J. Sally Liu [b]

[a] Environmental Engineering and Management, Asian Institute of Technology, Pathumthani, Thailand
[b] Department of Environmental and Occupational Health Sciences, University of Washington, Seattle, USA

HIGHLIGHTS

- Rice straw field burning was simulated using laboratory and *in situ* experiments.
- Emission factors in field burning were higher than laboratory burning.
- BTEX and PAHs in smoke showed distinguished profiles compared to ambient air.
- PCBs, OCPs, aldehydes were higher in smoke but without clear enrichment in profile.
- Results are relevant for current field spread burning emission in Asia.

ARTICLE INFO

Article history:
Received 6 February 2015
Received in revised form
26 July 2015
Accepted 3 August 2015
Available online 6 August 2015

Keywords:
Rice straw burning
Emission factor
Concentration profile
Gaseous pollutants
PAHs
Chlorinated compounds

ABSTRACT

Rice straw (RS) field burning, commonly practiced in Asia, produces large amounts of toxic air pollutants but has not been comprehensively characterized. This study conducted field and laboratory measurements for gaseous pollutants and semi-VOCs (16 PAHs, 16 chlorinated pesticides and 14 PCBs) in RS burning smoke to determine emission factors (EFs) and emission concentration profiles. Paddy burning experiments were done following common practices used by farmers in Southeast Asia and EFs were estimated using the carbon balance method. Laboratory hood experiments simulated burning of dry RS (moisture content ~ 5%) and normal RS (moisture ~ 23–30%). Semi-VOCs were analyzed separately in the particulate (PM) and gas phases, and the levels measured in smoke were compared with those in the paddy background and in general ambient air to identify enrichment of the compounds. Lower EFs of all pollutants were obtained for hood burning dry RS as compared to hood burning normal RS. EFs of all detected pollutants in the field burning were higher than hood burning. The EFs of field burning in mg kg^{-1} RS were 760 for benzene, 230 for toluene, 510 for SO_2, 490 for NO_2, 260 for total PAHs (88% in gas phase), 0.11 for total PCBs (59% in gas phase) and 0.23 for OCPs (62% in gas phase). The EF of aldehydes determined in the hood experiment was 80–150 mg kg^{-1} RS. As compared to ambient air, RS smoke had significant enrichment of light PAHs, fluoranthene in PM and acenaphthylene in gas phase. Smoke had a higher proportion of benzene in BTEX than roadside air. Levels of PCBs, OCPs and aldehydes were higher in the burning smoke compared to ambient air, but there was no significant enrichment of particular compounds. This study provides appropriate ranges of EFs for developing emission inventory of RS spread field burning.

1. Introduction

Rice is by far the most popular crop in Asia, where this staple provides 50–80% of the total calories consumed. Asian farmers shared about 90% of the total worldwide production, with two countries, China and India, producing more than 50% of the crop (Rice-Trade, 2014). Field open burning of rice straw (RS) has long been practiced as an inexpensive way of crop residue disposal and is used increasingly by farmers in Southeast Asia (SEA). To meet the domestic and export demand, SEA farmers grow 2–3 crop cycles per year that leaves only a short time period between two

* Corresponding author.
E-mail address: kimoanh@ait.ac.th (N.T. Kim Oanh).

http://dx.doi.org/10.1016/j.atmosenv.2015.08.005
1352-2310/

consecutive crop cycles, hence field burning becomes even more attractive as it helps to clear land quickly for the next crop planting. As a result, a huge amount of RS is disposed of annually by field open burning (Gadde et al., 2009). Furthermore, wealthier farmers tend to use less RS for cooking or animal feedstock (Cao et al., 2006) hence the RS field burning would continue to rise in the near future if no control measures are taken (Kim Oanh, 2012).

Combustion conditions for RS field open burning (RSOB) are largely uncontrolled, resulting in emission of incomplete combustion products. Consequently, large amounts of toxic air pollutants (fine particles, inorganic and organic gases) and climate pollutants including greenhouse gases (GHGs) and black carbon (BC) particles are emitted (Andreae and Merlet, 2001; Reid et al., 2004; Kim Oanh et al., 2011; and references therein). The toxic dioxins (PCDD/F), for example, have been reported to be released during RS burning (Gullett and Touati, 2003; Sanchis et al., 2014).

In Asia, RSOB contributes a considerable share to national emissions. Cao et al. (2006) and Yan et al. (2006) reported that field burning of crop residues (including RS) contributed around 7–10% to the China national emissions of BC and organic carbon (OC). In Thailand, the crop residue field burning was estimated to contribute 4–17% of the national emission of different species, and RSOB contributed more than 80% of the total emission from crop residue field burning (Kanabkaew and Kim Oanh, 2011).

Agricultural field burning activities are reported to adversely affect air quality in many locations around the world, including USA (Jiminez et al., 2007), Europe (Viana et al., 2008), and Asia (Yang et al., 2006; Tipayarom and Kim Oanh, 2007; Chen et al., 2008). In particular, emissions from RSOB have been reported to result in high personal exposures to air pollution (Wu et al., 2006), and resulted in adverse health effects (Torigoe et al., 2000). RSOB emissions also potentially cause regional and global climate effects, hence elimination of this source would result in co-benefits to both climate and environment (UNEP-WMO, 2011; Shindell et al., 2012).

Despite its high contribution to air pollution, RSOB is often overlooked in air quality management programs in Asia. It is therefore important to demonstrate the significance of this emission source and disseminate the information in order to effectively minimize the field burning activities. This in turn requires a comprehensive emission characterization of RSOB to determine emission factors (EFs) and emission profiles of particulate matter (PM) and toxic gases. A number of previous studies have been conducted using experiments, both with enrichment of pollutants in ambient air levels and in controlled laboratory conditions (Viana et al., 2008; Yang et al., 2006; Lee et al., 2008; Hays et al., 2005; Jenkins et al., 1996; Sheesley et al., 2003). However, these studies mainly focused on PM and its composition, whereas few studies have reported gaseous or semi-VOCs (volatile organic compounds) emissions from RS burning (Zhang et al., 2008; Cao et al., 2008). In particular, a comprehensive emission characterization of *in situ* RSOB burning in SEA for gaseous pollutants and semi-VOC has not been found in literature.

This study was conducted to partly fill in these data gaps. This paper reports emission factors for BTEX (benzene, toluene, ethylbenzene and xylenes), SO_2 and NO_2, aldehydes, semi-VOCs including polycyclic aromatic hydrocarbons (PAHs), organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs). Details on the particulate matter (PM) emission factors and PM profiles, together with CO & CO_2 emissions have been presented previously (Kim Oanh et al., 2011). The emission characterization was conducted through a set of experiments with *in situ* RSOB in paddy fields in Thailand, and simulated burning in a hood at the Asian Institute of Technology (AIT). The field experimental studies aimed to represent common practices of RSOB in SEA and are expected to provide appropriate ranges of EFs to be used for the emission inventory in the region.

2. Experimental design

Description of field sampling and measurements has been presented in our earlier paper that reports PM emission (Kim Oanh et al., 2011). Gaseous pollutants and semi-VOCs were measured in 10 out of 11 field experiments reported in the previous paper, i.e. fields 2–11, and in 3 hood experiments (hood 2, 3 and 4) out of 9 hood experiments, as detailed in Table S1, Supplementary information (SI). The field burning experiments in our study represent the RSOB practice commonly applied in SEA countries for paddies which have been mechanically harvested using combine harvesters. The machine leaves RS spread in windrows where it is burned when dried (after 1–7 days) hence named "spread burning". In addition, the RS pile burning is practiced in places where manual harvesting of rice is practiced, e.g. some regions of Vietnam or Indonesia, where RS after harvest is piled up at a paddy corner and burned largely under smoldering conditions. Our previous study (Kim Oanh et al., 2011) reported more than two times higher EFs of PM from pile burning as compared to spread burning. However, pile burning has declined in SEA as farmers have organized to have large paddies that allow mechanical ploughing and harvesting.

All the RS burning experiments were carried out during the RS burning seasons (dry season, December to April) in the period of 2003–2006. This section focuses only on sampling methods for the gaseous pollutants and semi-VOCs. Details on the experiment setup as well as sampling for RS biomass load, carbon content and moisture content have been described previously (Kim Oanh et al., 2011). A summary of parameters measured in the experiments is given in Table S2, SI. Briefly, PAHs and BTEX were measured in all hood and field experiments. PCBs and OCPs were monitored only in the field experiments. Aldehydes were measured in 2 hood experiments (hood 2 and 3) and one field experiment (field 4). Inorganic gases SO_2, NO_2, CO and CO_2 were measured in 7 field experiments (fields 5–11). Note that the field experiments simulated the actual RS field burning practice in the region hence they were expected to produce relevant EFs for the emission inventory purpose. Accordingly, more intensive measurements for semi-VOCs were conducted in the field experiments as compared to the hood experiments.

