Tree bark as bioindicator of metal accumulation from road traffic and air quality map: a
case study of Chiang Mai, Thailand

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Abstract

Trees have been recognized as air quality bioindicators, but they have still not been fully implemented in tropical areas. In this study, bark of *Cassia fistula* was used to inspect accumulation of air pollutants (metals) emitted from road traffic in the city of Chiang Mai, Thailand. The mean concentrations of metal accumulated on tree bark (ng/cm²) in descending order were Al (1,238) > Fe (707) > Zn (162) >> Cu (21.1) >> Pb (6.37) > Cr (2.14). Correlations of Enrichment Factors: EF_{TS} (metal concentrations on bark compared to those in soil) among metals were relatively strong ($r > 0.6$) meaning that they were probably generated from the same sources. Moreover, principal component analysis and cluster analysis of EF_{TS} values revealed that Al and Fe were generated from soil resuspension that were attached on vehicle wheels and on road surfaces, while Cr, Cu, Pb

and Zn resulted directly from vehicle emissions. The results lead to the conclusion that tree bark is a good bioindicator for air pollutant accumulation in this area. In addition, pollution indices, including total geoaccumulation index ($I_{GEO-tot}$) and pollution load index (PLI), were applied to generate air quality maps of the city. The maps illustrated that the most polluted areas in the city are the areas that have high traffic volume and building density, in which hospitals and schools are located. The degree of pollution presented in each area was influenced by both road traffic volume and density of buildings in relation to air ventilation capacity.

Keywords: *air pollution; bioindicator; Cassia fistula; pollution load index; total geoaccumulation index,*

1. Introduction

Metropolitan cities have been suffering with air quality degradation due to the rapid growth that is associated with urbanization. Road traffic is the most important anthropogenic source of atmospheric pollution in urban areas. It has been established that pollutant levels are directly related to the number of automobiles present on the roadways. Road traffic pollutants can be generated from various activities including internal combustion, corrosion of vehicle parts and resuspension of dust on road surface caused by vehicle-generated turbulence. Metal pollutants including Cr, Cu, Fe, Pb and Zn are known to be significant vehicular pollutants which are produced from both exhaust and non-exhaust actions of engines such as in fuel combustion, lubricant oil combustion, tire wear, crash barriers corrosion and brake lining wear (Thorpe and Harrison, 2008; Pulles et al., 2012). Moreover, an increase in particulate matter (PM) and soil metals such as Al has also

49 been observed due to transportation activity (Wilkinson et al, 2013). These soil metals (in
50 traffic area) are typically distributed from soil resuspension. Currently, the traffic volume in
51 the mega-cities of several countries in Asia is continuously increasing at alarming levels.
52 Consequently, these circumstances have resulted in enormous deteriorating impacts on
53 human health and urban ecosystem.

54 Chiang Mai City is a northern urban center located in Chiang Mai Province. It is
55 considered the second largest urban center in Thailand by population and attracts over 7
56 million visitors each year. This province is located in the Chiang Mai - Lamphun basin,
57 which is partially surrounded by high mountain ranges. The geographical features of the
58 province have forced the people of the city of Chiang Mai to face a serious situation with
59 regard to air quality degradation especially during the dry season. The possible sources of
60 air pollutants within 30 km radius from the city center are mobile source including on-road
61 vehicles as well as airplanes (Chiang Mai international airport located in urban area), area
62 source (biomass burning) and point source (Northern Industrial Estate). Biomass burning
63 was a major source of air pollutants in the dry season, while vehicle combustion (diesel and
64 gasoline emission) was the main source of air pollutants during the rainy season. However,
65 air pollutants emitted from engine-vehicles are also major concern as one of important air
66 pollution sources of the city for the whole year round (Chantara et al., 2012; Wiriya et al.,
67 2013). Moreover, Chiang Mai City is rapidly growing along with the number of vehicles on
68 the city's road system. The number of registered vehicles in December 2015 was 1.32
69 million vehicles with increasing rate by 6% per year since 2010. Therefore, the level of air
70 pollutants produced by road traffic would very likely become critical in the near future;
71 hence, the monitoring of those pollutants is necessary for this area.

According to the study of Schulz et al. (1999) and Janta et al. (2016), metals accumulated on the outer bark were deposited from ambient air. Using trees as an atmospheric bioindicator is widespread globally because the method is cheap, easy to use, and can potentially detect long-term contamination (Satake, 2001; Ferreira et al., 2012). Various tree species can be used. Examples of tree species that have been used successfully to monitor levels of aerial heavy metals were *Azadirachta indica* (Odukoya et al., 2000), *Zelkova serrata* (Hokura et al., 2009), *Casuarina equisetifolia*, *Delonix regia* (Ukpebor et al., 2010), *Fraxinus pennsylvanica* (Fujiwara et al., 2011), *Pinus massoniana* L. (Kuang et al., 2007). Even though, using of tree as air pollution bioindicator is implied in many areas. However, it is not much implemented in Southeast Asia (SEA) in which has high biodiversity. Consequently, the aims of this study were 1) the first of using a native tree species of SEA (*Cassia fistula*) for assessment of metals emitted from traffic activity, 2) Estimation of seasonal impact on metals accumulation on the bark, 3) Application of pollution indices including total geoaccumulation index ($I_{GEO-tot}$) and pollution load index (PLI) for comparing the degree of pollution between areas and indication of contamination zones by mapping of air quality in the study area in the city of Chiang Mai, Thailand and 4) Calculation of the influence of building areas and traffic volume on air quality. The results of the study should prove useful for local and governmental organizations in terms of urban air quality management.

91

92 **2. Materials and Methods**

93 2.1. Study areas

94 Study areas were located in Chiang Mai Province, which is the second largest
95 province in the north of Thailand. It is in mountainous northern Thailand with the
96 coordinates between 17.242° - 20.148°N (latitude) and 98.010° - 99.513°E (longitude) at
97 elevation 310 meters above sea level. This province covers area around 20,110 km² which
98 83% of the area is forest. The province has a population 1,640,479 people and population
99 density is 81.6 people per km². The average temperature and annual total rainfall are 27 –
100 28°C and 1,200 mm, respectively.

