1	Original Article
2	Organic and Elemental Carbons Characteristics in PM _{2.5} across Diverse
3	Landscapes
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15	Abstract
16	Air pollution, particularly in urban and industrial areas, is affecting human
17	health. Dust particles in the air are mostly composed of carbon particles, including
18	organic carbon (OC), and elemental carbon (EC). In this study, carbon compositions of
19	PM _{2.5} in different of land use surrounded Bangkok Metropolitan Region (BMR) area
20	were evaluated. A sampling was carried out during its episode using the gravimetric
21	method. They were analyzed for the organic and elemental carbon composition using
22	the thermal optical analysis following the U.S. EPA IMPROVE-A method. Results
23	found that organic carbon had the highest value in all sample areas. the OC/EC ratio in

PM_{2.5} ranged from 3.20 to 3.38. It can be concluded that the main sources of PM_{2.5} are emissions from gasoline and LPG exhaust, which come from vehicle and industrial combustion. Moreover, this study can provide supporting information for effective management and control of air pollution in urban areas.

Keywords: Organic carbon, Elemental carbon, Fine particulate matter, Pollution,

30 Urban.

1. Introduction

In recent years, air pollution has emerged as a significant concern and a prominent area of focus in atmospheric science research. According to the World Health Organization (WHO), a staggering 90% of the global population inhales highly polluted air, contributing to an alarming annual toll of 7 million deaths attributable to both outdoor and indoor air pollution. Particulate matter (PM), particularly PM_{2.5} with an aerodynamic diameter less than 2.5 μm, stands out as a key pollutant in air quality studies. The diminutive size of PM_{2.5} facilitates deep penetration into the human respiratory system, leading to adverse health effects upon prolonged exposure (Adães & Pires, 2019). Exposure to PM_{2.5} poses both short-term and long-term health risks. Short-term effects include irritation of the eyes, nose, throat, and lungs, accompanied by symptoms such as coughing, sneezing, runny nose, and shortness of breath. Furthermore, premature mortality can result from such exposure. Long-term consequences encompass adverse impacts on lung function and the exacerbation of medical conditions like asthma and heart disease (Department of Health, 2018).

Presently, Thailand is grappling with PM_{2.5} challenges in both urban and rural areas, particularly during the dry season spanning from November to February. The assessment of PM_{2.5} pollution levels in Bangkok relies on measurements obtained through the ambient air quality monitoring system conducted by the Thai Pollution Control Department. Additional data is sourced from the air quality monitoring network administered by the Bangkok Metropolitan Administration (BMA). These measured PM_{2.5} concentrations are juxtaposed with the national 24-hour average standard set at 15 µg m⁻³ (World Health Organization [WHO], 2021). Effectively managing and controlling PM_{2.5} pollution necessitates access to technical and scientific data concerning its characteristics, composition, and related factors. Such information plays a crucial role in facilitating the planning and implementation of strategies to mitigate potential emission sources in a manner that is both effective and suitable.

Carbon represents a key constituent of atmospheric PM_{2.5}, predominantly manifesting as organic carbon and elemental carbon. Elemental carbon in the atmosphere is emitted directly from primary anthropogenic sources, whereas organic carbon can be directly emitted from primary sources and undergo secondary formations within the atmospheric environment. The formation of secondary particulate matter occurs through atmospheric chemical reactions that involve high vapor pressure organics, ambient temperature, and sunlight in the atmosphere (Watson *et al.*, 1997). Utilizing the ratio between organic carbon (OC) and elemental carbon (EC) serves as a valuable tool in comprehending the transformation dynamics of pollutant emissions and carbonaceous particles. Research has demonstrated that an analysis of the correlation between OC and EC enables the identification of the source of carbonaceous aerosol. A robust correlation between OC and EC suggests similarities in pollution sources.

Consequently, this correlation can be effectively employed to qualitatively analyze the sources of carbon aerosol (Wang, Yu, Yang, & Fang, 2019).