2.1. Sampling in field burning experiments

The field burning experiments were conducted in the Pathumthani province which is located in the central part of Thailand, about 40 km North of Bangkok. The province has a large rice plantation area, 34% of its total area of 1526 km^2 (National Statistic Office, 2008). To minimize the effects of other local sources, only rice paddies located in the middle of large agricultural fields and far away from roads and residential homes were selected. In each field experiment, a paddy background (BG) sampling (taken for a period of 1–2 h, just prior to respective burning experiment) and a smoke plume sampling (taken during burning for a period 0.5–1 h) were conducted. The differences in pollutant concentrations between the two samplings were considered as the net contribution from the RS burning. To protect the instruments from heat, all sampling devices and continuous reading instruments were placed at a fixed downwind site, in a cleared plot of the respective experimental paddy. All gas sampling inlets were positioned 1.5 m above ground, near the other instruments (for wind, temperature, humidity, CO/CO_2, and PM) to ensure that they captured the same portion of the smoke plume (with the same dilution degree). In each field

experiment, for every parameter (BTEX, PAHs, OCPs/PCBs, aldehydes, and SO_2 and NO_2) one field blank (open but no air drawn through) and one trip blank (non-exposed, kept in a close box) were prepared and they were treated in the same way as the samples.

2.1.1. Semi-VOC sampling

Semi-VOCs were collected using an Andersen Hi-Vol. PUF sampler of Thermo Anderson Model PS-1 (225 L min^{-1}) following the US EPA Methods TO4A & TO13A (US EPA, 2011). Prebaked (at 550 °C for 4–5 h) glass fiber filters (GFF Ø110 mm) were used to collect the PM phase while pre-cleaned PUF/XAD-2 was used to collect the gaseous phase of semi-VOCs. PUF was used at the first 3 field experiments (fields 2 & 4 for PAHs, field 3 for OCPs/PCBs) but was replaced by XAD-2 in the last 7 experiments (fields 5–11) to facilitate segregation for analyses of the gas phase of both semi-VOC groups, PAHs and PCBs/OCPs. The pre-cleaning of PUF and XAD-2 was done by Soxhlet extraction, twice, each for 16 h at about 15 min per cycle. The first extraction used hexane while the second extraction used a mixture of diethyl ether/hexane (10% diethyl ether solution in hexane). The prepared PUF and XAD-2 were contained in the pre-cleaned (rinsed with methylene chloride 2 times) glass cartridge (of Hi-Vol. sampler), wrapped with aluminum foil and placed in separate air tight plastic bags until the start of sampling. For XAD-2 sampling, 50 g of XAD-2 resin was loaded over a thin supporting layer of PUF (<1 cm) in the glass cartridge (5.8 cm inner diameter) which made an XAD-2 layer of about 7 cm thickness.

2.1.2. BTEX sampling

BTEX sampling was done following NIOSH method 1501 (NIOSH, 1994). SKC–coconut shell charcoal tubes (6 mm × 70 mm length) packed with two sections of activated carbon (100 mg and 50 mg, respectively) were used for the sample collection. A calibrated pump was used at a flow rate of 0.2 L min^{-1}. The detail sampling procedure was described in our previous studies (Truc and Kim Oanh, 2007; Kim Oanh et al., 2013).

2.1.3. Aldehydes sampling

Sep-pak sorbent cartridges (C18 silica-based, Waters Corp., USA) were used to collect samples using a calibrated pump at 0.2–0.4 L min^{-1} which was the same as described by Liu Sally et al. (2001). The total volume of gas sampled in a tube for upwind field burning (taken simultaneously with downwind smoke plume and also considered as BG in this study) was around 15–25 L. Smaller sample volumes, 5–10 L, were used for sampling high smoke concentrations in field and hood experiments. For comparison, samples were also taken at roadside and at the AIT campus with the sampled volume of 70–150 L. The samples were transported, together with the blanks, in a box with dry ice for analysis at the University Washington (UW), Seattle, USA. The maximum period between sampling and analysis for aldehydes was about 1 month. Note that in addition to a trip blank and field blank used for every other parameter, for aldehydes, there was a trip blank that was always kept in the storage box during the shipment of unused Sep-paks from UW to AIT and sampled tubes from AIT back to UW. This blank yielded similar aldehyde concentrations as the other field and trip blanks with the levels ranged from below DL to a maximum of 0.45 μg per blank tube for acetone.

2.1.4. SO_2 and NO_2 sampling

These gases were monitored for field burning experiments using impinger absorption methods. Potassium tetrachloro-mercurate (TCM), (10 mL, 0.04 M aqueous solution) was used for SO_2 sampling (OSHA, 1992) while for NO_2 sampling, 30 mL solution of sodium hydroxide and sodium arsenite was used (OSHA, 1991). A pump was used to draw the sampled gas through the impinger at 0.5 L min^{-1}.

2.1.5. Continuous measurements

Continuous data were recorded for wind (Mechanical wind recorder), temperature and humidity (Thermo-Hydrometer, Delta TRAK®), CO and CO_2 (IAQ-CALC™, model 8760/876). As described in Kim Oanh et al. (2011), two continuous series of CO/CO_2 data were collected in the field experiments. The first data series was recorded at the fixed downwind site together with other field measurements and was used to determine the emission ratio for subsequent EFs calculation. The second data series contained CO/CO_2 measurements recorded near the flame and was used to determine the modified combustion efficiency.

2.2. Hood burning and stack sampling for gaseous pollutants

2.2.1. Semi-VOC

Both particulate (PPAHs) and gaseous phase (GPAHs) were determined for 3 hood experiments. As detailed previously (Kim Oanh et al., 2011), isokinetic samples were collected using a semi-VOC sampling train (Auto 5™, AST® Sampler) following US EPA modified Method 5. The isokinetic rates of the stack sampling in our study were 90 ± 10% which ensured the representative PM samples hence particulate phase of semi-VOCs. The PM samples were collected on pre-baked glass fiber filters (GFFs) which were segregated and a part was used for the PAH analysis. Gaseous PAHs were collected using pre-cleaned XAD-2. The experimental set-up and detail on the sample recovery were similar to those previously reported in our cookstoves study (Kim Oanh et al., 2002).

2.2.2. Other hood sampling

A pump was used to continuously collect an integrated sample of hood flue gas into Tedlar bags (series of 20 L bags, each placed inside a black bag) at a constant rate over the entire hood burning experiment. The sampled bulk gas was transferred to the adsorption tubes, using a pump, aldehydes (5–8 L) and BTEX (5–8 L) for subsequent analyses.

2.3. Sample analysis

Laboratory blanks, trip and field blanks were treated in the same way as the samples. The analytical results of field blanks were used to correct analyte concentrations reported in this paper.

2.3.1. Semi-VOC

The samples collected on GFF and XAD-2 in the field experiments were segregated into 2 halves: one for PAHs and the other for PCBs/OCPs analyses. GFF and XAD-2 samples from the hood experiments were analyzed for PAHs only. PUF, which was used in the 3 first field experiments, was analyzed alternatively for PAHs (field 2 and 4) and PCBs/OCPs (field 3) as seen in Table S2, SI. For the last 7 field samples where XAD-2 was used for sampling gas phase semi-VOCs, both groups of analytes were analyzed. GFF and XAD-2/PUF samples were analyzed separately to differentiate the particulate and gas phase concentrations of the semi-VOCs.

The 16 US EPA priority PAHs (from naphthalene to ideno(*1,2,3-c,d*)pyrene, as listed along with concentration results in Table 2) were analyzed at the AIT laboratory following US EPA Method TO13A (US EPA, 1999a) with the same detail given in Kim Oanh et al. (2002). Briefly, the samples were extracted by ultrasonification with dichloromethane; and quantified by High Performance Liquid Chromatography (HPLC). Before concentration (to the final volume of 1.5 mL) a 20 μL dimethyl sulfoxide (DMSO) was added to the

Table 1
Emission factors of pollutants (average ± SD).

