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Exposure Assessment for Biomass Smoke among "Rice in the Bamboo" Producing Workers: Comparison between $PM_{2.5}$, Levoglucosan and Methoxyphenols

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Abstract

This study focuses on comparing different measurements of biomass smoke exposure among "rice in the bamboo" producing workers in Thailand. Repeated measurements of $PM_{2.5}$, levoglucosan, and urinary methoxyphenols concentrations from a subsample of the exposed workers were analyzed. The analyses of variance components and variance ratios were calculated using ANOVA, and t-tests comparison on the before and after exposure levels. The results of the study revealed that levoglucosan measurement in the personal breathing zone was the most suitable measure of exposure to biomass smoke in this group of population. Urinary methoxyphenols offered no great advantage over environmental monitoring in this study. $PM_{2.5}$ did poorly for a choice of biomass smoke measurement.

Keywords: biomass smoke; exposure assessment; environmental monitoring; biomarker of exposure; epidemiological study

1. Introduction

The mechanism behind the associations of biomass smoke exposure and health effects are not fully understood (Fullerton *et al.*, 2008). Biomass fuel smoke has been, and will be a major health concern around the world as a result of extensive use of biomasses for alternative energy source (Smith, 2002; Boman *et al.*, 2006; Fullerton *et al.*, 2008). In most epidemiological studies, method of biomass smoke exposure has relied on particulate matter (PM) measurements, which can be biased (Naeher *et al.*, 2007). PM is the physical phase of all liquid and solid particles of air contaminants whereas biomass smoke consists of hundreds of chemical compounds not only in the form of solid particles such as soot and mineral dust but also including gasses, acid vapors, and volatile organic compounds (McDonald *et al.*, 2000; Schauer *et al.*, 2001; Fine *et al.*, 2002). To arrive at a more specific assessment of biomass smoke exposure, it should be measured as the whole mixture (Neaher *et al.*, 2007). Although there is a substantial number of compounds proposed as chemical markers for biomass smoke, levoglucosan (LG) and methoxyphenols (MPs) seem to be the most promising in terms of accuracy and method validations (Simpsons *et al*, 2004; 2005; Dills *et al*, 2006). LG, a sugar anhydride, was reported to be totally in the fine particle phase of wood smoke (Locker, 1988), and can be collected on air filter samples together with $PM_{2.5}$ (Simpson *et al*, 2004). Being formed during the pyrolysis of cellulose, LG is emitted in large quantities during wood combustion and can be found in most biomasses smoke pollutants (Fraser and Lakshmanan, 2000). LG is very stable under high temperature and can be detected in small quantity. As such, it is very useful in air pollution source apportionment, and long range transport studies (Simoneit and Elias, 2000). MPs, on the other hand, are volatile organic compounds. They are in both solid and gas phases, therefore, trapping them from air samples is not quite simple. MPs are more suitable to be used as a biomarker. They are readily absorbed via inhalation, remain mostly unchanged in the body, and excrete rapidly in the urine (Dills *et al.*, 2001; 2006).

There is still a controversy over the issue of whether use of biomarker or air sample is better for chemical exposure assessment studies. Biomarker seems to be more suitable when air sample is not possible or difficult to conduct (Neitzel *et al.*, 2008). Moreover, biomarker technique has been claimed to reduce misclassification bias in exposure assessment because it decreases the day-to-day variation of measurement of exposure within each subject (Rappaport *et al.*, 1995; Lin *et al.*, 2005). However, biomonitoring should not be

assumed a *priori* to be superior to air sampling for epidemiological studies (Liljelind *et al.*, 2003). Some biological monitoring procedures are invasive or even culturally embarrassing such as urine collecting and some are expensive to conduct.

