CHAPTER 3

Results and Discussion

3.1 Performance of Analysis Method by ICP-OES

The validation process of the method based on the ICP-OES technique was performed regarding accuracy, precision, and linearity using the experimental setting that provided the optimal conditions. Extraction method for ash validated with selected CRMs and spiked concentration to assess accuracy. Accuracy of the method, defined as the closeness of the mutually independent test results and reference values, which was determined in terms of the percentage of recovery (%R). Instrumental precision was evaluated as repeatability, LOD and LOQ. Repeatability was calculated in terms of percent relative standard deviation (%RSD) from means of the data obtained when 10 replicates with triple measurements of the mixed standard with concentration of 1 and 5 (μg/ml) were measured. Instrument precision tested and verified on the same day of samples analysis, while LOD and LOQ were defined from SD of means. The linearity of all elements were measured and plotted to make sure that the calibration curve is developed within a linear range. All are detailed as followings.

3.1.1 Accuracy of the method for elemental analysis

In order to confirm the elemental analysis method, certified reference material (CRM) was used. Three replications of 100 mg of pond sediment (NIES, No.2 300.21, Japan) were weighed by analytical balance with accuracy of 0.1 mg and extracted by using four acidic conditions: (1) HCl:HNO_3 (3:1 v/v) (Kröppl & Lanzerstorfer, 2013; Yafa & Farmer, 2006), 2) HNO_3:HF (3:2 v/v), 3) HNO_3:HCl:HF (3:1:0.5 v/v/v) (Yafa & Farmer, 2006), and 4) HNO_3:H_2O_2 (2:1 v/v) (Bakisgan, et al., 2009)) and applying the same procedure for all extraction conditions. Details of selected conditions are given in the Table 2.2 of Chapter 2.

Table 3.1 Recoveries of elements obtained from spiked solution concentration and CRM

Element	Spiking method*		CRM (No.2, 300.21)		
	Measured values ppm	%Recovery	Ref ** Values ppt	Measured values (g/kg)	%Recovery
Al	1.20 ± 0.03	80 ± 1.69	106	98.6 ± 4.4	93 ± 4.0
As	1.24 ± 0.03	83 ± 1.85	0.012	0.012 ± 0.009	97 ± 76
Ca	1.52 ± 0.04	101 ± 2.55	8.1	8.42 ± 0.92	104 ± 11
Cd	1.36 ± 0.03	91 ± 1.92	0.82	0.001 ± 0.001	122 ± 100
Co	1.35 ± 0.04	90 ± 2.51	0.027	0.032±0.001	119 ± 4
Cr	1.38 ± 0.03	92 ± 1.84	0.075	0.054 ± 0.001	72 ± 2
Cu	1.37 ± 0.03	91 ± 2.26	0.210	0.15 ± 0.002	76 ± 1
Fe	1.23 ± 0.02	82 ± 1.13	43.1	55.02 ± 1.45	84 ± 2
K	1.20 ± 0.02	80 ± 1.51	6.8	3.51 ± 0.17	52 ± 2
Mg	1.36 ± 0.02	91 ± 1.58	14.6	5.54 ±0.08	38 ± 1
Mn	1.39 ± 0.03	93 ± 2.01	0.77	0.87 ± 0.013	113 ± 2
Na	1.45 ± 0.04	97 ± 2.39	5.7	4.42 ± 0.02	76 ± 12
Ni	1.35 ± 0.02	90 ± 1.64	0.04	0.034 ±0.0002	85 ± 0.4
Pb	1.35 ± 0.03	90 ± 1.71	0.105	0.14 ± 0.003	134 ± 3
Sb	1.36 ± 0.03	91 ± 1.84	0.002	0.053 ±0.001	2670 ± 50
Si	1.35 ± 0.03	90 ± 1.84	210	0.021 ± 0.0	*<<1*
Sn	1.36 ± 0.01	91 ± 0.05	N/A	23.9 ± 0.1	N/A
V	1.40 ± 0.03	93 ± 1.97	0.250	0.193 ± 0.004	76 ± 2
Zn	1.36 ± 0.03	90 ± 1.75	0.343	0.283 ±0.01	82 ± 2

* Spiked concentration is 1.5 μg/ml.

** The values converted from CRM (No.2, 300.21) reference values.

N/A : The reference value is not available in the list for this element.

Percent recoveries of 20 elements were calculated comparing with reference values of CRM. The aqua-regia (HCl:HNO_3, 3:1, V/V) extraction condition was selected as optimum extraction condition (%R, Table 3.1), however some elements including K, Na, Mg, Si, As, Cd, Se and Sn showed very high or very low recovery (>36%) or were not detected. Therefore, a spiked method was introduced. Known concentration of mixed standards (1.5 μg/ml) of elements were spiked under the same extraction condition applied for CRM solution, details of percentage recovery (%R) of elements from both CRM and spiked solution are given in Table 3.1.

3.1.2 Performance of the ICP-OES

a) Repeatability

Repeatability or reliability test is the variation in measurements taken by a single person or instrument on the same item, under the same conditions, and in a short period of time. To confirm the precision of ICP-OES, repeatability of instrument was assessed using mixed standards solution. Two concentrations (1 and 5 μg/ml) of mixed standards were prepared and determined with 10 repeated measurements for each concentration.

Concentrations of 1 and 5 μg/ml were selected to represent both element in lower concentration and higher concentration, and the term was verified by calculation of percent relative standard deviation (%RSD), where highest %RSD (4.257%) in 1 μg/ml of mixed standard solution was found to Vanadium while in 5 μg/ml Zn shown higher %RSD (6.06%) comparing to others. Percent relative standard deviation (%RSD) from 1 and 5 μg/ml of mixed standard solution are 0.97-4.25 and 0.41-6.06 % respectively for all elements (Table 3.2), which are statistically in an acceptable range. %RSD (<5%) is very good and there will be no effect on the result. %RSD (<10%) is also statistically accepted and there will not be noticeable influence on the result since its include 95% of overall data distribution. Details of repeatability is given in (Table C.1 and 2, Appendix C) (Harvey, 2000).

Table 3.2 Repeatability of instrument measured from mixed elements standard.

	Prepared Concentration (1 μg/ml)		Prepared Concentration (5μg/ml)	
	Obtained values	% RSD	Obtained values	% RSD
Al	0.91 ± 0.02	2.47	5.1 ± 0.03	0.65
As	1.02 ± 0.10	9.80	ND	
Ca	0.80 ± 0.01	1.28	4.3 ± 0.03	0.67
Cd	0.87 ± 0.02	2.30	4.3 ± 0.02	0.46
Co	0.90 ± 0.01	1.29	4.3 ± 0.03	0.75
Cr	0.77 ± 0.01	1.09	3.8 ± 0.03	0.70
Cu	0.90 ± 0.02	1.82	4.4 ± 0.03	0.70
Fe	0.88 ± 0.01	0.97	4.4 ± 0.03	0.72
K	1.17 ± 0.02	2.01	7.4 ± 0.03	0.41
Mg	0.79 ± 0.01	1.34	4.3 ± 0.03	0.66
Mn	0.96 ± 0.03	3.49	4.7 ± 0.02	0.48
Na	0.83 ± 0.01	1.42	4.1 ± 0.04	0.87
Ni	0.97 ± 0.01	0.98	4.8 ± 0.03	0.59
Pb	0.86 ± 0.01	1.73	4.1 ± 0.04	0.92
Sb	0.50 ± 0.01	2.00	4.5 ± 0.03	0.67
Se	1.03 ± 0.03	2.91	5.1 ± 0.04	0.78
Si	0.59 ± 0.05	8.47	5.3 ± 0.05	0.94
Sn	0.91 ± 0.02	2.20	4.6 ± 0.03	0.65
V	1.22 ± 0.06	4.27	ND	
Zn	0.97 ± 0.01	1.15	4.7 ± 0.28	6.06

b) Limit of detection and limit of quantification

Measuring concentration of constituents of a sample is corresponding to the instrument limit of detection and limit of quantification. In this study LOD and LOQ were obtained respectively from three and ten times of SD from means using 10 measurements in triple replications of the lowest concentration which signals were recorded for the relevant element. LOD for all elements are below 0.047 (μg/ml) except As (0.119 μg/ml) and Se

(0.142 μg/ml) (Table 3.4). Both LOD and LOQ calculated using the linear regression equation given by standards calibration (Appendix B) for each element.

Table 3.3 LOD and LOQ of ICP-OES for each element.

Element	Wavelength (nm)	LOD (μg/ml)	LOQ (μg/ml)
Al	396.152	0.0067	0.0223
As	189.042	0.1191	0.3969
Ca	317.933	0.0277	0.0922
Cd	228.802	0.0040	0.0132
Co	236.379	0.0052	0.0174
Cr	267.716	0.0035	0.0118
Cu	324.754	0.0050	0.0165
Fe	239.563	0.0048	0.0160
K	766.491	0.0057	0.0189
Mg	285.213	0.0014	0.0045
Mn	257.610	0.0012	0.0040
Na	589.592	0.0024	0.0080
Ni	231.604	0.0412	0.137
Pb	220.353	0.0476	0.1588
Sb	206.833	0.0034	0.0114
Se	196.090	0.1428	0.4760
Si	288.158	0.0049	0.0163
Sn	189.991	0.0206	0.0688
V	310.230	0.0060	0.0199
Zn	213.856	0.0037	0.0125

c) Linearity

Sensitivity of the measurement for determination of each element in composition of targeted biomass was expressed by the slope of the linear regression equation (μg/ml). Linearity was assessed by the coefficients of determination (R^2) of linear curves that was considered acceptable when R^2

= 0.99X for individual elements. Linearity was assessed using mixed standard solutions with range of concentration from 0.01 to 100 (μg/ml), examples of linear curves are given in Figure 3.1, while linearity calibration curves of all elements can be found in (appendix A).

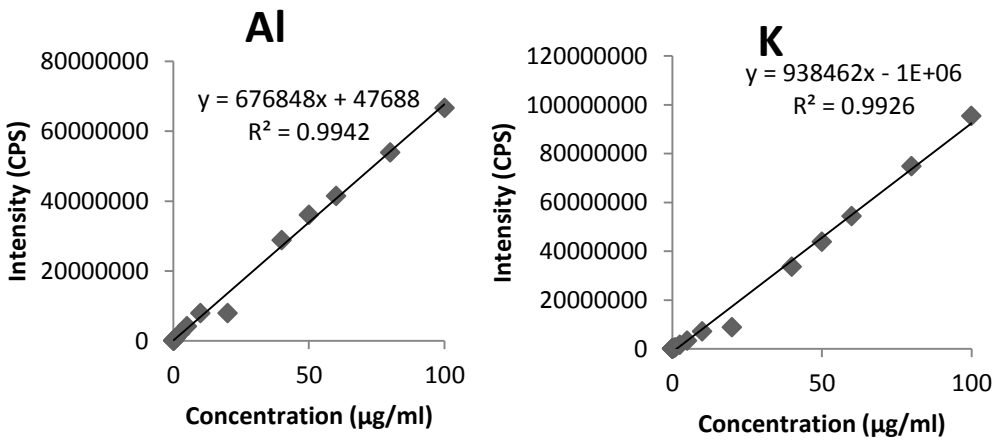

Figure 3.1 Examples of linearity calibration curves for Al and K.

3.1.3 Standard calibration curves

Using the data such as slop and coefficients of determination from linear graphs, the range of concentration from calibration curves was considered where the optimum and maximized linearity was obtained. Standard calibration curve of each element was developed by plotting of range (0.01-10 ppm) of concentrations (0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1.0, 2.5, 5.0,10.0 ppm) against their intensities, and value of coefficients of determination were R^2 = 0.999X (Table 3.6).

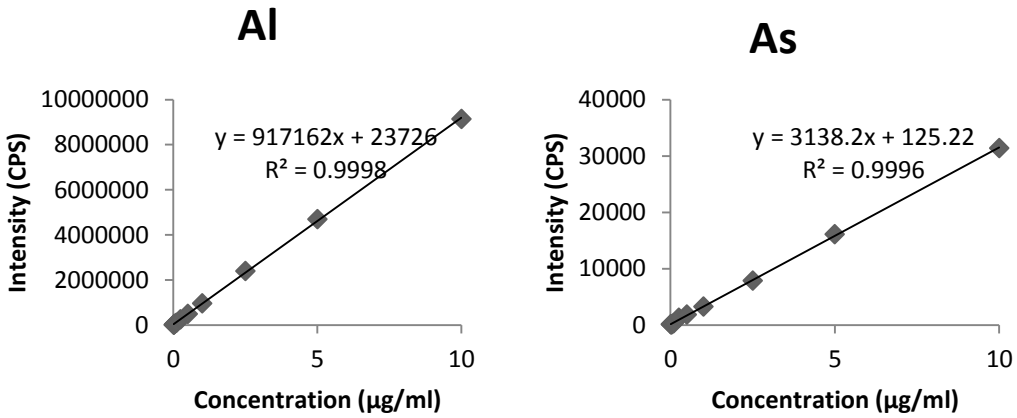

Figure 3.2 Examples of standard calibration curves of Al and As

As shown in Table 3.4, coefficients of determination for all elements are 1 or very close to 1 (1.0000 - 0.9996) which indicates maximum linearity of standard calibration curve. Examples of the standard calibration curves are given in Figure 3.2, and standard calibration curves of all elements can be found in APPENDIX B.