Pollutants		EF, g or mg per m^2 of paddy			EF, g or mg per kg RS (dry)				
		Hood dry (#2)	Hood normal (#3 & 4)	Field (n = 7)	Hood dry (#2)	Hood normal (#3 & 4)	Field (n = 7)	Literature data	
								Rice straw	Agro residue (f)
$PM_{2.5}$, g		0.2	3.2 ± 2.0	5.4 ± 1.0	0.54	5.3 ± 3.6	8.3 ± 2.2	3.8 (a)	
CO, g				62 ± 10			93 ± 10	180 ± 40(b); 64 ± 5(c)	92 ± 84
CO_2, g				803 ± 217			1177 ± 140	1216 ± 97 (b); 791 ± 13 (c)	1515 ± 177
Benzene, mg		46.5 ± 17	238.6 ± 97	531 ± 229	113 ± 41	362 ± 150	763 ± 266	870 ± 200 (b)	140
Toluene, mg		13.8 ± 3.1	101.1 ± 43	169 ± 2.5	33.4 ± 8.5	153 ± 67	232 ± 3.4	1080 ± 350 (b)	26
Ethylbenzene., mg		0.53	3.2	nd	1.3	4.8	nd		30
Xylenes, mg		3.5 ± 1.1	31.9 ± 9.0	nd	8.5 ± 2.6	48 ± 14	nd		10
SO_2, mg				370 ± 230			510 ± 320	180 ± 310 (g)	400
NO_2, mg				350 ± 170			490 ± 210	790 ± 50 (c, NO_2); 620 ± 400 (b, NO)	2500 ± 100 (NOx as NO)
Aldehydes, mg		33	98 ± 5.1		80	147 ± 8.0		3170 ± 880 (b, HCHO)	1400 (HCHO)
16 PAHs, mg	PPAH	nd	0.31 ± 0.44	21 ± 19	nd	0.83 ± 0.14	34 ± 35	1.02(a); 18.6(d); 3.0 (5% moist.) & 17.2 (20% moist.) (e)	
	GPAH	5.1	22.6 ± 12.9	156 ± 245	16.6	62 ± 50	230 ± 333		
	Total (G/T, %)	5.1 (100)	22.9 ± 12.9 (99)	177 ± 246 (88)	16.6 (100)	63 ± 49 (99)	264 ± 335 (88)	17.8(a)	25
14 PCBs, mg	PPCB			0.031 ± 0.033			0.049 ± 0.055		
	GPCB			0.045 ± 0.039			0.064 ± 0.053		
	Total (G/T, %)			0.077 ± 0.051 (59)			0.114 ± 0.076 (59)		
16 OCPs, mg	POCP			0.056 ± 0.034			0.086 ± 0.052		
	GOCP			0.083 ± 0.10			0.141 ± 0.194		
	Total (G/T, %)			0.138 ± 0.106 (62)			0.227 ± 0.20 (62)		

Note: G/T: share of gas phase to total semi-VOCs in percent; nd: not detected; blank cells: not analyzed/not available.
a: Jenkins et al. (1996); b: Christian et al. (2003), values for dry fuel, ash free; c: Zhang et al. (2008); d: Keshtkar and Ashbaugh (2007); e: Sanchis et al. (2014) for 5% and 20% moisture content of RS, included 9 PPAHs (Fth, BaA, BbF, BjF, BkF, BaP, IcdP, DahA and BghiP); f: Andreae and Merlet (2001): estimates based on laboratory studies; g: Cao et al. (2008).

extract solution to minimize PAH evaporation. The HPLC (HP1050 series) was equipped with a programmable fluorescence detector (FLD) and an ultraviolet detector (UV). A MERCK LiChroCART 4-4 Guard Column and LiChroCART 250-4 LiChrosphere PAH (4 × 244 mm) analytical column were used. A mixture of HPLC-grade water and acetonitrile (ACN) was used as the mobile phase. The solvent gradients (%ACN/HPLC water) were 60% during the first 5 min, gradually increased to 85% at the 20^{th} minute and kept until the 55^{th} minute, further increased to reach 100% at 58^{th} minute and kept until the 85^{th} minute. Acy, Ace, Flu and IcdP were quantified by UV detector while other PAHs by were quantified by FLD.

Sample preparation and analysis for PCBs and OCPs were the same as presented in a previous study (Pentamwa and Kim Oanh, 2008). In brief, the samples were Soxhlet extracted using a solvent mixture of 90% hexane and 10% diethyl ether and subsequently analyzed using a GC-ECD at AIT, following Method TO-4A (US EPA, 1999b). The GC-ECD (Model HP5890 Series II) was equipped with a capillary column (HP-5; 30 m × ID 0.32 mm × film thickness 0.25 μm). In total, 16 OCPs (from α-BHC to endosulfan sulfate, as detailed in Table 3) and 14 PCBs (from PCB 18 to PCB 209, as listed in Table 4) were analyzed.

The semi-VOCs were quantified using the respective external standards. The standards for PAHs were from SUPELCO while for PCBs and OCPs were from Dr. Ehrenstorfer Company. All solvents (HPLC grade) used were from J.T. Baker Company. For each compound, a standard curve was constructed using 5 different concentration levels. The calibration lines were obtained with R^2 of the linear regression of above 0.98.

Detection limits (DL) of the semi-VOCs were determined by repeated injections of reducing concentrations of standard solutions. The DL of PAHs in general were below 1.0 ng mL^{-1} but were higher for the first 3 compounds, i.e. Nap and Ace of 1.9 ng mL^{-1}, and Acy of 4.0 ng mL^{-1}. DL of the PCBs were in the range of 0.20–0.30 ng mL^{-1} while DL of OCPs were 0.06–0.35 ng mL^{-1}. Total sample extract was 1.5 mL and the injection volume was 20 μL for PAHs and 1 μL for PCBs/OCPs. The recovery rates of the compounds were determined by analyzing the spiked GFF and XAD-2 with known amount of the analytes. The average recovery was 70–120% for PAHs, 65–93% for PCBs and 60–87% for OCPs.

2.3.2. BTEX

BTEX were analyzed using NIOSH method 1501 (NIOSH, 1994). Briefly, the adsorbent content in a sample tube was desorbed using 1 mL carbon disulfide and allowed to stand with occasional shaking for 30 min. Before use the carbon disulfide solvent was cleaned by using concentrated sulfuric acid and concentrated nitric acid to remove benzene contamination (OSHA, 1980). A 14B GC equipped with a flame ionization detector (GC-FID) was used for BTEX quantification at the AIT laboratory. The injection volume was 1 μL and each sample was injected at least 2 times. The front and back adsorbent sections of the tubes used for burning smoke sampling, i.e. of higher BTEX concentration, were analyzed separately to check for possible breakthrough. Based on the NIOSH (1994) criteria, no breakthrough has occurred in our samples. A mixed BTEX standard (Fluka manufacturer) was used to prepare the calibration curves, each of 5 points, with R^2 above 0.99 for every BTEX species. The method could not separate *m*-xylene and *p*-xylene, therefore these two compounds are reported together. The method minimum detectable quantity for the BTEX compounds was in the range 0.20 ng–0.30 ng. The precision (ratio between the standard deviation and the average value) based on repeated injections of each sample was in the range from 8 to 13% for all the analytes (Truc and Kim Oanh, 2007).

2.3.3. Aldehydes

The sampled Sep-pak cartridges were analyzed at UW Seattle

Table 2
PAH concentration (average ± SD), ng m^{-3} (25 °C, 1 atm) and share (%, in brackets).