A few studies have demonstrated that $PM_{2.5}$ and LG are correlated in air samples. (Dills *et al.*, 2006; Neizel *et al.*, 2008) However, the relationship held true only in prolonged exposure monitoring such as more than 60% of the work shift (Neizel *et al.*, 2008). The authors also reported that LG was correlated less with MPs, but more with carbon monoxide. Their studies focused on transient exposure of firefighters where biological monitoring would be more suitable than air sampling. This study is confined to a group of traditional food producing workers who were constantly exposed to biomass smoke in higher magnitude on a daily basis. We extend this preliminary study to explore the within- and between-worker variance components and their ratios to define an appropriate measure of biomass smoke exposure among this group of population.

2. Materials and methods

2.1. Study area and subjects

This study was part of the health evaluation project conducted in San Sook municipality, Chonburi province, Thailand. This area is renowned for its "rice in the bamboo" by producing around 10,000 tubes per day. From our preliminary survey, this product generates around 5 million US dollars per year of income to the local community. "Rice in the bamboo" was traditionally produced by using biomass fuels such as wood and coconut husk. There were a few kitchens that still keep this traditional cooking process while others had eventually changed to use LPG oven. Because of personal inconvenience to the workers, only five kitchens agreed to participate in this preliminary study. The study subjects were drawn from the workers that comprised non current smokers who had not been diagnosed with kidney, hepatic diseases, diabetes, and hypertension. Eleven workers met the selection criteria and agreed to sign the consent form. The study protocol regarding human subjects was approved by the ethical review board of Burapha University, Thailand.

Figure 1. The cooking of "Rice in the bamboo"

2.2. Observation and interview

The researchers observed the working process, interviewed the workers on demographic information, health status, food and beverages consumption, smoking history, and environmental tobacco smoke exposure.

2.3. Exposure monitoring

2.3.1. Job Exposure Matrix (JEM)

We employed JEM to assign a *priori* grouping of workers by fuel type used and job (task team) for further analyses of exposure-response study in this occupation. The participating kitchens used two different fuel types. Three kitchens used wood and coconut husks, and two kitchens used charcoal. The cooking process of each kitchen was similar in that the bamboo tubes were lined up in rows on the cooking ground; biomass fuel was put along both sides of the row of the bamboo tubes, then the workers put on the fire. The cooking process ranged from 3-8 hours depending on the number of tubes produced. The kitchen structures were similar to one another, in that they were partially opened workshops with low level rooftop as shown in Fig. 1.

There were three major steps in the cooking process: 1) Preparation (before the fire started), 2) Mixing and adding the fuel, and 3) Removing the product (smoldering phase). Each worker usually rotated between each step. Mixing and adding the fuel would result in highest exposure in regard to proximity to the fire. Preparation and removing the product would experience less exposure. Monitoring protocols included environmental monitoring and urine sampling for biomarkers of exposure.

2.3.2. Air sampling and analysis

Three full-shift personal samplings were conducted on each subject at intervals of 2-5 days. Personal air sampling pumps (SKC model 224; SKC Inc., PA, USA.), and personal environmental monitors for $PM_{2.5}$ (MSP model 200 MSP Corp., MN, USA.) were used as the sampling instrument. Biomass smoke was collected on 37 mm. PTFE filters with PMP ring (SKC Inc., PA, USA).

Table 1. Demographic information of the study subjects (n=11)

Gender:	Male	6
	Female	5
Age (years)	Median	53 (range 29-68)
Height (cm.)	Mean	56.57
Weight (kg.)	Mean	66
Smoking history	Ex-smoker	2
	Never smoke	9
Years in trade (years)	Mean	18
Daily work hour (hours)	Mean	6
Food and alcohol consumption during the study period		Number of subjects
Alcoholic beverages		4
Wood smoke flavoring		none
Exposure to environmental tobacco smoke		2

Sampling and analytical procedures were based on NIOSH Method 0500 (NMAM, 1994). The filters were pre-weighed at the Ministry of Public Health, Thailand. After air sampling was conducted, each filter was loaded into a separate petri dish (SKC Inc., PA, USA), kept frozen (-20°C), and shipped for further analyses at the Environmental Health Laboratory, University of Washington, USA. The filters were first analyzed for $PM_{2.5}$ by gravimetric analysis, then underwent the analyses of LG by gas chromatography-mass spectometry (GC/MS) as described previously (Simpson *et al*., 2004). Briefly, filters were extracted by sonication in ethyl acetate, reduced the extract volume in Turbo Vap bath under N_2, derivertized with a slating reagent (TMSI), and analyzed by GC/MS. Field blank filters were also included with each batch for quality control.

