CHAPTER 6
ESTIMATION OF EMISSION FACTOR OF CARBONACEOUS COMPOUNDS

6.1 Materials and Methods

6.1.1 Emission Concentration

Emission information is obtained in two forms of emission ratios and emission factors. The emission ratio and emission factor relate the emission of a compound of interest and the emission to the amount of fuel burned, respectively. The raw data is retrieved from the real-time equipment. The unit of CO (ppm), CO_2 (ppm) and BC ($\mu g/m^3$) concentrations were converted to mg/m^3 of emission concentrations after subtracting the background concentrations as shown below.

$$CO, CO_2\ (ppm) \times MW/V_{gas} = CO, CO_2\ (mg/m^3) \quad \text{Equation 6.1}$$

$$BC\ (ng/m^3) \times 10^{-6} = BC\ (mg/m^3) \quad \text{Equation 6.2}$$

where: MW is molar weight, i.e. 28g/mol for CO and 44 g/mol for CO_2 and V_{gas} is the volume of i mole of gas interest at measurement T°, which can be calculated by

$$V_{gas} = (V_{25}/T_{25}) \times T_{gas} \quad \text{Equation 6.3}$$

where: V_{25} is the volume of air at 25°C (24.45 L/mole), T_{25} is the temperature at 25°C in unit K (25+273.15 = 298.15 K) and T_{gas} is the temperature of gas/or smoke plume at measurement T (°C) plus T (273.15 K).

The estimation of emission concentrations of $PM_{2.5}$ were considered by the equation below,

$$PM_{2.5}\ (mg/m^3) = PM_{2.5}\ (\text{emission concentration-background concentration}) \quad \text{Equation 6.4}$$

The concentrations of gases CO_2 and CO in unit ppm was calculated by subtracting the median of background concentration before changing to concentration in mg/m^3. In the same manner, the temperature of the emission concentration of these gases, the median value of background temperature was subtracted from the temperature of gases released from biomass burning before used to estimate the volume of emission air.

After calculating the concentration, BC and $PM_{2.5}$ concentrations were converted in the unit of mg/m^3, and we can estimate the emission in unit $g/kg_{\text{dry biomass burned}}$ using the following equation:

$$E_i = M_i \times EF_i \qquad \text{Equation 6.5}$$

where: E is the emission air pollutant i (g/m^3), EF is emission factor of i ($g_{species}/kg_{\text{dry biomass burned}}$) and M is amount of biomass burned (g).

The amount of biomass consumed was estimated by the area burned, biomass fuel loads and combustion completeness (Garivait *et al.*, 2008) calculated as follows:

$$M = A \times BL \times CC \qquad \text{Equation 6.6}$$

where: A is area burned (hectares), BL is biomass fuel loads (kg) and CC is the combustion completeness (%).

Combustion completeness is estimated by weight of the aboveground biomass before burning and record as B_{before}. Then set up a prescribed burn and collect residue after burned, which consists of unburned part and ash part. The unburned part is weighed and recorded as B_{after}.

$$CC(\%) = \frac{B_{before} - B_{after}}{B_{before}} \times 100 \qquad \text{Equation 6.7}$$

where: CC is combustion completeness (%), B_{before} represents amount of aboveground biomass before burned (g/m^2), B_{after} is amount of unburned part of biomass after burned (g/m^2).

In this study, the biomass fuel loads and combustion completeness were used to calculate based on Equation 6.6 or estimated directly from the ratio of emission and biomass fuel consumed, which can be written as:

$$EF_i = \frac{E_i}{B_C} \qquad \text{Equation 6.8}$$

where: E is the emission air pollutant i (mg/m^3), EF is emission factor of i ($mg_{species}/g_{\text{dry biomass burned}}$) and B_C is biomass fuel consumed per volume (g/m^3). Finally, the unit of emission factor was converted to unit $g/kg_{\text{dry biomass burnt}}$.

