CHAPTER 3

RESULTS AND DISCUSSION

3.1 PM_{10} levels in the studied houses

The PM_{10} levels were measured using personal air sampler (SKC, USA.). The position of personal air sampler in the houses was located about 1.5 meters above the ground. The pumped volume flow rate was 2.0 L/min. The sampling duration in each house was performed for 12 hr for 3 days a week on Monday, Wednesday, and Friday between 06.00 pm to 06.00 am of next morning and the mean levels was obtained for each house. The sampling period was in October 2011 for wet season and January 2012 for dry season. The PM_{10} levels on a quartz filter was determined gravimetrically by weighing the quartz filter before and after sampling using a 5 decimal places microbalance in a clean room at 25 ˚C and less than 50% relative humidity. The PM_{10} levels of each studies and control houses in wet and dry season are shown in Table 3.1.

Table 3.1 PM_{10} levels collected from the studied and control houses during wet and dry season. In each season, PM_{10} samples were collected 3 days

House number	Number of days collected in each season	Mean±SD PM_{10} levels (μg/m^3)	
		Wet season (October, 2011)	Dry season (January, 2012)
S_1	3	255.2±7.1	102.9±63.5
S_2	3	95.0±53.7	112.9±52.6
S_3	3	94.0±20.1	67.7±16.1
S_4	3	131.0±69.6	156.2±114.1
S_5	3	157.1±146.5	202.9±208.5
S_6	3	61.5±26.1	106.9±42.4
S_7	3	43.9±12.2	145.7±68.1
S_8	3	69.9±36.9	221.9±213.9
S_9	3	48.3±13.3	161.1±54.1
S_10	3	209.3±162.4	137.4±29.6
S_11	3	115.8±7.8	190.4±142.1
S_12	3	86.3±9.5	195.9±139.7
S_13	3	250.8±164.3	189.9±40.9
S_14	3	124.8±56.2	283.7±252.4
Mean±SD	**42**	**124.5±70.1**	**162.5±56.5**
Control	6	43.0±18.2	49.6±9.0

In wet season, the lowest and highest of PM_{10} level of the studied houses using wood for cooking were 43.9 (S_7) and 255.2 (S_1) μg/m^3, respectively, while of that the control house was 43.0 μg/m^3. In dry season, the lowest and highest of PM_{10} concentration of the studied houses were 67.7 (S_3) and 283.7 (S_14) μg/m^3, respectively, while of that the control house was 49.6 μg/m^3. The PM_{10} levels of the studied houses are statistically significantly higher than the level of control house in both wet and dry seasons ($p<0.05$). However, there is no significant difference

between the mean PM_{10} levels in wet and dry seasons (p=0.140). Figure 3.1 shows the filters collected from studied and control houses. The different physical characteristic of two filters was obviously visible with the naked eye.

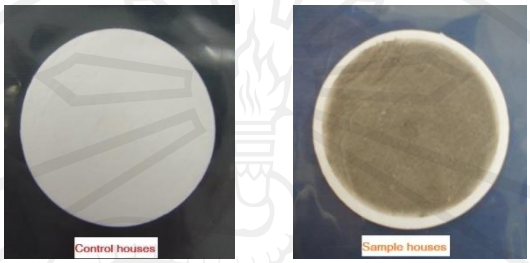

Figure.3.1 PM_{10} on quartz filter collected from the control house, 43.0±18.2 µg/m^3 (wet season) and a studied houses No.1, 255.2±7.1 µg/m^3 (wet season).

3.2 Analytical characteristics

In the present work, the method validation was presented in terms of precision, repeatability, and reproducibility, limit of detection (LOD), limit of quantitation (LOQ), recovery and linearity of calibration curve**.**

3.2.1 Chromatograms of levoglucosan and 2-methoxyphenol analyses

The chromatograms of levoglucosan and 2-methoxyphenol analysis are shown in Figure. 3.2 and 3.3, respectively.