2.3.3. Urine sampling and analysis

Urine specimens were collected from each of the eleven workers. The participants were asked to provide urine samples at intervals of two to five days in parallel with the air sampling. For two days prior to urine collection, and for the duration of this study, the subjects were asked not to consume food cooked on open fires or charcoal or food containing biomass smoke flavoring such as vanilla or cloves. First morning urine samples (prior to work), and after work urine samples were collected from each subject in clean separate containers. An aliquot part (40 mL) of the sample was transferred to the 50 mL polypropylene tubes. The samples were stored frozen (-20°C) and shipped to the University of Washington for analysis. Urine samples were analyzed for creatinine by colorimetric assay (Beckman Coulter Inc.) at the University of Washington Medical Center, Chemistry Division. MPs were analyzed at the Environmental Health Laboratory by the procedures described by Dills *et al.* (2001; 2006) and Simpson *et al*. (2005). Brief summary of the procedure included acid hydrolysis to deconjugate the MPs. Deuterated standard compounds were added to the urine samples prior to extraction to determine analytical recoveries in each sample. Then, the samples were applied to ion exchange solid phase extraction and analyzed by GC/MS. Method blanks, method spike, and benchmark were included in each batch of the samples to monitor accuracy and precision.

2.4. Statistical analysis

In addition to descriptive statistics, correlation analysis, and linear regression model, a one-way random-effect model was employed to estimate the between-worker ($_{bw}S^2$) and the within-worker ($_{ww}S^2$) variance components. The kitchen and worker were treated as random effect factors. Variance component analyses were performed by using Minitab 15 Statistical Software (Minitab Inc.).

3. Results

3.1. Subject characteristics

The demographic information of the study participants was described in Table 1. There were six males and five females with a median age of 53 (range: 29-68). All subjects worked in the kitchens seven days a week for an average of six hours per day. One subject worked for twelve hours a day. The majority of the workers reported of drinking occasionally. During the study period, four subjects had alcoholic beverages. None reported that they had eaten food cooked on open fires or charcoal or food flavored with vanilla or cloves.

Table 2. Concentrations of $PM_{2.5}$ and LG by kitchen and fuel type

Fuel type/Kitchen	n	$PM_{2.5}$ (μg/m³)		LG (μg/m³)	
		AM(SD)	GM	AM(SD)	GM
Wood & husk					
Kitchen 1	8	1729.65 (741.89)	1556.51	53.05 (15.68)	51.20
Kitchen 2	5	1046.82 (331.01)	1009.39	30.67 (9.80)	29.52
Kitchen 3	4	654.59 (357.97)	529.75	10.61 (7.90)	7.64
Total	17	1278.86 (710.54)	1063.48	36.48 (21.41)	27.83
Charcoal					
Kitchen 4	5	676.84 (218.77)	643.42	3.27 (2.79)	2.59
Kitchen 5	3	393.64 (197.40)	361.44	5.04 (1.38)	4.93
Total	8	570.64 (244.89)	518.32	3.93 (2.41)	3.30

AM, arithmetic mean; SD, standard deviation; GM geometric mean

3.2. Environmental monitoring

Twenty five air filter samples were available for the analyses of $PM_{2.5}$ and LG. The number of samples ready for the analysis was fewer than expected because some participants denied putting on the sampling pumps after experiencing the inconveniences during the first few days. However, each participant provided at least two samples of the air measurement. According to the gravimetric analysis procedure, the filters were pre-weighed at the Reference Laboratory and Toxicology Center, Ministry of Public Health in Thailand and post-weighed at the University of Washington. A few field blanks and laboratory blanks were used in the calculations of $PM_{2.5}$ concentrations to adjust for inter-laboratory differences. After the analysis of $PM_{2.5}$, the filters were analyzed for LG with the analytical recoveries of 65-92%.