6.1.2 Carbon Mass Balance Estimation Method

The carbon mass balance (CMB) of a chemical reaction is defined as:

$$C_{\text{input}} = C_{\text{output}} \qquad \text{Equation 6.9}$$

In case of biomass combustion, Equation 6.9 can be expressed as:

$$C_{biomass} = C_{ash} + C_{oxidized\ or\ released} \qquad \text{Equation 6.10}$$

where: $C_{biomass}$ is the amount of carbon in biomass consumed (gC/m^2) and C_{ash} is the amount of carbon in ash and residues after burning such as charred leaf (gC/m^2), $C_{oxidized\ or\ released}$ is the amount of carbon oxidized or released to the atmosphere (gC/m^2),

The carbon content of biomass fuel was used to estimate the amount of carbon oxidized and released in the emission. The CMB or carbon mass balance method (Ward *et al.*, 1979 and Radke *et al.*, 1990) was used to calculate the carbon oxidized related to the carbon in biomass before and after burning. The general equation to calculate the CMB in biomass combustion is illustrated in Equation 6.10:

The CMB method was used to estimate the emission factor of CO_2 because carbon dioxide is the main form of carbon released to the atmosphere with a share higher than 90% of the total carbon released (Reid *et al.*, 2004; Andreae and Merlet, 2001). In this study, the emission of assumed to be 95% of the total carbon released. The emission factor of CO_2 can be written as:

$$EF_{CMB-CO2}(g/kg_{dry\ biomass\ burned}) = \frac{0.95 \times C_{oxidized} \times 44 gCO_2}{12 gC} \qquad \text{Equation 6.11}$$

where: *0.95* is a factor of carbon released from the leaf litter in to the atmosphere, $C_{oxidized}$ is quantify directly from field experiment based on CMB method ($C_{oxidized} = C_{biomass} - C_{ash+charred\ leaf}$) in unit g/kg $_{\text{dry biomass}}$, *44* g CO_2 is the molecular weight of CO_2 in unit g and *12* g C is the molecular weight of carbon in unit g.

Also, we used the CMB method to obtain the dilution factor of pollutant released to the atmosphere by the ratio of emission factor estimation from CMB method to emission factor calculation from the field experiment.

$$Dilution\ factor_{CO_2} = EF_{CMB-CO_2}/EF_{FE-CO_2} \qquad \text{Equation 6.12}$$

where: $EF_{CMB\text{-}CO2}$ and $EF_{FE\text{-}CO2}$ are the emission factor of CO_2 that calculated from the CMB method by Equation 6.10 and emission factor estimation from field experiment, respectively.

Finally, the emission factors of all pollutant released to the atmosphere in the unit of g/kg $_{\text{dry biomass burned}}$ can be calculated by multiplying the dilution factor from Equation 6.12.

6.1.3 Emissions of Carbonaceous Aerosols (BC and OC)

BC and OC are the solid components of particulate matter found in the fine fraction of the atmospheric particles ($PM_{2.5}$). The emissions of BC and OC from forest fires were estimated by the BC to total carbon (TC) ratio. OC is calculated by

$$TC=BC+OC \qquad \text{Equation 6.13}$$

where: *TC* is total carbon, *BC* is black carbon and *OC* is organic carbon, respectively. BC is measured by real-time measurement using Aethalometer. TC is assumed to represent 60% of the $PM_{2.5}$ total mass (Ward *et al.*, 1992)

6.2 Results and Discussion

6.2.1 Background and Emission Concentration of Gases and Black Carbon

Background Concentrations

Table 6.1 presents the median values of background concentration of CO_2, BC and $PM_{2.5}$ that retrieved from the real-time equipment set up in the field equipment box (FEB) in DDF1, MDF1 to 3. Background concentration of DDF1 is comparable to these found for the 3 plots in MDF.

Table 6.1 Background concentrations of CO_2, CO, BC and $PM_{2.5}$ from prescribed fires in DDF and MDF (plots)

Forest type	Background concentrations			
	CO_2 (ppmv)	CO (ppmv)	BC (mg/m^3)	$PM_{2.5}$ (mg/m^3)
DDF1	458.25	4.33	0.006	0.08
MDF1	636.00	0.88	0.001	0.07
MDF2	796.50	1.59	0.004	0.15
MDF3	365.00	3.37	0.004	0.10

Table 6.2 Emission concentrations of CO_2, CO, BC and $PM_{2.5}$ from prescribed fires in DDF and MDF (plots)