The measurement of elemental carbon (EC) associated with atmospheric soot employs the technique known as Thermal-Optical Analysis (TOA). In TOA, variations in the optical properties of carbon within particulate matter (PM) are monitored to discern the thermal separation of carbon, specifically EC, from organic carbon (OC) within the sample (Joseph, 2008).

This research focused on measuring ambient PM_{2.5} across various land uses surrounding the BMR area. High-volume air samplers were employed to collect samples on quartz filters. Subsequently, thermal-optical analysis was conducted to quantify the levels of organic and elemental carbon within the samples. The findings suggest that PM_{2.5} primarily originates from organic carbon, resulting from the aggregation or transformation of gases. Additionally, carbon elements are formed through the combustion of fuels, as inferred from the results.

While there has been significant research on the chemical compositions and sources of PM_{2.5} in Thailand, there remains a scarcity of studies focusing on the characteristics of organic carbon (OC) and elemental carbon (EC) in PM_{2.5}, particularly in distinct landscape types such as residential and industrial areas. The objectives of this study were to assess the concentrations of organic and elemental carbons in PM_{2.5} across varied landscapes and to gauge the potential contributions of primary and secondary PM_{2.5} sources through an analysis of the EC/OC ratio. This study entails thorough measurements of PM_{2.5} within the encompassing BMR area, spanning various land use categories. The collected samples are subjected to analysis to determine the fractions of organic carbon (OC) and elemental carbon (EC) in PM_{2.5}. The outcomes of this research

are expected to contribute valuable insights into discerning potential emission sources of $PM_{2.5}$ across different land uses, facilitating more effective management of air pollution.

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2. Materials and Methods

2.1 Sampling site description

The study focuses on various land uses surrounding the BMR area, encompassing Nakhonpathom, Nonthaburi, and Samutsakorn, as illustrated in Figure 1. The geographical details of the sampling sites are outlined in Table 1. The selection of sampling sites deliberately represents two distinct land use categories: industrial areas and general or residential areas. This study adheres to the criteria outlined in the Acid Deposition Monitoring Network in East Asia report from 2000 for categorizing the study area based on land use types. The classification considers areas at both the onsite scale (within a 150-meter radius from the sampling point) and the local scale (within a 10-kilometer radius from the sampling point) (Acid Deposition Monitoring Network in East Asia [EANAT], 2000). For the Lapawan9 village (LPW 9) site, it is designated as a general area due to the onsite scale having a volume of vehicles passing through the site less than or equal to 1,000 vehicles per day, with a corresponding local scale volume of vehicles also less than or equal to 50,000 vehicles per day. Conversely, the Rai Khing Child Center (RKCC) site and Thepnorarat (TNSC) site are classified as industrial areas because of the presence of industrial factories surrounding the sampling sites on the local scale. Specifically, the RKCC site hosts various manufacturers engaged in the production of plastic packaging, glue starch with tapioca starch, warehouses, electrical transformers, general welding, freezing plants, as well as butchery and slaughterhouses.

Similarly, the Thepnorarat (TNSC) site is surrounded by freezing plants, stainless steel product facilities, plastic utensil manufacturing, wooden utensils and furniture production, as well as the production of frozen ready meals from meat and aquatic animals. PM_{2.5} levels at the sampling sites were assessed using the gravimetric method. Quartz filters were meticulously weighed before and after sample collection, utilizing a microbalance with an accuracy of 0.1 μg at the Automobile Emission Laboratory of the Pollution Control Department. The collection period for PM_{2.5} samples spanned 24 hours each day over 15 consecutive days at each sampling site, taking place from December 14, 2020, to February 19, 2021.