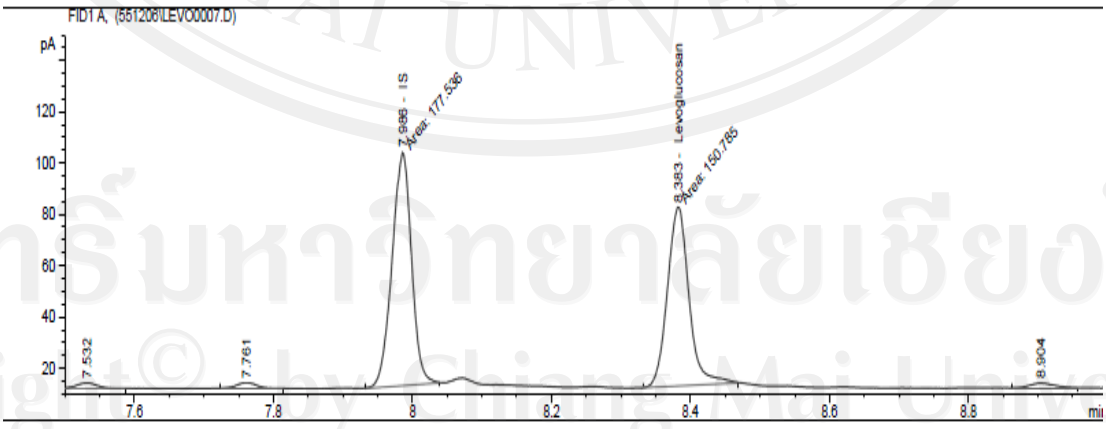

Figure.3.2 A chromatogram of levoglucosan in PM_{10} sample obtained from GC-FID

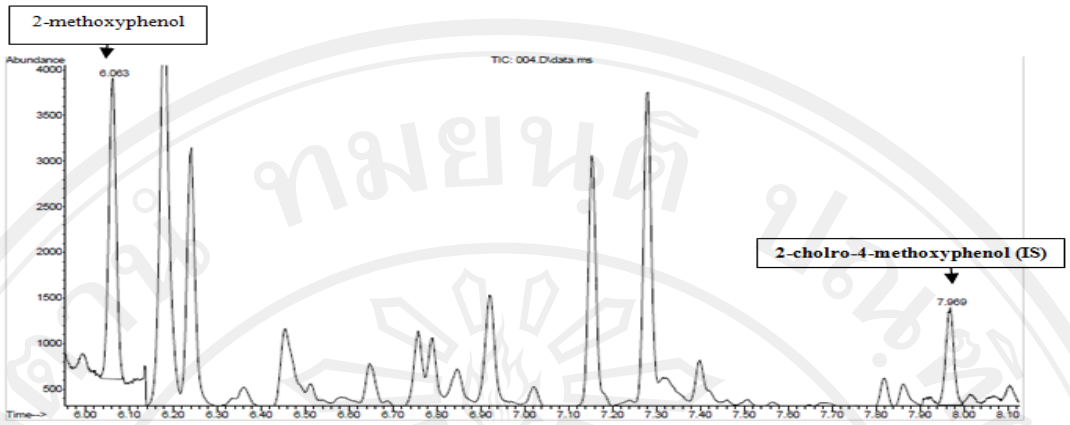

Figure.3.3 A chromatogram of 2-methoxyphenol in PM_{10} sample obtained from GC-MS

3.2.2 Calibration curve of spiked levoglucosan standard solution

The levoglucosan standard solution, 1000 mg/L, was spiked onto 8 clean quartz filters with 1, 2, 5, 10, 20, 50, and 100 µL in order to obtained the final concentrations at 0 (solvent blank), 1, 2, 5, 10, 20, 50, and 100 mg/L in EA prior GC-FID analysis. In the meantime, Fixed concentration of an internal standard was prepared by adding 20 µL of 1,000 mg/L methyl β-D-xylopyranoside onto the filters gave final concentration of 20 mg/L. The standards were extracted using the same protocol of sample filters and then derivatized and analyzed using the GC-FID. The extracted calibration curve was plotted between the concentration of the levoglucosan and area ratio of levoglucosan and methyl β-D-xylopyranoside. Linearity regression equation and correlation (R^2) were shown in Figure.3.4