Compound[a]	Net field burning (n = 9)		Hood dry (#2)		Hood normal (#3 & 4)		AIT, dry season (n = 26)		BG[b] (n = 10)	
	PPAHs	GPAHs	PPAHs	GPAHs	PPAHs	GPAHs	PPAHs	GPAHs	PPAHs	GPAHs
Naph	378 ± 580 (19)	641 ± 547 (4.2)	nd	332,509 (65)	nd	650,988 ± 477,008 (51)	15.1 ± 9.1 (69)	20.3 ± 12.8 (39)	nd	305 ± 357
Acy	nd	12,576 ± 1638 (82.3)	nd	65,660 (13)	nd	232,746 ± 64,915 (18)	0.02 ± 0.06 (0.1)	0.60 ± 0.22 (1.1)	nd	nd
Ace	8.9 ± 28.1 (0.4)	27 ± 84 (0.2)	nd	nd	nd	nd	nd	nd	3 ± 3.3	1391 ± 1252
Flu	nd	165 ± 438 (1.1)	nd	nd	nd	52,956 ± 74,890 (4.1)	0.05 ± 0.1 (0.2)	1.28 ± 0.52 (2.5)	0.6 ± 0.7	363 ± 305
Phen	35.6 ± 86.5 (1.7)	334 ± 868 (2.2)	nd	78,798 (15)	nd	242,938 ± 67,558 (19)	0.31 ± 0.1 (1.4)	15.1 ± 5.44 (29)	4.4 ± 4.5	166 ± 86
Anth	14.2 ± 18.6 (0.7)	64 ± 116 (0.4)	nd	6580 (1.3)	47 ± 67 (0.24)	16,855 ± 23,836 (1.3)	0.13 ± 0.18 (0.6)	1.31 ± 0.73 (2.5)	0.1 ± 0.2	27 ± 60
Fth	876 ± 673 (43)	1302 ± 1743 (8.5)	nd	nd	3886 ± 398 (20)	32,579 ± 46,074 (2.5)	0.38 ± 0.12 (1.7)	7.02 ± 1.9 (13.5)	210 ± 215	149 ± 152
Pyr	258 ± 420 (13)	157 ± 245 (1.0)	nd	26,646 (5.2)	3296 ± 787 (17)	38,149 ± 17,696 (3.0)	0.34 ± 0.28 (1.6)	4.56 ± 1.3 (8.7)	3.8 ± 6.5	60 ± 111
BaA	94.1 ± 96.8 (4.6)	13 ± 30 (0.1)	nd	844 (0.2)	3241 ± 173 (17)	3532 ± 864 (0.3)	0.36 ± 0.08 (1.6)	0.54 ± 0.19 (1.0)	2.6 ± 2.6	0.6 ± 1.4
Chry	134 ± 176 (6.5)	4 ± 12 (0.03)	nd	nd	2937 ± 580 (15)	7096 ± 4481 (0.6)	0.45 ± 0.17 (2.0)	0.97 ± 0.26 (1.9)	1.1 ± 1.8	0.8 ± 2.1
BbF	70.3 ± 77 (3.4)	nd	nd	nd	2719 ± 3845 (14)	nd	1.21 ± 0.54 (5.5)	0.28 ± 0.23 (0.5)	nd	nd
BkF	26.7 ± 26.4 (1.3)	nd	nd	nd	1576 ± 2229 (8.1)	nd	0.94 ± 0.44 (4.3)	0.22 ± 0.18 (0.4)	nd	nd
BaP	90.8 ± 89.1 (4.4)	nd	nd	nd	1812 ± 2563 (9.3)	nd	0.84 ± 0.26 (3.8)	nd	nd	nd
DahA	45.9 ± 53.5 (2.2)	nd	nd	nd	nd	nd	0.19 ± 0.28 (0.9)	nd	nd	nd
BghiP	10.9 ± 11.2 (0.5)	nd	nd	nd	nd	nd	0.77 ± 0.32 (3.5)	nd	nd	nd
IcdP	nd	nd	nd	nd	nd	nd	0.89 ± 0.37 (4.0)	nd	nd	nd
Total	2043 ± 1016	15,282 ± 16,441	nd	511,036	19,515 ± 5241	1,277,838 ± 494,923	22.0 ± 9.2	52.2 ± 14.1	225 ± 215	2461 ± 1354
G/T, %	88 ± 13		100		98 ± 2		70		93 ± 6	

'Hood dry' refers to the experiment with RS moisture of 5%; 'Hood normal' refers to those with RS moisture similar to the field experiments, 23–30%; nd: not detected.
[a] Abbreviations of PAHs: 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).
[b] BG: background levels in the RS burning season; BG samples were collected prior each filed sampling.

Table 3
OCP concentration (average ± SD), ng m^{-3} (25 °C, 1 atm) and share (%, in brackets).

Compounds	Paddy BG (n = 8)		Burning smoke net (plume-BG) (n = 8)		AIT, dry season 2003 (n = 5)	
	POCPs	GOCPs	POCPs	GOCPs	POCPs	GOCPs
α-BHC	0.077 ± 0.084 (16)	0.06 ± 0.049 (13)	0.069 ± 0.091 (13)	0.277 ± 0.298 (9)	nd	nd
β-BHC	nd	nd	nd	0.170 ± 0.291 (6)	0.025 ± 0.025 (5)	0.019 ± 0.028 (3)
γ-BHC	0.002 ± 0.006 (0.7)	0.007 ± 0.016 (1)	0.009 ± 0.018 (2)	0.066 ± 0.172 (2)	nd	0.005 ± 0.011 (1)
δ-BHC	nd	nd	nd	0.006 ± 0.017 (0.2)	nd	nd
Heptachlor	0.135 ± 0.125 (28)	0.160 ± 0.249 (35)	0.102 ± 0.155 (19)	0.193 ± 0.252 (7)	nd	0.132 ± 0.193 (18)
Aldrin	0.123 ± 0.099 (26)	0.114 ± 0.073 (25)	0.155 ± 0.218 (29)	0.195 ± 0.157 (7)	0.455 ± 0.319 (95)	0.522 ± 0.125 (71)
Heptachlor epoxide	0.123 ± 0.123 (26)	0.082 ± 0.065 (18)	0.157 ± 0.214 (29)	2.04 ± 2.56 (69)	nd	nd
Endosulfan I	0.003 ± 0.008 (1)	nd	0.041 ± 0.124 (8)	nd	nd	nd
DDE	nd	nd	nd	nd	nd	0.009 ± 0.021 (1)
Dieldrin	nd	nd	nd	nd	nd	0.052 ± 0.012 (7)
Endrin	nd	nd	nd	nd	nd	nd
Endosulfan II, PCB149 & 118	0.242 ± 0.39 (NI)[a]	0.895 ± 0.489 (NI)	0.043 ± 0.098 (NI)	nd	nd	nd
DDD	nd	0.017 ± 0.041 (4)	nd	0.003 ± 0.008 (0.1)	nd	nd
Endrin aldehyde	0.012 ± 0.031 (2)	0.013 ± 0.033 (3)	nd	nd	nd	nd
DDT	nd	nd	nd	nd	nd	nd
Endosulfan sulfate	nd	nd	nd	nd	nd	nd
Total OCP (exclude Endo.II)	*0.476 ± 0.448*	*0.452 ± 0.562*	*0.533 ± 0.389*	*2.95 ± 2.62*	*0.479 ± 0.320*	*0.739 ± 0.233*
G/T, %	*50 ± 25*		*80 ± 22*		61	

[a] NI: endosulfan II were overlapped with PCB149 and PCB118 hence three compounds were excluded from the total for share estimation; nd: not detected..

by HPLC following the method described in Liu Sally et al. (2001). Seven compounds were quantified including formaldehyde, acetaldehyde, acrolein, acetone, crotonaldehyde, glyoxal and methylglyoxal. Sep-pak cartridges were desorbed in acetonitrile using a SUPELCO visi-prep vacuum manifold (Sigma–Aldrich Corp., USA). The Sep-pak cartridges were attached to the manifold

Table 4
PCB concentration (average ± SD), ng m^{-3} (25 °C, 1 atm), and share (%, in brackets).

Compound	Background field (n = 8)		Burning smoke net (plume-BG) (n = 8)		AIT, dry season 2003 (n = 5)	
	PPCBs	GPCBs	PPCBs	GPCBs	PPCBs	GPCBs
PCB 18	0.041 ± 0.077 (2)	0.082 ± 0.202 (4)	0.049 ± 0.115 (2)	0.003 ± 0.009 (0.1)	0.023 ± 0.031 (21)	0.108 ± 0.066 (14)
PCB 31	1.335 ± 1.155 (66)	1.655 ± 1.25 (71)	2.143 ± 2.594 (67)	1.874 ± 2.673 (63)	0.013 ± 0.01 (12)	0.144 ± 0.055 (18)
PCB 28	0.148 ± 0.185 (7)	0.149 ± 0.253 (6)	0.217 ± 0.365 (7)	0.056 ± 0.06 (2)	0.037 ± 0.023 (35)	0.240 ± 0.103 (30)
PCB 52	0.249 ± 0.213 (12)	0.279 ± 0.315 (12)	0.327 ± 0.457 (10)	0.119 ± 0.179 (4)	nd	0.125 ± 0.033 (16)
PCB 44	0.203 ± 0.233 (10)	0.124 ± 0.137 (5)	0.195 ± 0.18 (6)	0.387 ± 0.385 (13)	0.03 ± 0.008 (28)	0.119 ± 0.042 (15)
PCB 101	0.037 ± 0.056 (2)	0.02 ± 0.05 (1)	0.037 ± 0.073 (1)	0.019 ± 0.054 (1)	0.004 ± 0.008 (3)	0.045 ± 0.015 (6)
PCB 153	0.019 ± 0.039 (1)	0.021 ± 0.051 (1)	0.009 ± 0.017 (0.2)	nd	nd	0.009 ± 0.005 (1)
PCB138	nd	nd	nd	nd	nd	0.007 ± 0.006 (1)
PCB 180	nd	nd	0.140 ± 0.302 (4)	0.359 ± 0.933 (12)		
PCB 170	nd	nd	nd	nd		
PCB 194	nd	nd	nd	0.068 ± 0.191 (2)		
PCB 209	nd	nd	0.07 ± 0.143 (2)	0.087 ± 0.23 (3)		
Total	*2.03 ± 1.22*	*2.33 ± 1.34*	*3.19 ± 2.69*	*2.97 ± 2.88*	*0.107 ± 0.041*	*0.797 ± 0.145*
G/T, %	*56 ± 16*		*49 ± 37*		88	

and acetonitrile was slowly added. The extract from each sample was collected in a vial inside the manifold. Individual calibration standards of the DNPH-derivatives were purchased from Sigma–Aldrich. A stock solution containing the seven aldehyde DNPH-derivatives was prepared in acetonitrile, then diluted to form the calibration series of 5 concentration levels. The calibration curve of each compound had R^2 of linear regression of above 0.99.