2.2 Sample analysis

Following the determination of mass concentration, samples underwent thermal-optical analysis to quantify the composition of organic and elemental carbon in PM_{2.5}. The analysis was conducted at the Environmental Science Research Centre, Chiang Mai University, adhering to the IMPROVE_A protocol for OC EC measurement. This method involves the thermal volatilization of carbonaceous material loaded onto a quartz fiber filter, which is heated in a quartz tube sample oven. The oven temperature undergoes a gradual increase in a pure helium atmosphere through four steps: 140 °C, 280 °C, 480 °C, and 580 °C. Subsequently, an oxidative atmosphere containing 98% helium and 2% oxygen is applied during three temperature steps: 580 °C, 740 °C, and 840 °C, following the protocol (Chow *et al.*, 2007). The devolatilized carbon extracted from the sample punch undergoes oxidation to CO₂, facilitated by MnO₂, within a primary catalyst oven at a temperature of 915 °C. Subsequently, in a secondary catalyst oven, the CO₂ is reduced to methane with hydrogen, employing a nickel catalyst (Fung, Chow, & Watson, 2004). The carbon liberated from the sample is continuously

measured as a methane equivalent via a flame ionization detector (FID). Concurrently, the sample's darkness is monitored for pyrolysis correction, utilizing a 632.8 nm He-Ne laser and a photodetector.

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In the initial stage of the thermal-optical analysis, the temperature is incrementally raised within the range of 550 °C to 870 °C in a pure helium atmosphere. This elevation induces the volatilization of thermally unstable organic carbon (OC), allowing for its measurement, even though some OC may undergo pyrolysis at these temperatures. Conversely, elemental carbon (EC) remains firmly bound to the filter, as it solely volatilizes through sublimation at temperatures approximately 650 °C (Peterson & Richards, 2002) in the absence of oxidants or reactions. Throughout this phase, alterations in the transmittance/reflectance of the samples are continuously monitored using a He-Ne laser. As the pure helium phase progresses, the pyrolysis of OC results in the formation of char, which constitutes EC and absorbs light, thereby causing a reduction in transmittance/reflectance values from their baseline. In the subsequent phase of the analysis, occurring in a 2% O₂ in He atmosphere, the introduced oxygen oxidizes both the pyrolytically formed char and the inherent EC content of the sample. This process releases them from the filter, enabling their quantification. Consequently, the filter's transmittance/reflectance values experience an increase in this phase. Upon the laser signal returning to its baseline value, the instrument automatically designates this point as the "split point," crucial for correcting the char produced during the initial phase of analysis. The elemental carbon (EC) detected from the beginning of the He/O₂ phase up to the "split point" is considered pyrolytic and is added to the overall organic carbon (OC) amount. Meanwhile, the EC detected after the "split point" is recognized as the native EC content of the sample, following the approach (Bautista et al., 2015). To

contextualize the temperature steps and durations employed in this study using the IMPROVE_A method, a comparison with other methods (NIOSH and EUSAAR_2) is presented in Table 2. The calculation of OC and EC involves summing the quantities obtained at different combustion temperatures. OC is defined as OC1+OC2+OC3+OC4+OP, while EC is defined as EC1+EC2+EC3-OP.

3. Results and Discussion

3.1 OC and EC Analysis

The analytical findings regarding the organic carbon (OC) and elemental carbon (EC) contents in PM_{2.5} samples, gathered at the Lapawan9 village (LPW 9), Rai Khing Child Center (RKCC), and Thepnorarat (TNSC) sampling sites, are illustrated in Figure 2 and detailed in Table 3.

The measured results revealed that OC3 made the highest contribution among all the collected samples. OC3 primarily originated from exhaust emissions of gasoline and liquefied petroleum gas (LPG) dust, followed by OC2 and OC4. OC4 consisted of OC3, while OC2 was emitted from the combustion of fuel oil and coal. Consistently, Organic Carbon 3 (OC3) emerges as the predominant carbon fraction in all studied areas, with the most significant contribution observed in the general area (LPW 9) at 36%. This finding implies a substantial influence of sources related to engine combustion, likely stemming from vehicular emissions and industrial machinery. Varied Contributions of OC2: The contribution of Organic Carbon 2 (OC2) fluctuates among areas, with its highest percentage (25%) identified in the RKCC industrial zone. This variability indicates a notable impact of fuel oil and coal combustion in industrial settings, potentially associated with specific industrial processes. Industrial Influence on OC3 and OC4: In both industrial areas (RKCC and TNSC), the percentages of OC3 and OC4

surpass those in the general area (LPW 9). This underscores the influence of industrial activities on particulate matter composition, suggesting contributions from combustion processes within factories. Limited Presence of EC3: Elemental Carbon 3 (EC3) is conspicuously scarce across all areas, with minimal or zero percentages. This scarcity could be attributed to the research method employed, which might have affected the detection of certain carbon fractions, especially at high temperatures.