Table 2 shows descriptive statistics of $PM_{2.5}$ and LG concentrations by kitchen. On average, LG levels from the study samples were about 19% of $PM_{2.5}$ levels (29% from coconut husk and wood smoke samples, 0.7% from charcoal smoke samples). $PM_{2.5}$ levels were relatively higher, with two orders of magnitude among kitchens that used wood and coconut husk than those that used charcoal. Kitchen number one had the highest $PM_{2.5}$ level, whereas kitchen number five had the lowest level. For LG concentrations, the levels were 10 times higher on average, among kitchens that used wood and coconut husk as compared to the ones that used charcoal.

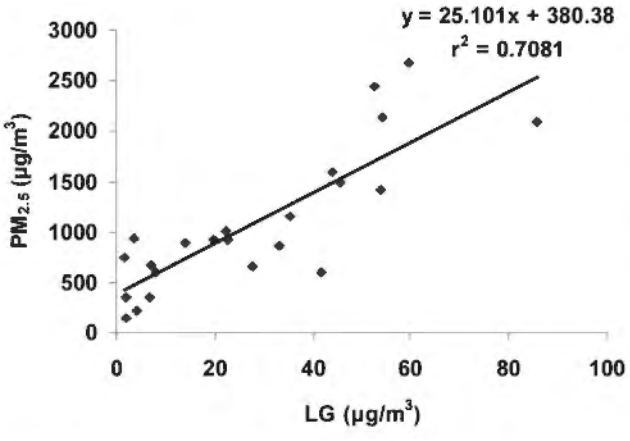

Figure 2. Correlation between $PM_{2.5}$ and LG

Fig. 2 depicts the correlation between $PM_{2.5}$ and LG concentrations. Pearson's correlation indicated that the two substances were highly correlated ($r^2 = 0.809$, $p<0.001$)

3.3. Biological monitoring

Due to urine collection problems such as forgetting to provide the first morning urine sample, consuming food cooked on charcoal, exposure to environmental tobacco smoke, and forgetting to collect the urine in the provided containers. A hundred urine samples (50 pre- and 50 post-shifts) were collected from the participants, but 72 urinary MPs results were available to be used for data analyses. MPs analytical recoveries varied from 25-125% for all valid data. Urinary MPs results below the limit of detection were discarded. Each individual MPs results were normalized by creatinine concentration to ensure that MPs concentrations were not affected by variations in urinary concentration. Pre-, post- and cross-shift (post-pre) concentrations of 17 MPs adjusted for creatinine were calculated (Tables 3-5). Cross-shift changes in the creatinine normalized levels of the 17 urinary MPs were calculated as post-shift minus pre-shift levels. Paired t-tests ($\alpha = 0.05$) for pre- and post-shift in each urinary MP were conducted to see the changes. Among the wood and coconut husk group, the levels of MPs increased for eleven compounds with statistical significance (Table 3). Among the charcoal group, MPs increased for two compounds (Table 4). And for the unexposed reference group, MPs increased only for one compound (Table 5).

Table 3. Creatinine-adjusted urinary methoxyphenols for wood & husk group (μg methoxyphenol/mg creatinine)