Table 3.4 Linear equation of calibration curve with coefficient of determination.

Element	Wavelength (nm)	Linear equation y =	Coefficient of Determination R^2
Al	396.152	917162x + 23726	0.9998
As	189.042	3138x +125.2	0.9996
Ca	317.933	19247x – 277.9	0.9999
Cd	228.802	189509x + 24113	0.9999
Co	236.379	75297x + 439.7	1.0000
Cr	267.716	493874x + 3528.8	0.9999
Cu	324.754	370081x + 1168.6	1.0000
Fe	239.563	195730x – 651.4	0.9999
K	766.491	2579721x – 213181.5	0.9990
Mg	285.213	18512x + 594.7	0.9998
Mn	257.610	1886862x + 56,499	0.9998
Na	589.592	28599833x - 824,161	0.9998
Ni	231.604	52811x + 911.6	0.9999
Pb	220.353	22980x + 493.3	0.9999
Sb	206.833	72293x + 1,286.7	0.9999
Se	196.090	4968x + 456	0.9999
Si	288.158	175912x - 157.72	1.0000
Sn	189.991	12278x + 94.4	0.9999
V	310.230	533329x + 6208	1.0000
Zn	213.856	181871x + 2046.8	0.9999

3.2 Emission of $PM_{2.5}$ from Biomass Burning

Emission Factor (EF) is a representative value attempting to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. These factors are usually expressed in terms of the mass of pollutant emitted per unit mass of dry biomass used (g or $mg/kg_{dry\text{-}biomass}$) (Sillapapiromsuk et al., 2013). $PM_{2.5}$ EF biomass type samples were assessed by burning biomass samples 15 times for each biomass in open system combustion chamber separately with a sufficient time gaps between two burning experiments to let the combustion chamber cool down, in order to avoid risk of memory effects from previous burning experiment during $PM_{2.5}$ sampling. Range of EFs of $PM_{2.5}$ emitted from RS, MR, DDF and MDF were 1.50-6.57, 1.12-3.47, 2.91-4.42 and 2.43-8.68 g/kg, respectively (Table 3.5). The highest EF of $PM_{2.5}$ was found in site 4 of MDF and the lowest in site 4 of MR. Based on the evidence from burning experiments the EF of $PM_{2.5}$ from MDF was highest from study site 4 due to higher volume of smoke produced during the burning experiments from biomass in this study site. The lowest EF of $PM_{2.5}$ from study site 4 of MR can be explained as impact of EF of K as agricultural biomass burning tracer (Khamkaew et al., 2016) on EF of $PM_{2.5}$ which was lowest in this site comparing to K in composition of $PM_{2.5}$ from other study sites for MR. ANOVA test between means of sites for biomass types revealed that for RS site 4 was significantly different from sites 2 and 3, while site 3 was also significantly different from sites 1 and 5. As shown in Table 3.5 EF of $PM_{2.5}$ from site 3 was from EF of $PM_{2.5}$ from 1, 4 and 3, similar perception is true between 2 and 4 which are explained as fluctuation of K content between study sites leaded to show significance difference of EF of $PM_{2.5}$. And the same discussion is correct when comparing means EF of $PM_{2.5}$ emitted from study site of MR, which means of EF of $PM_{2.5}$ from site 5 of MR. Moreover, site 4 of MDF were significantly different from other four study sites but difference between means of EF of $PM_{2.5}$ emitted from DDF were insignificant among study sites. EF of $PM_{2.5}$ and other constituents are not fluctuating between all study sites of MDF except study site 4 and likewise all study sites of DDF, therefore they were not significantly different from each other excluding study site 4 of MDF.

Table 3.5 EFs of $PM_{2.5}$ (mean ± SD) of biomass types by location.

Biomass types	$PM_{2.5}$ EF (g/kg) by study sites				
	Site 1	Site 2	Site 3	Site 4	Site 5
RS	*2.10 ±0.70*^{ab}	4.72±1.00^{bc}	6.57±1.83^{c}	1.50±0.20^{a}	*3.46±0.72*^{ab}
MR	*2.26±0.15*^{ab}	*2.06±0.73*^{b}	*1.66±0.65*^{b}	*1.12±0.14*^{b}	3.47±0.29^{a}
DDF	*2.91±0.50*^{a}	*3.94±0.16*^{a}	*3.12±1.45*^{a}	*3.50±0.27*^{a}	*4.42±2.74*^{a}
MDF	*3.01±0.63*^{a}	*2.43±0.71*^{a}	4.60±2.75^{ab}	8.68±3.48^{b}	*3.19±0.46*^{a}

$^{a, b, c}$ same superscripts, underline and italic express similarity between means. Different superscripts show significant difference ($p < 0.05$)

Figure 3.3 shows EFs of $PM_{2.5}$ from burning of 4 biomass types. It was found that MDF biomass samples had highest EF of $PM_{2.5}$ (4.44 ± 2.94 g/kg $_{\text{dry biomass}}$) which was very similar (4.50 ± 1.64 g/kg $_{\text{dry biomass}}$) to previous studies (Yokelson et al., 2011) for tropical forest, and is very higher than EF of PM_{10} (1.52 ± 0.65 and 1.22 ± 0.29 g/kg $_{\text{dry biomass}}$) studied for leaf litter in Chiang Mai province (Sillapapiromsuk et al., 2013; Wiriya et al., 2016), respectively. The average $PM_{2.5}$ EF (2.11 ± 0.90 g/kg $_{\text{dry biomass}}$) of MR was the lowermost, still very closed to previous literatures (3.84 ± 1.02 g/kg $_{\text{dry biomass}}$) (Shen et al., 2013) and considerably higher than EF of PM_{10} (0.90 ± 0.31 and 0.59 ± 0.13 g/kg $_{\text{dry biomass}}$) emitted from MR burned in closed system combustion chamber which were studied by (Sillapapiromsuk et al., 2013; Wiriya et al., 2016), respectively. Emission factors of PM2.5 from RS and DDF were most likely the same and were 3.67 ± 2.10 and 3.59 ± 0.78 (g/kg $_{\text{dry-biomass}}$) respectively. EF of $PM_{2.5}$ from RS was smaller than EF of $PM_{2.5}$ (7.7, 8.3, 12.95 and 13.10 g/kg) attained by previous studies (Hays et al., 2005; Amaral et al., 2016; Gadde et al., 2009; Oanh et al., 2011; Zhang et al., 2017), respectively, however it noticeably higher than EF of PM_{10} (0.69 ± 0.23 and 0.89 ± 0.25 g/kg $_{\text{dry biomass}}$) studied by (Sillapapiromsuk et al., 2013; Wiriya et al., 2016), respectively. The results for EF of $PM_{2.5}$ show that forest leaf litters emitted higher amount of $PM_{2.5}$ per unit of dry biomass comparing to emission from RS and MR, hence, burning of forests' leaf litter emit more pollutant and can contribute more to form haze during forest fire.

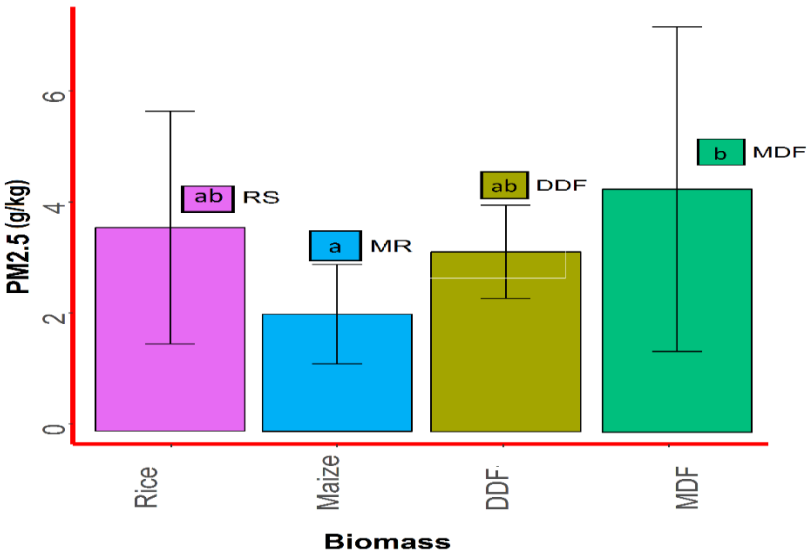

Figure 3.3 EF of $PM_{2.5}$ from burning of four biomass types.
[a & b], superscripts show similarity. Different superscripts show significantly ($p < 0.05$) different.

Result from analysis of variance indicated that the means of EF of $PM_{2.5}$ from various biomasses were significantly ($P < 0.05$) different. While the pairing wise analysis of variance verifies that means of $PM_{2.5}$ emitted from MDF was significantly higher and different from mean of EF of $PM_{2.5}$ emitted from MR which was the lowest, but the difference between means of all other pairs were insignificant. Values of EFs of $PM_{2.5}$ for biomass samples within one sampling location were similar and deviation from means was small. The measured values of $PM_{2.5}$ EF for the same type of biomass samples collected from different locations varied, that resulted to greater values for SD from means particularly for MDF and RS with high %RSD value.

3.2.1 Emission of $PM_{2.5}$ and its elemental composition from rice straw burning

An average mass of 1.14 ± 0.01 kg of rice straw was burned in each burning experiment, the burning process was 81 ± 2% completed in average and emitted 1.49 ± 0.76 mg of $PM_{2.5}$. About 200 ± 20 g of ash remained from the burning, while average of dilution factor (DF) was 2440 ± 210. EF of $PM_{2.5}$ for RS burning was 3.67 ± 2.10 g/kg $_{\text{dry-biomass}}$. Biomass samples details, $PM_{2.5}$ weight and EF and burning experiments of RS are given in Table 3.6.

Table 3.6 Overall details about RS burning experiments.

site	Sample Code	Dry biomass (kg)	%Burn	Remained Ash (g)	$PM_{2.5}$ (mg)	DF	$PM_{2.5}$ EF (g/kg)
	1100-1	1.01	76	240	0.82	2210	1.81
1	1100-2	1.01	78	220	0.64	2530	1.63
	1100-3	1.02	78	230	1.02	2907	2.95
	1200-1	1.00	81	190	2.00	2530	5.05
2	1201-2	1.01	81	190	2.14	2590	5.54
	1201-3	1.01	79	220	1.44	2510	3.62
	1300-1	1.01	82	180	2.74	2600	7.13
3	1300-2	1.00	81.	190	3.05	2660	8.13
	1300-3	1.01	82	190	2.08	2220	4.61
	1400-1	1.01	82	180	0.65	2210	1.43
4	1400-2	1.00	79	210	0.62	2190	1.35
	1400-3	1.01	80	210	0.79	2210	1.75
	1700-1	1.01	84	170	1.29	2310	2.98
5	1700-2	1.02	83	180	1.34	2400	3.22
	1700-3	1.01	84	170	1.76	2470	4.34
	Average	1.14	81	200	1.49	2440	3.67
	SD	0. 01	2	20	0.78	210	2.10

This study detected 9 metals in the composition of $PM_{2.5}$ emitted from RS during open burning simulation in open system combustion chamber. Potassium (K) was the most abundant element of the measured elements. EFs of K ranged (190-850 mg/kg $_{\text{dry biomass}}$). K together with Mg, Na, Sn and Zn were detected in composition of $PM_{2.5}$ emitted from all biomass of all sampling locations. Cr was detected in samples from study sites of 1 and 4, while Sb (1, 2, 4 and 5) and Si (2-5) were present in some samples of four sampling sites. Ca was only detected in study site 3, while was not detect in other sites so there can be some unknown error such dust from field or contamination in extraction and elemental measurement impacting EF of Ca from RS (Table 3.7). K as biomass tracer (Khamkaew et al., 2016; Pachon et al., 2013.) is uptaken in large amount by rice from soil and root environment which is mainly supplied by inorganic fertilizers

(Sarkar et al., 2017). Though other detected elements in composition of $PM_{2.5}$ are essential elements in structure of rice (Pinto et al, 2016), but they are toxic for exposure when interring in ambient air.

Table 3.7 EFs of elements (mean ± SD) of $PM_{2.5}$ emitted from RS burning.