3.2 Average OC and EC and its OC/EC Ratio

The mean concentrations of Organic Carbon (OC) and Elemental Carbon (EC) recorded at each sampling site are depicted in Figure 3. The analytical findings revealed that the average OC levels measured at LPV9 (a), RKCC (b), and TNSC (c) were 21.66 μg m⁻³, 19.64 μg m⁻³, and 29.22 μg m⁻³, respectively. The highest OC concentration, reaching 39.291 μg m⁻³, was observed at the industrial site (TNSC). The measured OC concentrations at LPV9 (general area) and RKCC (industrial area) exhibited notable similarity. In terms of total EC concentrations, RKSC recorded the lowest value, followed by LPV9 and TNSC, respectively.

Figure 3 displays the mean concentrations of Organic Carbon (OC) and Elemental Carbon (EC) at each sampling site. According to the analytical results, the average OC levels recorded at LPV9 (a), RKCC (b), and TNSC (c) are 21.66 μg m⁻³, 19.64 μg m⁻³, and 29.22 μg m⁻³, respectively. The highest OC concentration, reaching 39.291 μg m⁻³, was observed at the industrial site (TNSC). Notably, measured OC concentrations at LPV9 (general area) and RKCC (industrial area) exhibited considerable similarity. In terms of total EC concentrations, the lowest value was recorded at RKSC, followed by the concentrations measured at LPV9 and TNSC, respectively.

Figure 4 illustrates the ratio of primary and secondary particulate origins from organic carbon (OC), while elemental carbon (EC) is categorized as primary particulate. The results indicated that at the LPW9 sampling point, the carbon fraction of primary particulate was 6.80 μg m⁻³, and the carbon fraction of secondary particulate was 23.32 μg m⁻³. Evaluating the OC/EC ratio [(OC1+OC2+OC3+OC4+OP)/(EC1+EC2+EC3-OP) = 23.32/6.80 or 3.43], it is deduced that approximately 77.53% of the PM_{2.5} measured at this general area originated from secondary particulate sources (Chow *et al.*, 2007). Applying the same methodology, the contribution of secondary particulate in PM_{2.5} measured at the industrial area was approximately 76.38% (at RKCC) and about 77.31% (at TNRS), respectively.

The measured OC/EC ratio in this study ranged from 3.23 to 3.45. Comparison with Table 4 suggests that the primary source of PM_{2.5} in both general and industrial areas is likely the exhaust emissions from gasoline and liquefied petroleum gas (LPG) used as fuel in vehicles and industrial combustion (Table 4). These findings align with similar studies conducted in major cities in China, Hong Kong, and Taiwan (Cao *et al.*, 2005; Lin & Tai, 2001). Notably, in Taiwan, measurements in the general area indicated an OC/EC ratio of about 7.0, pointing to biomass burning as the dominant contributor to PM_{2.5} concentrations (Meng *et al.*, 2007) (Table 5). The carbon fractions identified in this study indicated the highest percentage contribution from OC3, followed by OC2, OC4, EC1, OC1, and EC2, respectively. OC1 was predominant in samples associated with biomass burning, while OC3 and OC4 were relatively abundant in road dust profiles (Chow *et al.*, 2004). OC2 was abundant in samples related to coal combustion, and EC1 was enriched in motor-vehicle exhaust samples (Cao *et al.*, 2005).

Additionally, EC2 and EC3 were carbon fractions associated with coal combustion and motor-vehicle exhaust, respectively (Yu, Xu, & Yang, 2002).