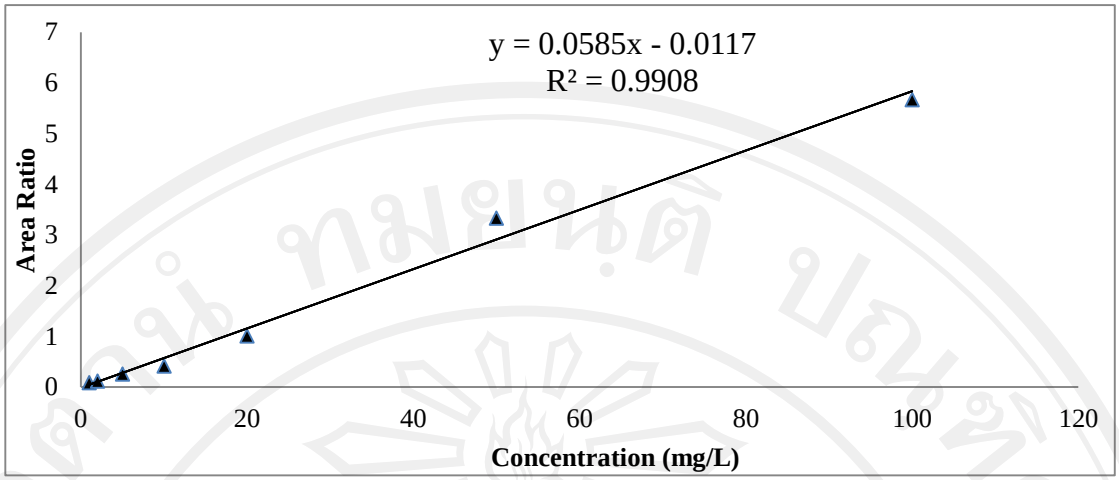

Figure.3.4 A linear regression of extracted calibration curve of levoglucosan standards

3.2.3 Calibration curve of spiked 2-methoxyphenol standard solutions

The 2-methoxyphenol standard solution, was spiked onto 8 clean quartz filters to obtain the final concentrations at 0 (solvent blank), 2, 5, 10, 20, 50, 100 and 200 µg/L. Internal standard was also spiked onto the filters by adding 50 µL of 1 mg/L of 2-chloro-4-methoxyphenol. The standards were extracted using the same protocol of sample filters and then derivatized and analyted using the GC-MS. The extracted calibration curve was plotted between the concentrations of 2-methoxyphenol and area ratio of the 2-methoxyphenol and 2-chloro-4-methoxyphenol. Linearity regression equation and correlation (R^2) were shown in Figure.3.5.

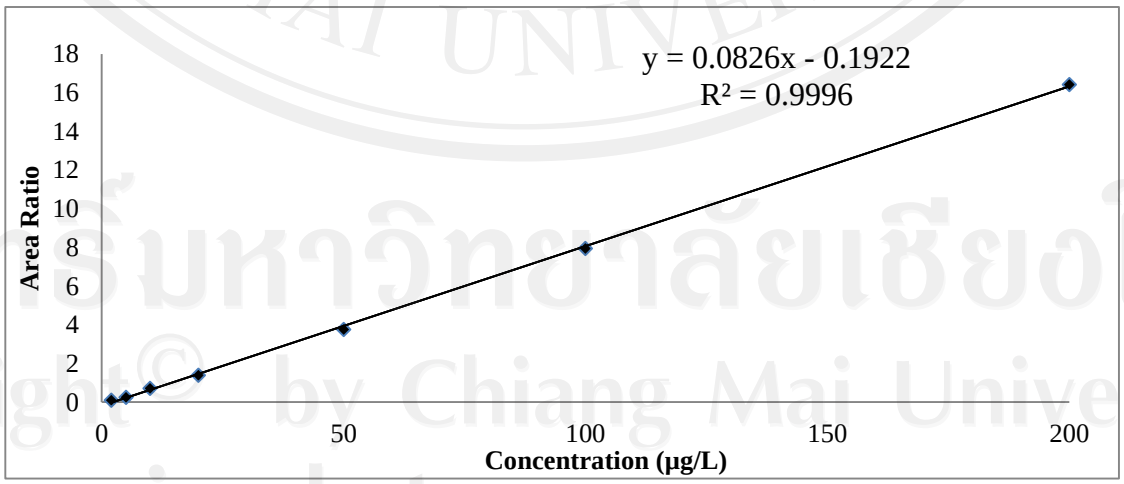

Figure.3.5 Linear regression of extracted calibration curves of 2-methoxyphenol standards