	EFs of PM2.5 (g/kg $_{\text{dry biomass}}$) and elements (mg/kg $_{\text{dry biomass}}$)					
	Site 1	Site 2	Site 3	Site 4	Site 5	Average
$PM_{2.5}$	*2.10±0.70^{ab}*	4.72±1.00^{bc}	6.57±1.83^{c}	1.50±0.20^{a}	*3.46±0.72^{ab}*	**3.67±*2.10***
Ca	ND	ND	21.22±0.18	ND	ND	-
Cr	*5.5±0.79*	ND	ND	*4.14±0.35*	ND	**4.69±0.72**
K	*430±140^{b}*	*380±60^{ab}*	*670±60^{c}*	190±10^{a}	*850±100^{c}*	**500±260**
Mg	*10.54±2.88^{a}*	*15.26±4.62^{a}*	*16.12±0.25^{a}*	*8.17±1.98^{a}*	*5.02±2.46^{a}*	**11.02±4.7**
Na	*46.3±7.49^{a}*	*48.2±30.53^{a}*	*36.44±22.37^{a}*	*33.55±3.4^{a}*	*23.77±5.92^{a}*	**37.65±9.96**
Sb	7.06±0.99	3.5±4.19	ND	5.78±0.19	ND	-
Si	ND	ND	ND	0.52±0.22	ND	-
Sn	*3.11±1.16^{a}*	*2.62±1.36^{a}*	*2.2±1.37^{a}*	*2.55±0.32^{a}*	*2.79±0.87^{a}*	**2.65±0.33**
Zn	*2.55±2.06^{a}*	*0.98±0.7^{a}*	*1.87±0.79^{a}*	*1.59±0.54^{a}*	*1.03±0.69^{a}*	**1.6±0.65**
TE	510±130^{ab}	470±130^{ab}	*740±90^{bc}*	250±6^{a}	*880±110^{c}*	**570±250**

$^{a,\ b,c}$ same superscripts and Italics express similarity between means. Different superscripts show significant difference ($p < 0.05$). ND: Not Detected.

Analysis of variance (ANOVA) indicated that EFs of K were significantly ($p < 0.05$) different between EF of K from site 1 was significantly smaller comparing to sites 3,4 and 5, while site 4 was different from site 2, 3 and 5 and site 2 is also different from sites 3 and 5. Means of total EFs (TE) from site 1 and 2 were different from sites 3 and 5, also difference between site 3 and sites 4 and 5 were significant, moreover site 4 was significantly different from site 5. Furthermore, Means of EF of Sb was different between sites 1, 2 and 4, while difference between means of other element for study sites were insignificant. As shown in Figure 3.7, K as biomass burning tracer (Khamkaew et al., 2016; Pachon et al., 2013, 2013) was the major element detected in all RS samples, EF

of K (500 ± 260 mg/kg$_{dry\text{-}biomass}$) covered 86.98% mass of all measured elements in composition of $PM_{2.5}$ emitted from RS. Other elements in descending order of percentage were Na (6.49%) > Ca (2.79%) > Mg (1.90%) > Sb (0.56%) > Cr (0.49%) > Sn (0.46%) > Zn (0.28%) and Si (0.07%). Presence of some toxic and heavy metal in composition of $PM_{2.5}$ emitted from RS samples have potential to harm human, affect environment and reduce air quality of atmosphere (Tchounwou, et al., 2012). Emission factors of K element measured in this study was higher but very similar to EF of K in composition of PM_{10} studied by (Chaichana, 2011), furthermore EF of K element and other measured elements in this study were very similar but higher comparing to some previous studies (Oanh et al., 2011; Turn et al., 1997). Emission factor (EF) of $PM_{2.5}$ emitted from RS showed a significant ($p < 0.05$, 0.01, $r = 0.55$) correlation to EF of K in composition of $PM_{2.5}$. Since K is most abundant element so it has high effect on mass of total measured element, therefore, $PM_{2.5}$ had exactly the same trend of correlation with Total amount elements as was shown with EF of K in composition of $PM_{2.5}$ emitted from RS burning (Figure 3.4). Therefore potassium content of rice straw can directly impact the EF of $PM_{2.5}$ from RS.

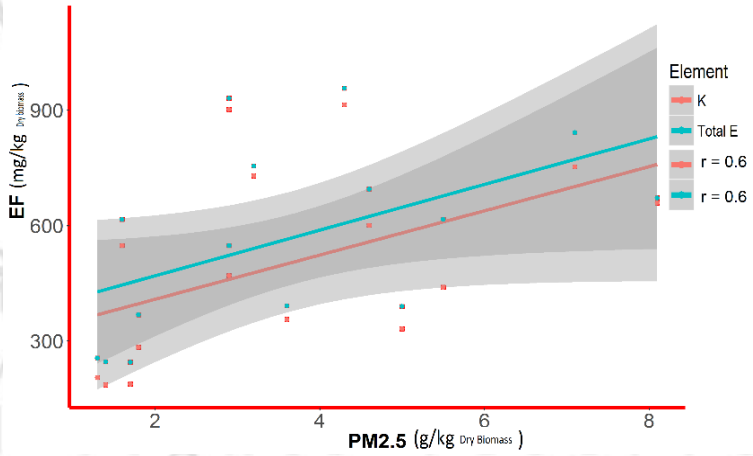

Figure 3.4 Correlation of $PM_{2.5}$ with K emitted from RS burning

3.2.2 Emission of $PM_{2.5}$ and its elemental composition from MR burning

Emission factor of $PM_{2.5}$ from 15 burning experiments of MR with an average mass of 0.9 ± 0.04 (kg) of biomass was 2.10 ± 0.90 (g/kg $_{dry\text{-}biomass}$) which was lower than Emission factor of $PM_{2.5}$ from RS, while percent burned (91 ± 2 %) of biomass of MR was higher than RS (81 ± 2 %), and average

3.2.3 Emission of $PM_{2.5}$ and its elemental composition from DDF burning

Dry dipterocarps forest (DDF) is one of the major forest types over Upper Northern Thailand (UNT), that experiencing forest fire every now and then particularly during the dry seasons. To estimate the emission of $PM_{2.5}$ from Dry dipterocarps forest, 15 samples of leaf litters from 5 different locations collected during the dry season. Average emission factor of $PM_{2.5}$ from 15 burning experiments of DDF biomass samples was 3.58 ± 0.87 (g/kg $_{\text{dry biomass}}$) which was very similar to emission of $PM_{2.5}$ from RS (3.7 ± 2.1 g/kg $_{\text{dry biomass}}$) when biomass burning was 84 ± 4 % completed. EFs of $PM_{2.5}$ were very similar within samples from same location. Details burning experiments of DDF presented in Table 3.10.

Table 3.10 Overall details about DDF burning experiment.

site	Sample Code	Dry biomass (kg)	%Burn	Remained Ash (g)	$PM_{2.5}$ (mg)	DF	$PM_{2.5}$ EF (g/Kg)
1	3103-1	1.02	89	110	1.21	2420	2.93
	3103-2	1.01	84	160	1.66	2100	3.48
	3103-3	1.02	90	110	0.96	2600	2.50
2	3106-1	1.03	84	160	1.92	2180	4.18
	3106-2	1.03	90	100	1.73	2230	3.86
	3106-3	1.01	88	120	1.91	2110	4.04
3	3107-1	1.01	92	80	0.95	2420	2.29
	3107-2	1.02	90	110	0.96	2390	2.30
	3107-3	1.01	87	140	2.09	2340	4.89
4	3108-1	1.01	91	90	1.37	2420	3.32
	3108-2	1.02	88	120	1.60	2420	3.87
	3108-3	1.03	84	160	1.49	2330	3.46
5	3110-1	1.03	84	160	1.65	2290	1.69
	3110-2	1.00	88	120	3.23	2320	3.81
	3110-3	1.02	79	220	0.91	2380	2.70
Average		1.02	84	130	1.58	2330	3.58
SD		0.01	4	40	0.60	130	0.87

As shown in Table 3.11, from 8 elements detected in composition of $PM_{2.5}$ emitted from DDF, the EF of K (220 ± 30 mg/kg $_{dry\ biomass}$) was very high comparing to other elements with range of 200-240 mg/kg $_{dry\ biomass}$. Comparing to agricultural biomass (RS and MR) EFs of in K emitted form DDF were not fluctuating considerably between studies sites. Average EF of K in composition of $PM_{2.5}$ emitted from DDF was considerably lower than EF of K (500 ± 260 mg/kg $_{dry\ biomass}$) in composition of $PM_{2.5}$ emitter from RS burning. The lowest emission factor from DDF found for Si (0.29 ± 0.23 mg/kg $_{dry\ biomass}$). Similar to MR, Ca which was detected in RS samples was not present in composition of $PM_{2.5}$ emitted from DDF. Potassium contents of $PM_{2.5}$ emitted from DDF as biomass burning tracer was lower comparing to $PM_{2.5}$ emitted from RS and MR that can be explained that source of K in forest biomass is only soil its unlikely to used inorganic fertilizer for forests to supply K.

Table 3.11 EFs of elements (mean ± SD) of $PM_{2.5}$ emitted from DDF burning.

	EFs of $PM_{2.5}$ (g/kg $_{dry\ biomass}$) and elements (mg/kg $_{dry\ biomass}$)					
	Site 1	Site 2	Site 3	Site 4	Site 5	Average
$PM_{2.5}$	*2.91±0.50*^{a}	*3.94±0.16*^{a}	*3.12±1.45*^{a}	*3.50±0.27*^{a}	*4.42±2.74*^{a}	**3.58±*0.78***
Ca	ND	ND	ND	ND	ND	-
Cr	*3.81±1.98*^{a}	*3.29±1.74*^{a}	*2.08±1.24*^{a}	*3.97±0.9*^{a}	*2.28±2.02*^{a}	**3.08±0.87**
K	*210±30*^{a}	*200±20*^{a}	*210±30*^{a}	*240±20*^{a}	*200±20*^{a}	**220±30**
Mg	ND	ND	ND	6.57±5.82	ND	-
Na	*18.55±0.57*^{a}	*36.33±11.25*^{a}	*4.86±5.46*^{a}	*37.1±21.79*^{a}	ND	**23.92±13.43**
Sb	*5.33±1.84*^{a}	*4.65±1.73*^{a}	*3.3±1.42*^{a}	*5.39±1.16*^{a}	*3.76±1.91*^{a}	**4.48±0.93**
Si	0.13±0.11	ND	ND	ND	ND	-
Sn	*2.05±0.88*^{a}	*2.91±0.82*^{a}	*2.08±0.55*^{a}	*1.66±0.63*^{a}	*1.39±0.31*^{a}	**2.02±0.58**
Zn	*1.53±0.86*^{a}	*1.27±0.25*^{a}	*2.45±1.17*^{a}	*3.22±2.27*^{a}	*1.2±0.35*^{a}	**1.93±0.87**
TE	*240±30*^{a}	*240±40*^{a}	*220±40*^{a}	*300±50*^{a}	*210±40*^{a}	**240±30**

$^{a, b, c}$ same superscripts and Italics express similarity between means. Different superscripts show significant difference ($p < 0.05$). ND: Not Detected.

Comparing means of EFs of elements between study sites showed no significant difference for all elements in composition of $PM_{2.5}$ emitted from DDF. Similar to RS and MR burning, K (84.55 %) was most abundance element in percent of emission factors of elements in the composition of $PM_{2.5}$ emitted from DDF. EFs of other elements in descending order of percentage were Na (9.60%) > Mg (1.18%) > Sb (1.80%) > Cr (1.24%) > Sn (0.81%) > Zn (0.76%) and Si (0.08%) (Figure 3.7). Comparing abundance of elements in composition of $PM_{2.5}$ emitted from DDF with pervious literatures it was found that trend of elements remained the same value found for chemical elements in leaf litter of Dipterocarpaceae trees (Breulmann et al., 1999). EFs of metals such as Sb, Cr, and Zn are high enough to reduce quality of air and pose risk to human health and environment. Assessing correlation of $PM_{2.5}$ and elements in composition of $PM_{2.5}$ emitted from DDF burning showed that $PM_{2.5}$ was negatively correlated to EF of K ($r = -0.44$, $p < 0.05$) and EF of Zn ($r = -0.57$, $p < 0.05$) (Figure 3.6). EF of $PM_{2.5}$ from DDF in contrast to RS and MR is negatively influenced by EF of K, which increase in K content will lead to decrease in EF of $PM_{2.5}$, similar relation found between EF of $PM_{2.5}$ and EF of Zn in composition of $PM_{2.5}$ emitted from DDF leaf litter burning.