Forest type	Emission concentrations			
	CO_2 (ppmv)	CO (ppmv)	BC (mg/m^3)	$PM_{2.5}$ (mg/m^3)
DDF1	889.76	50.16	0.423	5.16
MDF1	916.00	26.45	0.027	4.64
MDF2	982.00	23.11	0.212	6.21
MDF3	562.00	20.04	0.076	2.13

Emission Concentrations

The emission concentrations in Table 6.2 were conducted from prescribed fires in both DDF and MDF plots. The emission data of gases and aerosols from experiment set up

in DDF3 and 4 are not reported problem of field equipment measurements during fire. The pollutants of interest in the emissions from tropical deciduous forest fire consist of CO_2, CO, BC and $PM_{2.5}$. These emission values in Table 6.2 were subtracted from the background concentration reported in Table 6.1.

Table 6.3 Net emission concentrations of CO_2, CO, BC and $PM_{2.5}$ from prescribed fires in DDF and MDF (plots)

Forest type	Net emission concentrations (mg/m^3)				TC in $PM_{2.5}$ ($mg\ C/m^3$)	OC[a] (mg/m^3)	CO/CO_2	$BC/PM_{2.5}$
	CO_2	CO	BC	$PM_{2.5}$				
DDF1	721.48	48.82	0.42	5.09	3.05	2.63	0.068	0.082
MDF1	564.84	36.30	0.09	11.82	7.09	7.00	0.084	0.053
MDF2	463.93	29.77	0.25	7.71	4.63	4.38	0.064	0.032
MDF3	321.46	19.38	0.24	4.60	2.76	2.52	0.060	0.052

[a] calculation from OC= TC-BC

Table 6.3 presents the net emission concentrations that were converted to units of mg/m^3 in both DDF and MDF plots (detailed real-time measurement profiles are reported in Appendix D). In DDF1, CO_2 and CO emission concentrations are higher than MDF plots. MDF3 is released CO_2 lower than the other plots of the same forest type. The average of CO_2, CO, BC and $PM_{2.5}$ concentrations in MDF are 450.78±70.60, 28.48±4.98, 0.19±0.05 and 8.04±2.09, respectively. The CO/CO_2 ratio showed that the CO produced is higher than CO_2 in all plots. The highest $BC/PM_{2.5}$ ratio was found for the DDF plots which showed that BC is high concentration released from DDF fires than MDF fires but still lower than the concentration of OC (Table 6.3). On the other hand, for of MDF plots, $BC/PM_{2.5}$ ratio is lower than DDF and the OC concentration are 7.00, 4.38 and 2.52 mg/m^3 in MDF1, MDF2 and MDF3, respectively. It was showed that the emission concentration of OC in MDF is higher than 90%. In addition, the TPM collected on filter in MDF is brown color (Chapter 5) that is the major composition of OC.

6.2.2 Emission Factors

The emission factor of pollutants released from prescribed fire in both DDF and MDF is illustrated in Table 6.4. The dilution factor of in DDF is very close to 1000 and in

MDF it never exceeded 1000 (Table 6.4). Although the behavior of the fires and the moisture content is very close in both DDF and MDF, the dilution factors are still different in both forests. In DDF, plots the emission factor of CO_2 is the highest in DDF1 followed by DDF3 and DDF4 which should be related to the fireline intensity presented in Table 4.2, indicating that in the DDF1, DDF3 and DDF4 the fireline intensity were 95.48, 36.90 and 36.06 kW/m, respectively. It can be suggested that the fireline intensity influence to the emission factor of CO_2. The information of fireline intensity seems to represent one of parameters that can support to predict the emission factor of CO_2 released from forest fire, and is suggested to the taken in account in a model development in the future. The overall CO_2 emission factors are the same order magnitude for all DDF plots. In addition, the emission factor of CO_2 in both DDF3 and DDF4 plots was calculated based on CMB in biomass (Equation 6.10) because of problems of field equipment measurements as mentioned previously.

In the MDF plots, the emission factor of CO_2 is the highest in the MDF2 followed by MDF1 and MDF3, which is also in the same order as the fireline intensity presented in Table 4.4 forMDF1, MDF2 and MDF3 are 45.57, 111.92 and 32.49 kW/m, respectively. The emission factor of CO, BC, OC and $PM_{2.5}$ were also the highest in MDF2 due to the highest fuel load, fireline intensity and combustion completeness as well (Table 4.4). The fireline intensity in MDF3 and MDF4 were lower than 50 kW/m.