The general area in Thailand (LPW9) displays elevated Total Carbon (TC), Organic Carbon (OC), and Elemental Carbon (EC) concentrations compared to analogous general areas in China, Hong Kong, Shenzhen, and Taiwan. In contrast, industrial areas in Thailand (RKCC and TNRS) exhibit comparable TC and OC levels to general areas in other regions, but with notably higher EC concentrations, suggesting a discernible impact of industrial emissions. The OC/EC ratio demonstrates variability across locations, with industrial areas generally exhibiting higher ratios than general areas. Taiyuan, China, stands out with markedly higher TC and OC levels, indicative of potentially intensive industrial activities and emissions. These cross-regional comparisons underscore the regional diversity in particulate matter composition, influenced by local sources, industrial activities, and variations in measurement methodologies.

In their 2013 study, Duangkaew et al. identified potential sources of OC1–OC4 and EC1–EC3, as outlined in Table 6 (Duangkaew, Limpaseni, & Suwattiga, 2013). The investigation delved into the sources of PM_{2.5}, with details presented in Table 7 based on the derived source profiles. It is important to highlight that multiple methodologies exist for assessing aerosol source profiles. For instance, the measurement of radiocarbon (14C) in carbonaceous aerosols offers independent and quantitative insights into the contributions of biomass burning and fossil fuels to regional emission budgets. This approach complements data from satellite remote sensing and in situ field measurements (Wiggins *et al.*, 2018).

4. Conclusions

This study concentrated on examining the source contributions of ambient $PM_{2.5}$ in both general and industrial areas surrounding the Bangkok Metropolitan Region (BMR). The findings revealed a hierarchical order of major emission sources influencing total $PM_{2.5}$ concentrations, with gasoline and LPG exhaust being the predominant contributors, followed by fuel oil and coal combustion, biomass burning, and diesel exhaust.

Our results highlight the prevalence of secondary particulate matter, with organic carbon exhibiting a secondary origin and elemental carbon emanating primarily from direct emissions. This observation aligns with the visible presence of fine particulate matter resembling black soot, commonly associated with primary emissions from diesel vehicles. In contrast, gasoline and LPG vehicles were identified as sources of volatile organic compounds, which undergo chemical transformations, transitioning from a gaseous to a fine particulate phase.

Furthermore, our investigation underscored that the contribution of organic carbon (OC) to PM_{2.5} in Bangkok and its vicinity predominantly originated from gasoline and LPG exhausts. As a result, targeted control measures should not only address primary emission sources but also consider other sources potentially emitting precursors of secondary PM_{2.5} formation. This study emphasizes the critical importance of understanding pollutant source contributions specific to each area before formulating strategies to mitigate their concentrations. To facilitate effective PM_{2.5} pollution management, the development of an emission inventory for the target PM_{2.5} in the concerned area is crucial, aiding in the identification and elaboration of emission sources.

Acknowledgments

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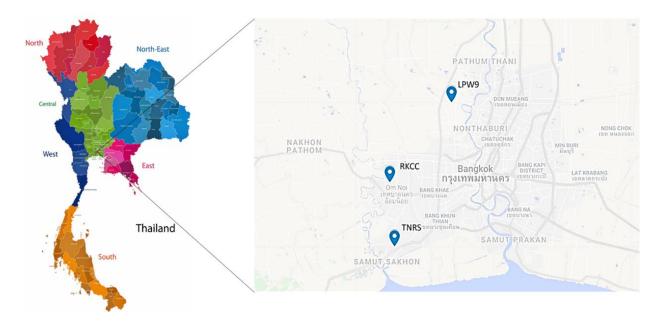
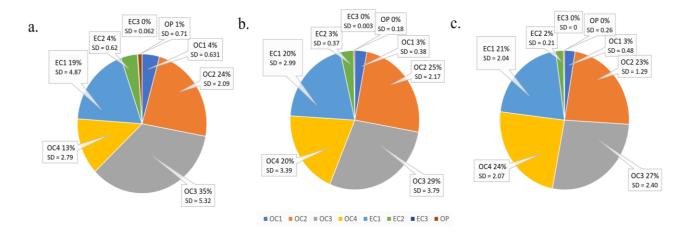


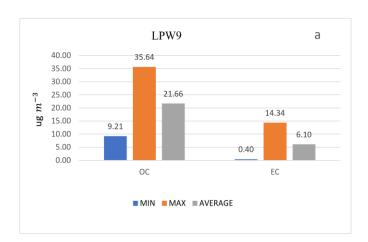
Figure 1 Location of sampling sites.