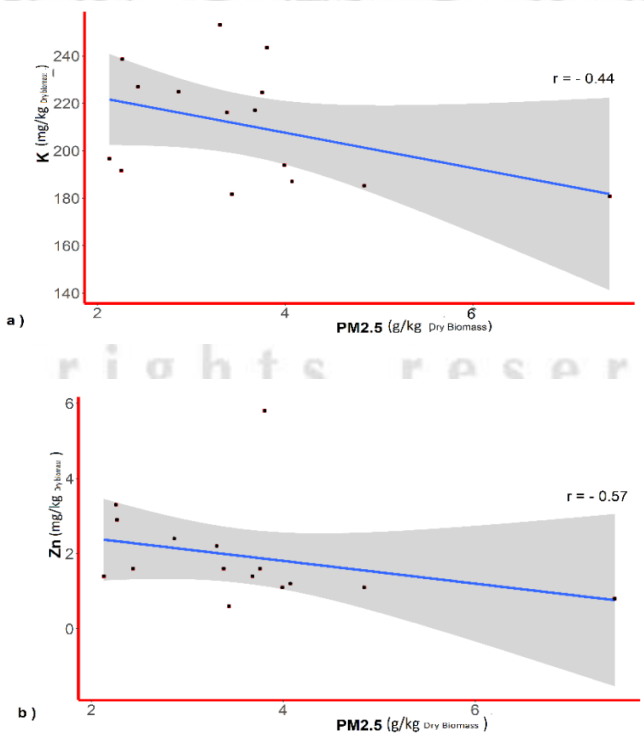

Figure 3.6 Correlation of $PM_{2.5}$ emitted from DDF with, a) K and b) Zn

3.2.4 Emission of $PM_{2.5}$ and its elemental composition from MDF burning

Mixed deciduous forest (MDF) is covering huge areas of UNT that contributes to $PM_{2.5}$ emission during forest fire. 15 burning experiments of MDF forest leaf litter were studied during this research. About 1 kg of leaf litter was burned in each burning experiment, the burning process was 88 ± 4 % completed in average which 140 ± 40 g of ash remained from biomass burning and emitted 1.92 ± 1.18 mg of $PM_{2.5}$. The average $PM_{2.5}$ emission factor of MDF was 4.44 ± 2.94 (g/kg $_{\text{dry bio mass}}$) while EFs of $PM_{2.5}$ of burning experiments of MDF biomass samples ranged 2-12 (g/kg $_{\text{dry biomass}}$) (Table 3.12).

Table 3.12 Overall details about MDF burning experiments.

site	Sample Code	Dry biomass (kg)	%Burn	Remained Ash (g)	$PM_{2.5}$ (mg)	DF	$PM_{2.5}$ EF (g/kg)
1	3202-1	1.00	88	130	1.56	2070	3.23
	3202-2	1.01	88	130	1.42	2480	3.54
	3202-3	1.00	87	136	0.85	2720	2.32
2	3203-1	1.01	89	120	1.55	2100	3.26
	3203-2	1.00	88	130	1.82	1160	2.12
	3203-3	1.01	89	110	1.41	1390	1.97
3	3207-1	1.00	88	130	1.22	2720	3.32
	3207-2	1.01	87	140	1.01	2720	2.75
	3207-3	101	88	130	3.17	2470	7.82
4	3208-1	1.01	88	130	2.39	2100	5.02
	3208-2	1.01	89	120	3.95	2350	9.29
	3208-3	1.01	90	110	4.90	2440	11.97
5	3209-1	1.01	80	210	1.08	2600	2.81
	3209-2	1.00	79	220	1.38	2690	3.71
	3209-3	1.00	81	190	1.15	2700	3.09
	Average	1.01	88	140	1.92	2310	4.44
	SD	0.01	4	40	1.18	480	2.94

Measured EF of $PM_{2.5}$ from MDF in this study was very closed to $PM_{2.5}$ EF (4.50 g/kg $_{\text{dry biomass}}$) studied for tropical forest by (Yokelson et al., 2011), the

only amount reported by (Amaral et al., 2016) in reviewing particulate matter emission from biomass. Furthermore this EF of was very closed but higher than EF of PM_{10} (3.30 ± 0.17 g/kg) emitted from leaf litter burning in combustion chamber studied by (Chaichana, 2011), while very higher than EF of PM_{10} (1.52 ± 0.65 and 1.22 ± 0.29 g kg^{-1}) studied by (Sillapapiromsuk, et al., 2013 and Wiriya, et al.,, 2016) respectively. Average EF of K (270 ± 70 mg/kg $_{dry\ biomass}$) in composition of $PM_{2.5}$ emitted from MDF was very similar to DDF. Likewise, the lowest emission factor was belonging to Si (0.27 ± 0.1 mg/kg $_{dry\ biomass}$) and remaining elements also showed the same trends. Comparison of means of EFs of elements was done (ANOVA). EF of K and total EF of elements showed the same trend which study site 1 as lowest EF of K measured was significantly ($p < 0.05$) different from study site 3 where the highest EF of K was found, while other pairs were not different from each other. EF of Zn in composition of $PM_{2.5}$ emitted from site 3 was different from sites 1, 2 and 4, while EFs of Cr, Mg, Na, and Sb were not different between all study sites (Table 3.13).

Table 3.13 EFs of elements (mean ± SD) of $PM_{2.5}$ emitted from MDF burning.

	EFs of $PM_{2.5}$ (g/kg $_{dry\ biomass}$) and elements (mg/kg $_{dry\ biomass}$)					
	Site 1	Site 2	Site 3	Site 4	Site 5	Average
$PM_{2.5}$	*3.01±0.63*^{a}	*2.43±0.71*^{a}	*4.60±2.75*^{ab}	8.68±3.48^{b}	*3.19±0.46*^{a}	**4.44±2.94**
Ca	12.12±10.5	ND	ND	ND	ND	-
Cr	*4.87±0.85*	*2.97±0.92*	*2.5±3.23*	ND	ND	-
K	*260±30*^{ab}	*210±80*^{a}	390±90^{b}	*262±30*^{ab}	*240±90*^{ab}	**270±70**
Mg	*8.68±2.95*^{a}	*4.29±2.53*^{a}	*11.82±0.05*^{a}	*2.18±2.37*^{a}	ND	**7.02±3.81**
Na	*44.83±5.98*^{a}	*27.07±9.17*^{a}	*34.79±10.61*^{a}	*24.29±5.12*^{a}	*37.53±18.38*^{a}	**33.7±8.25**
Sb	*6.47±1.19*^{a}	*3.99±1.14*^{a}	*2.84±3.11*^{a}	*6.25±0.08*^{a}	*3.42±3.5*^{a}	**4.59±1.67**
Si	0.22±0.22	ND	ND	ND	ND	-
Zn	*2.98±0.55*^{a}	*1.81±0.25*^{a}	6.22±1.02^{b}	*2.29±0.36*^{a}	*4.2±1.82*^{ab}	**3.5±1.77**
TE	*330±20*^{ab}	250±80^{a}	*430±110*^{b}	*300±30*^{ab}	*290±30*^{ab}	**320±70**

$^{a, b, c}$ same superscripts, underline and italics express similarity between means. Different superscripts show significant difference ($p < 0.05$). ND: Not Detected.

EF of K in composition of $PM_{2.5}$ emitted from MDF as biomass burning tracer was higher than DDF but lower comparing to $PM_{2.5}$ emitted from RS and MR, that can be explained that source of K in forest biomass is only soil and some natural minerals; it is most improbable to use inorganic fertilizer for forests to supply K.

Percent EFs of elements in composition of $PM_{2.5}$ emitted from MDF showed exactly the same trend as of $PM_{2.5}$ emitted from DDF with relatively the same EFs values, the exceptions were presence and absence of Ca and Sn in composition of $PM_{2.5}$ emitted from MDF while they were absent and present in the composition of $PM_{2.5}$ emitted from DDF, respectively. EFs of element in composition of $PM_{2.5}$ emitted from MDF in descending order were K (82.15%), Na (10.18%) > Mg (2.12%) > Ca (1.90 %), Sb (1.39%) > Cr (1.13%) > Zn (1.06%) and Si (0.08%) (Figure 3.7).

Percentage of some toxic metal are high in composition of $PM_{2.5}$ emitted from MDF that can be harmful for long time exposure and can be potential risk for environments (Plum et al., 2010; Tchounwou et al., 2012). No significant correlation found for EF of $PM_{2.5}$ with other measured elements in composition of $PM_{2.5}$ emitted from MDF. While EF of K with EF of Zn ($r = -0.77$, $p < 0.01$) and EFs Cr with Sb ($r = 0.85$, $p < 0.01$) were strongly correlated to each other, which can be explained that EF of $PM_{2.5}$ from MDF is independent from EFs of elements measure in its composition.

3.2.5 Comparison of $PM_{2.5}$ and its elemental composition emitted from BB

Average values of EFs of $PM_{2.5}$ emitted from studied biomasses were not much different from each other, however MDF emitted higher $PM_{2.5}$ (4.44 ± 2.94 g/kg $_{\text{dry biomass}}$), though similar studies were not done for specific forest of MDF previously to compare with, but this EF of $PM_{2.5}$ was almost the same as EF of $PM_{2.5}$ from dry biomass of tropical forest in Mexico (4.50 ± 1.64 g/kg $_{\text{dry biomass}}$) studied by (Yokelson et al., 2011) and the only amount reported by (Amaral et al., 2016) in reviewing particulate matter emission from biomass. Furthermore this EF of was very closed but higher than EF of PM_{10} (3.30 ± 0.17 g/kg) emitted from leaf litter burning in combustion chamber studied by (Chaichana, 2011), while

very higher than EF of PM_{10} (1.52 ± 0.65 and 1.22 ± 0.29 g kg^{-1}) studied by (Sillapapiromsuk et al., 2013 and Wiriya et al., 2016) respectively. The lowest EF of $PM_{2.5}$ (2.11 ± 0.90 g/kg $_{dry\ biomass}$) was found for MR which was not very different than EF (3.47 ± 0.25 g/kg $_{dry\ biomass}$) of total particulate matter (TPM) study for maize as biomass fuel by (Saud et al., 2013) and EF of $PM_{2.5}$ (3.84 ± 1.02 g/kg $_{dry\ biomass}$) in corn by (Shen et al., 2010), but was very lower than EF of PM_{10} (5.08 ± 1.52 g/kg) emitted from MR burning in combustion chamber studied by (Chaichana, 2011). Still very higher than EF of PM_{10} (0.90 ± 0.31 and 0.59 ± 0.13 g kg^{-1}) studied by (Sillapapiromsuk et al., 2013 and Wiriya et al., 2016) respectively. Furthermore, EF of $PM_{2.5}$ from RS (3.67 ± 2.10 g/kg $_{dry\ biomass}$) and DDF (3.58 ± 0.78 g/kg $_{dry\ biomass}$) were not significantly ($p < 0.05$) different.

EF of $PM_{2.5}$ from RS measured in this research was smaller than EF of $PM_{2.5}$ of (7,7, 8.3, 12.95 and 13.1) reported by previous studies (Turn et al., 1997;Gadde et al., 2009; Hays et al., 2005; Zhang et al., 2017) respectively, but this EF of $PM_{2.5}$ from RS was higher than EF of PM_{10} (0.59, 0.69 ± 0.23 ,0.89 ± 0.25 g/kg $_{dry\ biomass}$) studied for RS in Chiang Mai respectively by (Chiachana, 2011; Sillapapiromsuk, et al., 2013; Wiriya et al., 2016). The results for EF of $PM_{2.5}$ showed that EF of $PM_{2.5}$ from forest leaf litter burning (DDF and MDF) (4.02 ± 0.57 g/kg $_{dry\text{-}biomass}$) was higher than that from agricultural residues burning (MR and RS) (2.89 ± 1.10 g/kg $_{dry\text{-}biomass}$). Therefore, forest leaf litters contribute more in emission of $PM_{2.5}$ per unit of dry biomass comparing to emission from agricultural (RS and MR) biomass, hence, burning of forests' leaf litters can form haze and reduce air quality during forest fire.

Comparing means (ANOVA) of $PM_{2.5}$ showed that EF of $PM_{2.5}$ emitted from MDF (as highest EF of $PM_{2.5}$) was significantly ($p < 0.05$) different from MR (as lowest EF of $PM_{2.5}$) from each other, while all other pairs were not significantly different from each other. K was most abundant element in composition of both agricultural (< 85 %) and forest (< 80 %) biomass (Figure 3.7).

