EXCELLENT PUBLISHERS

International Journal of Current Research and Academic Review

ISSN: 2347-3215 Special Issue-2 (January-2015) pp. 84-90

www.ijcrar.com

Proportion of trace elements from airborne PM_{10} in Chiang Mai City using Pixe technique

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KEYWORDS

Picea smithiana, Pixe technique, airborne PM_{10}, ecological and ethnomedicinal

A B S T R A C T

The effect of the global climate change was assessed in the Swat Valley of Northern Pakistan, to understand the future of one of the important tree species i.e. *Picea smithiana (Wall.) Boiss. Picea smithiana* is of a significant ecological and ethnomedicinal importance to the area. The Maximum entropy (MaxEnt) modelling technique of species prediction and distribution was applied, using HADCM3 A2a global climate change scenario. It was concluded that by the 2080 there will be a significant change in the distribution and density of the species. The results obtained show a "good model" for both present and future models, gaining the AUC values of 0.972 and 0.977respectively. The results indicate that mean temperature of coldest quarter (bio_11) and temperature of the warmest month (bio_5) climatic variables have the highest contribution to the AUC values in the present model, while the mean temperature of warmest quarter (bio_10) and bio_3 have significant contribution to the future prediction model of the species and thus positively correlated with the distribution and density of the species. The predicted changes in the distribution and density of the species in the future prediction model can have immense ecological and socioeconomic impact.

Introduction

Since the smog episode in 2007, upper northern Thailand provinces have been facing high level of air pollution especially during February to March.

Air pollution has been reportedly affecting people health with increasing incidence rate of patient with respiratory disease. The number of patients admitted with airway problems was higher than that of previous years (Pollution control department. 2011). Eight provinces of upper northern Thailand including Chiang Mai, Chiang Rai, Lamphun, Lampang, Phrae, Nan, Phayao, Mae Hong Son and one of lower northern part of Thailand, Tak province have had elevated levels of particulate matters with aerodynamic diameter less than 10 micrometer (PM_{10}) exceeded the control level (>120 µg m^{-3}, 24 hours average level).

Main causes of airborne PM_{10} and smog/haze are forest fire in both from in-bound and neighboring countries i.e. Lao, Myanmar, Vietnam and Cambodia. The other source is burning of post-harvest biomass, branch and paddy remains such as rice and corn fields (Pengchai *et al.*, 2009). To date, study about sources of air pollutants did not clarify of their origins, or even cause and effect to personal health.

Thus, the objective of this study is to use a nuclear analytical technique called Proton Induce X-Ray Emissions (PIXE) which fast and non-destructive technique to identify source of air pollution composition from each sources.

Materials and Methods

Study design: It was a cross-sectional study of PM_{10} collection from 4 March 2010 to 7 May 2010.

Study sites: There were 2 sampling sites. One was located at the ground floor of the Research Institute for Health Sciences (RIHES) Building 3, Chiang Mai University main campus as a clean area. The other site was at Wat Nantaram (WT) School, Saraphi district, a sub-urban of Chiang Mai city.

Apparatus: GENT Air Samplers [International Atomic Energy Agency (IAEA), Austria] were employed to collect PM_{10} samples using micropore polycarbonate filters, diameter 47 mm, 8.0 µm (Nuclepore, Track-Etch membrane, Whatman, USA). The sampler was installed about 1.5 meters above the ground with metal case as shown in Figure 1.PIXE and GUPIXWIN software.

PM_{10} collection method: The Gent Air Sampler was collecting PM_{10} for 24 hour samples with the flow rate of 15 liter per minute. The PM_{10} level on the filter was estimated by gravimetric method. Pre-weight filter was installed in the filter holder before start timer and adjust air flow rate and closing top cover of air sampler. After 24 hours collected sample, the filter was kept at least24 hours in the vacuum desiccator for moisture removal. The filter was weighed again as post weighted. PM_{10} level was calculated as following.

Total PM_{10} (µg/m^3) = [1000 × (post weight - pre weight) g]/(15 l min-1 × 1,440 min × 10^6)

Controlled combustion chamber study

Eight dried plant samples which commonly found in upper northern Thailand were collected and burned in the controlled combustion chamber at Division of Environmental Science, Faculty of Science, Chiang Mai University, Thailand (Wiriya *et al.*, 2013). Eight plants included bamboo (*Bambusa vulgaris*), longan (*Dimocarpus longan*), lychee (*Litchi chinensis*), corn (*Zea mays*), grass (*Echinochloa crusgalli*), teak (*Tectona grandis*), rice (*Oryza sativa*) and Yangna (*Dipterocarpus alatus*). PM_{10} samples were collected from the chamber.