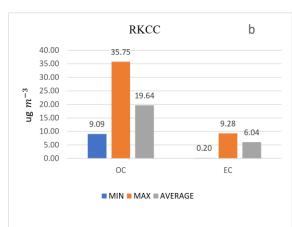


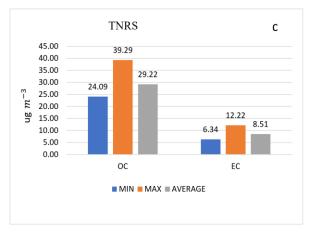
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Figure 2 Average percentage of OC and EC in sample site (a) LPW9, (b) RKCC

389 and (c) TNSC.







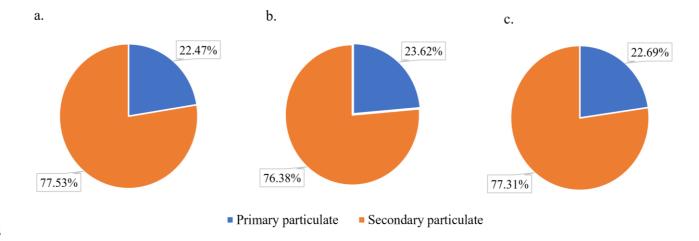
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Figure 3 Average OC and EC concentrations at the sample sites (a) LPW9, (b) $\,$

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RKCC, and (c) TNSC.



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Figure 4 Ratio of primary and secondary particulates of PM_{2.5} at the sampling sites

from OC and EC analysis (a) LPW9, (b) RKCC and (c) TNSC.

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Table 1 Information of the sampling site characteristics.

Province	Land use Sampling site		Location of sa (UTM:	•
			X	Y
Nonthaburi	General area	LPW9	655.375	1539.793
Nakhon Pathom	Industrial area	RKCC	638.411	1518.870
Samut Sakhon	Industrial area	TNSC	639.794	1502.030

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Table 2 Temperature steps and durations of NIOSH, IMPROVE_A, and

400 EUSAAR_2 (Cavalli, Viana, Yttri, Genberg, & Putaud, 2010).

	NIOSH	IMPROVE_A	ESAAR_2
Step	T(C), duration(s)	T(C), duration(s)	T(C), duration(s)
OC1	310, 80	140, 150-580	200, 120
OC2	475, 60	280, 150-580	300, 150

G.	NIOSH	IMPROVE_A	ESAAR_2
Step	T(C), duration(s)	T(C), duration(s)	T(C), duration(s)
OC3	615, 60	480, 150-580	450, 180
OC4	870, 90	580, 150-580	650, 180
EC1	550, 45	580, 150-580	500, 120
EC2	625, 45	740, 150-580	550, 120
EC3	700, 45	840, 150-580	700, 70
EC4	775, 45	-	850, 80
EC5	850, 120	-	-
EC6	870, 120	<u>-</u>	-

403 Table 3 Percentage of average carbon fraction in OC and EC.

Land use	Carbon fractions (µg m ⁻³)	Percentage of OC and EC (%)
	OC1 (1.22)	4%
	OC2 (6.61)	24%
	OC3 (9.84)	36%
(General area)	OC4 (3.70)	13%
LPW 9	EC1 (5.21)	19%
	EC2 (1.16)	4%
	EC3 (0.03)	0%
	OP (1.19)	4%
Industrial area	OC1 (0.78)	3%