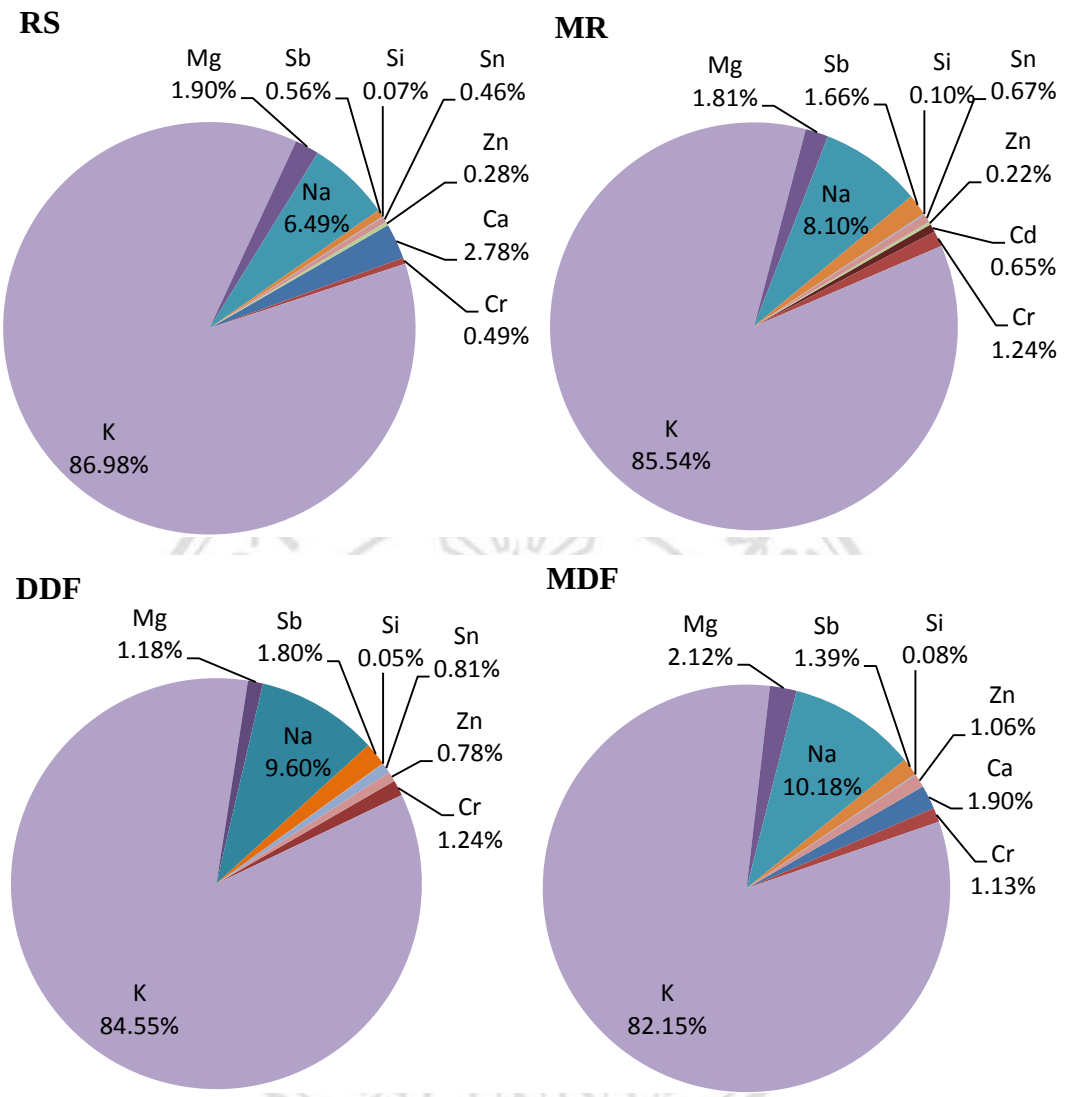

Figure 3.7 Percentage of elements in composition of $PM_{2.5}$ emitted from BB.

EF of K and most of elements in composition of $PM_{2.5}$ emitted from RS were higher comparing to other biomass samples and flowed by MR > MDF > DDF, this trend was clearly noticeable in total EF of measured elements. Average EFs of elements in composition of $PM_{2.5}$ measured by this research are considerably higher than EFs elements in composition of $PM_{2.5}$ from relevant biomass type studied by (Turn et al., 1997) using combustion wind tunnel for assessing EFs of various agricultural and forests biomasses and as well as EFs of some elements in composition of PM_{10} studied for RS and MR by (Chaichana, 2011).

Table 3.14 EFs of $PM_{2.5}$ and its elemental composition (mean ± SD).

	EFs of $PM_{2.5}$ ($g/kg_{dry\ biomass}$) and element ($mg/kg_{dry\ biomass}$) (n=15)			
	Agricultural biomass		Forest biomass	
	RS	MR	DDF	MDF
$PM_{2.5}$	*3.67±2.10*[ab]	2.11±0.90[a]	*3.58±0.78*[ab]	*4.44±2.94*[b]
Ca	*26.87±26.32*	ND	ND	*6.3±5.08*
Cr	*4.69±0.72*[a]	*4.73±1.41*[a]	*3.08±0.87*[a]	*3.73±0.98*[a]
K	504±257[a]	*327±179*[ab]	*211±16*[b]	*272±68*[ab]
Mg	*11.02±4.7*[a]	*8.66±3.52*[a]	*3.68±2.66*[a]	*7.02±3.81*[a]
Na	*37.65±9.96*[a]	*30.93±19.85*[a]	*23.92±13.43*[a]	*33.7±8.25*[a]
Sb	*4.09±3.09*[a]	*6.36±1.63*[a]	*4.48±0.93*[a]	*4.59±1.67*[a]
Si	*0.47±0.58*[a]	*0.38±0.19*[a]	*0.29±0.23*[a]	*0.27±0.1*[a]
Zn	*1.6±0.65*[ab]	0.84±0.33[a]	*1.93±0.87*[ab]	*3.5±1.77*[b]
Sn	*2.65±0.33*[a]	*2.55±0.64*[a]	*2.02±0.58*[a]	ND
Cd	ND	2.47±0.51	ND	ND
Total	569±246[a]	*376±183*[ab]	*243±32*[b]	*322±68*[ab]
$\%(m_{PM2.5}/m_E)$	15	13	7	7

[a, b, c] same superscripts, underline and italics express similarity between means. Different superscripts show significant difference ($p < 0.05$). ND: Not Detected.

K as biomass tracer (Khamkaew et al., 2016; Pachon et al., 2013, 2013) is uptaken in large amount from soil and root environment which in agricultural crops is mainly supplied by inorganic fertilizers (Sarkar et al., 2017) et al., 2017), but for forest biomass the source of K is soil and mineral in soil composition. Though all other detected elements in composition of $PM_{2.5}$ of both agricultural and forest biomasses are essential elements in structure of plants (Pinto et al., 2016), except Cd which is highly toxic element (Godt et al., 2006). Emission of the toxic elements in composition of $PM_{2.5}$ to air emitted from both biomass types, make them potential risk for health for long exposure and as well as environmental impacts.

Homogeneity test (ANOVA) between means of elements in composition of $PM_{2.5}$ showed that EF of K and total EF of elements emitted from RS were significantly ($p < 0.05$) different from EF of K and total EF of elements emitted

from DDF, respectively, while EF of K and total EF of elements of other biomass types were not different from each other. So, the ANOVA test verify that EF of K from RS was significantly higher than EF of K from DDF which basically because source of K in RS is from inorganic fertilizer while for forest source of K is only soil and some mineral in soil, and high EF of K and its weight on total EF of elements further influencing total EF of elements to follow the same trend as EF of K. Zn is an essential and micronutrient in plants and is mainly present in the soil, EF of Zn in composition of $PM_{2.5}$ emitted from MR was significantly lower and different from MDF. All other measure elements were not significantly ($p < 0.05$) different between studied biomass types (Table 3.14).

As shown in Figure 3.8, composition of emitted $PM_{2.5}$ from all investigated biomasses of agriculture and forest were complex mixture of various elements including some heavy metals. EF of K was significantly high in both agriculture (86.23 %) and forest (83.55%) biomass samples. Other elements in $PM_{2.5}$ compositions of agricultural biomass in descending order were Na, Mg, Ca, Sb, Cr, Sn, Cd, Zn and Si, while those of forest were Na, Mg, Sb, Cr, Ca, Zn, Sn and Si.

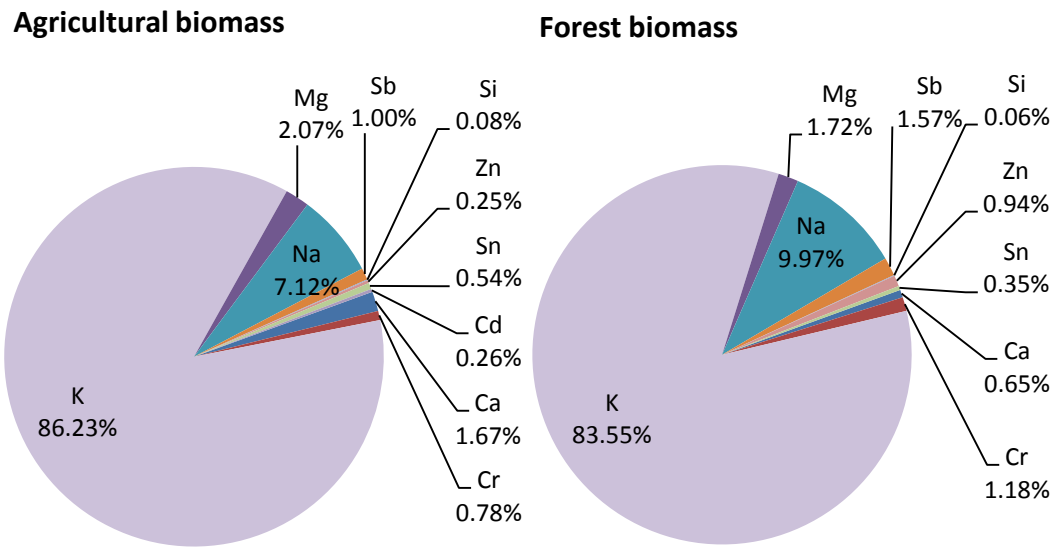

Figure 3.8 Overall elements percentage in composition of $PM_{2.5}$ from BB.

Percentage of elements in composition of $PM_{2.5}$ depended on the type of assessed biomass not to the mass of $PM_{2.5}$ emitted. Ratio of mass of elements in composition of $PM_{2.5}$ and average mass of emitted $PM_{2.5}$ showed adverse order to EF of $PM_{2.5}$ from investigated biomasses. In Figure 3.9, four inner layers from center toward outside show mass of $PM_{2.5}$ for biomass types (MDF, DDF, RS MR, respectively) determined by different colors and the red color in each layer indicates percentage of measured elements in composition of $PM_{2.5}$ emitted from related biomass type. The outer layer of graph presents percentage of ratio of measured elements in each biomass and total amount of measured elements (m of each biomass / m total).

Total measured elements in composition of $PM_{2.5}$ emitted from MR burning was including 16% mass of $PM_{2.5}$ emitted from MR, which was higher comparing to other biomass types although MR showed lowest EF of $PM_{2.5}$. Total elements measured comprising 15% of $PM_{2.5}$ emitted from RS but for DDF and MDF both 7% while EF of $PM_{2.5}$ from MDF burning was highest. Which can be explained, that in contrast to MDF that emitted more $PM_{2.5}$ per unite of dry biomass, MR emitted lower $PM_{2.5}$, but the health impact and health risk of $PM_{2.5}$ emitted from MR would be higher due to complexity (containing more toxic elements) of composition of emitted $PM_{2.5}$.

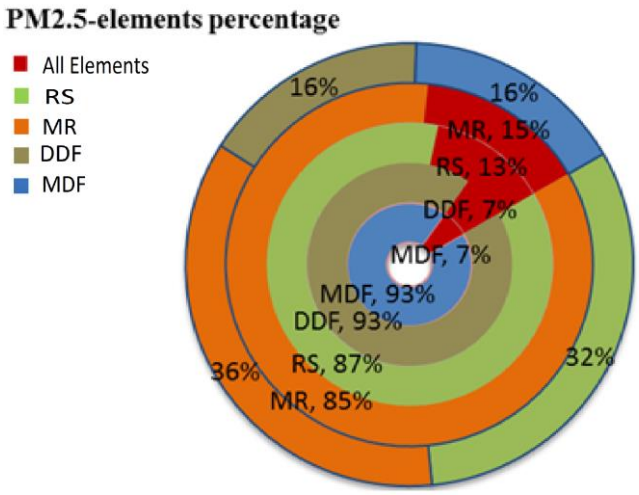

Figure 3.9 Ratio of elements in composition of $PM_{2.5}$ emitted from BB.

Presence of Cd, Cr, And Sn as toxic elements in the composition of $PM_{2.5}$ emitted MR increases its toxicity comparing other assessed biomass samples (Godt et al., 2006; Tchounwou et al., 2012). As shown in the outer layer of Figure 3.9, $PM_{2.5}$ emitted from agricultural biomass can have more health and environmental impact comparing to $PM_{2.5}$ emitted from forest leaf litters since emitting more elements and higher amount of toxic elements.

3.3 Elemental Composition of Ash Samples from BB

Ash samples were collected after each burning experiment and were analyzed for elemental composition of ash for each biomass type. Composition of ash samples from all biomass types were almost alike with few exceptions in some, but amount of constituents varied based on origin of biomass samples. Underneath are the details of findings from ash elemental analysis of screened biomass samples for this research.

3.3.1 Composition of ash sample from RS burning

Concentration and number of elements detected in ash samples of RS was very high comparing elements in $PM_{2.5}$ emitted from RS. In composition of ash samples remained from RS burning, K (10830 ± 4530 mg/kg $_{\text{dry biomass}}$) was most plentiful element. Potassium is a mineral nutrient essential to plants especially K content of many high-yielding crops such as rice, therefore, K is supplied by inorganic fertilizers and uptaken in high amount by rice. Other major elements in ash remained from RS burning were Ca, Mg, Mn, Fe and Al with EFs of 4370 ± 480, 1880 ± 200, 1150 ± 710, 855 ± 477 and 730 ± 430, respectively.