2.3.4. SO_2

SO_2 was measured using the colorimetric method described by OSHA (1992). The absorbent solution for SO_2 (TCM contained in impinger) was stored for 20 min for ozone destruction prior to analysis. The complex was made to react with pararosaniline and formaldehyde to form the intensely colored pararosaniline methylsulphonic acid. Sulfamic acid was used to destroy nitrite resulting from oxides of nitrogen. A UV/Vis Spectrophotometer (Hitachi Model U-2001) with silicon photodiode was used to measure the absorbance of the solution at 548 nm.

2.3.5. NO_2

NO_2 was measured the method described by OSHA (1991). The concentration of nitrite ion produced during sampling was determined colorimetrically by reacting the nitrite ion with phosphoric acid, sulfanilamide, and N-(1-napthyl)-ethylenediamine dihydrochloride. The absorbance of the colored azo-dye was also measured by UV spectrophotometry described above, at 550 nm.

Calibration curves, each with 5 concentration levels, were prepared for SO_2 and NO_2, ($R^2 > 0.997$). A field blank was analyzed for every sample. Analyte concentrations were calculated taking into account the blanks and absorption efficiency following the guidelines given in OSHA (1992) and OSHA (1991), respectively.

2.4. Emission factor determination

Emission factors are presented as mg m^{-2} of paddy burned and mg kg^{-1} of dry RS burned, which are convertible given representative data on the dry RS biomass density (average of 0.58 ± 0.14 kg m^{-2} paddy). In each hood experiment, an area of 3 m^2 of the rice paddy collected with the paddy surface soil was burned, hence RS loading was the same as in the field experiments of the RS spread burning.

EFs from the hood experiments were directly determined based on the measurements of flue gas volume and pollutant mass concentration (Eq. (1)).

$$EF = Conc\left(mg/m^3\right) * Flowrate\left(m^3/min\right) * Burning\ time(min) / Area\ burned\left(m^2\right) \quad (1)$$

EFs in the field experiments were determined using the carbon balance/emission ratio method which is commonly used in biomass open burning studies (Lee et al., 2008 and references therein). As detailed in our previous paper (Kim Oanh et al., 2011), the method basically calculates the carbon emitted with carbon containing species, i.e. CO_2, CO, CH_4, non-methane VOC and particulate C, based on the difference in C measured in the paddy biomass before and after burning. The EFs of other species are then determined using the concentration ratio of the selected species to a reference species, either CO_2 or CO, measured simultaneously in the emission plume. The modified combustion efficiency, $MCE = CO_2/(CO + CO_2)$, calculated using the measurements near the flame in all our field experiments was above 0.9 (Kim Oanh et al., 2011), indicating the flaming combustion phase, hence CO_2 was selected as the reference species following the suggestion by Reid et al. (2004). Details on the calculation steps for EFs in the field experiments are presented in Textbox 1, SI.

3. Results and discussion

3.1. Emission factors

Table 1 presents EFs obtained for the field and hood burning experiments. Hood 2 experiment burned spread dry RS (5% moisture) hence named “hood dry” while the other two hood experiments (hood 3 and hood 4) burned spread RS with moisture content of 23% and 30%, respectively, which was in the same moisture range of RS in the field experiments (Table S1, SI) hence named “hood normal”. EFs presented for the field experiments were based on the results of 7 field experiments (5–11) which had the online CO_2 and CO data required for the EF calculation. Reported aldehydes EFs are the results of the hood experiments because the only field experiment (field 4) having aldehydes measured but had no CO_2/CO data for the EF calculation.

The hood dry experiment produced lower EFs for all compounds compared to the hood normal experiments. The field experiments had the highest EFs, well above those for the hood normal that burned RS with a similar moisture content, and this may be explained by more uncontrolled combustion conditions in the field burning experiments. For example, the ambient air conditions

measured at the sampling sites of temperature, relative humidity, and wind speeds and directions (Table S1, SI) were varying largely between experiments. Wind speeds and directions were observed to strongly influence the RS field burning conditions whereas the hood burning was not significantly affected by wind. Comparing the different experiments, the EFs of gases and semi-VOC followed the same order as for $PM_{2.5}$ that is provided in Table 1 for reference while the detail on PM emission has been presented previously in Kim Oanh et al. (2011). EF data from other published studies are also illustrated in Table 1 for comparison.

3.1.1. BTEX

Among the BTEX species, benzene had the largest EF. Our average EF for benzene in the field experiments is in the same range of the reported values for the simulated RS burning (Christian et al., 2003), whereas the EF we observed for toluene was about 4 times lower. Andreae and Merlet (2001) compiled EFs of BTEX for agricultural residues (not specifically for RS) which are lower than our values for both benzene (about 5 times) and toluene (about 10 times). Xylenes and ethylbenzene were not enriched in the field experiments, i.e. similar levels were measured in both paddy BG and the smoke plume, hence the net contributions from burning were close to zero and their emissions were negligible. The EFs of these compounds, estimated based on the hood experiments, were in the same range as reported elsewhere in the literature for agricultural residues.

3.1.2. Aldehydes

EFs of aldehydes, 80–147 mg kg^{-1} RS, are reported as the total of the seven compounds analyzed. The EFs were determined only for the hood experiments (field 4 had aldehydes concentration data but no CO/CO_2 records for the EF calculation). Our EF results for "total aldehydes" were 20–40 times lower than reported EFs for formaldehyde alone by Andreae and Merlet (2001) and by Christian et al. (2003). It would be helpful to have aldehydes measurements for field burning, which (consistent with the other pollutants measured) is expected to generate higher EFs for aldehydes as compared to the more controlled hood experiments. Thus, more measurements for aldehydes are still required in future studies.

3.1.3. NO_2 and SO_2

The SO_2 EF obtained in the field experiments in this study, 510 ± 320 mg kg^{-1} RS, is compatible with the average value of 180 ± 310 mg kg^{-1} RS by Cao et al. (2008), in hood simulated burning, and quite close to the value of 400 mg kg^{-1} of agro residue reported by Andreae and Merlet (2001). As for NO_2, the EF obtained in the field experiments was 490 ± 210 mg kg^{-1}. Note that our method measured only NO_2 (not NOx) and our results were in the range of NO_2 EF of 330 ± 170 mg kg^{-1} RS by Cao et al. (2008) and 790 ± 50 mg kg^{-1} RS by Zhang et al. (2008). Zhang et al. (2008) measured both NO and NO_2 in laboratory experiments and reported the EFs for NO of 1.02 g kg^{-1} RS and NO_2 of 0.79 g kg^{-1} RS which yielded a ratio NO_2/NO of 0.77 and NO_2/NOx of 0.44. This high contribution of NO_2 to NOx may be expected due to the low combustion temperature of RS which was also the case of our field experiments. Based on this ratio, the NO emission would be estimated at 630 ± 270 and NOx at 1120 ± 480 mg kg^{-1} RS, which is similar to the ranges of NO_X values reported in the literature.

3.1.4. PAHs

The majority of PAHs measured were present in the gas phase (above 80%). Our EFs for the hood normal samples were comparable with the values reported by Jenkins et al. (1996), also produced in a controlled combustion of RS, i.e. about 1 mg kg^{-1} RS of PPAHs and 17.8 mg kg^{-1} RS for total PAHs (TPAHs), TPAHs is the sum of PPAHs and GPAHs. The average EFs of PPAHs obtained in our field burning (7 experiments) were comparable with that reported by Keshtkar and Ashbaugh (2007) of 18.6 mg kg^{-1} RS (no gas phase data reported in the study). Sanchis et al. (2014) reported EFs of 9 PAHs in PM_{10} of 17 mg kg^{-1} RS with 20% moisture content. These 9 PAHs (listed in the footnote of Table 1) contributed about 60% of the total 16 PPAHs measured in our study hence the estimated EFs for the 9 PPAHs in our field experiments would be approximately 20 mg kg^{-1} RS, i.e. close to the result by Sanchis et al. (2014).

3.1.5. PCBs and OCPs

EFs were determined based on data obtained for 7 field experiments. The result showed EFs of 114 ± 76 μg kg^{-1} RS for total PCBs and 227 ± 200 μg kg^{-1} RS for total OCPs. The presence of these toxic substances in the RSOB smoke should be of concern for health effect study. Note that these persistent OCPs are 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). The use of the OCPs analyzed in this study was banned in Thailand by around 2002 (FDA, 2007) but enforcement may still be an issue. For example, the ban of all active isomers of endosulfan was imposed in 2004 but the use of endosulfan was still reported afterward (Panuwet et al., 2012). Thus, the persistent OCPs remained in paddy soil from the past intensive applications and more recent applications may be re-emitted during the burning. Likewise, the PCBs deposited in soil may also be re-emitted during the field burning activity.