Table 6.4 Emission factors of CO_2, CO, BC and $PM_{2.5}$ and emission ratio of gas to aerosols from prescribed fire in DDF plots.

Forest type	Emission factor (g/kg $_{dry\ biomass}$)						Dilution factor	MCE
	CO_2	CO	BC	OC	$PM_{2.5}$	TC		
DDF1	1,449.07	98.05	0.84	5.29	10.22	6.13	864	0.93
DDF3	1,414.96	ND	ND	ND	ND	ND	ND	ND
DDF4	1,384.42	ND	ND	ND	ND	ND	ND	ND
Average	1,416.15							
SE	18.64							

ND means no data.

Table 6.5 Emission factors of CO_2, CO, BC and $PM_{2.5}$ and emission ratio of gas to aerosols from prescribed fire in MDF plots.

Forest type	Emission factor (g/kg $_{dry\ biomass}$)						Dilution factor	MCE
	CO_2	CO	BC	OC	$PM_{2.5}$	TC		
MDF1	1,149.07	73.85	0.19	14.23	24.04	14.42	335	0.90
MDF2	1,216.79	78.09	0.65	11.49	20.23	12.14	717	0.89
MDF3	1,071.15	64.57	0.79	8.40	15.23	9.19	465	0.92
Average	1,145.68	72.17	0.54	11.37	19.86	11.92	505	0.90
SE	42.08	3.99	0.18	1.68	2.52	1.51	112	0.01

Modified Combustion Efficiency (MCE)

Emission factor of CO_2, CO, BC and $PM_{2.5}$ were calculated from the real-time emissions released from prescribed fire and using the reference gas of CO_2 to quantify the dilution factor. The amount of biomass burned in DDF1, MDF1, MDF2 and MDF3 are constant values as 430.41, 265.28, 533.11 and 171.94 g $_{dry\ biomass}$ and the dilution factor are 864, 335, 717 and 465, respectively. The overall of combustion phase that was showed in Tables 6.4 and 6.5 and Figures in Appendix D in both DDF and MDF is flaming dominant that related to the literature reports CC>0.90 for flaming biomass burning and 0.75<CC<0.85 for smoldering (Babbitt *et al.*, 1996). MCE can be low for a value of reason, including high moisture content of leaf litter and degree of fuel packing. However, in this study the moisture content of leaf litter less than 10% in both DDF and MDF. It suggested that the degree of fuel packing influence the variation of combustion phase dominant in both forest types.

Emission Factor of Carbonaceous Aerosols

The emission concentrations of OC are calculated from TC in $PM_{2.5}$ with assumption that TC represented 60% of the total mass of $PM_{2.5}$, as indicated by Ward *et al.* (1992). In DDF1, the emission factor of OC is 6.11 $g/kg_{dry\ biomass}$. For MDF plots, the emission factor of OC in MDF1, MDF2 and MDF3 are 7.12, 11.99 and 4.43 $g/kg_{dry\ biomass}$, respectively. The average of emission factor of OC in MDF is the same order of magnitude with DDF plots. The emission factor of BC is 0.07, 0.73 and 0.28 $g/kg_{dry\ biomass}$ in MDF1, MDF2 and MDF3, respectively. The BC/$PM_{2.5}$ ratio showed that the BC released from DDF plot prescribed fires is higher than from MDF plots. This is continued by the colour

of TPM collected on filter being black to gray in DDF plots (Figure 5.1 and 5.2). The relationship between fireline intensity and emission factor of BC showed good agreement for DDF1, MDF2 and MDF3 plots except MDF2. The greater BC emission factor in DDF1 and MDF2 suggested that the fireline intensity is one of the parameters influencing the emissions of BC, and it would be recommended to develop a numerical model to predict the emission of BC using the fireline intensity data in the future. In addition to the fireline intensity but also the leaf litter type that is produced from the different of forest type is influence the carbon released and emission factor of gas and aerosol from forest fire. However, the emission factor of the other composition in aerosols such as water-soluble and elemental cannot quantify due to the field equipment for TPM collected on filter had problem during sampling.