101 The study area was conducted on the main roads in the city of Chiang Mai (18.788°N
102 and 98.988°E). The city covers 152 km² and has a population of approximately 240,000.
103 The population density is 1,600 people/km². Traffic density ranged between 3,000 – 80,000
104 vehicles per day. This area was represented the polluted area (local site) in which it was
105 divided into urban and sub-urban area based on population density and human activities
106 (Bootdee et al., 2012). The urban area was categorized with a 5 km radius from the center,
107 consisting of residential areas, schools and businesses. The sub-urban area was comprised
108 of residential areas, agricultural areas and parks. Moreover, Phrao District, Chiang Mai
109 Province (19.366°N and 99.202°E) was selected as a background site for comparison due to
110 its low level of human activities and pollution. It is located about 90 km from Chiang Mai
111 City in the north and has about 60 times less population density (25 people/km²) than the
112 city of Chiang Mai.

113 2.2. Sample collection

114 2.2.1 Tree-type selection

115 *C. fistula* is selected because it is a tree species native to Southeast Asia and the
 116 Indian subcontinent. This tree is deciduous and fast growing tree. When young, it has
 117 smooth and thin bark which the outermost layer can be easily peeled off, and its bark
 118 change to scaly in old trees . The *C. fistula* is commonly planted along the road, both inside
 119 and outside of towns, for decoration and shading. Therefore, determination of metals on the
 120 bark of *C. fistula* planted near roadsides can be expected to show the level of pollutants
 121 influenced by road traffic.

122 The sampling trees were selected from *C. fistula* species planted along roads at a
 123 distance of less than 3 m from the road edge. The trees with the age around 4 - 20 year old
 124 or diameter at breast height (DBH) in the range 5 - 30 cm were chosen for this study
 125 because the metal accumulation on the bark was not related the age of the tree within this
 126 range (Janta et al. 2016). Moreover, the selected trees must have a smooth bark surface.
 127 The criteria for selection of trees as a bioindicator for metals accumulation was mentioned
 128 previously in Janta et al. (2016).

129 2.2.2 Tree bark sample collection

130 A total of 115 *C. fistula* (< 3 m distance from the road) were selected for sampling.
 131 Their geographical coordinates were recorded in order to indicate their locations. Sampling
 132 locations in urban area (the inner pink circle) and sub-urban area (the outer part of the pink
 133 circle) are shown in Fig. 1a. Bark sampling was carried out during two periods; January
 134 2014 (dry season and high tourist season) and September 2014 (wet season). In the first

135 sampling, 79 and 36 trees (green circle symbols on the map) were collected from urban and
136 sub-urban areas, respectively. In the second sampling, 26 trees (urban) and 14 trees (sub-
137 urban) were selected from some of the first sampling trees (black triangular symbols in the
138 map). For the background area, four trees were selected and sampled in September 2014.

139 Bark samples were collected from the selected trees at around 1.5-2.0 m above
140 ground level. Approximately 20 cm² of the outermost layer of the bark (gray color) was
141 collected from trees with a plastic spatula. The bark from second sampling was collected
142 from near the same level as the first sampling (Fig. 1b). The samples were kept in
143 polyethylene bags and stored in a refrigerator at 4.0°C.

144 2.2.2 Soil sample collection

145 Topsoil (0-10 cm depth) samples (40 samples) were collected from the area near the
146 sampling trees of the second sampling. Each sample came from a mix of 3 random points
147 around the selected trees.

148 2.3. Metal extraction

149 2.3.1 Bark sample extraction

150 The bark samples were dried in an oven at 60°C for 2 hr and then cooled. The dried
151 samples were weighed by 4 digits balance. Sample weights ranged between 50 and 270 mg.
152 The samples were transferred into the inner layer of a double-layer Teflon digestion tube,
153 while the outer layer was filled with 4 ml of concentrated extra pure grade HNO₃. The
154 samples were heated at 140°C for 4 hr. The residue was diluted with 10 ml of 0.1 mol/L
155 HNO₃ (Qiuquan et al., 2003).

156 2.3.2 Soil sample extraction

157 The soil samples were dried at 80°C for 24 hr in a hot-air oven. The dried soil
158 samples were sieved with 0.5 mm pour size nylon. One hundred mg of each sample were
159 digested with 4 ml of HCl: HNO₃ (3:1) in the Teflon digestion tube at 180°C for 5 hr
160 (modified from Khamkaew et al, 2016). After digestion, the residue was adjusted to 25 ml
161 with 0.31 mol/L HNO₃. In the case of Fe and Al analysis, the method was developed from
162 US EPA, 3052. The samples were digested with 5 ml of HF: HNO₃ (2:3) for 5 hr at 180°C
163 in an oven. After that, the solution was transferred and heated again on a hot plate at 60 –
164 65°C for 20 min for HF removal. Afterward, the residue was adjusted to 25 ml with
165 deionized water.

166 2.4. Analysis of metals on bark and soil samples and their quality control

167 The digested solutions of bark and soil samples were filtered through 0.45 µm nylon
168 filters. They were analyzed for metal content by inductively coupled plasma optical
169 emission spectrometry (ICP-OES), Perkin Elmer Optima 3000 (Norfolk, Massachusetts,
170 USA). The target metals included Al, Cr, Cu, Fe, Pb and Zn.