Ca, Mg, Mn, Fe and Al all are essential elements playing key roles in plants physiology except Al which is toxic for plants (Panda et al., 2009) Ca, Fe and Mn are key elements in plants growth and Mg is important element of chlorophyll and essential for photosynthesis. Source of later five major elements is soil and soil minerals, very unlikely to supply them through fertilizers. Comparing means (ANOVA) of elements between sites it was found that EFs of K as most abundant element and all other elements in composition of ash from RS burning were

significantly different between sites except As, Ca, Fe and Mg which they were not significantly different between all study sites.

Table 3.15 EF of Elemental composition (mean±SD) of ash remained from RS burning.

Element	EF of elements (mg/kg $_{\text{dry biomass}}$) (n = 3)					
	Site 1	Site 2	Site 3	Site 4	Site 5	Average
Al	*480±60*^{ab}	*1320±140*^{a}	*210±10*^{ab}	*950±990*^{ab}	690±40^{b}	**730±430**
As	*3.82±1.7*^{a}	*3.65±1.79*^{a}	*3.82±2.47*^{a}	*3.96±0.87*^{a}	*3.57±1.18*^{a}	**3.76±0.15**
Ca	*4090±392*^{a}	*3781±279*^{a}	*4238±91*^{a}	*4862±353*^{a}	*4859±233*^{a}	**4370±480**
Co	*4.91±1.5*^{a}	*5.29±0.37*^{a}	1.07±0.24^{b}	*6.05±0.45*^{a}	*2.17±0.12*^{ab}	**3.9±2.16**
Cr	*2.02±0.61*^{a}	*2.27±0.23*^{a}	1.05±0.06^{b}	*2.19±0.16*^{a}	1.63±0.15^{b}	**1.83±0.5**
Cu	*3.41±0.62*^{a}	1.85±0.14^{c}	*2.67±0.08*^{ab}	2.37±0.15^{bc}	1.03±0.11^{d}	**2.27±0.89**
Fe	919±160^{a}	1240±130^{a}	250 ±10^{a}	1370±120^{a}	500±40^{a}	**855±477**
K	*14900±1520*^{a}	9460±770^{c}	*14080±400*^{ab}	3652±270^{bc}	12070±570^{d}	**10830±4530**
Mg	*1850±190*^{a}	*1940±140*^{a}	*1540±50*^{a}	*2058±160*^{a}	*2010±90*^{a}	**1880±200**
Mn	*1260±121*^{a}	730±59^{b}	*2350±55*^{a}	762±56^{b}	670±30^{b}	**1150±710**
Na	*120±8.11*^{c}	*120±10*^{c}	40±1.0^{a}	80±10^{b}	270±10^{d}	**120±90**
Pb	*13.22±2.52*^{a}	*13.89±0.7*^{a}	1.93±0.37^{b}	2.77±0.99^{b}	5.63±1.5^{b}	**7.49±5.71**
Sb	*1.64±0.66*^{a}	*2.14±0.16*^{a}	0.35±0.09^{b}	*2.08±0.16*^{a}	*1.38±0.1*^{ab}	**1.52±0.72**
Si	*2.28±0.23*^{bc}	*3.93±0.35*^{c}	1.23±0.06^{a}	*3.49±0.45*^{bc}	*2.24±0.03*^{b}	**2.63±1.08**
Sn	6.27±0.66^{b}	*5.13±0.62*^{c}	4.81±0.27^{a}	*4.93±0.07*^{c}	4.29±0.3^{b}	**5.09±0.73**
V	*1.49±0.5*^{a}	*3.07±0.23*^{ab}	0.43±0.06^{b}	2.89±0.31^{b}	1.46±0.18^{b}	**1.87±1.1**
Zn	39.89±1.5^{b}	*43.13±3.64*^{c}	44.3±0.49^{a}	*41.6±3.32*^{c}	24.84±0.9^{b}	**38.75±7.95**
TE	*23720±2150*^{a}	*18670±1530*^{a}	*22780±610*^{a}	*13800±1050*^{a}	21120±870^{b}	**20020±3970**

$^{a, b, c, d,}$ same superscripts, underline and italics express similarity between means. Different superscripts show significant difference ($p < 0.05$).

EF of K despite not fluctuating very much between study sites except study site 4 which was significantly lower comparing with other study sites, still EF of K from site 1 was different from sites 2, 4 and 5, EF of K from site 2 was different from sites 3 and 5 and EF of K from site 5 was different from all other sites. Total EF (TE) of element in composition of ash from RS of site 5 was significantly ($p < 0.05$) different from all other sites while they were not different from each other

(Table 3.15). Out of 17 detected elements in composition of ash remained from RS burning 6 elements (K, Ca, Mg, Mn, Fe and Al), were major elements which included more than 96% mass of detected and measured elements, which understandable for all of them as macronutrient and essential elements except Al that show various toxicity (Panda et al., 2009).

EF of K (10837 ± 4258 mg/kg $_{\text{dry biomass}}$) from RS consisted 54% of all elements' EFs. Percentage EFs of other major elements (Ca, Mg, Mn, Fe and Al) were 22, 9, 6, 4 and 4 % respectively. Between minor elements EF of Na (0.62 mg/kg $_{\text{dry biomass}}$) was significantly higher than EFs of other elements (Figure 3.13, RS). Arsenic as very toxic substance (Ratnaike, 2003; Tchounwou et al., 2012) was found in composition of ash from RS samples, it needs to be studied more closely, the concern is how much it can mix with atmospheric air since its high toxicity can be harmful for exposure. Number and EFs of heavy metal were very high in ash samples that can inter into air through flying ashes particles in various sizes and degrade the ambient air quality. Emission factor of $PM_{2.5}$ has negative and relatively strong correlation with EFs of Co and Fe ($r = -0.63, -0.53$, $p < 0.05$) in ash samples of RS (Figure 3.10).

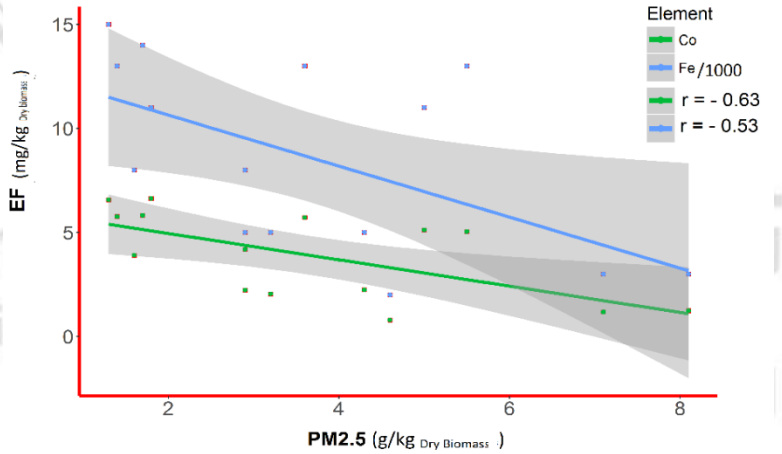

Figure 3.10 $PM_{2.5}$ correlation with Co and Fe in ash from RS burning

3.3.2 Composition of ash sample from MR burning

Emission factor of K (13106 ± 6171 mg/kg $_{\text{dry biomass}}$) from MR ash samples was higher than EF of K (10830 ± 4530 mg/kg $_{\text{dry biomass}}$) in ash sample of RS. Similar to ash sample of RS, in composition of ash samples remained from MR

other major elements were Ca, Mg, Mn, Fe and Al with EFs of 4370 ± 480, 1880 ± 200, 1150 ± 710, 855 ± 477 and 730 ± 430, respectively. Reason and role of major elements are explained in section 3.3.1. In case of minor elements, Zn showed highest EF, while Sb lowest EF between. Analysis of variance test (ANOVA) comparing means of elements between study sites indicated that EFs of K as most abundant element and all other elements in composition of ash from MR burning were significantly different between study sites except Cr, Cu, Na, Zn and Mg which they were not significantly different between all study sites. EFs of K from sites 1 and 3 were not different from each other, but EF of K from site 2 was different from site 4 and 3.

Table 3.16 EF of Elemental composition (mean±SD) of ash remained from MR burning.

Element	EF of elements ($mg/kg_{Dry\ biomass}$) (n = 3)					
	Site 1	Site 2	Site 3	Site 4	Site 5	Average
Al	*150±10*^{a}	610±110^{c}	360±50^{b}	*200±49*^{ab}	*290±80*^{ab}	**320±180**
Ca	*2280±170*^{b}	1240±210^{a}	3670±260^{c}	5030±440^{d}	*1870±530*^{ab}	**2820±1520**
Co	0.71±0.02^{a}	*2.58±0.46*^{b}	*1.92±0.38*^{b}	1.01±0.15^{a}	1.05±0.07^{a}	**1.45±0.77**
Cr	*0.29±0.05*^{a}	*0.57±0.12*^{a}	*0.65±0.14*^{a}	*0.43±0.18*^{a}	*0.51±0.14*^{a}	**0.49±0.14**
Cu	*6.27±0.39*^{a}	*3.73±0.54*^{a}	*7.7±0.77*^{a}	*7.05±2.28*^{a}	*5.49±2.77*^{a}	**6.05±1.54**
Fe	180±20^{a}	630±110^{c}	*440±70*^{bc}	*250±60*^{ab}	200±60^{a}	**340±192**
K	*13980±1100*^{bc}	*12090±1890*^{b}	20890±1560^{c}	3470±290^{a}	*15100±4530*^{bc}	**13120±6310**
Mg	*1980±150*^{a}	*1620±250*^{a}	*1600±120*^{a}	*3270±280*^{a}	*950±270*^{a}	**1880±860**
Mn	*120±10*^{a}	*86.14±14.17*^{ab}	62.79±5.59^{b}	*120±10*^{a}	*84.63±28.12*^{ab}	**94.71±24.87**
Na	*1.28±0.16*^{a}	*4.56±1.04*^{a}	*4.02±2.47*^{a}	*2.94±1.56*^{a}	*2.2±0.88*^{a}	**3.00±1.33**
Pb	*4.11±0.41*^{ab}	*4.19±1.17*^{ab}	*5.79±1.92*^{b}	1.75±0.32^{a}	1.59±0.64^{a}	**3.49±1.79**
Sb	0.18±0.05^{a}	*0.46±0.11*^{ab}	*0.54±0.1*^{b}	*0.29±0.15*^{ab}	*0.38±0.12*^{ab}	**0.37±0.14**
Si	0.47±0.08^{a}	1.56±0.27^{c}	*1.2±0.15*^{bc}	*0.83±0.26*^{ab}	*0.9±0.11*^{ab}	**0.99±0.41**
V	0.06±0.01^{a}	0.89±0.19^{c}	*0.46±0.06*^{b}	*0.2±0.16*^{ab}	*0.31±0.12*^{ab}	**0.38±0.32**
Zn	*6.57±0.3*^{a}	*6.69±1.23*^{a}	*10.6±2.59*^{a}	*9.39±3.83*^{a}	*6.62±3.44*^{a}	**7.97±1.89**
TE	*18700±1470*^{a}	*16300±2570*^{a}	27070±2060^{b}	*12380±1060*^{a}	*18510±5500*^{a}	**18590±5380**

$^{a, b, c, d,}$ same superscripts, underline and italics express similarity between means. Different superscripts show significant difference ($p < 0.05$).

EF of K from site 4 was different from sites 1, 3 and 5; the reason for significance difference was fluctuation of EF of K between sites. Total EF (TE) of elements in composition of ash remained from MR samples of site 3 was significantly ($p < 0.05$) higher different from all other sites while the difference between means of all other study sites were insignificant (Table 3.16). EF factor of calcium showed most difference between sites, except site 2 and 5 which were not different from each other, means of EF of Ca from all other study sites were significantly ($p < 0.05$) different. Percentage of EFs of major elements from MR ash in descending order were K (70.49%), Ca (15.16%), Mg (10.15%), Fe (1.83%) and Al (1.74%) Mn (0.50%), those covered 99.87% of overall EFs of measured elements in composition of ash remained from MR burning. EFs of minor elements only covered 0.13% mass of measured elements. Amount and EFs of heavy metals in composition of ash remained from MR burning were considerably lower in comparison with ash remained from RS burning (Figure 3.13). Emission factor of $PM_{2.5}$ showed a relatively strong and negative correlation with EFs of Mg ($r = -0.72$, $p < 0.01$), Ca ($r = -0.63$, $p < 0.01$) and Zn ($r = -0.55$, $p < 0.01$ (Figure 3.11) detected in composition of ash remained from burning of MR.

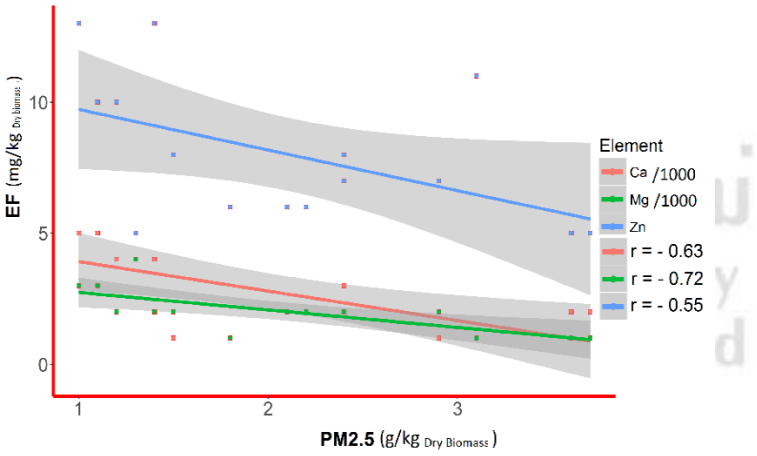

Figure 3.11 $PM_{2.5}$ correlation with Ca, Mg and Zn in ash from MR burning.