Trace element analysis: PM_{10} samples from plant burning in controlled chamber and ambient air of RIHES and WT School were analyzed by PIXE at the Ion Beam Physics & Application Research Unit of Chiang Mai University. Samples were exposed high energy beam with 3 MeV Photon energy for 6 min.

The GUPIXWIN was application software using for analyzing trace elements data collected from PIXE. The concentrations of trace elements which derived from hitting high energy beam in specific area (13.46 cm^2) were calculated in $ngcm^{-2}$. Total sample area of PM_{10} collected filter was the total volume of ambient air collected for 24 hours (1,440 min) via Gent air sampler with 15 liters per min and then convert to $\mu g\ m^{-3}$ or ppm by the following formula.

$$\text{Concentration } (\mu g/m^3) = (A\ ngcm^{-2} \times 10^3 \times 13.46\ cm^2)/(15m^3\ min^{-1} \times 1{,}440min)$$

A = Concentration of trace element in specific analyzed area of proton beam in PIXE technique ($ng\ cm^{-2}$)

Cluster analysis: The proportions between trace elements and Ca were calculated and then tested for cluster analysis using computer-based software. Euclidean distance and dendogram were used to group the samples.

Result and Discussion

The mean±SDPM_{10}level of 24 hours average at WT school sampling site was significantly higher than those from the RIHES sampling site (Table 1). Thailand and World Health Organization (WHO) Standard PM_{10} level of 24 hour average are 120 and 50 μgm^{-3}, respectively (U.S. Environmental Protection Agency, 2006; Pollution Control Department, 2011). Therefore, mean PM_{10} levels of these 2 sites are not exceeded Thailand standard but WT sampling site had mean PM_{10} level exceeded WHO standard level. The result from RIHES site indicated that the main campus of Chiang Mai University deserves to be a clean area while WT site which is sub-urban area of Chiang Mai city indicated slightly particulate air pollution. However, both sites had the highest PM_{10} level which exceeded Thailand standard on 16 Mar 2010.

PM_{10} filters of 8 plants burning and 2 sampling sites (RIHES and WT School) were analyzed for trace elements using PIXE technique and GUPIX software. The concentrations of 10 trace elements are shown in Table 2.

PM_{10} bound trace elements from burning leaves of 8 plants (bamboo, longan, lychee, corn, grass, teak and rice and Yangna) in control combustion chamber were measured. Six elements including Al, S, Cl, K, Ca, and Fe were found in all types of plants. Cr was detected in corn, rice, teak and Yangna and Ti was found in teak and Yangna. Si was not found in corn while Mn was not detected in any plant burning. Comparing the concentration, rice burning gave the highest concentration of Al, S, Cl, K and Ca.

All 10 elements were found in PM_{10} samples from RIHES and WT school sites. Most concentrations of trace elements from both sites were not much different from each other. Specially, Ca concentration from RIHES site (230.3 $\mu g\ m^{-3}$) was 3.5-fold lower than from WT school site (1,006 $\mu g\ m^{-3}$) and Cr concentration from RIHES site (31.84$\mu g\ m^{-3}$) was 4-fold higher than WT School (8.54$\mu g\ m^{-3}$).

Since Ca is the abundance of elements in Earth's crust, the proportions between other elements and Ca were calculated and shown in Table 3

Euclidean distance was used to measure distance between samples. The low Euclidean distance (closing to 0) shows high similarity between the samples. The results are shown in Table 6 and Figure 2.

It was noticeably that values of same sample on the diagonal were 0, since a case does not differ from itself. Therefore, distance between WT School and RIHES samples at 0 suggested the same cluster of trace elements pattern from these two sites. Considering the dendogram, there were 5 clusters consisted of 1 (WT School and RIHES), 2 (rice, teak and Yangna), 3 (bamboo and grass), 4 (longan and corn) and 5 (lychee).Cluster 1 was more similar to cluster 2 than cluster 3, 4 and 5, respectively. This can be explained that the major source of PM_{10} in WT School and RIHES sites may be from rice, teak and Yangna burning. Whereas bamboo and grass might be the subordinately possible sources and longan and corn were the minor source.

PM_{10} concentrations from RIHES and WT School sites in this study (57.1 and 80.9 µg m^{-3}, respectively) were slightly higher than the previous study which reported PM_{10} concentration (40.4 µg m^{-3}) collected in Chiang Mai and Lumphun provinces in dry season, 2006 (Chantara *et al.*, 2010). It could be from the different number of hotspot which occurred in each year. However, in March of the same year (2010), PM_{10} concentrations in this study were very high as well as another study which collected samples in Chiang Mai University (Wiriya *et al.*, 2013).