	Pre-shift			Post-shift			Cross-shift			Paired t-test
	n	*mean*	SD	*n*	*mean*	SD	*n*	*mean*	SD	*p*
Guaiacol	44	0.611	0.679	44	1.062	0.862	44	0.451	0.863	0.001*
Methylguaiacol	43	0.143	0.361	43	0.287	0.351	43	0.144	0.289	0.002*
Ethylguaiacol	44	0.043	0.059	44	0.196	0.174	44	0.153	0.168	<0.001*
Syringol	44	0.291	0.489	44	0.848	0.735	44	0.558	0.765	<0.001*
Eugenol	41	0.880	1.633	41	0.546	0.762	41	-0.334	1.453	0.149
Propylguaiacol	43	0.016	0.030	43	0.116	0.387	43	0.100	0.387	0.097
Vanilin	44	0.072	0.157	44	0.061	0.131	44	-0.011	0.040	0.086
cis-isoeugenol	35	0.022	0.032	35	0.115	0.102	35	0.092	0.110	<0.001*
Methylsyringol	42	0.020	0.032	42	0.194	0.176	42	0.175	0.181	<0.001*
trans-isoeugenol	44	0.056	0.056	44	0.199	0.172	44	0.142	0.186	<0.001*
Acetovanillone	44	0.248	0.219	44	0.389	0.316	44	0.141	0.350	0.011*
Ethylsyringol	35	0.023	0.025	35	0.129	0.113	35	0.106	0.122	<0.001*
Guaiacylacetone	43	0.499	1.304	43	0.101	0.272	43	-0.397	1.276	0.048*
Allylsyringol	43	0.031	0.033	43	0.056	0.048	43	0.052	0.058	0.007*
Propylsyringol	36	0.004	0.005	36	0.262	0.021	36	0.022	0.021	<0.001*
Acetosyringone	44	0.027	0.044	44	0.025	0.020	44	-0.002	0.051	0.804
Propionylsyringone	40	0.016	0.024	40	0.014	0.012	44	-0.002	0.028	0.594

* Significant level: $p<0.05$

Table 4. Creatinine-adjusted urinary methoxyphenols for charcoal group (μg methoxyphenol/mg creatinine)

	Pre-shift			Post-shift			Cross-shift			Paired t-test
	n	*mean*	SD	*n*	*mean*	SD	*n*	*mean*	SD	*p*
Guaiacol	7	0.655	0.475	7	1.442	0.917	7	0.951	0.790	0.019*
Methylguaiacol	7	0.112	0.092	7	0.552	0.599	7	0.440	0.552	0.048*
Ethylguaiacol	7	0.023	0.019	7	0.106	0.133	7	0.082	0.130	0.143
Syringol	7	0.239	0.191	7	0.143	0.066	7	-0.096	0.199	0.246
Eugenol	7	0.162	0.223	7	0.108	0.111	7	-0.054	0.134	0.332
Propylguaiacol	7	0.045	0.086	7	0.008	0.009	7	-0.037	0.086	0.297
Vanilin	7	0.022	0.018	7	0.032	0.012	7	0.010	0.015	0.105
cis-isoeugenol	6	0.020	0.018	6	0.020	0.012	6	-0.001	0.008	0.842
Methylsyringol	7	0.035	0.041	7	0.032	0.023	7	-0.002	0.023	0.800
trans-isoeugenol	7	0.061	0.044	7	0.061	0.032	7	0.001	0.031	0.975
Acetovanillone	7	0.186	0.175	7	0.434	0.364	7	0.249	0.282	0.085
Ethylsyringol	7	0.016	0.015	7	0.019	0.012	7	0.003	0.015	0.620
Guaiacylacetone	7	0.032	0.043	7	0.027	0.023	7	-0.005	0.054	0.813
Allylsyringol	7	0.103	0.186	7	0.107	0.388	7	0.067	0.206	0.419
Propylsyringol	6	0.003	0.001	6	0.003	0.002	6	0.001	0.001	0.209
Acetosyringone	7	0.016	0.012	7	0.014	0.011	7	-0.001	0.008	0.670
Propionylsyringone	7	0.004	0.007	7	0.011	0.003	7	0.006	0.005	0.121

* Significant level: $p<0.05$

Table 5. Creatinine-adjusted urinary methoxyphenols for unexposed reference group (μg methoxyphenol/mg creatinine)