3.3.3 Composition of ash sample from DDF burning

Despite 6 major elements in composition of ash from RS and MR remained exactly the same in composition of ash left over from burning of DDF leaf litter,

but a clear increase observed in EF of Ca (15240 ± 7770 mg/kg $_{\text{dry biomass}}$) and decrease in EF of K (4260 ± 600 mg/kg $_{\text{dry biomass}}$) in ash samples of DDF comparing to ash from RS and MR. Though K and Ca in composition of tree play the same role as plants in agricultural crops but source of K in tree is natural composition of soil similarly for Ca which present in high concentration in soil and also Ca in composition of ash of leaf litter is influenced from soil as the samples were collected from ground under trees.

Table 3.17 EF of Elemental composition (mean±SD) of ash remained from DDF burning.

Element	EF of elements (mg/kg$_{\text{Dry biomass}}$) (n = 3)					
	Site 1	Site 2	Site 3	Site 4	Site 5	Average
Al	*830±210*^{abc}	*1340±240*^{bc}	360±100^{a}	*680±200*^{ab}	1500±470^{c}	**940±470**
Ca	11700±2870^{a}	7870±1820^{a}	*15200±4540*^{ab}	*13150±4300*^{ab}	*28300±11140*^{b}	**15240±7770**
Co	*5.74±1.48*^{ab}	*5.12±1.15*^{a}	1.61±0.34^{b}	*4.19±1.26*^{a}	*6.41±2.38*^{ab}	**4.61±1.87**
Cr	*2.51±0.59*^{ab}	3.74±1.17^{b}	*1.11±0.24*^{a}	*1.13±0.38*^{a}	*2.74±1.08*^{ab}	**2.25±1.13**
Cu	6.06±1.49^{a}	5.19±1.32^{a}	*9.09±2.31*^{ab}	*6.68±2.15*^{ab}	*14.83±5.82*^{b}	**8.37±3.89**
Fe	*1160±320*^{bc}	*980±180*^{abc}	300±70^{a}	*560±180*^{ab}	1430±480^{c}	**890±450**
K	*4580±1100*^{a}	*4450±1030*^{a}	*4800±1450*^{a}	*3260±1050*^{a}	*4220±1480*^{a}	**4260±600**
Mg	*4100±1000*^{a}	*3810±880*^{a}	*3190±960*^{a}	*2740±900*^{a}	*2970±1100*^{a}	**3360±570**
Mn	*840±200*^{ab}	*1070±240*^{ab}	1590±470^{b}	*520±170*^{a}	*690±260*^{a}	**940±410**
Na	*9.17±2.03*^{a}	*7.49±1.82*^{a}	*11.27±3.03*^{a}	*8.58±2.76*^{a}	*8.52±3.37*^{a}	**9.01±1.4**
Ni	*5.19±1.26*^{a}	*2.66±0.67*^{a}	10.15±2.55^{b}	*2.63±0.86*^{a}	*5.17±1.89*^{a}	**5.16±3.06**
Pb	15.58±4.5^{a}	*5.76±1.39*^{b}	*6.16±3*^{b}	*2.72±0.75*^{b}	*3.05±1.27*^{b}	**6.65±5.22**
Sb	*2.05±0.5*^{ab}	3.17±1.01^{b}	*0.47±0.12*^{a}	*0.79±0.36*^{a}	2.25±0.9a^{b}	**1.75±1.11**
Si	*2.33±0.7*^{a}	*2.5±0.62*^{ab}	*1.04±0.13*^{a}	*1.69±0.48*^{a}	5.09±1.97^{b}	**2.53±1.54**
V	*1.79±0.52*^{a}	*1.79±0.56*^{a}	*0.49±0.07*^{a}	*0.84±0.26*^{a}	*3.84±1.39*^{a}	**1.75±1.3**
Zn	*16.13±4.01*^{a}	*12.95±2.96*^{a}	*19.4±5.18*^{a}	*14.2±4.5*^{a}	*21.66±8.16*^{a}	**16.87±3.62**
TE	*23280±5720*^{a}	*19580±4410*^{a}	*25510±7600*^{a}	*20950±6810*^{a}	*39190±14940*^{a}	**25700±7870**

$^{a, b, c, d,}$ same superscripts, underline and italics express similarity between means. Different superscripts show significant difference ($p < 0.05$).

EFs of major elements in composition of ash from DDF in descending order were Ca (15240 ± 7770 mg/kg $_{dry\ biomass}$), K (4260 ± 600 mg/kg $_{dry\ biomass}$), Mg (3360 ± 570 mg/kg $_{dry\ biomass}$), Mn (940 ± 410 mg/kg $_{dry\ biomass}$), Al (940 ± 470 mg/kg $_{dry\ biomass}$), and Fe (890 ± 450 mg/kg $_{dry\ biomass}$). As mentioned in section 3.3.1 all major elements are vital nutrients for plant except Al, as an example role of K in plants including enzyme activation, photosynthesis, water use efficiency, starch formation and protein synthesis. From 10 minor elements in composition of ash from DDF EF of Zn is highest and EFs of Sb and V are lowest. Results of analysis of variance test (ANOVA) comparing means of elements between sites showed that EFs of K and total elements (TE) EFs follow the same trend and were not significantly different between study sites and similar results were found for Na, Mg and Zn. EF of Ca as highest EF in composition of ash remained from DDF leaf litter burning was significantly ($p < 0.05$) different between site 5 and all other study sites, while EF of Ca between 2-4 were not significantly ($p < 0.05$) different from each other (Table 3.17).

In composition of ash samples remained from DDF burning, percentage of major elements were Ca (59.32%), K (16.59%), Mg (13.08%), Al and Mn both (3.67%) and Fe (2.45%) which include 99.77% mass of all measured elements, the rest 10 elements only contributed 0.23% to mass of overall assessed elements. Composition of DDF ash samples contains more elements comparing to $PM_{2.5}$ emitted from the same samples but percentage of minor elements were noticeably low in ash samples comparing to $PM_{2.5}$. No significant correlation was found between emitted $PM_{2.5}$ from DDF and EFs of elements in composition of its ash samples.

3.3.4 Composition of ash sample from MDF burning

Emission factors of elements emitted from MDF ash samples and composition of ash samples behaved similar to EFs of elements emitted from DDF ash samples, though MDF emitted higher $PM_{2.5}$ per unit of dry biomass than DDF. EFs (mg/kg $_{dry\ biomass}$) of major elements from high to low were Ca (17570±6310), K (4730±2130), Mg (3060±1190), Al (1090±330), Fe (894±599)

and Mn (310±260). From 10 minor elements in composition of ash remained from MDF burning, EF of Zn was highest and EF of Sb was lowest (Table 3.18).

Table 3.18 EF of Elemental composition (mean±SD) of ash remained from MDF burnin.

Element	EF of elements (mg/kg $_{\text{dry biomass}}$) (n = 3)					
	Site 1	Site 2	Site 3	Site 4	Site 5	Average
Al	1330±40^{bc}	1510±60^{c}	*1020±50^{ab}*	*810±60^{a}*	*760±290^{a}*	**1090±330**
Ca	*22920±1030^{a}*	15840±780^{b}	*23720±990^{a}*	17290±1510^{b}	8100±3150^{c}	**17570±6310**
Co	8.62±0.25^{a}	2.66±0.26^{b}	*7±0.29^{c}*	*2.9±0.26^{c}*	*2.82±0.13^{c}*	**4.8±2.81**
Cr	6.26±0.13^{a}	0.94±0.11^{d}	*2.41±0.1^{b}*	0.77±0.15^{d}	1.59±0.18^{c}	**2.39±2.26**
Cu	*13.08±0.37^{ab}*	*14.15±0.61^{a}*	11.03±0.57^{c}	11.86±1.18^{bc}	6.41±0.41^{d}	**11.31±2.98**
Fe	1850±60^{a}	550±60^{b}	*1120±40^{c}*	*490±40^{c}*	*460±180^{c}*	**894±599**
K	3800±150^{c}	7580±390^{a}	*5600±310^{b}*	*4820±460^{bc}*	1830±710^{d}	**4730±2130**
Mg	*3980±180^{a}*	*3380±160^{ab}*	*3729±160^{ab}*	3220±290^{b}	990±400^{c}	**3060±1190**
Mn	*150±10^{ab}*	*240±10^{b}*	390±20^{c}	720±60^{d}	70±40^{a}	**310±260**
Na	*10.35±0.32^{a}*	8.01±0.68^{b}	7.99±0.32^{b}	8.02±1.06^{b}	3.94±0.43^{c}	**7.66±2.31**
Ni	12.98±0.66^{a}	*0.45±0.06^{b}*	12.64±0.63^{a}	*0.71±0.05^{b}*	*1.34±0.18^{b}*	**5.62±6.57**
Pb	1.27±0.17^{a}	9.51±1.44^{c}	*4.31±0.15^{b}*	*5.99±1.11^{b}*	*5.49±1.03^{b}*	**5.31±2.98**
Sb	6.04±0.12^{a}	0.67±0.06^{d}	*2.19±0.05^{b}*	0.44±0.07^{d}	1.39±0.19^{c}	**2.15±2.28**
Si	5.73±0.09^{a}	1.4±0.17^{d}	*5.15±0.23^{b}*	1.27±0.08^{d}	2.71±0.16^{c}	**3.25±2.09**
V	*4.3±0.16^{a}*	0.53±0.02^{c}	*4.18±0.17^{a}*	0.73±0.12^{c}	1.75±0.26^{b}	**2.3±1.83**
Zn	23.18±1.04^{b}	*19.23±0.95^{ab}*	43.99±2.06^{d}	37.83±4.1^{c}	*13.99±0.92^{a}*	**27.64±12.73**
TE	*34140±1450^{ab}*	*29160±1470^{ab}*	*35670±1570^{a}*	27420±2420^{b}	12260±4770^{c}	**27730±9290**

$^{a, b, c, d,}$ same superscripts, underline and italics express similarity between means. Different superscripts show significant difference ($p < 0.05$).

Results of analysis of variance test (ANOVA) comparing means of elements between sites showed that EFs of Ca from study sites 1 and 3 were significant ($p < 0.05$) different from study sites 2 and 4 while both groups were different form EF of Ca from study site 5. EFs of total elements (TE) of study site 3 was different form study sites 4 and 5, and EF of TE of study site 5 was different from study

sites 1, 2 and 4 (Table 2.18). Emission factor of $PM_{2.5}$ from MDF showed significant ($p < 0.05$) negative correlation with EF of Al in ash samples of MDF.

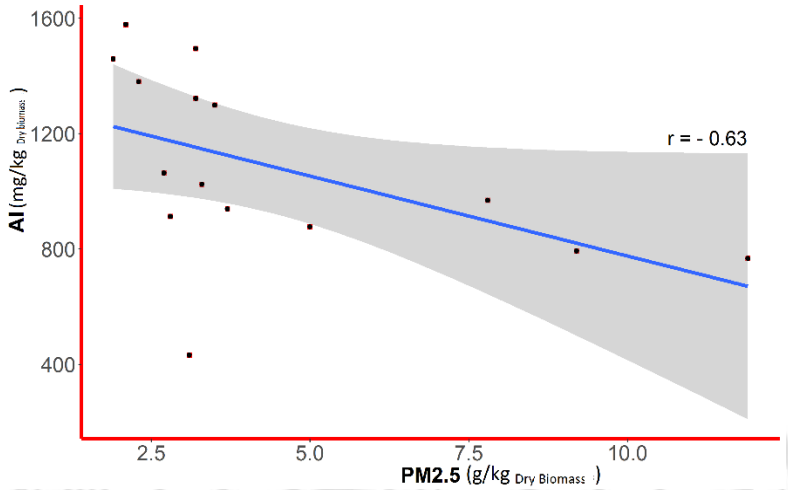

Figure 3.12 $PM_{2.5}$ correlation with Al in ash from MDF burning.

3.3.5 Elemental composition of ash samples from BB

Comparing number of detected elements in composition of ash samples from agricultural residues (RS and MR) and forest leaf litter samples from dry dipterocarps and mixed deciduous forests, As and Sn which were detected in composition of ash remained from burning RS were not found in composition of ashes from other biomass samples. Ni which was present in composition of ash from forest leaf litters was absent in composition of ash left over from agricultural biomass samples.

Though the 6 major elements (Al, Ca, Fe, K, Mg and Mn) remained the same in composition of ash from agricultural and forest biomasses, but the most abundant element in composition of ash from agricultural biomass was K, while in forest biomass it was Ca. Other constituents in composition of ash from both biomass types did show considerable difference (Figure 3.13).