171 Prior to metal analysis of the samples, quality control for extraction and analysis of
172 metals was performed by using 3 types of certificated reference materials (CRM). There
173 were two types of botanical CRM, including apple leaf 1515 from the National Institute of
174 Standard and Technology (NIST) (Gaithersburg, Maryland, USA) and pepperbush leaf
175 No.1 from the National Institute for Environmental Studies (NIES) (Tsukuba, Japan). The
176 other CRM was clay soil 051 from R.T. Corporation (RTC) (Laramie, Wyoming, USA).
177 The CRMs were extracted by acid extraction under high temperature and pressure. The

acids used, including nitric acid (HNO₃) and hydrochloric acid (HCl), were obtained from Merck (Gernsheim, Germany), while hydrofluoric acid (HF) was purchased from Sigma-Aldrich (Saint Louis, Missouri, USA). The extraction method for botanical CRM was applied from Qiuquan et al. (2003), while the soil CRM was developed from Khamkaew et al. (2016) and a standard method (US EPA, 3052). The five replicates for each type of CRM were extracted with 200 mg (apple leaf), 350 mg (pepperbush leaf), and 100 mg (clay soil). Recovery of the 6 target metals are presented in Table 1. The analyzed values were compared with the certified values and found that recovery of metals ranged from 79 ± 3 to $115 \pm 15\%$. In order to check for sensitivity of the instrument, a standard solution (1.00 µg/ml) was re-measured at every 20 sample-measurement throughout the analysis in each batch.

Limit of detection (LOD) for the ICP-OES in each metal was obtained by measurement of 0.10 µg/ml of standard solution (7 times). Afterward, the standard deviation of the seven sample measurements was multiplied by three. The detection limits of Al, Cr, Cu, Fe, Pb and Zn were 0.032, 0.005, 0.004, 0.003, 0.023 and 0.005 µg/ml, respectively.

2.5 Pollution level classification

2.5.1 Enrichment Factors

Enrichment Factors (EFs) are a common index used to estimate the anthropogenic impact on an environment. EFs are the relative comparison between normalized metal concentration in *C. fistula* bark sample with either the concentration in the bark from a background area (EF_B) or in soil (EF_{TS}). In this study, Mn was selected as normalizing

metal because this metal has few inputs from anthropogenic activities on a regional scale (Zhang et al., 2014). The calculations for Enrichment Factors are shown below (Abril et al., 2014):

$$EF_B = \frac{[X_i] \times [\bar{X}_{Mn,B}]}{[X_{Mn}] \times [\bar{X}_{i,B}]} \quad (1)$$

$$EF_{TS} = \frac{[X_i] \times [\bar{X}_{Mn,S}]}{[X_{Mn}] \times [\bar{X}_{i,S}]} \quad (2)$$

where $[X_i]$ ($\mu\text{g/mL}$) is the individual concentration of the interest metal in *C. fistula* bark sample, while $[X_{Mn}]$ ($\mu\text{g/mL}$) is the individual concentration of Mn in the bark sample. $[\bar{X}_{i,B}]$ ($\mu\text{g/mL}$) and $[\bar{X}_{i,S}]$ ($\mu\text{g/mL}$) are average concentration of the interest metal in the bark from background area and soil from local site, respectively. Meanwhile, $[\bar{X}_{Mn,B}]$ ($\mu\text{g/mL}$) and $[\bar{X}_{Mn,S}]$ ($\mu\text{g/mL}$) are average concentrations of Mn in the background bark and soil from local site, respectively. According to Bergamaschi et al. (2002), any metal that has an EF value greater than 1 is indicative that the metal did not originate from the surrounding soil and might be present due to long range transport by either natural or/and anthropogenic sources. On the other hand, a value higher than 10 is significant and indicates an anthropogenic source (Ferreira et al., 2012).

2.5.2 Air pollution indices

The total geoaccumulation index ($I_{\text{GEO-toi}}$) and potential load index (PLI) were applied to identify contaminants in the study area and background area that were relative.

(a) Geoaccumulation index

The geoaccumulation index (I_{geo}) was proposed by Müller in 1969 and is a calculation of the concentration enrichment of metals above the background or baseline concentration (Abraham and Parker, 2008). This index was applied to assess the pollution status in soil (Chen et al., 2015), sediment (Abraham and Parker, 2008) and tree bark (Guéguen et al., 2012) in many areas. I_{geo} is expressed as follows (Abraham and Parker, 2008):

$$I_{geo} = \log_2 \left(\frac{[X_i]}{1.5 \times [\bar{X}_{i,B}]} \right) \quad (3)$$

where $[X_i]$ ($\mu\text{g/mL}$) is individual concentration of an interest metal in the study area, while $[\bar{X}_{i,B}]$ ($\mu\text{g/mL}$) is average concentration of an interest metal in a background area. The factor 1.5 is introduced to detect very small anthropogenic influence (Chen et al., 2015). Müller classified the geoaccumulation index into 7 classes with different pollution degrees. Class 0 (none to weakly polluted): $I_{geo} \leq 0$; Class 1 (weakly to moderately polluted): $0 < I_{geo} \leq 1$; Class 2 (moderately polluted): $1 < I_{geo} \leq 2$; Class 3 (moderately to strongly polluted): $2 < I_{geo} \leq 3$; Class 4 (strongly polluted): $3 < I_{geo} \leq 4$; Class 5 (strongly to excessively polluted): $4 < I_{geo} \leq 5$; Class 6 (excessively polluted): $5 < I_{geo}$ (Guéguen et al., 2012; Chen et al., 2015).

Moreover, a new index for the total geoaccumulation index ($I_{GEO-tot}$) was proposed by Guéguen et al. (2012). It was a combination of I_{geo} for all observed metals:

$$I_{GEO-tot} = \sum_i I_{geo,i} / n = \log_2 (PLI/1.5) \quad (4)$$

where n is the number of total observed metals. This index is useful for easy specification of pollution levels in each study area.

(b) Potential Load Index

In a study by Salah et al., (2012), Contamination Factor (CF) was applied for metal contamination level expression in sediment. This factor was defined as (Salah et al., 2012):

$$CF = [X_i] / [\bar{X}_{i,B}] \quad (5)$$

where $[X_i]$ ($\mu\text{g/mL}$) is individual concentrations of an interest metal in the study area. $[\bar{X}_{i,B}]$ ($\mu\text{g/mL}$) is average concentrations of an interest metal in the background area. The 4 levels for CF value and the details of contamination level were mentioned in Salah et al. (2012): Low contamination level ($CF < 1$); moderate contamination level ($1 \leq CF < 3$); considerable contamination level ($3 \leq CF < 6$); very high contamination level ($CF \geq 6$).