3.2.4 Precision

The relative standard deviation of individual results was determined from different days, different analysts, different calibration curves, and different batches of reagents. Precision is usually defined in terms of reproducibility and repeatability:

Repeatability was done by 5 injections of 20 μ L of 100 mg/L of levoglucosan standard with 20 μL of 1,000 mg/L of methyl β-D-xylopyranoside for GC-FID and 10 μ L of 1 mg/L of 2-methoxyphenol standard with 50 μ L of 1 mg/L of 2-chloro-4-methoxyphenol for GC-MS analyses. Mean and standard deviation (SD) values were calculated and the result is shown in Table 3.2. The %RSDs of levoglucosan (2 mg/L) and 2-methoxyphenol (0.01 mg/L) were 5.8% and 11.1% which in the acceptable range of 6% and 15%, respectively (Horwitz, 2000).

Table 3.2 Repeatability of levoglucosan and 2-methoxyphenol measurement

No. of measurement	**Concentration**	
	Levoglucosan (mg/L)	**2-methoxyphenol (μg/L)**
1	1.7	10.4
2	1.9	8.4
3	2.3	8.2
4	2.0	10.3
5	2.0	9.0
Average	**1.9**	**9.3**
SD	**0.1**	**1.0**
%RSD	**5.8**	**11.1**

1) Reproducibility

The reproducibility of levoglucosan (20 mg/L) and 2-methoxyphenol (0.04 mg/L) was done by calculating the RSD using means and SD from 7-batch analysis. The result is shown in Table 3.3.

Table 3.3 Reproducibility of levoglucosan and 2-methoxyphenol measurements

No. of measurement	Concentration	
	Levoglucosan (mg/L)	**2-mehoxyphenol (µg/L)**
1	17.1	35.5
2	17.5	34.7
3	17.3	34.8
4	16.9	37.4
5	16.4	35.9
6	17.2	33.7
7	17.6	34.8
Average	**17.2**	**35.3**
SD	**0.4**	**1.2**
%RSD	**2.4**	**3.4**

The %RSDs of levoglucosan (20 mg/L) and 2-methoxyphenol (0.04 mg/L) were 2.4% and 3.4% which in the acceptable range of 6% and 15%, respectively (Horwitz, 2000).

3.2.5 Recovery

Five replications at 3 levels which were low, medium and high concentrations (2, 10 and 100 mg/L for levoglucosan and 10, 50 and 200 µg/L for 2-methoxyphenol). The results were shown in Table. 3.4. The results showed good recoveries acceptable ranging of AOAC (Horwitz, 2000) in the range of 75.2-97.1% for levoglucosan and 91.7-92.2% for 2-methoxyphenol.

Table 3.4 Mean ±SD recoveries (n=5) of levoglucosan and 2-methoxyphenol spiked onto clean filters

Level	% Recovery (means±SD)
Levoglucosan (n=5)	
Low Concentration (2 mg/L)	93.6±5.4
Medium Concentration (10 mg/L)	75.2±2.2
High Concentration (100 mg/L)	97.1±1.3
2-methoxyphenol (n=5)	
Low Concentration (10 µg/L)	92.1±10.3
Medium Concentration (50 µg/L)	92.2±7.6
High Concentration (200 µg/L)	91.7±0.9

3.2.6 Limit of detection (LOD)

In present work, LOD (limit of detection) and LOQ (limit of quantitation) were determined using the intercept of the regression line between the concentration of standard concentrations and SD which were derived from 5 replicates of each concentration. The concentrations of levoglucosan standard solution were prepared in 1, 10 and 100 mg/L with 20 mg/L internal standard and concentrations of 2-methoxyphenol standard solution were prepared in a 10, 50 and 200 µg/L with 50 µg/L internal standard. LOD and LOQ are 3 and 10 times of Y-intercept, respectively. The LOD and LOQ results are shown in Table 3.5