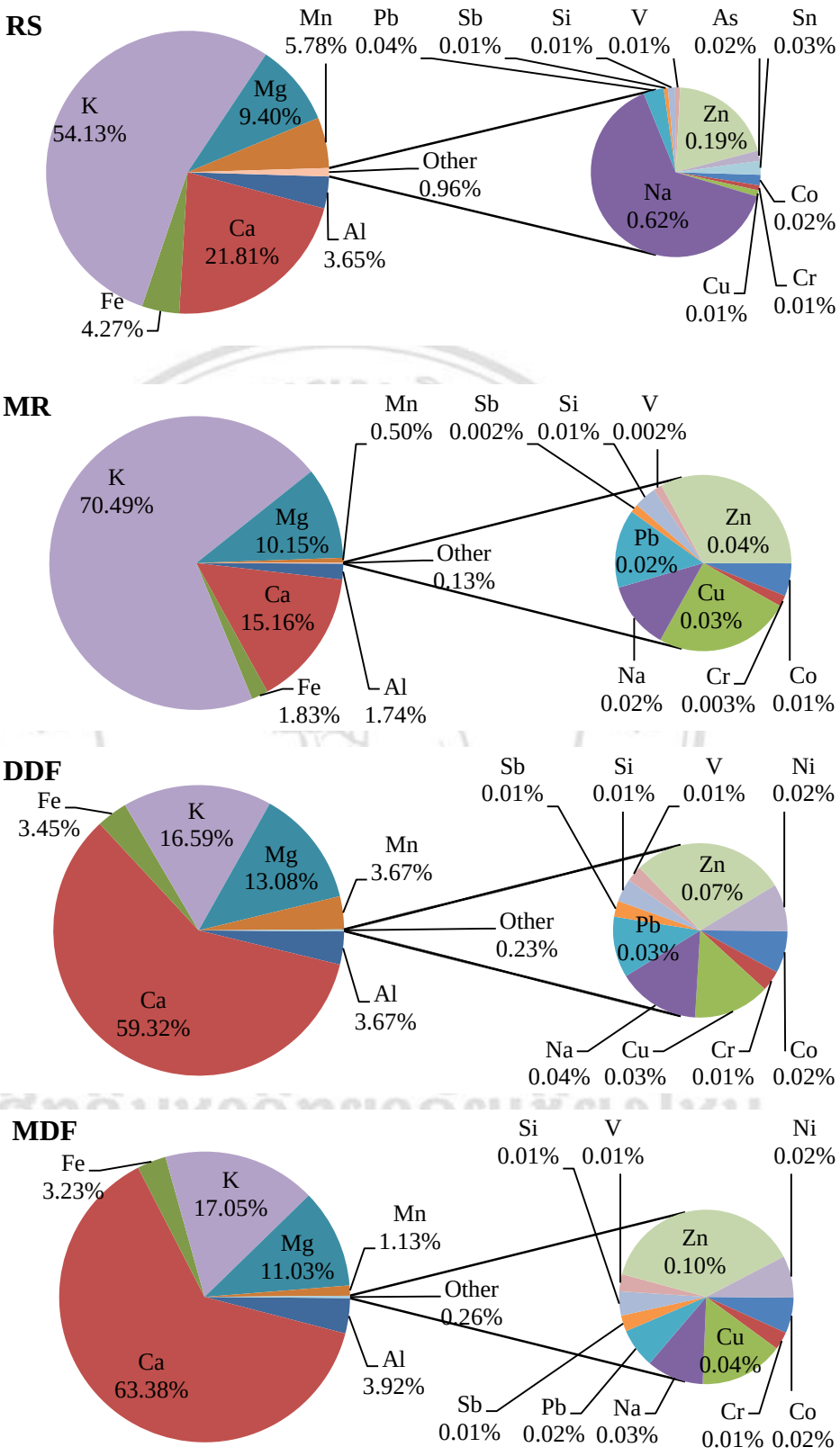

Figure 3.13 Percent of elements in composition of ash samples from the burning of all biomass types.

EFs of mentioned major elements from agricultural biomass samples were considerably higher than that in flying ash studied by (Lanzerstorfer, 2015) while the trend from higher EF to lower was identical, and similar trend was true for EFs of major elements from ash of forest biomass. The major elements in composition of ash from agricultural were higher than EFs of same elements in bottom ash of power plant studied by (Dahl et al., 2010) except Ca and Mg which were lower. EFs of Ca, K, Mg, Al, Fe and Mn from ash of forest studied in this study were lower comparing to EFs of same elements from ash of various forest biomass types studied by (Wang & Dibdiakova, 2014) despite the trend from higher to lower EFs remained alike. From major elements in composition of ash from agricultural biomass K was most abundant element which is understandable as main ion of plant and is up taking large amounts of potassium (K), which is mainly supplied from inorganic fertilizer (Sarkar et al., 2017). K and calcium ions plays a crucial role in regulation of xylem cell expansion and a significant influence of Ca ion on the onset of cambial reactivation after winter dormancy as well as on wood structure and chemistry (Fromm, 2010). Magnesium (Mg) is an important nutrients, involved in many enzyme activities and the structural stabilization of tissues, and Mg deficiency in plants cause severe health problem (Guo et al., 2016). Al is one of the plentiful elements in earth crust and its toxicity is a major concern particularly during acidic rain and in the texture of acidic soil (Singh et al., 2017). Fe and Mn are important nutrient (essential elements) for growth of plants and for food production and productivity respectively. Excess manganese is toxic (Millaleo et al., 2010), so burning of biomass can increase mobility of manganese and increase concentration in the lower agricultural and forest areas. EFs of remaining 11 elements (Na > Zn > Pb > Cu > Co > Sn > As > Si > Cr > V > Sb) from ash agricultural biomass and 10 elements (Zn > Cu > Na >Pb> Ni > Co > Si > Cr > V > Sb) from ash of forest biomass were very low comparing to two 6 major element. For most of minor elements, the measured EFs in the composition of ash from agricultural biomass combustion are lower compared to the results published by (Aguiar del Toro et al., 2009; Smriti Singh et al., 2011) except As. Elements in the composition of ash from forest were very closed and higher than result reported by (Sano et al., 2013). Most of elements

appeared with lower EF are toxic and have significant environmental impact (Estrellan & Iino, 2010; Tchounwou et al., 2012; Winship, 1988).

Table 3.19 Elemental composition of ash remained from BB (mean ± SD).

Element	EF of elements (mg/kg$_{Dre\ biomass}$) (n = 15)			
	Agricultural biomass		Forest biomass	
	RS	MR	DDF	MDF
Al	730±400^{a}	320±170^{c}	*940±490*^{ab}	*1100±300*^{b}
Ca	4400±500^{a}	2800±1400^{a}	15200±8800^{b}	17600±6000^{b}
Co	*3.90±2.09*^{a}	1.46±0.76^{b}	*4.61±2.13*^{a}	*4.80±2.61*^{a}
Cr	*1.82±0.52*^{ab}	*0.49±0.17*^{a}	2.25±1.24^{b}	2.4±2.09^{b}
Cu	*2.27±0.86*^{a}	6.05±2.00^{b}	8.37±4.45^{b}	11.31±2.82^{c}
Fe	*900±400*^{a}	340±190^{b}	*890±480*^{a}	*900±560*^{a}
K	10,800±4,260^{a}	13,100±6,170^{a}	*4,300±1,200*^{b}	*4,700±2,000*^{b}
Mg	*1,900±200*^{a}	*1,900±800*^{a}	3,400±100^{b}	3100±1100^{b}
Mn	1200±700^{a}	*93.55±25.34*^{b}	940±460^{a}	*314±241*^{b}
Na	124±80^{a}	*3.00±1.73*^{b}	*9.01±2.6*^{b}	*7.66±2.21*^{b}
Pb	*7.49±5.42*^{a}	*3.49±1.89*^{a}	*6.65±5.31*^{a}	*5.31±2.87*^{a}
Sb	*1.51±0.73*^{ab}	*0.37±0.1.89*^{a}	1.75±1.17^{b}	2.15±2.11^{b}
Si	*2.64±1.03*^{a}	0.99±0.41^{b}	*2.53±1.66*^{a}	*3.25±1.94*^{a}
V	*1.87±1.05*^{a}	0.38±0.31^{b}	*1.75±1.35*^{a}	*2.30±1.70*^{a}
Zn	38.75±7.62^{a}	7.79±2.84^{b}	16.87±5.57^{c}	*27.64±11.93*^{d}
Ni	ND	ND	5.16±3.15	5.62±6.09
Sn	5.09±0.77	ND	ND	ND
As	3.76±1.44	ND	ND	ND
Total	*20000±3800*^{a}	*18600±5600*^{a}	*25700±10400*^{ab}	27700±8900^{b}

$^{a, b, c, d,}$ same superscripts, underline and italics express similarity between means. Different superscripts show significant difference ($p < 0.05$).

Analysis of variance test showed that EFs of K in composition of agricultural biomass residues (RS and MR) and forest leaf litters biomass (MDF and DDF) burning experiments are significantly ($p < 0.05$) different from each other, while EF of K did not show significantly different among RS and MR (agricultural residues) and DDF and MDF (forest leaf litters). EF of Ca as most plentiful element in composition of forest biomass followed the same trend as EF

of K in both agricultural and forest biomass. EF of Mg showed exactly the same behavior to EFs of K and Ca. Only means of EFs of Pb were not significantly different between ash samples of all biomass types while EFs of Zn are significantly different between all biomass types, details are given in Table 3.19. Percent EFs of six major elements in composition of ash samples from agricultural biomass burning in descending order were K (62.01 %), Ca (18.61 %), Mg (9.76 %), Mn (3.24 %), Fe (3.10 %) and Al (2.73 %) and in forest biomass were Ca (61.42 %), K (16.83 %), Mg (12.02 %) , Al (3.80 %), Mn (3.35 %) and Fe (3.33 %). EF of major elements in both agricultural and forest biomasses totally comprised more than 99% of overall mass of detected and measured elements. As shown in Figure 3.14, EF of Na was dominant in minor elements of ash from agricultural biomass, while EF of Zn was highest in ash from forest biomass.

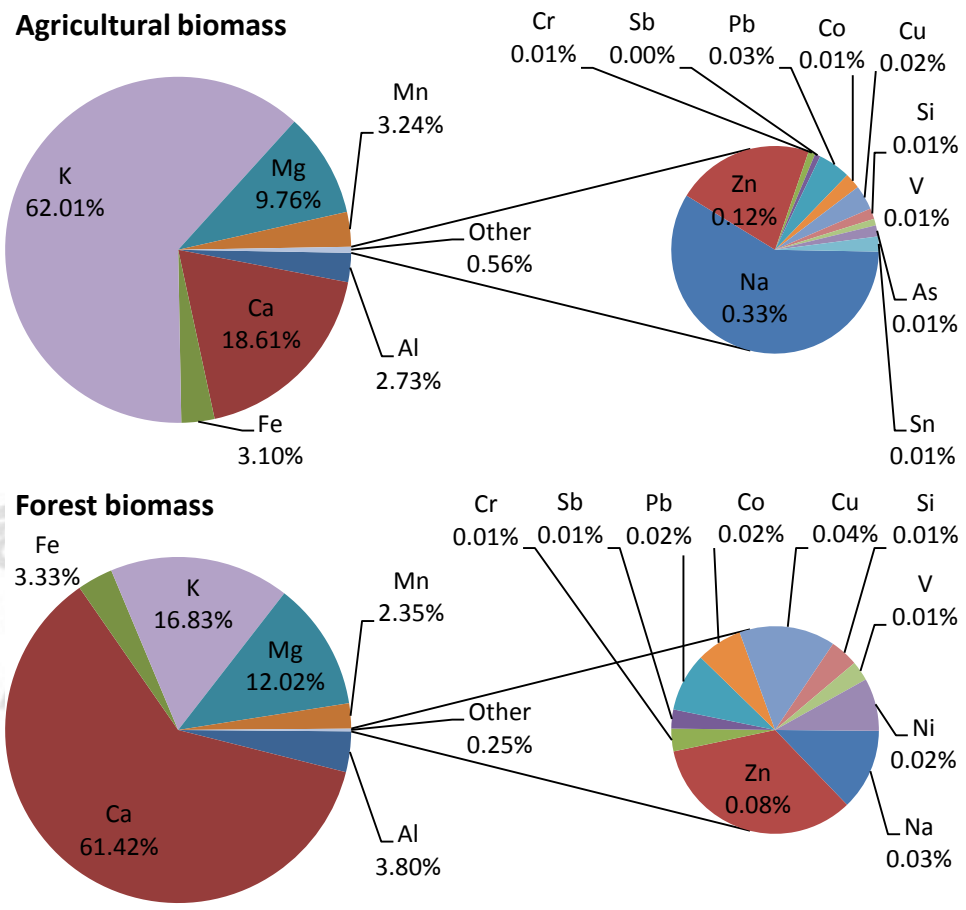

Figure 3.14 Overall percentage of elements in ash samples.