Potential Load Index (PLI) was use to evaluate overall metal contamination in the study area. This index was later applied as a soil and lichen bioindicator in various areas such as Nigeria, China, Indonesia and Ghana. The calculation of PLI is shown below (Guéguen et al. (2012) :

$$PLI = (CF_{i1} \times CF_{i2} \times CF_{i3} \times \dots \times CF_{in})^{1/n} \quad (6)$$

where CF is contamination factor; i is species of interest metal; n is the number of interest metal. According to Guéguen et al. (2012), contamination was divided into 7 levels: Background concentration ($PLI = 0$); unpolluted ($0 < PLI \leq 1$); unpolluted to moderately polluted ($1 < PLI \leq 2$); moderately polluted: $2 < PLI \leq 3$; moderately to highly polluted: $3 < PLI \leq 4$; highly polluted: $4 < PLI \leq 5$; very highly polluted: $5 > PLI$ (Chen et al., 2015).

In this study, the concentration of metal was assumed to be equal to the zero limit of detection value when its concentration was lower than the limit of detection for calculation of metal content on bark. On the other hand, the concentration for limit of detection was applied for EFs, CF and I_{geo} calculation.

2.6 Calculation of building area and traffic volume

The relationship between metals accumulated on tree bark with traffic volume and building area were evaluated in order to estimate the influence of both parameters on metal accumulation in each area. Information for vehicle volume on main roads and building areas in the study area were obtained from various sources. The average daily vehicle volume on the main roads of Chiang Mai city (2009 – 2012) was obtained from Sopajaree et al., (2011), while the accumulated vehicle volume over 24 hrs was obtained from the Chiang Mai Traffic Control and Training Center of Chiang Mai Municipality, the Office of Chiang Mai Rural Roads and the Office of Chiang Mai Highways. The main road network in Chiang Mai city was created by use of digitization road lines from a web-mapping service at Google.com. The GIS database for buildings in Chiang Mai as of 2004 was performed by digitization of the building shapes from high-resolution aerial photography. The database was provided by the Department of Civil Engineering, Faculty of Engineering, Chiang Mai University and Geo-Information and Space Technology Centre (Northern Region).

In order to estimate the effects of road traffic, a 500 m x 500 m grid was drawn over the study area covering the main road network and the infrastructure, i.e. buildings. Each grid cell was assigned with a unique ID that ranged from #1 – #1088 (starting from left to right column and down to top row of the map). The features of main roads and buildings

were identified within the grid to produce datasets of short line lengths of the road and buildings contained within each grid. Total traffic volume in each grid was calculated from a summation of multiplication for traffic volume on main roads (R_n) with the ratio between length of the main road in each grid and original length of the main road ($L_{n,i}/L_n$) (Fig. 3a). The total building area was the summation of the area of all buildings existing in the grid (Fig. 3b).

2.7 Statistical analysis and metal distribution map construction

Statistical pair testing was used to compare metal concentrations between wet and dry seasons in order to observe the effects of rain. The square root of 2 was used to transform metal concentrations in order to achieve normal distribution. Pearson Correlation was performed to evaluate the relationships among metal species, while Spearman's Rank was applied to find the correlations among pollution indices, traffic volume and building area. Moreover, multivariate statistical techniques including Principal Component Analysis (PCA) and Cluster Analysis (CA) were performed to indicate potential sources of metals in the study area. Furthermore, pollutant indices with GPS coordinates of the sampling points, traffic volume and building area were imported into the GIS software to generate a pollutant distribution map. The GIS software used in this study was freeware available online at <http://www.qgis.org/en/site/forusers/download.html>.

3. Results and Discussion

3.1 Metal concentrations on tree bark and soil samples

Metal concentrations from the *C. fistula* bark samples collected during two seasons are presented in Table 2. The metal concentrations found in the tree bark samplings from urban areas of Chiang Mai city were 1.5 times higher than those in sub-urban areas. However, no significant difference between the areas was observed. Concentrations of metals on the bark in urban and sub-urban areas were 2 – 27 times higher than those from the background site. Most metals concentrations found in the city and background site were not significantly different, except for Al and Fe. The cause might be due to the high variation of metal content among sampling points in Chiang Mai City from traffic volume and air ventilation at each point. However, the accumulation patterns for each metal species at both sites were similar. The metal with the highest concentration found on bark samples at most of the sampling points was Al. Its concentration in Chiang Mai City ranged from 180 – 6,975 ng/cm² (dry season) and 30 – 5,408 ng/cm² (wet season), while a very low concentration (53 – 186 ng/cm²) was found at the background area. The descending order of metal concentrations at both sites was the same (Al > Fe > Zn >> Cu >> Pb > Cr). The results revealed that the metal with highest concentration (Al) accumulated on the bark was generated from soil. However, metals emitted from vehicles (Fe and Zn) were also the majorities observed on tree bark (Apeagyei et al., 2011).

In order to evaluate the effects of rain on metal accumulation on tree bark, metal concentrations on bark samples in both dry and wet seasons were compared (Table 2). It was found that the concentrations of most of the metals were not different between seasons. An exception was found only in the case of Al and Fe, which concentrations in the wet

season were higher than those in the dry season. Al and Fe originated mainly from the soil. In the wet season, dirt on the road is mixed with rain water and can be flushed off, splashed and deposited on tree trunks located near the road. Al and Fe, which are known as the soil-generated metals, attached on the road and the wheels in the dust form. When the dirt becomes dried, those metals can re-suspend, distribute and deposit on tree trunks at road side due to the vehicles movement. Therefore, it might be the main reason of Al and Fe rising in the wet season. Even though, metals accumulated on tree bark are removed by the rain. However, they are also accumulated from wet deposition by leaching metals from atmosphere to attach on the bark. Therefore, the free deposit formed on the tree bark had a quick renewal rate and could be fully recovered in a few months (Catinon et al., 2012). Additionally, Cruz et al. (2012) also found significant accumulation of Zn on *Cryptomeria japonica* bark exposed to a polluted area during the summer. However, there was no significant difference of metals (Cr, Fe and Zn) accumulation on the bark between exposed periods in the summer and winter seasons in Portugal.