Table 6.6 Comparison of emission factors of compounds of interest emitted from DDF and MDF fires

Forest type	EF(g/kg $_{\text{dry biomass burned}}$)					
	CO_2	CO	BC	$PM_{2.5}$	TPM	OC
DDF	1,416±19	98	0.84	10.22	-	5.29
MDF	1,146±42	72±4	0.54±0.18	19.86±2.52	-	11.37±1.51

Comparison of emission factors of compounds of interest emitted from DDF and MDF fires. The average values of the emission factor of CO_2, CO, BC and $PM_{2.5}$ in DDF and MDF are presented in Table 6.6. The emission factors of CO_2 and CO in DDF were higher than in MDF. The ratios of BC and $PM_{2.5}$ showed that the flaming phase was dominant and the average of combustion completeness was also higher than 80% in DDF plots (Table 4.2).

The comparison of emission factors data in Table 6.6 showed that the overall emissions factor of CO_2 in other research studies were higher than in this study. The tropical forest and extra tropical forest, especially BC and $PM_{2.5}$ emission that found factors and the ratio of CO to CO_2 are of the same order magnitude with MDF experiment. OC emission factor from DDF is the lowest while the ratio of BC to $PM_{2.5}$ is the highest (Tables 6.6 and 6.3).

6.2.3 Estimation of the Emission Factors by Other Methods

Carbonaceous aerosols released from burning of leaf litters in DDF and MDF have also different fractions of BC and OC. Emissions of BC released from DDF are higher concentration than MDF. This suggested that the composition of leaf litter plays an important role in the replace of carbonaceous aerosols to the atmosphere. The estimation method of emission factor of a pollutant emitted from forest fire can be compared to other methods.

Table 6.7 Mass of carbon associated with each of the analyzed pollutant, mass of biomass consumed, and % carbon associated to CO_2 released from leaf litter burning in DDF and MDF plots

Plot	Carbon (mg/m^3)						Mass of biomass consumed (g/gC)	$\%C_{CO2}$
	$m_{C\text{-}CO2}$	$m_{C\text{-}CO}$	$m_{C\text{-}BC}$	$m_{C\text{-}PM2.5}$	$m_{C\text{-}OC}$	$m_{C\text{-}total}$		
DDF1	196.75	20.92	0.42	3.05	2.63	220.72	2.40	89.14
MDF1	153.38	15.71	0.09	7.09	7.00	176.17	3.03	87.06
MDF2	109.26	12.78	0.25	4.63	4.38	126.91	2.86	86.09
MDF3	95.55	9.08	0.24	2.76	2.52	107.63	3.25	88.78

The amount of carbon associated with each analyzed compound reported in calculated using the equation established by Neto et al. (Neto *et al.*, 2009). The amount of carbon associated to CO_2 in DDF1, MDF1, MDF2 and MDF3 plot was 196.75, 153.38, 109.26 and 95.55 mg/m^3, respectively. The total amount of carbon emitted from both DDF and MDF plots was calculated from the biomass consumed for each gram of carbon emitted reported in Table 6.7. The amount of carbon associated in CO_2, CO and BC was the highest in DDF1. The amount of carbon associated to CO_2 in MDF plot was varied from 95 to 150 mg/m^3. The fraction of $PM_{2.5}$ which includes BC and OC were estimated from the total carbon associated to $PM_{2.5}$. The total carbon (TC) was assumed to represent 60% of total was of $PM_{2.5}$ following the finding of Ward et al. (Ward *et al*, 1992). The OC mass is one of the fractions of TC mass associated to $PM_{2.5}$. The overall of OC mass in MDF is higher than in DDF1. Based on the mass of carbon associated with BC in MDF cases, which is two times lower than that in DDF1, it was suggested that the emission factor of BC released from DDF is higher than that from MDF, and the emission factor of

OC released from MDF is more dominant than OC released from DDF as well. The mass percent of mass of carbon associated to CO_2 is of the same range for all plots, and also never exceeded 90% when calculated from the total mass of carbon associated to CO_2, CO, and $PM_{2.5}$ (Table 6.7).

$$m_{C-CO2}(mg/m^3) = \frac{[CO_2] \times M_{CO2} \times 10^3 mg \times 12\ gC}{V_{co2} \times 10^{-3} m^3 \times 44g\ CO_2}$$
$$= 196.75\ \text{mg/m}^3,$$

where: $[CO_2]$ is the net concentrations of CO_2 in ppmv V_{CO2} is 24.5 L for 1 mole of CO_2 at 25 °C and 1 atm, and M is the molecular weight of CO_2.