Land use	Carbon fractions (μg m ⁻³)	Percentage of OC and EC (%)
RKCC	OC2 (6.38)	25%
	OC3 (7.36)	29%
	OC4 (5.07)	20%
	EC1 (5.26)	20%
	EC2 (0.84)	3%
	EC3 (0.001)	0%
	OP (0.400)	2%
	OC1 (0.99)	3%
	OC2 (0.83)	23%
	OC3 (10.24)	27%
Industrial area	OC4 (9.05)	24%
TNSC	EC1 (7.90)	21%
	EC2 (0.73)	2%
	EC3 (0.00)	0%
	OP (0.649)	2%

405 Table 4 OC/EC ratio and its relevant emission source.

Source	OC/EC ratio	Reference
		(Schauer, Kleeman, Cass, & Simoneit,
Gasoline and LPG exhaust	1.0 - 4.0	1999; Schauer, Kleeman, Cass, &
		Simoneit, 2001)
Diesel exhaust	< 1	(Schauer <i>et al.</i> , 1999; Schauer <i>et al.</i> ,
Diesei Callaust	\ 1	(Schauer et al., 1777, Schauer et al.,

Source	OC/EC ratio	Reference
		2001)
Biomass combustion	7.0 - 8.0	(Zhang, Cao, Lee, Shen, & Ho, 2007)
Wood combustion	16.8 – 40.0	(Schauer et al., 2001)
Residential cooking produced	32.9 – 81.9	(He et al., 2004)

Table 5 Comparison of TC, OC, and EC with other Asian cities (Gu et al., 2010).

T	TC	OC	EC	OCITIC	Measure	D. C
Location	(μg m ⁻³)	(μg m ⁻³)	(μg m ⁻³)	OC/EC	method	Reference
General area	27.6	21.3	6.4	3.45	IMPROVE_A	This study
(LPW9),						
Thailand						
Industrial area	25.6	19.5	6.1	3.23	IMPROVE_A	This study
(RKCC),						
Thailand						
Industrial area	37.7	29.1	8.6	3.41	IMPROVE_A	This study
(TNRS),						
Thailand						
Industrial area	17.3	12.2	5	2.4	IMPROVE_T	(Cao et al.,
Guangzhou,					OR	2005)
China						
General area	14.4	9.6	4.7	2.3	IMPROVE_T	(Cao et al.,
Shenzhen,					OR	2005)

Location	TC	OC	EC	OC/EC	Measure	Reference
	$(\mu g m^{-3})$	(μg m ⁻³)	(μg m ⁻³)		method	
China						
General area	23.2	16.3	6.9	2.4	IMPROVE_T	(Cao et al.,
Zhuhai, China					OR	2005)
General area	25.1	17	8.1	2.1	IMPROVE_T	(Cao et al.,
Hong Kong					OR	2005)
General area	14.4	10.4	4	2.6	Elemental	(Lin & Tai,
Kaohsiung,					analyzer	2001)
Taiwan						
General area	33.5	28.9	4.8	7.0	IMPROVE_T	(Meng et al.,
Taiyuan, China					OR	2007)

408 Remarks: TC = Total carbon

409

Table 6 Potential source of carbon fractions (Duangkaew et al., 2013).

Carbon fractions	Potential Source
OC1	Biomass burning
OC2	Coal combustion
OC3	Gasoline and LPG exhaust
OC4	Road dust
EC1	Motor vehicle exhaust
EC2 Diesel exhaust	
EC3	Coal combustion and motor vehicle exhaust

412 Table 7 Potential source contribution of PM_{2.5}

Sampling site	Representativeness	Source contribution
LPV9	General area	- Mobile exhausted source (23%)
		- Road dust (13%)
		Gasoline and LPG exhaust (36%)
		Biomass burning (4%)
		- Coal combustion (24%)
RKCC	Industrial area	- Mobile exhausted source (23%)
		- Road dust (20%)
		Gasoline and LPG exhaust (29%)
		- Biomass burning (3%)
		- Coal combustion (25%)
TNRS	Industrial area	Mobile exhausted source (23%)
		- Road dust (24%)
		Gasoline and LPG exhaust (27%)
		- Biomass burning (3%)
		- Coal combustion (23%)

Gasoline and LPG exhaust come from factories that use oil and gas as fuel for their

⁴¹⁴ operations.