Metal concentrations for soil samples collected along the roads in the city of Chiang Mai revealed that the soil samples contained high concentrations of Fe (1,000 – 31,000 mg/kg) and Al (1,200 – 25,800 mg/kg). Zn was found in a medium range (32.9 - 353 mg/kg). Concentrations of Cr, Cu and Pb were quite low (41.8 ± 17.9 , 23.7 ± 13.9 , 34.6 ± 22.8 mg/kg, respectively).

3.2 Enrichment factors of metals

Enrichment factors (EF) for metals accumulated on the bark of *C. fistula* were calculated in order to evaluate accumulation rates and sources of metals. The mean values for EF_B and EF_{TS} are shown in Table 3. The EF_B values for metals in descending order

were Fe (20.2), Al (9.07), Zn (1.62), Cu (1.44), Cr (1.37) and Pb (1.13). EF_B values are used to present the accumulation rate of metals (Abril et al., 2014) and classified into 5 classes (Frati et al., 2005). It was found that the EF_B value for Al and Fe had fallen into severe accumulation rate ($EF_B > 1.75$), while those for Cr, Cu and Zn were in the same class of accumulation (1.25 - 1.75). The EF_B of Pb was in a normal rate (0.75 - 1.25). The EF_{TS} value was used to indicate sources of metals as being from either natural or anthropogenic sources. Based on the EF value of metals, a value higher than 1 can be considered from long-distance transport phenomena, from other natural and/or anthropogenic sources (Bergamaschi et al., 2002), while a value greater than 10 is indicative of anthropogenic influence (Ferreira et al., 2012). Therefore, the possible source of Zn ($EF_{TS} = 3.37$), Cu ($EF_{TS} = 2.56$) and Pb ($EF_{TS} = 1.46$) is from long-range transport of either natural or/and anthropogenic sources, whereas mean EF_{TS} value of Al, Cr and Fe (0.25, 0.26 and 0.11 respectively) were less than 1, meaning that they originated from the surrounding crustal (Bergamaschi et al., 2002).

3.3 Correlations between metals on bark samples

Correlations among metal concentrations on bark samples from Chiang Mai city were analyzed. Significantly strong correlations for Al-Fe ($r = 0.915$) were observed. Nevertheless, significantly weak to medium correlations ($r = 0.193 - 0.639$) were observed between almost all metals. Therefore, the concept of EF_{TS} was applied in order to reduce the effects of unique characteristics for each area by integrating the normalized concentration from both natural source metal (Mn) and local soil source. The correlations between normalized metal concentrations to EF_{TS} values were strongly correlated ($p <$

0.01) ($r = 0.629 - 0.940$) for almost all metals. The results indicated that all metals might be generated from the same sources or activities.

3.4 Source estimation of metals accumulated on the bark

Principal component analysis (PCA) of EF_{TS} was used in order to identify possible sources for the metals. The varimax rotation of principal component patterns was applied to improve the differentiation between sources. The results are shown in Table 4. Only factor loading higher than 0.5 was specified to be statistically significant (Chantara et al., 2012). Loadings having a value greater than 0.70 are marked in bold. There were two loadings with 93% variance. The first component had high loading for Cr, Cu, Pb and Zn, which likely originated from automobiles (McKenzie et al., 2009; Pulles et al., 2012), while Al and Fe had high loading in the second component. They are released from crust materials (Yongjie et al., 2009; Enamorado-Báez et al, 2015). Apart from that, Fe is also used in the composition for brake pads and tires on vehicles (Thorpe and Harrison, 2008; Apeagyei et al., 2011).

Cluster analysis (CA) was used to identify the group of metals found on bark samples. The analyzed metals were grouped based on their concentrations in the samples. Consequently, metals in the same group illustrated similar source origins. First of all, the individual EF_{TS} values were transformed by dividing the values with the maximum value for each metal species (maximum magnitude of 1 method) in order to avoid overpowering of the higher concentration on classification of the metal into groups. Then, the average linkage (between-groups linkage) and Squared Euclidean distance were calculated for cluster classification. Six metals were paired and divided into three groups (Fig. 3). In the first cluster (Cluster I), Al and Fe were closely linked. The result was well in agreement

394 with PCA analysis, in which both metals were in the same component. Moreover, the
395 accumulation characteristic of Fe on the bark (increasing of concentration in the wet season
396 and severe accumulation rate and crustal source from EFs classification) was the same as
397 Al. Consequently, Fe and Al should have originated from the same source. Al is well
398 known as an abundant metal composite in the Earth's crust, comprising 7% of its mass
399 (Dong et al., 2002). Therefore, the source of Fe found in this study should come from the
400 soil. The second group (Cluster II) consisted of Cr and Pb, while the third group (Cluster
401 III) was Cu and Zn. According to Pulles et al., (2012), Cr, Cu, Pb, and Zn are the dominant
402 metal species distributed from lubricant oil combustion in exhaust emissions. Moreover,
403 Cu, Pb and Zn are used as reliable tracers for the presence of vehicle source (Thorpe and
404 Harrison, 2008), leading to the conclusion that vehicles were a possible source of those
405 metals in Clusters II and III. It can be revealed that source approximation by CA and PCA
406 provided the same results. The result of metal classification in this study was similar to the
407 result from using *Parmotrema reticulatum* (lichen) as biomonitor for atmospheric
408 deposition of potentially harmful elements (PHEs) in the Greater Auckland Region of New
409 Zealand (Boamponsem et al., 2016). Therefore, two groups of metals were categorized
410 based on their sources; Al and Fe were soil resuspension (soil pollutants), while Cr, Cu, Pb
411 and Zn were vehicle (vehicle pollutants). Additionally, it could be summarized that the
412 metals accumulated on the bark were mainly originated from soil resuspension.