The carbon mass associated with the other pollutants released from biomass burning in each plot was calculated in a similar manner as shown in Table 6.8.

$$EF_{CO2}(g/kg_{dry\ biomass}) = \frac{C_1 \times 44 \times 1000}{12 \times g_{biomass\ burned} \times C}$$
$$= 1{,}361.85\ \text{g/kg}_{\text{dry biomass}}$$

where: C_1 is the mass of carbon emitted in the form of CO_2 (=196.75 mg/m^3), $g_{biomass\ burned}$ is calculated from each gram of carbon released from the amount of biomass burned (Table 6.6) and C is the total carbon mass of all carbon-bound pollutants released (=220.72 mg/m^3) as illustrated in Table 6.7.

Table 6.8 Emission factors in unit gram of gas per kilogram of dry biomass burned.

Plot	Emission factor (g/kg $_{\text{dry biomass}}$)				
	EF_{CO2}	EF_{CO}	EF_{BC}	$EF_{PM2.5}$	EF_{OC}
DDF1	1,361.85	92.15	0.79	5.76	4.97
MDF1	1,053.54	68.65	0.18	13.28	13.11
MDF2	1,103.69	82.16	0.68	12.75	12.06
MDF3	1,001.63	60.56	0.68	7.89	7.21

The emission factors in Table 6.8 were calculated from the data of real time measurements from the field experiment and based on the equation of Neto et al. (Neto *et al.*, 2009). The emission factor of CO_2 is the highest in DDF1 followed by MDF2, MDF1 and MDF3 that was 1361.85, 1104.69, 1053.54 and 1001.63 $g/kg_{dry\ biomass}$, respectively. The difference of emission factor calculated by two different methods is due to the percentage of carbon emitted in the form of CO_2 in this study was assumed to be 95% of the total carbon released from the biomass burning. While the emission factors of CO_2 from Table 6.8 were based on the percentage directly calculated from the carbon associated to CO_2, CO and $PM_{2.5}$ directly measured. The percentage of carbon associated to CO_2 shown in Table 6.7 was lower than 95% of the assuming carbon associated in the form CO_2 of this study.