3.2. Emission concentration profiles

3.2.1. BTEX

Benzene was the most abundant of the BTEX compounds measured in hood and net field burning smoke, 64–77%, followed by toluene (21–27%). In the hood experiments, xylenes contributed about 5–8% to the total BTEX while ethylene contributed less than 1% (Table S3, SI). The BTEX profiles in the RS burning smoke were different from that measured at roadside in Bangkok (Kim Oanh et al., 2013) which is also presented in Table S3, SI for comparison. The roadside BTEX had the highest proportion of toluene (54%), followed by benzene (20%), xylenes (18%) and the lowest was ethylbenzene (8%).

3.2.2. PAHs

Levels of PPAHs and GPAHs in burning smoke plume captured at the fixed sampling point are presented in Table 2. The PAH concentrations obtained at the AIT campus in dry season (Chothicha, 2008) are also presented for comparison. The PAH sampling point at the AIT campus was located inside the campus, about 500 m from the highway and at minimum 2–5 km from any rice paddy depending on the direction, therefore it can represent the general ambient air of the study area.

High levels of GPAHs were obtained in the flue gas of the hood experiments. The differences in the PAH concentrations between hood dry and hood normal smoke were significant with dry RS emitting much lower levels of PAHs, which showed the influence of the RS moisture content. RS moisture content has been shown to influence the PM emission in our previous study (Kim Oanh et al., 2011). Sanchis et al. (2014) reported that burning RS with higher moisture content emitted more PAHs and dioxins.

The dilution of the smoke plume sampled during field experiments, varied substantially due to the uncontrolled wind conditions, and this may have led to the substantial variations in the levels of PAHs (and other pollutants) that we observed. The PAH levels in smoke samples were about 2–10 times above those in BG samples for most compounds and for several PPAHs the smoke

levels were above 100 times higher (Table 2). The BG samples were taken at the experimental paddies prior to each field burning experiment, hence they reflected the fluctuating ambient PAH levels in the study area during these intensive RS field burning periods. This also explained the higher PAHs levels observed in BG samples than those measured at the general air at the AIT campus. The field burning smokes had PPAH levels significantly above those at AIT, above 20 times for every compound. The levels of low molecular weight (LMW) or light PAHs with 4 or less benzene rings (i.e. from napththalene to chrysene in Table 2) had enrichment of above 100 times for PPAHs as compared to the AIT levels, in particular, fluoranthene was 2200 times and pyrene was 750 times. GPAHs also had a high enrichment for LMW PAHs in the smoke, e.g. fluoranthene for 185 times, fluorene for 130 times and 30 times for pyrene, as compared to the AIT levels. This suggested that these light PAHs in both phases were mainly associated with the RS burning activities.

High molecular weight PAHs with more than 4 benzene rings (last 6 compounds in Table 2) were not detected in the gas phase of RS burning smoke in both field and hood experiments. In the PM phase, all PAHs, except IcdP, were detected in the field burning experiments, while for the hood normal experiments only compounds with more than 3 benzene rings (anthracene onward) were detected and at higher concentrations than the field experiments. No PPAHs were detected in the hood dry experiment. Overall GPAHs were more abundant than PPAH, averaged at 88% of total PAHs for field burning, 100% for hood dry and 98% of hood normal experiments.

Fluoranthene was the most abundant among the PPAHs, 43% in the field burning and 20% for the hood normal smoke. Other PPAH compounds also had significant contributions, e.g. pyrene, 13% for field burning, and those ranging from pyrene to benzo(a)pyrene (BaP) in Table 2, shared 8–17% in the hood normal smoke. The enrichment of these PAHs, especially fluoranthene in PM, serves as useful markers to identify the contribution from fresh RS smoke to ambient PM pollution as discussed previously (Kim Oanh et al., 2011). Acenaphthylene was the most abundant of the GPAHs in the field experiment smoke (82%) followed by fluoranthene (8.5%). GPAHs from hood burning had a high proportion of acenaphthylene (13–18%) and phenanthrene (15–19%), while other compounds commonly contributed less than 3% each. Naphthalene was the most prevalent PAH in the ambient air and hood burning smoke but had a relatively small share in the net field burning smoke. However, due to its general abundance in the atmosphere this compound is not considered as a relevant marker of the RS burning emission.

Although the obtained PPAH and GPAH profiles were not exactly the same for the field and hood experiments, in both cases fluoranthene was the major PPAH and acenaphthylene was the major GPAH. The differences observed in PAH concentration profiles between the field burning and hood burning smoke may be attributed to the different combustion conditions discussed above. Our findings on the predominance of relatively LMW PAHs in particles emitted from RS burning agrees with previous studies (Hays et al., 2005; Jenkins et al., 1996; Sheesley et al., 2003; Korenaga et al., 2001). Chen et al. (2008) found significant enrichment, 1.54–2.57 times, of combustion related PAHs measured at a rural site in Central Taiwan during RS burning periods, with remarkable increase in shares of the TPAHs (21 species) observed for fluorene, phenanthrene, fluoranthene and pyrene. As for agricultural debris open burning in general, Kakareka and Kukharchyk (2003) also reported a high share of phenanthrene and fluorene in GPAHs emitted.

High levels of PAHs in the RS burning smoke may pose a health risk for people living near the rice plantation area during the RS burning period, due to exposure to these carcinogenic pollutants. In total, the field burning smoke had the levels of PPAHs of about 90 times and GPAHs of 300 times above those measured at AIT. BaP, a known carcinogen, was detected at high levels in the PM phase in both field burning (90 ng/m^3) and hood normal smoke (1800 ng/m^3), significantly above that at AIT (0.8 ng/m^3).

3.2.3. OCPs

The OCPs were determined only for BG and field experiment smoke which are presented with the levels previously measured at AIT for comparison (Table 3). The OCPs (and PCBs) monitoring at AIT was done at the AIT meteorological station, located in the middle of the AIT agricultural field, which is about 500 m from the sampling site for PAHs presented above. The monitoring at the AIT site was done in the dry season 2003 using the same Hi-Vol. method with 24 h sampling (Giang, 2003).

There was no significant difference in total OCPs in PM phase (POCPs) between the field burning smoke (net contribution), BG, and ambient air at AIT, i.e. about 0.5 ng m^{-3}. In the gas phase (GOCPs), the levels of all 16 compounds in the field burning smoke was about 3 ng m^{-3}, higher than that in paddy BG samples and ambient AIT samples, respectively (Table 3).

Out of 16 OCPs analyzed in this study, only 8 compounds were consistently detected in PM phase of both paddy BG and field burning smoke samples. There was no significant enrichment of POCPs by the RS burning activities. In the gas phase, the same 8 OCPs were detected in BG samples, whilst 2 additional compounds (β-BHC and δ-BHC) were detected at low levels in the field burning smoke. Paddy burning activities with elevated temperature may enhance vaporization of OCPs from soil and this may explain the higher proportions of GOCPs in the net burning smoke than in BG samples or ambient air.

The OCPs concentration profiles were similar for both field burning smoke and BG samples with high proportions of heptachlor, aldrin, heptachlor epoxide and α-BHC in both PM and gas phase. Samples collected at the AIT campus (Giang, 2003) had only two OCPs detected in the PM phase, aldrin (95%) and β-BHC (5%), while the gas phase had more detectable compounds with aldrin being the most abundant (71% of total GOCPs) followed by heptachlor (18%). As mentioned, these toxic OCPs have been banned in Thailand for already some years hence the presence of particular OCPs in different places may be due in large part to historical applications. Levels of aldrin found at AIT were about 3 times higher than the BG and net field burning smoke which may be attributed to past applications of aldrin for gardening and in the agricultural activities in areas surrounding the campus. As mentioned above, the presence of OCPs in the RS burning smoke may reflect both more recent and far past intensive applications of these persistent OCPs which remained in paddy soil and were subsequently re-emitted during the burning.

3.2.4. PCBs

In total 14 PCBs were analyzed but two compounds (PCB149 and PCB118) were overlapped with the Endosulfan II peak and they are reported together in Table 3. Therefore, the concentration profiles are discussed for the remaining 12 PCBs (Table 4). For comparison, the PCBs levels measured at the AIT meteorological station are also presented. Levels of PCBs in paddy BG and field burning smoke were almost equally distributed in both PM and gas phase, totaled at 2–3 ng m^{-3}, and were significantly above the levels measured at AIT (0.1 ng m^{-3} in PM and 0.8 ng m^{-3} in gas phase).

As shown in Table 4, mainly lower molecular weight/higher volatility PCBs were detected in both PM and gas phase of BG samples, AIT samples and the RS burning smoke samples. In the field burning smoke, several additional PCBs were also detected,

Table 5
Aldehydes concentrations (average ± SD), μg m^{-3} (25 °C, 1 atm), and share (%, in brackets).