3.5 Assessment of metals using pollution indices

3.5.1 Geoaccumulation index of metals

The index was used to determine the level of metal contamination by comparing the concentrations accumulated on tree bark between Chiang Mai City with the background area. Individual and total geoaccumulation in the city are presented in Table 5. The individual I_{geo} values for vehicle pollutants were relatively lower than for soil pollutants. The value for I_{geo} can be categorized into 2 classes. Cr ($I_{geo} = -0.21$) and Pb ($I_{geo} = -0.40$) were classified as non- to weak polluted class ($I_{geo} \leq 0$), while Cu ($I_{geo} = 0.46$) and Zn ($I_{geo} = 0.19$) were categorized as weak to moderate class ($0 < I_{geo} \leq 1$). The I_{geo} values for both soil pollutants, Al (2.5) and Fe (3.6), fell into the class of moderately to strongly ($2 < I_{geo} \leq 3$) and strongly ($3 < I_{geo} \leq 4$) polluted, respectively. According to a study by Guéguen et al., (2012), the bark of *Tilla* trees were used as a bioindicator around an industrial area within a 15 km large radius in the Rhine Valley (French–German boundary). The I_{geo} values for Cu and Zn in this study were equal to the rural areas of the Rhine Valley. The values were 2 times lower than those in traffic and urban area, whereas the I_{geo} values for Cr and Pb were lower than those in all areas. On the other hand, the I_{geo} values for soil pollutants (Al and Fe) were comparable to those in traffic areas and urban areas. The lower degree of pollutant metals in this study might be from different vehicle types, vehicle volumes and the composition of fuel and lubricant.

$I_{GEO-tot}$ can be used to present soil and vehicle pollutants. It was found that vehicle pollutants such as Cr, Cu, Pb and Zn with a $I_{GEO-tot}$ value equal to 0.01 were classified as mildly to moderately polluted, while soil pollutants ($I_{GEO-tot}$ value = 3.06) fell into the highly polluted class.

3.5.2 Contamination factor and potential load index of metals

The status of pollutant contamination in Chiang Mai city was estimated by using contamination factor (CF) and potential load index (PLI). The calculated CF and PLI values are shown in Table 6. Soil pollutants (Al and Fe) should have relatively high CF values similar to I_{geo} values. The CF value of Fe (CF = 25.5) and Al (CF = 11.8) can be classified as very high contamination (CF > 6). All vehicle pollutants (Cr, Cu, Pb and Zn) were at the moderately contaminated level ($1 \leq CF \leq 3$). Moreover, the mean PLI value of soil pollutants (17.2) was classified at the highly polluted level, while that of the vehicle pollutants (1.60) was grouped into the unpolluted to moderately polluted level. The PLI value for vehicle pollutants in this study was comparable to the value found in soil samples at Yibin City, China, where high influence was found from industry and traffic (Guo et al., 2012).

The output from both indices revealed the contamination status in Chiang Mai city. Based on vehicle pollutants, it was unpolluted to moderately polluted, while it was moderately to highly polluted according to the level of soil pollutants. The results demonstrated that Chiang Mai city was polluted by road traffic, including fuel combustion, the corrosion of vehicle parts and soil resuspension distributed from the vehicle wheels as well as road surface. The city was polluted by contaminants in soil resuspension more than from vehicle emissions. However, individual value for the indices by sampling point varied from very low to high. Therefore, pollutant indices for each sampling point were presented in a spatial distribution map.

3.6 Spatial distribution map of soil and vehicle pollutants

Regarding the results of pollution assessment in Chiang Mai city, spatial distribution maps of PLI and $I_{\text{GEO-tot}}$ based on soil and vehicle pollutants were constructed to present patterns for metals distribution (Figs. 4–5). Moreover, vehicle volume in the road and building areas of the city were also considered together with both indices. Daily vehicle volume on the main roads of Chiang Mai city varied from 3,000 – 8,000 vehicles. The volume in the middle part of the city (18,000 vehicles) was relatively lower than in the outer (26,000 vehicles) and sub-urban areas (29,000 vehicles). In the city, roads are short and narrow. Therefore, traffic volume was lower than in sub-urban areas, where roads are wider and longer. Considering total building area in each square (0.25 km^2), it was found that the urban building areas were higher than that in sub-urban, especially an area within 3 km radius from the city center. Building area was found to be related to population density. It was 3 times higher in urban areas ($\sim 3,000 \text{ people/ km}^2$) than in sub-urban areas ($\sim 1,000 \text{ people/ km}^2$). Both building area and population density were related to $I_{\text{GEO-tot}}$ values for vehicle pollutants, which indicated that urban areas ($I_{\text{GEO-tot}}$ values = 0.08) were more polluted than sub-urban areas ($I_{\text{GEO-tot}}$ values = -0.15). The results were in agreement with previous results reported by Xia et al. (2011). They used a spatial distribution map of Beijing, China to present a contamination pattern of vehicle pollutants (Cu, Pb and Zn), which decreased from the center of the city out to the suburban areas. Table 7 presents the number of pollutant indices distributed in each polluted level between urban and sub-urban areas. The difference in polluted level of vehicle pollutants between urban and sub-urban areas was distinguished from classification by $I_{\text{GEO-tot}}$ values. It was found that 56% of all samples were classified as polluted level ($I_{\text{GEO-tot}}$ values > 0.00) in urban areas, while 31%

was observed in sub-urban areas. $I_{\text{GEO-tot}}$ values provided classification between urban and sub-urban indicated that $I_{\text{GEO-tot}}$ index was appropriate for classification of polluted level among different types of areas. On the other hand, the use of PLI value was unable to distinguish contamination levels between areas. This conclusion was based on statistical analysis, in which no significant difference ($p \geq 0.05$) between urban and sub-urban areas was found. Therefore, $I_{\text{GEO-tot}}$ was better than PLI in terms of pollution degree classification.