Table 3.5 LOD and LOQ of levoglucosan and 2-methoxyphenol

Standard	LOD	LOQ
Levoglucosan (mg/L)	0.3	0.9
2-methoxyphenol (µg/L)	0.5	1.6

3.3 Levoglucosan concentration in PM_{10} samples

A total of PM_{10} samples collected in KCK during the wet and dry season of 2011-2012 were analyted for levoglucosan and 2-methoxyphenol. The results presented in microgram of levoglucosan per cubic meter air ($\mu g/m^3$) and nanogram of 2-methoxyphenol per cubic meter air (ng $/m^3$)were shown in Table 3.6 and 3.7, respectively.

Table 3.6 Concentration of levoglucosan s in PM_{10} samples from the studied and control houses during wet and dry season. In each season, PM_{10} samples were collected 3 days.

House number	Number of days collected in each season	Mean±SD levoglucosan ($\mu g/m^3$)	
		Wet season	Dry season
S_1	3	22.1±12.5	2.2±3.5
S_2	3	1.9±2.1	7.7±5.1
S_3	3	1.7±0.5	9.9±6.6
S_4	3	8.0±5.3	9.3±5.9
S_5	3	1.9±3.1	2.7±1.1
S_6	3	1.3±0.9	7.4±6.9
S_7	3	2.5±1.8	22.6±26.7
S_8	3	2.5±1.8	6.1±27.5
S_9	3	5.5±5.7	2.9±3.4
S_10	3	7.9±1.6	19.3±1.5
S_11	3	1.9±1.6	5.6±4.8
S_12	3	21.5±25.1	2.6±4.6
S_13	3	5.2±4.6	7.8±0.5
S_14	3	1.7±2.0	2.2±3.5
Mean±SD	**42**	**6.2±7.1**	**8.7±6.9**
Control	6	Not detected	0.2±0.2

The mean concentration of levoglucosan in studied houses in wet and dry seasons was 6.2±7.1 μg/m^3 and 8.7±6.9 μg/m^3, respectively. While, the mean concentration of levoglucosan measured in control houses was 0.2±0.2 μg/m^3 in dry season, but it was not detected in wet season (Table 3.6).

In wet season, the lowest and highest concentration of levoglucosan of the studied houses were 1.3 (S_7) and 22.6 (S_1) μg/m^3, respectively. In dry season, the lowest and highest concentration of levoglucosan of the studied houses were 2.2 (S_1) and 22.6 (S_8) μg/m^3, respectively. However, there is no significant difference between the levoglucosan concentrations in wet and dry seasons (p=0.35). The mean concentration of levoglucosan measured in control houses was 0.2 μg/m^3 for dry season while, there was not detected in wet season.

Since the majority of the PM_{10} present in KCK was due to wood smoke, this result was expected. This suggests that these compounds are useful tracers for wood smoke in particulate matter. The Pearson correlation of the association between PM_{10} concentrations and levoglucosan was 0.57 (Figure 3.6).