	Ambient air (n = 3)	Roadside, rush hours (n = 3)	Field 4 upwind (n = 1)	Field 4 burning net (n = 2, duplicate)	Hood dry (n = 1)	Hood normal (n = 2, duplicate)
Formaldehyde	9.63 ± 0.86 (47)	15.7 ± 4.4 (43)	5.0 (16)	54.3 ± 1.2 (16)	1431 (58)	1709 ± 821 (43)
Acetaldehyde	5.43 ± 2.85 (26)	10.5 ± 2.8 (29)	15.1 (50)	79.9 ± 10.7 (24)	165 (7)	354 ± 118 (9)
Acrolein	nd	nd	nd	14.2 ± 0.0 (4)	134 (5)	423 ± 186 (11)
Acetone	1.68 ± 2.72 (8)	2.1 ± 2.0 (6)	nd	26.6 ± 4.4 (8)	nd	nd
Crotonaldehyde	1.55 ± 0.7 (8)	2.1 ± 0.4 (6)	3.1 (10)	19.7 ± 0.3 (6)	13 (1)	150 ± 149 (4)
Glyoxal	1.08 ± 0.57 (5)	2.9 ± 0.8 (8)	4.8 (16)	63.6 ± 4.4 (19)	122 (5)	182 ± 73 (5)
Methylglyoxal	1.13 ± 0.68 (6)	3.3 ± 1.1 (9)	2.5 (8)	72.1 ± 4.9 (22)	606 (25)	1154 ± 518 (29)
Total	20.5 ± 4.19	36.6 ± 5.7	30.4	330.4 ± 13.4	2471	3972 ± 1009

PCB 180 and PCB 209 in both phases, and PCB 194 in the gas phase. These compounds may be enriched in the RS burning smoke samples due vaporization of PCBs from soil to air caused by the elevated temperature of paddy burning activities.

PCB 31 was the most abundant compound in the PM and gas phase of every BG and burning smoke samples. With the exception of PCBs 180, 194 and 209, the proportions of individual PCBs were similar between the BG and burning smoke samples, especially in the PM phase. Overall, the share GPCB in the field burning smoke (49 ± 37%) was almost the same as in the BG samples (56 ± 16%).

3.2.5. Aldehydes

Aldehydes were measured in gas samples collected in the hood (dry and normal), field burning upwind (simultaneously collected with smoke samples hence can be considered as BG) and field burning smoke. The levels of aldehydes measured at the roadside of the Paholyothin highway passing the AIT gate (hourly sampling for morning/evening rush hours) and hourly ambient levels at the AIT meteorological station are presented for comparison (Table 5). With the exception for acetone, levels of aldehydes found in the hood smoke and field smoke were well above those measured at other sites including the roadside. This suggests that RS burning emitted these compounds. The aldehydes concentration profiles were however quite similar among all the samples. The most abundant compounds were formaldehyde and acetaldehyde but in burning smoke higher contributions of methylglyoxal were also observed, i.e. above 22% as compared to 6–9% in the ambient and roadside samples. Acrolein was not detected in all ambient and roadside samples but was present at high levels in the smoke samples. Thus, both methylglyoxal and acrolein appeared to be associated with the RS burning smoke. Acetone was detected at considerable levels in the field smoke samples, and at low levels in ambient samples but in the hood smoke samples it was lower than blanks. However, due to the high level of acetone in blanks (~0.45 μg per blank cartridge) mentioned above the low levels of this compound could be determined with a high uncertainty. Hood burning of dry RS emitted less aldehydes than hood 3 with normal RS moisture content. There was not much literature data available for the aldehydes emission from RS burning hence further research is required to fill in the data gap, especially for the emission factors and emission profiles from actual field burning conditions.

4. Conclusions

Field open burning of rice straw emitted higher amount of BTEX and semi-VOCs than the hood burning due to the more uncontrolled combustion of the paddy fire. Moisture content of the rice straw had a significant effect on the emission factors and emission profiles of semi-VOC in the smoke, which was evident from the results of hood experiments burning dry rice straw compared to those burning normal rice straw.

Our results of emission factors for benzene, NO_2 and SO_2 were in the same range as those reported in the literature but were lower for toluene, ethylbenzene and xylenes. The aldehydes EFs were also lower than literature reported values, but our results were obtained based on the hood burning experiments only. The field burning conditions of RS are expected to emit higher EFs of the incomplete combustion products including aldehydes, hence more measurements should be conducted for the aldehydes characterization.

The gas phase of semi-VOCs emitted from RS burning contributed the majority (88%) of total PAHs emission but less to total OCPs and PCBs emission (about 60%). Levels of semi-VOCs in the RS burning smoke were significantly higher than the paddy background and the ambient air in the study area. The increase in abundance of light PAHs such as fluoranthene (in PM phase) and acenaphthylence (in gas phase) suggests these compounds may serve as useful markers to identify the contribution of fresh rice straw burning smoke in the ambient air. Levels of several OCPs and PCBs were higher in the smoke samples compared to ambient air and this may arise due to vaporization of these compounds from the paddy soil where they have accumulated from the past applications of OCPs and deposit of PCBs.

Benzene was the most abundant BTEX compound found in the burning smoke, while toluene was about 1/3 of that of benzene. The BTEX profiles in the RS burning smoke were different than those measured at roadside where toluene levels were about 2 times higher than benzene. In the RS burning smoke, levels of aldehydes were significantly higher and with more abundance of methylglyoxal and acrolein as compared to a busy roadside and the ambient air. However, formaldehyde and acetaldehyde were found to be the most predominant of the seven aldehydes measured in all samples.

Because emission of the pollutants characterized in this study (semi-VOCs, BTEX and NOx) strongly depends on burning conditions, the results of this study regarding EFs and concentration profiles from the field experiments are relevant for the spread RS field burning practice in the region. High levels of the toxic substances observed in RS burning smoke would cause high exposure to people during the paddy burning season, and may lead to adverse health consequences. Reduction or elimination of this open burning source should result in benefits to air quality, health, and climate.

Acknowledgment

The authors would like to thank the Swedish International Development Agency for providing financial support to the research through the AIRPET project coordinated by AIT. Further acknowledgement is extended to the NIH Research Grant # D43 TW0642 funded by the Fogarty International Center, National Institutes on Environmental Health Services, NIOSH, and the Agency for Toxic Substances and Disease Registry, that made sampling and analysis for aldehydes possible. The students and staff of the air quality research group at the Asian Institute of Technology and other partners are acknowledged for the assistance in field burning activities.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.08.005.

References

Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. Glob. Biogeochem. Cycles 15 (4), 955–966.

Cao, G., Zhang, X., Zheng, F., 2006. Inventory of black carbon and organic carbon emissions from China. Atmos. Environ. 40, 6516–6527.

Cao, G., Zhang, X., Gong, S., Zheng, F., 2008. Investigation on emission factors of particulate matter and gaseous pollutants from crop residue burning. J. Environ. Sci. 20, 50–55.

Chen, K.-S., Wang, H.-K., Peng, Y.-P., Wang, W.-C., Chen, C.-H., Lai, C.-H., 2008. Effects of open burning of rice straw on concentrations of atmospheric polycyclic aromatic hydrocarbons in Central Taiwan. J. Air Waste Manag. Assoc. 58, 1318–1327.

Chothicha, S., 2008. A Comparative Study on Airborne Polycyclic Aromatic Hydrocarbons in Bangkok and Seoul (Dual Degree Program with KIST, Korea) (AIT Master thesis).

Christian, T.J., Kleiss, B., Yokelson, R.J., Holzinger, R., Crutzen, P.J., Hao, W.M., Saharjo, B.H., Ward, D.E., 2003. Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels. J. Geophys. Res. 108 (D23), 4719.

Food and Drug Administration (FDA), 2007. Thailand's National Chemicals Management Profile (2005). Chemical Safety Group Thailand Focal Point for WHO/IPCS, and IFCS, Food and Drug Administration, Ministry of Public Health of Thailand. Available from: http://ipcs.fda.moph.go.th/e_ipcs/profile/2005/summary.htm?var=2005#t2.

Gadde, B., Bonnet, S., Menke, C., Garivait, S., 2009. Air pollutant emissions from rice straw open field burning in India, Thailand and the Philippines. Environ. Pollut. 157, 1554–1558.

Giang, P.H., 2003. Chemical Composition of Airborne Particles and Organic Compound Phase Distribution: A Regional Comparative Study (AIT thesis, EV – 03–15).

Gullett, B., Touati, A., 2003. PCDD/F emissions from burning wheat and rice field residue. Atmos. Environ. 37, 4893–4899.

Hays, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullett, B.K., 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. Atmos. Environ. 39, 6747–6764.