In order to distinguish the contamination level of each road, new intervals for $I_{\text{GEO-tot}}$ and PLI values in the map were adjusted by setting the interval from the range of contamination level (Fig. 4). $I_{\text{GEO-tot}}$ and PLI indices showed the same high value at Grid No #596 (20 columns from left hand side and 19 rows from bottom side), which was ~ 3 km away from the city center in a northeast direction. This area contains a big intersection with heavy traffic congestion. There are schools, hospitals and a bus terminal in this area. The values for $I_{\text{GEO-tot}}$ and PLI in the grid were 2.27 and 7.21, respectively. Both indices indicated that the ring-road at ~ 1 km west of city center (the pink circle in Fig. 4), close to hospitals and high schools, contained the highest traffic pollutant contamination. The main reason was high traffic density, especially during rush hours and due to low air ventilation in the area caused by high building density.

Fig. 5 presents $I_{\text{GEO-tot}}$ and PLI indices for soil pollutants. The highest values for both indices ($I_{\text{GEO-tot}} = 5.75$ and $\text{PLI} = 80.96$) were found at Grid No # 596. The result was similar to the traffic pollutants, but the soil pollutant indices were unable to be differentiated between urban and sub-urban areas. However, the highest soil pollutants in contaminated areas were found in the same area as a result of traffic pollutants (pink circle).

Pollution indices, $I_{\text{GEO-tot}}$ and PLI indices for vehicle pollutants were significantly correlated ($p < 0.01$) with both building area ($r_s = 0.383$) and traffic volume ($r_s = 0.269$), while not significantly correlated with the indices for soil pollutants. The result indicated that both building area and traffic volume were related to the accumulation of vehicle pollutants on *C. fistula* bark. Building area was related to building density as the major parameter influencing pollutant accumulation because high density value resulted in low air circulation. Consequently, there was a high chance for pollutant accumulation in that area. However, correlations between both parameters and pollutant indices were relatively weak. This may due to uncontrollable parameters, including vehicle flow, wind direction, wind velocity, building arrangements and shapes, aspect ratio (building height to street width) and tree planning, which influence pollutant dispersion (Buccolieri et al., 2011; Hang et al., 2016).

4. Conclusion

Metals (Al, Cr, Cu, Fe, Pb and Zn) accumulated on *C. fistula* bark planted on the roadsides in the city of Chiang Mai were analyzed for assessment of metals emitted from traffic activity. It was found that Al was the metal with the highest concentration, while Cr was the lowest existing metal. The results from PCA and CA also illustrated that metals accumulated on roadside tree bark originated directly from vehicles particles and from soil resuspension circulated from road traffic. The pollution indices, including PLI and $I_{\text{GEO-tot}}$, illustrated that urban areas were more contaminated from traffic pollutants than from suburban areas, while soil pollutants were randomly distributed in both areas based on the PLI and $I_{\text{GEO-tot}}$ values. Some areas of the city with high traffic density, such as hospitals and

525 school areas, might need effective management for a road traffic system to provide more air
 526 ventilation and reduce pollutant accumulation.

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Table 1. Recoveries of metals obtained from certified reference materials (n=5)

	NIES no.1 (Pepperbush)			NIST 1515 (Apple leaves)			RTC 051 (Cray soil)		
	Certified value (mg/kg)	Mean $\pm$ SD (mg/kg)	%Recovery $\pm$ SD	Certified value (mg/kg)	Mean $\pm$ SD (mg/kg)	%Recovery $\pm$ SD	Certified value (mg/kg)	Mean $\pm$ SD (mg/kg)	%Recovery $\pm$ SD
Al	<i>a</i>			286	278 $\pm$ 4	97 $\pm$ 1	5530	5396 $\pm$ 742	98 $\pm$ 13
Cr	1.3	1.5 $\pm$ 0.2	115 $\pm$ 15	<i>a</i>			246	283 $\pm$ 12	115 $\pm$ 4
Cu	12	11 $\pm$ 1	92 $\pm$ 4	5.64	4.87 $\pm$ 0.02	86 $\pm$ 1	59	54 $\pm$ 3	91 $\pm$ 5
Fe	205	168 $\pm$ 10	82 $\pm$ 6	83	72 $\pm$ 4	87 $\pm$ 5	4520	3853 $\pm$ 221	85 $\pm$ 5
Pb	5.5	4.4 $\pm$ 0.2	79 $\pm$ 3	0.470	ND	ND	44	37 $\pm$ 3	83 $\pm$ 9
Zn	340	304 $\pm$ 12	89 $\pm$ 4	12.5	11.7 $\pm$ 0.9	94 $\pm$ 8	44	46 $\pm$ 2	104 $\pm$ 5

Note: a = no certified value; ND = Not detect (<LOD).

Table 2. Metal concentrations on *C. fistula* bark samples

Sampling sites/season (Sample no.)		Metal concentration (ng/cm ²)					
		Al	Cr	Cu	Fe	Pb	Zn
Statistic ANOVA test							
CM/Dry season							
Urban (n=79)	Mean	1312 ^a	2.38 ^a	22.4 ^a	734 ^a	8.54 ^a	173 ^a
	Max -Min	6975- 180	29.1 -ND	65.0-5.1	2725-63	133-ND	609-39
Sub-urban (n=36)	Mean	1075 ^{ab}	1.60 ^a	18.4 ^{ab}	649 ^a	1.58 ^a	137 ^{ab}
	Max -Min	4044-190	10.9-ND	49.4-6.4	2208-63	23-ND	644-31
Background area (n=4)	Mean	105 ^b	ND ^a	9.0 ^b	28 ^b	ND ^a	82 ^b
	Max -Min	186-53	ND	20.4-2.7	67-ND	ND	113-66
Statistic paired t-test							
CM/Dry season *							
(n=40)	Mean	892 ^a	1.38 ^a	19.6 ^a	534 ^a	3.08 ^a	151 ^a
	Max -Min	4044-180	6.9-ND	49.4-7.6	2024-64	16.2-ND	644-31
CM/Wet season *							
(n=40)	Mean	1252 ^b	0.90 ^a	23.7 ^a	705 ^b	4.45 ^a	171 ^a
	Max -Min	5408-30	7.4-ND	65.6-2.5	2214-46	34.6-ND	475-ND