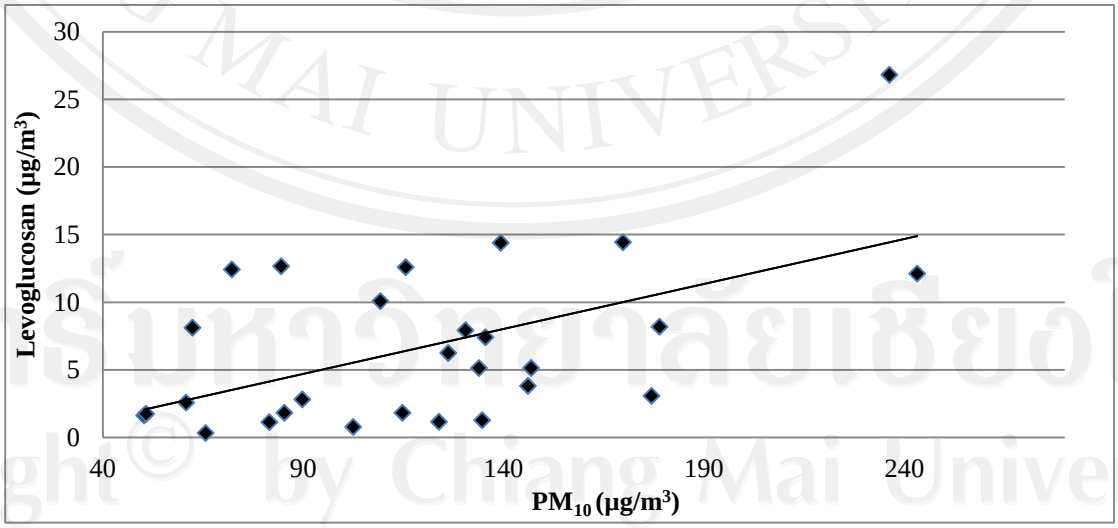

Figure.3.6 Correlation between concentrations of levoglucosan and PM_{10} measured in both seasons (r = 0.57)**.**

3.4 2-Metoxyphenol concentrations in PM_{10} samples

Table 3.7 Concentration of 2-methoxyphenol in PM_{10} samples from the studied and control houses during wet and dry season. In each season, PM_{10} samples were collected 3 days.

House number	Number of days collected in each season	Mean±SD 2-methoxyphenol (ng/m^3)	
		Wet season	Dry season
S_1	3	30.1±14.7	7.7±2.4
S_2	3	20.8±6.9	12.8±4.2
S_3	3	17.7±12.3	10.2±6.4
S_4	3	17.5±8.4	9.8±2.3
S_5	3	31.3±13.4	15.5±3.5
S_6	3	13.4±5.0	18.5±8.0
S_7	3	23.9±18.8	16.1±5.9
S_8	3	23.2±3.4	30.4±27.1
S_9	3	9.2±1.8	14.0±11.6
S_10	3	23.9±14.1	20.0±14.5
S_11	3	23.3±4.4	9.4±3.1
S_12	3	10.2±2.7	6.6±0.8
S_13	3	13.9±8.7	12.3±7.8
S_14	3	31.2±41.4	23.4±29.1
Mean±SD	**42**	**20.7±7.4**	**14.7±6.6**
Control	6	10.9±7.4	7.9±4.1

The mean concentration of 2-methoxyphenol in studied houses in wet season and dry season were 20.7±7.4 ng/m^3 and 14.7±6.6 ng/m^3, respectively. While, the mean concentration of 2-methoxyphenol measured in control houses was 10.9±7.4 ng/m^3 and 7.9±4.1 ng/m^3 in wet season and dry season, respectively. In wet season, the lowest and highest concentration of 2-methoxyphenol of the studied houses were 10.2

(S_12) and 31.3 (S_5) ng/m^3, respectively. In dry season, the lowest and highest concentration of 2-methoxyphenol of the study houses were 6.6 (S_12) and 30.4 (S_8) ng/m^3, respectively. However, there were significant difference between 2-methoxyphenol concentrations in wet and dry seasons ($p<0.05$).

In present study, the levels of 2-methoxyphenol showed poor correlation with PM_{10} concentration ($p=0.22$). This study did not support 2-methoxyphenol as a tracer for wood smoke (Figure.3.7).