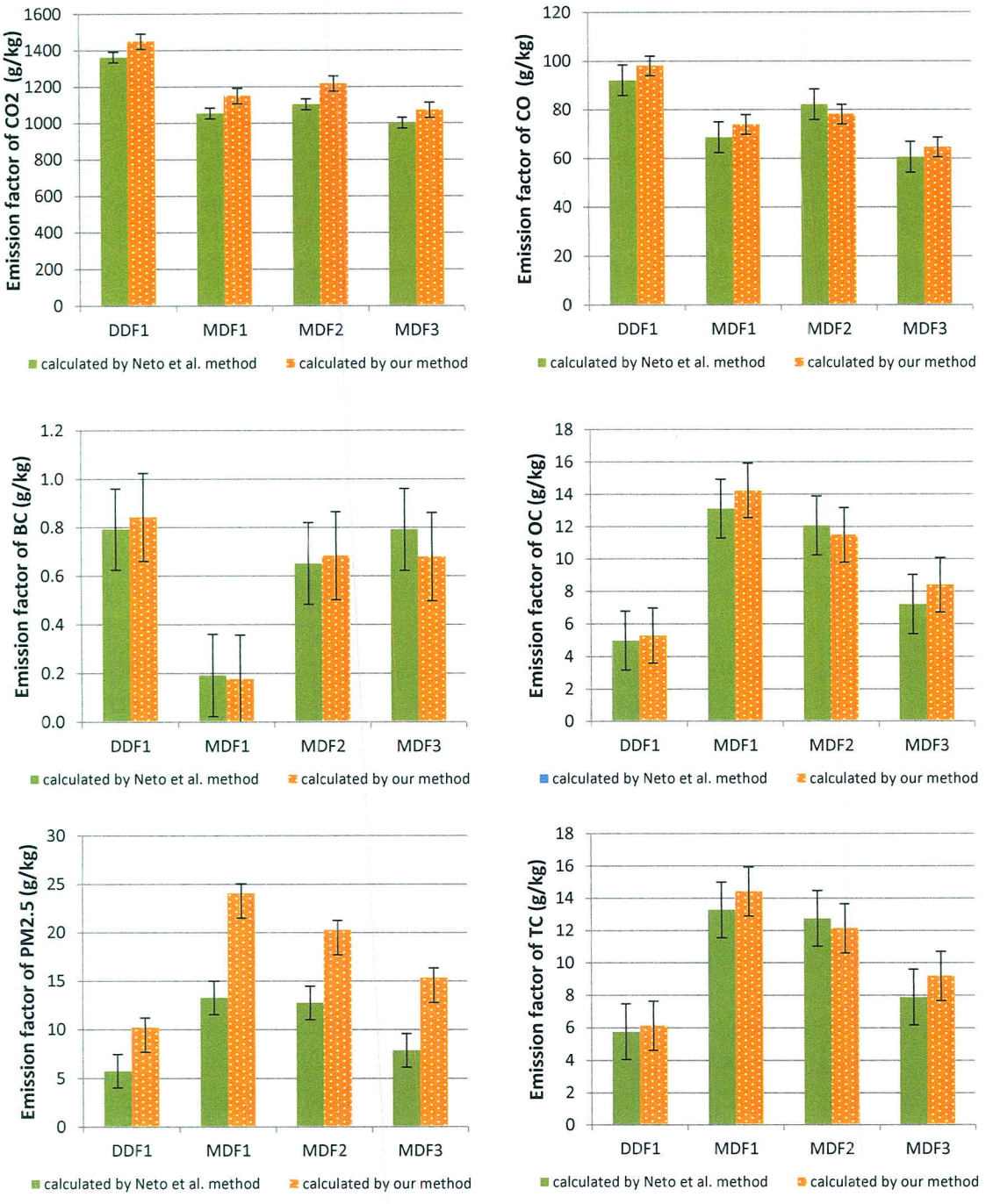

Figure 6.1 Comparison of emission factors of CO_2, CO, BC, CO, $PM_{2.5}$ and TC calculated by Neto et al. method (Neto *et al.*, 2009) and by our method

The emission factor of $PM_{2.5}$ found in this study is higher than the reference experiment method that directly calculated from the real-time measurement data from the field. On the other hand, the emission factor of carbon associated to $PM_{2.5}$ represents the emission factor of TC. Then based on the $PM_{2.5}$ to be composed of 60% carbon, the

emission factor of $PM_{2.5}$ in this study is the same order of magnitude with the emission factor of $PM_{2.5}$ computed by Neto et al. (Neto *et al.*, 2009) method as shown in Figure 6.1.

6.3 Summary of Findings

- The emission factor estimation from field experiments should use in the CMB method because the emission concentration was diluted in the atmosphere.
- CO_2 is the major gas emitted from burning and used as reference gas to estimate the dilution factor.
- Carbonaceous aerosols in $PM_{2.5}$ emitted from DDF are majorly composed of BC (>60%), while in MDF the organic carbon dominated. It was shown that the BC/TC ratio in DDF is higher than MDF and other research studies.
- The emission factor of CO_2 in both DDF and MDF plots is related to the fireline intensity and combustion completeness.
- The biomass fuel physical and chemical properties, and the combustion phase were found to influence the amount of pollutant released to the atmosphere. Each gram of carbon released from biomass burned was also different.
- The emission factors of carbonaceous aerosols from forest fires were estimated from the fraction of $PM_{2.5}$ related to the fireline intensity. The greater fireline intensity is suggested to release a higher amount of BC, and so higher BC emission factor.
- The direct emissions were calculated as the leaf litters consumed during the fires and area burned in Mae Nam Phachi Wildlife Sanctuary, Ratchaburi Province during 2007-2010.