	Pre-shift			Post-shift			Cross-shift			Paired t-test
	n	*mean*	SD	*n*	*mean*	SD	*n*	*mean*	SD	*p*
Guaiacol	4	0.455	0.196	4	0.235	0.197	4	-0.220	0.390	0.340
Methylguaiacol	4	0.019	0.018	4	0.015	0.009	4	-0.004	0.031	0.832
Ethylguaiacol	4	0.018	0.009	4	0.032	0.019	4	0.014	0.012	0.088
Syringol	4	0.031	0.009	4	0.041	0.015	4	0.009	0.024	0.564
Eugenol	4	0.055	0.027	4	0.027	0.014	4	-0.016	0.022	0.244
Propylguaiacol	4	0.002	0.001	4	0.342	0.189	4	-0.339	0.588	0.423
Vanilin	4	0.021	0.001	4	0.064	0.085	4	0.042	0.085	0.394
cis-isoeugenol	4	0.012	0.009	4	0.023	0.011	4	-0.001	0.008	0.682
Methylsyringol	4	0.011	0.017	4	0.191	0.375	4	-0.002	0.023	0.387
trans-isoeugenol	4	0.060	0.047	4	0.032	0.014	4	-0.001	0.031	0.269
Acetovanillone	4	0.072	0.047	4	0.039	0.011	4	0.134	0.006	0.003*
Ethylsyringol	4	0.009	0.008	4	0.016	0.015	4	0.007	0.016	0.436
Guaiacylacetone	4	0.013	0.004	4	0.045	0.002	4	0.031	0.070	0.292
Allylsyringol	4	0.026	0.015	4	0.019	0.011	4	-0.007	0.011	0.429
Propylsyringol	4	0.003	0.003	4	0.025	0.042	4	0.022	0.040	0.429
Acetosyringone	4	0.014	0.007	4	0.012	0.007	4	-0.001	0.008	0.622
Propionylsyringone	4	0.006	0.001	4	0.011	0.006	4	0.006	0.005	0.184

* Significant level: $p<0.05$

The separate analyses for correlations of the 17 MPs were conducted by fuel type. Among wood & coconut husk group, compounds in the guaiacyl family (guaiacol, methylguaiacol, and ethylguaiacol), syringyl family (methylsyringol, ethylsyringol, propylsyringol, acetosyringone, and propionylsyringone) and some euginyl family were significantly correlated (Table 6). Among the charcoal using group, no significant correlation was detected, except for guaiacol and propionylsyringone (Table 7).

The regression analyses showed that summed guaiacols correlated mostly with LG ($r^2 = 0.59$, $p<0.001$), but for summed syringols it was not correlated ($r^2 = 0.07$), as detailed in Table 8. Figs 3-5 depicted the correlations and linear regression models between MPs and LG. Based on these analyses, the summed guaiacols was selected as the surrogate of biomass smoke exposure in this study.

3.4. Comparison of $PM_{2.5}$, LG, and MPs

Table 9 shows the estimated within- and between-worker variance components and the corresponding variance ratios of $PM_{2.5}$, LG, and MPs concentrations. The variance components for the between-worker ($_{bw}S^2$) were higher for LG and MPs but showed the opposite direction for $PM_{2.5}$. This indicated that there was a larger day-to-day variation of exposure within each worker (the same

Table 6. Pearson's correlation coefficient of cross-shift creatinine adjusted MPs for wood & coconut husk group

GU	1.000	SY	0.074	EUG	0.238	VAN	0.113
MTGU	0.378*	MESY	0.344*	CISOEU	0.388*	ACETV	0.159
ETGU	0.407**	ETSY	0.403*	TISOEU	0.536**		
PRGU	-0.753*	PRSY	0.337*				
GUACE	-0.276	ALLSY	0.138				
		ACETSY	0.561**				
		PRSYON	0.559**				

* Significant level: $p < 0.05$
** Significant level: $p < 0.01$

Table 7. Pearson's correlation coefficient of cross-shift creatinine adjusted MPs for charcoal group