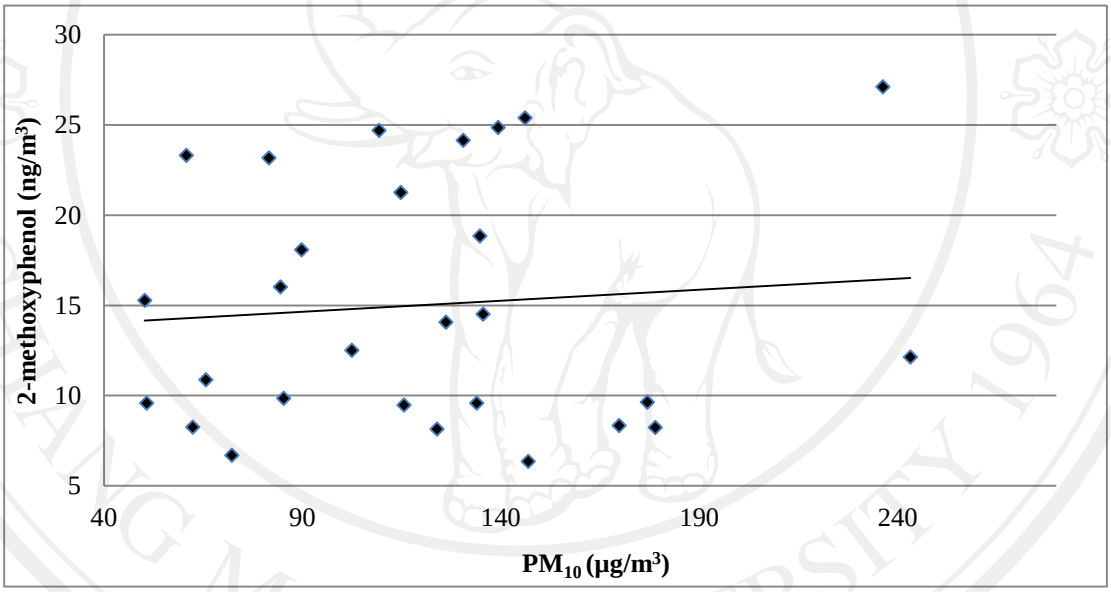

Figure.3.7 Correlation between concentrations of 2-methoxyphenol and PM_{10} measured in both seasons (r = 0.22).

Means of PM_{10} and levoglucosan were not different between dry and wet seasons but means of 2-methoxyphenol were significantly different between two seasons ($p = 0.034$, one tail t-test). In wet season, 2-methoxyphenol was higher than in dry season. Indoor burning is common lifestyles of hilltribes in northern Thailand. People in KCK village use wood for indoor cooking and warming through the whole year. These wood burning produce air pollutants which impact to KCK villagers' health.

Moreover, house characteristics with poor ventilation in this study site enhance the exposure to air pollutants among these villagers.

PM_{10} amounts in same house varied over a wide range. There was found that PM_{10} amount was highest on Friday. From the survey, all members in family are together on Friday and many activities including of cooking by using wood more occurred on this day.

Table 3.8 Concentrations of levoglucosan and 2-methoxyphenol from the present and other studies

Study	Sample type	Levoglucosan	2-methoxyphenol
Simpson et al., 2004	Ambient air from Washington, USA.	0.2 µg/m^3	-
Jordan et al., 2006	Ambient air from Launceston, Australia	2-15 µg/m^3	<0.2-22.0 ng/m^3
Bergauff et al., 2007	Ambient air from western Montana USA.	3.0 µg/m^3	4.3 ng/m^3
Present study, 2012	Indoor air from KCK (wet) season	6.2±7.1 µg/m^3	20.7±7.4 ng/m^3
	Indoor air from KCK (dry) season	8.7±6.9 µg/m^3	14.7±6.6 ng/m^3

The results of levoglucosan and 2-methoxyphenol in present studies were 10-fold higher than in the other studies which found that the concentration of levoglucosan and 2-methoxyphenol (n=10) were 3.0 µg/m^3 and 4.3 ng/m^3, respectively. Since the house characteristics in KCK village is one multi-purpose closed room with poor ventilation which might differ from the house characteristics in others, the indoor concentration of these two compounds were difference between in two studies.

3.5 The limitation of the present study

1) Indoor air sample collection was performed in 12 hr, from 6 pm to 6 am of next day. This was due to the limitation of the air sampler battery that last only 12 hours and electricity was not yet provided in KCK village. Sample collection from 6 am to 6 pm should be performed in order to obtain 24 hr average air sample.

2) The control house which using clean energy i.e. LPG was available only one house though it was proved that using clean energy providing less PM_{10}, levoglucosan and 2-methoxyphenol concentrations.