Iwata, H., Tanabe, S., Sakai, N., 1994. Geographic distribution of persistent organochlorines in air, water and sediment from Asia and Oceania and their implications for global redistribution from lower latitudes. Environ. Pollut. 85, 15–33.

Jenkins, B.M., Jones, A.D., Turn, S.Q., Williams, R.B., 1996. Particle concentrations, Gas–particle partitioning, and species. Intercorrelations for polycyclic aromatic hydrocarbons (PAH) emitted during biomass burning. Atmos. Environ. 30 (22), 3825–3835.

Jiminez, J., Claiborn, C., Dhammapala, R., Simpson, C.D., 2007. Developing a source fingerprint for burning of wheat and Kentucky bluegrass stubble in eastern Washington and northern Idaho. Environ. Sci. Technol. 41 (22), 7824–7829.

Kakareka, S.V., Kukharchyk, T.I., 2003. PAH emission from the open burning of agricultural debris. Sci. Total Environ. 308, 257–261.

Kanabkaew, T., Kim Oanh, N.T., 2011. Development of spatial and temporal emission inventory for crop residue field burning. Environ. Model. Assess. 16 (5), 453–464.

Keshtkar, H., Ashbaugh, L.L., 2007. Size distribution of PAH particulate emission factors from agricultural burning. Atmos. Environ. 41, 2729–2739.

Kim Oanh, N.T., 2012. Integrated approach to rice straw management for reduction of field burning activity (Chapter 13), in the book. In: Integrated Air Quality Management: Asian Case Studies. Taylor and Francis Group, CRC Press, ISBN 9781439862254.

Kim Oanh, N.T., Nghiem, L.H., Phyu, Y.L., 2002. Emission of polycyclic aromatic hydrocarbons, toxicity, and mutagenicity from domestic cooking using sawdust briquettes, wood and kerosene. Environ. Sci. Technol. 36, 833–839.

Kim Oanh, N.T., Thuy, L.B., Tipayarom, D., Manadhar, B.R., Pongkiatkul, P., Simpson, C.D., Sally Liu, L.-J., 2011. Source characterization of aerosol emission from field burning of rice straw. Atmos. Environ. 45, 493–502.

Kim Oanh, N.T., Kongpran, J., Hang, N.T., Parkpian, P., Hung, N.T.Q., Lee, S.B., Bae, G.N., 2013. Characterization of gaseous pollutants and $PM_{2.5}$ at fixed roadsides and along vehicle traveling routes in Bangkok metropolitan region. Atmos. Environ. 77, 674–685.

Korenaga, T., Liu, X.X., Huang, Z.Y., 2001. The influence of moisture content on polycyclic aromatic hydrocarbons emission during rice straw burning. Chemosphere Glob. Change Sci. 3, 117–122.

Lee, J.J., Engling, G., Candice Lung, S.C., Lee, K.Y., 2008. Particle size characteristics of levoglucosan in ambient aerosols from rice straw burning. Atmos. Environ. 42, 8300–8308.

Liu Sally, J., Dills, R.L., Paulsen, M., Kalman, D.A., 2001. Evaluation of media and derivatization chemistry for six aldehydes in a passive sampler. Environ. Sci. Technol. 35, 2301–2308.

National Statistic Office, Statistical data 2008, National Statistic Office of Thailand. TNSO, Bangkok, Thailand.

NIOSH, 1994. Manual of Analytical Methods, fourth ed. (Hydrocarbons, Aromatic).

OSHA, Occupational Safety and Health Administration, 1980. Benzene. Retrieved from: http://www.osha-slc.gov/dts/sltc/methods/organic/org012/org012.html.

OSHA, 1991. Nitrogen Dioxide in Workplace Atmospheres (Ion Chromatography): Method ID-182. Branch of Inorganic Methods Development, OSHA Salt Lake Technical Center, Utah.

OSHA, 1992. Sulfur Dioxide in Workplace Atmospheres (Impregnated Activated Beaded Carbon): Method ID-200. Branch of Inorganic Methods Development, OSHA Salt Lake Technical Center, Utah.

Panuwet, P., Siriwong, W., Prapamontol, T., Ryan, P.B., Fiedler, N., Robson, M.G., Barr, D.B., 2012. Agricultural pesticide management in Thailand: situation and population health risk. Environ. Sci. Policy 17, 72–81.

Pentamwa, P., Kim Oanh, N.T., 2008. Levels of pesticides and PCBs in selected homes in Bangkok metropolitan region, Thailand. Ann. N. Y. Acad. Sci. 1140, 91–112. Environmental Challenges in the Pacific Basin, V 1140.

Reid, J.S., Koppmann, R., Eck, T.F., Eleuterio, D.P., 2004. A review of biomass burning emissions, part II: intensive physical properties of biomass burning particles. Atmos. Chem. Phys. Discuss. 4, 5135–5200.

Rice-Trade, 2014. Major Rice Producing Countries, Published by Rice Trade B2B Marketplace. Online information at: http://www.rice-trade.com/major-rice-producing-countries.html (accessed in December 2014).

Sanchis, E., Ferrer, M., Calvet, S., Coscoll, C., Yus, V., Cambra-Lopez, M., 2014. Gaseous and particulate emission profiles during controlled rice straw burning. Atmos. Environ. 98, 25–31.

Sheesley, R.J., Schauer, J.J., Chowdhury, Z., Cass, G.R., Simoneit, B.R.T., 2003. Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia. J. Geophys. Res. 108 (D9), 4285.

Shindell, D., Kuylenstierna, Johan C.I., Vignati, E., van Dingenen, R., Amann, M., Klimont, Z., Anenberg, S.C., Muller, N., Janssens-Maenhout, G., Raes, F., Schwartz, J., Faluvegi, G., Pozzoli, L., Kupiainen, K., Höglund-Isaksson, L., Emberson, L., Streets, D., Ramanathan, V., Hicks, K., Kim Oanh, N.T., Milly, G., Williams, M., Demkine, V., Fowler, D., January 2012. Simultaneously mitigating near-term climate change and improving human health and food security. Science 13, 183–189. http://dx.doi.org/10.1126/science.1210026.

Tipayarom, D., Kim Oanh, N.T., 2007. Effects from open rice straw burning emission on air quality in the Bangkok metropolitan region. J. Sci. Asia 33 (3), 339–345.

Torigoe, K., Hasegawa, S., Numata, O., Yazaki, S., Matsunaga, M., Boku, N., Hiura, M., Ino, H., 2000. Influence of emission from rice straw burning on bronchial asthma in children. Pediatrics 42, 143–150.

Truc, V.T.Q., Kim Oanh, N.T., 2007. Roadside BTEX and other gaseous air pollutants in relation to emission sources. Atmos. Environ. 41, 7685–7697.

UNEP-WMO, 2011. Integrated Assessment of Black Carbon and Tropospheric Ozone. UNEP and World Meteorological Organization (WMO), Nairobi, Kenya, ISBN 92-807-3141-6.

US EPA, 1999a. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS). Compendium Method TO-13A. U.S Environmental Protection Agency, Center for Environmental Research Information. Office of Research and Development, Cincinnati, OH 45268.

US EPA, 1999b. Compendium Method TO-4A: Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-detector Detection (GC/MD). U.S Environmental Protection Agency, Center for Environmental Research Information. Office of Research and Development, Cincinnati, OH 45268. Available from: http://www.docstoc.com/docs/7827128/EPA-R.

US EPA, 2011. Ambient Air Sampling, SESD Operating Procedure. SESDPROC-303–R4. Available online at: http://www.epa.gov/region4/sesd/fbqstp/Ambient-Air-Sampling.pdf (accessed Feb. 2015).

Viana, M., López, J.M., Querol, X., Alastuey, A., García-Gacio, D., Blanco-Heras, G., López-Mahía, P., Piñeiro-Iglesias, M., Sanz, M.J., Sanz, F., Chi, X., Maenhaut, W., 2008. Tracers and impact of open burning of rice straw residues on PM in eastern Spain. Atmos. Environ. 42, 1941–1957.

Wu, C.F., Jimenez, J., Claiborn, C., Gould, T., Simpson, C.D., Larson, T., Liu, S.-J., 2006. Agricultural burning smoke in eastern Washington: part II: exposure assessment. Atmos. Environ. 40, 639–650.

Yan, X., Ohara, T., Akimoto, H., 2006. Bottom-up estimate of biomass burning in mainland China. Atmos. Environ. 40, 5262–5273.

Yang, H.H., Tsai, C.-H., Chao, M.R., Su, Y.L., Chien, S.M., 2006. Source identification and size distribution of atmospheric polycyclic aromatic hydrocarbons during rice straw burning period. Atmos. Environ. 40, 1266–1274.

Zhang, H., Ye, X., Cheng, J., Yang, X., Wang, L., Zhang, R., 2008. A laboratory study of agricultural crop residue combustion in China: emission factors and emission Inventory. Atmos. Environ. 42, 8432–8441.