GU	1.000	SY	0.764	EUG	0.238	VAN	0.867*
MTGU	0.171	MESY	-0.420	CISOEU	-0.728	ACETV	0.711
ETGU	0.119	ETSY	-0.102	TISOEU	-0.187		
PRGU	-0.230	PRSY	-0.417				
GUACE	0.421	ALLSY	0.690				
		ACETSY	-0.539				
		PRSYON	-0.680				

* Significant level: $p<0.05$

person) than between workers (different persons) for $PM_{2.5}$. In contrast, LG and MPs levels had smaller variability within-worker, but larger between-worker variations. Variance ratio of LG was very small (0.45) whereas the variance ratio of $PM_{2.5}$ was almost 20 times larger (8.12). For MPs, the variance ratio of summed guaiacols was 0.85 which was twice of that of LG.

4. Discussion

The strong correlation between $PM_{2.5}$ and LG concentrations was detected from air samples of those who used wood and coconut husk fuel. LG levels from the study samples were about 29% of $PM_{2.5}$ levels. Although it is certain that LG is formed during the pyrolysis of lignin, no reports of LG concentration from coconut husk burning were documented. Comparing to a study done by Neitzel and coworkers (2008), they found that LG levels from forest fire smoke in Southeastern United States were about 8% of $PM_{2.5}$ levels. The proportion of LG level is worth mentioning because we can use LG concentration as an exposure estimate for biomass smoke in future exposure-response studies.

Significant association was detected between LG and summed guaiacols ($r^2 = 0.59$, $p<0.001$) but not for summed syringols. This finding is in consistent with the results reported by Dills *et al.* (2006), Clark *et al.* (2007), and Neitzel *et al.* (2008), in that not all MPs are good for biomarkers of biomass smoke. The study showed that there was a significant increase in guaiacols in all of the cross-shift creatinine adjusted samples for both types of fuel. Syringols were significantly increased only for subjects who used wood and coconut husks fuel.

This study focuses on the selection of whether environmental monitoring or biomarker would be appropriate to characterize personal exposures in a subsample of population that is exposed to biomass smoke from the cooking process of "rice in the bamboo" in Thailand. We compared a few samples of repeated measurements of $PM_{2.5}$ and LG from air samples and urinary MPs, one of the promising biomarkers of exposure to biomass smoke. Based on the methods recommended by Rappaport *et al.* (1995), variance components and variance ratios of the within-worker and between-worker were analyzed. Results obtained from the study indicated that the variance ratios for LG (0.45) and MPs (0.85) were less than 1. This suggested that the inter-individual (between- workers) differences in both air samples (as indicated by LG) and urinary biomarker (MPs) were much larger than those of the day-to-day variability in one person. For future