PIXE technique which is high sensitive and non-destructive analytical technique is useful to identify trace element in PM_{10} samples. PM10 samples from WT School and RIHES were found major trace elements such as Al, Si, S, Cl, K, Ca, Ti, Cr, Mn and Fe. PM10 concentrations

The ratio of proportion of elements are characterizing for each sample are apply to evaluate source of biomass burning because of each sampling sites was different related the plants in each area. Since Ca was abundant element, it was used to standardize the concentrations of the elements. K which is the major element in fertilizer was highly detected in the commercial plants such as longan, corn and rice. Heavy metals such as Cr, Ti and Mn were not found in any plant samples. Noticeably, Mn, octane-added material in gasohol fuel, was presented in PM_{10} samples from RIHES and WT school sites but not found in any samples from plant burning.

The previous study pointed that the vegetative burning was the largest PM_{10} contributor in Chiang Mai and Lamphun ambient air (Pengchai *et al.,* 2009). However, it did not identify the type of plant. This study had selected the predominantly-found plant around Chiang Mai-Lamphun basin. Teak, bamboo, grass and Yangna are forest trees normally found in Saraphi and Suthep hill areas where WT School and RIHES sites take place, respectively, whereas rice, corn, longan and lychee are important commercial crops in both areas. From the cluster analysis, the highly possible sources of PM10 in WT School and RIHES sites were from burning of rice, teak, Yangna, bamboo and grass. Since teak, Yangna, bamboo and grass are all forest plants, the main source of PM_{10} in these sites was forest fire. According to hotspot data (Forest fire statistics, 2010), sample collecting period was in dry season and at the same time as highest forest fires occurring in these area. Field burning is a normal part of field preparation for cultivation of field crops such as rice and corn. Therefore, in these areas, PM_{10} from lychee and longan burning was not as much as rice and corn burning.

Conclusions

The PM_{10} samples collected from WT School were slightly higher than RIHES site because PM_{10} from WT school may be affected by traffic whereas RIHES site which places in the University is a cleaner area. Euclidean distance showed that the source of PM_{10} in both sites of this study was from forest fire and burning of local plants including rice, teak, Yangna, bamboo and grass. This study offers the proportion of trace elements from PIXE technique to identify source of PM_{10}.

Table.1 The mean of PM10 level of 24 hours average at WT school and RIHES sampling sitescollected from 4 March 2010 to 7 May 2010

Sampling site	PM_{10}weight mass (µgm^{-3})		
	Mean (± SD)	Min-Max	Day with highest PM_{10}
RIHES (n=30)	57.1 (±38.5)	5.0-125.0	16 Mar 2010
WTschool (n=16)	80.9 (±49.5)	27.3-205.7	16 Mar 2010

Table.2 Trace elements of PM10from 8 plants burning in control combustion chamber and 2 sampling sites (RIHES and WT School)

PM_{10} sample	Concentrations of trace elements (µg m^{-3})									
	AL	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe
Plant burning										
Bamboo(*Bambusa vulgaris*)	928.9	205.9	113.5	56.63	51.98	14.91	ND	ND	ND	39.72
Longan (*Dimocarpus longan*)	572.5	204.6	95.62	349.1	463.1	17.67	ND	11.65	ND	17.28
Lychee (*Litchi chinensis*),	954.0	244.7	150.3	59.21	31.32	4.26	ND	0.00	ND	16.34
Corn (*Zea mays*)	786.8	ND	73.27	162.3	236.2	9.30	ND	1.62	ND	21.41
Grass (*Echinochloa crusgalli*)	670.5	134.3	38.72	30.93	28.22	5.08	ND	0.00	ND	5.77
Teak (*Tectona grandis*)	1,083	248.1	99.85	1,649	1,423	196.2	5.67	11.57	ND	70.09
Rice (*Oryza sativa*)	1,108	437.8	803.2	1,852	3,449	205.5	ND	ND	ND	0.72
Yangna (*Dipterocarpus alatus*)	876.4	154.8	98.38	143.6	219.8	19.70	4.95	6.05	ND	14.66
Sampling site										
RIHES	1,592	590.6	196.5	22.62	210.7	230.3	18.72	31.84	7.55	181.1
WT school	1,176	671.2	237.5	19.65	191.6	1,006	19.76	8.54	8.73	189.3

ND =Not detected

Table.3 Proportions of the concentrations between each trace element to potassium