*Note: * The Same tree; ND = Not detect (<LOD); ^{a,b} significantly different (p < 0.05)*

670 **Table 3.** Enrichment factors of metals in relation to background values (EF_B) and soil
 671 (EF_{TS})

EFs	Classes	Meaning	Mean EFs (n =115)					
			Al	Cr	Cu	Fe	Pb	Zn
EF _B	0–0.25 ^a	Severe loss						
	0.25–0.75 ^a	Loss						
	0.75–1.25 ^a	Normal					1.13	
	1.25–1.75 ^a	Accumulation		1.37	1.44			1.62
	>1.75 ^a	Severe accumulation	9.07			20.2		
EF _{TS}	< 1 ^b	Surrounding soils	0.25	0.26		0.11		
	1 – 10 ^b	long distance transport phenomena, from other natural and/or anthropogenic sources			2.56		1.46	3.37
	>10 ^c	anthropogenic sources						

672 Reference: ^aFrati et al., 2005; ^bBergamaschi et al., 2002; ^cFerreira et al., 2012

673

674 **Table 4.** Principal components analysis of metal enrichment factor

	Components	
	1	2
Al	0.421	0.888
Cr	0.826	0.484
Cu	0.798	0.516
Fe	0.376	0.908
Pb	0.889	0.382
Zn	0.883	0.303
% of Variance	53.42	39.19
Cumulative %	53.42	92.62
Possible source	vehicle	Soil resuspension

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676

677

678

679 **Table 5.** Geoaccumulation index by using *C. fistula* bark (n = 115)

	I_{geo}						$I_{GEO-tot}$	
	Soil pollutants		Vehicle pollutants				Vehicle	Soil
	Al	Fe	Cr	Cu	Pb	Zn		
Mean	2.52 ^a	3.59 ^b	-0.21 ^w	0.46 ^x	-0.40 ^y	0.19 ^z	0.01 ^a	3.06 ^b
SD	1.15	1.29	0.64	0.71	0.46	0.77	0.45	1.20
Min	0.20	0.61	-0.58	-1.43	-0.58	-1.98	-0.87	0.41
Max	5.47	6.03	3.09	2.25	2.95	2.39	2.27	5.75

680 ^{a,b and w, x,y,z} Significantly different from pair and ANOVA test ($p < 0.05$).

681

682 **Table 6.** Contamination factor (CF) and potential load index (PLI) of metals (n=115)

	CF						PLI	
	Soil pollutants		Vehicle pollutants				Vehicle	Soil
	Al	Fe	Cr	Cu	Pb	Zn		
Mean	11.83 ^a	25.53 ^b	1.51 ^x	2.33 ^y	1.25 ^x	1.97 ^z	1.60 ^a	17.16 ^b
SD	10.86	20.35	1.43	1.23	1.09	1.19	0.77	14.31
Min	1.73	2.29	1.00	0.56	1.00	0.38	0.82	1.99
Max	66.68	98.31	12.76	7.16	11.58	7.84	7.21	80.96

683 ^{a,b and x,y,z} Significantly different from pair and ANOVA test ($p < 0.05$)

684

685 **Table 7.** Classification of pollution indices value in each contamination level

Ranges	Pollution degree	Number of indices (%)			
		Vehicle pollutants		Soil pollutants	
$I_{GEO-tot}$		Urban ^a	Sub-urban ^b	Urban ^a	Sub-urban ^a
≤ 0.00	None to weakly polluted	35 (44%)	25 (69%)		
0.01-1.00	Weakly to moderately polluted	42 (53%)	11 (31%)	4 (5%)	1 (3%)
1.01-2.00	Moderately polluted			13 (16%)	7 (19%)
2.01-3.00	Moderately to strongly polluted	2 (3%)		18 (23%)	10 (28%)
3.01-4.00	Strongly polluted			23 (29%)	11 (31%)
4.01-5.00	Strongly to excessively polluted			18 (23%)	5 (14%)
> 5.00	Excessively polluted			3 (4%)	2 (6%)
PLI		Urban ^a	Sub-urban ^a	Urban ^a	Sub-urban ^a
0.00	Background concentration				
0.01-1.00	Unpolluted	3 (4%)	3 (8%)		
1.01-2.00	Unpolluted to moderately polluted	64 (81%)	30 (83%)	1 (1%)	
2.01-3.00	Moderately polluted	10 (13%)	3 (8%)	3 (4%)	1 (3%)
3.01-4.00	Moderately to highly polluted			5 (6%)	1 (3%)
4.01-5.00	Highly polluted			5 (6%)	4 (11%)
> 5.00	Very highly polluted	2 (3%)		65 (82%)	30 (83%)

686 ^{a,b} significantly different between area in each pollutant source ($p < 0.05$)

Figure 1. Map of Chiang Mai city: (a) Sampling points; (b) tree bark sampling

Dendrogram using Average Linkage (Between Groups)
Rescaled Distance Cluster Combine

Possible sources

CASE Label	Num	0	5	10	15	20	25
Soil resuspension	Al	1					
	Fe	2					
	Cr	3					
Vehicle	Pb	4					
	Cu	5					
	Zn	6					

Figure 3. Hierarchical dendrogram of EF_{TS} of the six metals

699

700 **Figure 4.** Spatial distribution map of pollution indices for vehicle pollutants: (a) $I_{GEO-tot}$ of
 701 vehicle pollutants; (b) PLI of vehicle pollutants

Figure 5. Spatial distribution map of pollution indices for soil pollutants: (a) $I_{GEO-tot}$ of soil pollutants; (b) PLI of soil pollutants