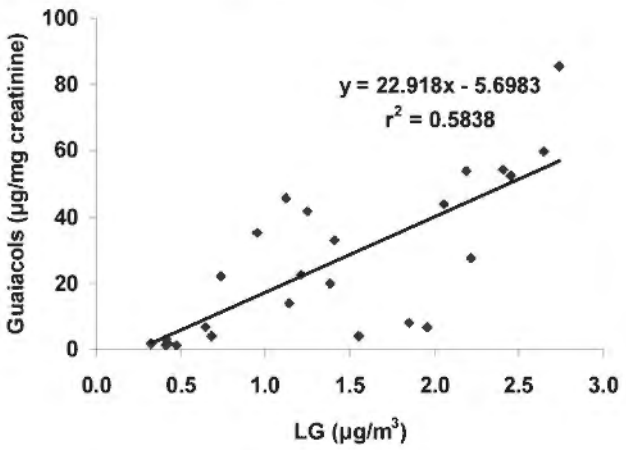

Figure 3. Regression of guaiacols on LG

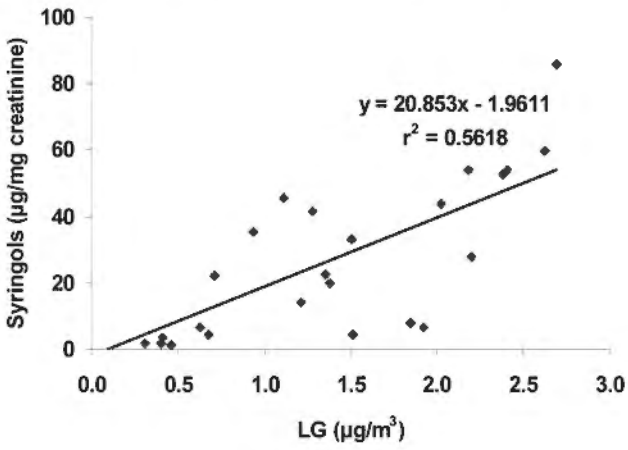

Figure 4. Regression of syringols on LG

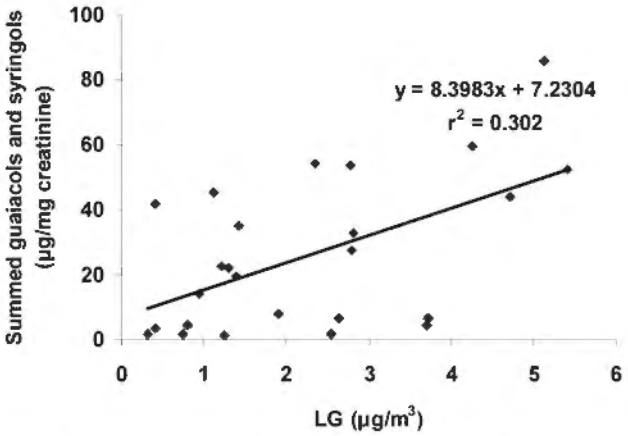

Figure 5. Regression of summed guaiacols and syringols on LG

Table 9. Estimated variance components and variance ratio for $MP_{2.5}$, LG and MPs measurements

Substance	n	${}_{ww}S^2$	${}_{bw}S^2$	Variance Ratio
$PM_{2.5}$	25	0.268	0.033	8.12
LG	25	0.142	0.314	0.45
MPs	36	0.379	0.446	0.85

n = number of samples;
${}_{ww}S2$ = within-worker variance component;
${}_{bw}S2$ = between-worker variance component, estimated from log transformed data;
variance ratio = ${}_{ww}S2/{}_{bw}S2$

epidemiological studies of exposure-response in this population, it is more important to emphasize on the study sample size to represent the population studied rather than obtaining repeated measurement of the same individual. The variance ratio for LG was smaller than that of urinary MPs. This indicated that environmental monitoring for LG would be superior to biological monitoring for MPs. Moreover, sampling and assay demands of urinary MPs are greater than those associated with LG. $PM_{2.5}$ should not be used because of the large variance ratio. However, the results presented here were confined to monitoring in a small group of biomass smoke exposed workers and should not be generalized to all populations. It is suggested that further studies should be conducted in different populations, such as in other occupations, to compare the results of these measurements.

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Table 8. Regression models for cross-shift creatinine adjusted summed guaiacols, summed syringols, LG, and $PM_{2.5}$

Model	Predictor	Dependent variable	n	Coefficient	95% CI	Coefficient *p*	r^2
1	LG	Summed guaiacols	25	0.025	0.016 - 0.035	0.001**	0.587
	LG			0.720	0.400 - 1.040		
2	$PM_{2.5}$	Summed guaiacols	25	0.001	0.000 - 0.001	0.001**	0.461
	$PM_{2.5}$			0.600	0.162 - 1.038		
3	LG	Summed syringols	19	0.012	-0.010 - 0.034	0.278	0.069
	LG			0.776	-0.022 - 1.573		
4	$PM_{2.5}$	Summed syringols	19	0.001	0.000 - 0.001	0.069	0.181
	$PM_{2.5}$			0.428	-0.449 - 1.305		

** $p<0.01$

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