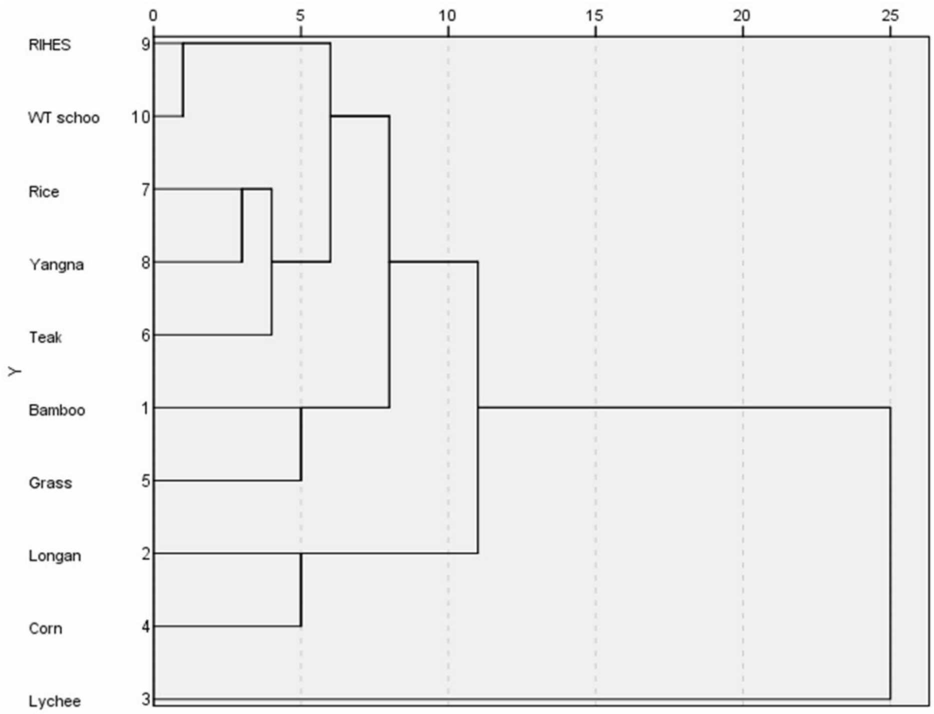
PM_{10} samples	Proportions							
	Si/Ca	S/Ca	Cl/Ca	K/Ca	Ti/Ca	Cr/Ca	Mn/Ca	Fe/Ca
Plant burning								
Bamboo(*Bambusa vulgaris*)	13.8	7.6	3.8	3.5	0.0	0.0	0.0	2.7
Longan (*Dimocarpus longan*)	11.6	5.4	19.8	26.2	0.0	0.7	0.0	1.0
Lychee (*Litchi chinensis*),	57.4	35.3	13.9	7.4	0.0	0.0	0.0	3.8
Corn (*Zea mays*)	0.0	7.9	17.4	25.4	0.0	0.3	0.0	2.3
Grass (*Echinochloa crus-galli*)	26.4	7.6	6.1	5.6	0.0	0.0	0.0	1.1
Teak (*Tectona grandis*)	1.3	0.5	8.4	7.2	0.0	0.1	0.0	0.4
Rice (*Oryza sativa*)	2.1	3.9	9.0	16.8	0.0	0.0	0.0	0.0
Yangna (*Dipterocarpus alatus*)	7.9	5.0	7.3	11.2	0.2	0.3	0.0	0.7
Sampling site								
RIHES	2.6	0.8	0.1	0.9	0.1	0.1	0.0	0.8
WT School	0.7	0.2	0.0	0.2	0.0	0.0	0.0	0.2

Table.4 Euclidean Distance amongtrace elements from 8 plants and PM10 samples from RIHES and WT school sites

Case	Proximity Matrix: rescaled Euclidean Distance									
	Bamboo	Longan	Lychee	Corn	Grass	Teak	Rice	Yangna	RIHES	WT school
Bamboo	.000	.166	.592	.181	.035	.052	.076	.024	.041	.054
Longan	.166	.000	.721	.030	.177	.131	.062	.083	.239	.257
Lychee	.592	.721	.000	.932	.381	.936	.886	.731	.942	1.000
Corn	.181	.030	.932	.000	.259	.099	.035	.079	.203	.212
Grass	.035	.177	.381	.259	.000	.146	.156	.081	.142	.166
Teak	.052	.131	.936	.099	.146	.000	.021	.016	.023	.025
Rice	.076	.062	.886	.035	.156	.021	.000	.014	.072	.078
Yangna	.024	.083	.731	.079	.081	.016	.014	.000	.042	.052
RIHES	.041	.239	.942	.203	.142	.023	.072	.042	.000	.000
WT school	.054	.257	1.000	.212	.166	.025	.078	.052	.000	.000

Figure.1 Gent Air sampler at sampling site for collecting PM_{10}

Figure.2 Dendogram of rescaled Euclidean distance



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