

Contribution of Primary and Secondary PM_{2.5} at a Near Road Monitoring Station in Bangkok during the 2020 COVID-19 Lockdown

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Abstract

PM_{2.5} samples were collected at a near road air monitoring station during the first and harsh lockdown in Bangkok. The sampling campaign was set to gain the insight information on chemical speciation of PM_{2.5} during this rare event when most activities in Bangkok cease, and to establish a low episode of PM_{2.5} and its chemical component. The sampling was carried out during April and May 2020 with a Federal Reference Method (FRM) air sampler. Twenty-one metals were characterized by an inductively coupled plasma mass spectrometry (ICP-MS). Nine soluble ions were analyzed by an ion chromatography (IC), and a thermal-optical analysis for organic carbon (OC), and elemental carbon (EC). Daily PM_{2.5} concentrations at the sampling station ranged from 20.3 to 44.4 µg/m³ with the median of 26.3 ± 7.4 µg/m³. Secondary aerosol species accounted about 65% of PM_{2.5} mass and 14% for the primary aerosols, and unaccounted component was about 21%. OC was the major component of the secondary aerosol (59%), followed by sulfate ion (33%), ammonium ion (5%), and nitrate ion (3%). Sulfur dioxide as a precursor gas was well correlated with sulfate ion ($r = 0.8, p < 0.05$). EC accounted about 47% of the primary aerosol, followed by other water-soluble ions (27%), and elemental component (26%). Daily concentration of PM_{2.5} at the near road location in Bangkok during the low episode remained higher than the new guideline suggested by WHO (15 µg/m³). Lower the contribution of the secondary species of PM_{2.5} is crucial for the reduction of PM_{2.5} mass in the area and it is very challenging to achieve the target recommended by the guideline.

Keywords: Primary aerosols; Secondary aerosols; Low episode; COVID-19 pandemic; Bangkok

1. Introduction

Recent high episodes of PM_{2.5} have become a public health concern among ten million inhabitants in Bangkok, Thailand. The 2018 – 2020 episodes were unprecedented and gained attention nationwide over the widespread of atmospheric pollution the country has seen in the past decade, much higher than the 24-hr national ambient air quality standard of 50 µg/m³. The events, at some point, have caused panic and stimulated the extensive use of face mask and air purifier in daily life. The government has response with mitigation measures to curbe the emissions from various anthropogenic sources, e.g., diesel vehicle restriction,

open burning ban. However, more effective strategies are much needed to understand the PM_{2.5} problems in Bangkok. For instant, the background levels of PM_{2.5}, chemical compositions, or source contributions should provide insight information of the problems. The urban background PM_{2.5} in Bangkok is difficult to estimate due to constant high activities year-round, but the opportunity of quantifying the PM_{2.5} urban background came when the stringent lockdown of Bangkok was enforced in April 2020 from the surge of COVID-19 cases in Thailand.

PM_{2.5} is a complex mixture of various chemicals, causing visibility reduction

resolution of 1 µg (XPR series, Metler Toledo, Switzerland).

A Federal Reference Method (FRM) air sampler was used to collect PM_{2.5} at a required flow rate of 16.67 L/min (PQ200, BGI, Inc., USA). A primary flow calibrator was used as the calibrator prior to the sampling (deltaCal BGI, Inc., USA) to ensure the corrected flow rate during the sampling. The sampler was set and ran for 24 hours each day. The filters were retrieved the next day and put in the 50 mm petri dish. The filters were equilibrated in a desiccator at the same relative humidity and temperature in the similar manner as previously described procedures. Post-weight was determined after completed the filter equilibration for at least 24 hours. Later the filters were divided and subsequently extracted for quantitative analysis.

2.3 Quantifying chemical composition of PM_{2.5} sample

Ten water soluble ions including NH₄⁺, Na⁺, Mg²⁺, K⁺, Ca²⁺, NO₃⁻, SO₄²⁻, Cl⁻, and F⁻ were analysed by an ion chromatography (IC) (Dionex, Model ICS5000, ThermoFisher Inc., USA). The filter was submerged in 20 mL of deionized water and sonicated for 30 minutes and maintained the temperature at less than 25°C with ice in the sonicator. The sample solution was filtrated through 0.45 µm pore size of a nylon filter.

Twenty-one elements including Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, and Zn, were quantified by an Inductively Couple Plasma-Mass Spectroscopy (ICP-MS) (Model 7700, Agilent Technologies, USA). Another portion of the filter was digested with SupraPur® nitric acid

(Merck KGaA, Germany) in a microwave (MAR6™, CEM Corp., USA). The sample solution was later filtered with 0.45 µm pore size of nylon filter before analysis.

OC and EC concentrations were measured by a thermal-optical method using a carbon analyzer (Sunset Laboratory Ltd., USA) based on NIOSH method (Method-5040).

3. Results and Discussion

3.1 PM_{2.5} concentration during low episode

The sampling campaign during the lockdown was scheduled for every other day between 8 April 2020 and 24 May 2020 with the total of 18 samples. Daily average of PM_{2.5} concentrations ranged from 20.3 to 44.4 µg/m³ with the average of 29.6 ± 7.4 µg/m³ and the median of 26.3 µg/m³. Every PM_{2.5} samples were lower than the 24-hr national ambient air quality standard of 50 µg/m³, but all the samples were exceeded the new 2021 WHO air quality guideline. A trend analysis shows that the median PM_{2.5} concentrations in the previous year in April and May were significantly higher at 40% relative to the median of PM_{2.5} concentrations in 2018. The findings suggested that limited activities during the lockdown decreased PM_{2.5}. In Asia, the mean of PM_{2.5} concentrations during the city lockdown in Thailand ranked second while the minimum of mean concentration of PM_{2.5} was observed in Singapore (Li and Tartarini, 2020). Vietnam and China had higher levels of mean PM_{2.5} concentrations (Nguyen *et al.* 2021; Xia *et al.* 2021). Mean PM_{2.5} concentrations in the U.S. and Brazil were less than 15 µg/m³ (Berman and Ebisu, 2020; Nakada and Urban, 2020).

Table 1. The PM_{2.5} concentrations during COVID-19 lockdown in various country

Country	Mean PM2.5 concentration, µg/m ³	References
Bangkok, Thailand	29.6	This study
Singapore	11.0	Li and Tartarini, 2020
Chengdu, China	37.8	Xia <i>et al.</i> , 2021
Hanoi, Vietnam	43.4	Nguyen <i>et al.</i> , 2021
US	13.9	Berman and Ebisu, 2020
São Paulo state, Brazil	12.5	Nakada and Urban, 2020

3.2 Primary and Secondary PM_{2.5}

The PM_{2.5} samples were quantitatively analyzed for water soluble ions (WSIs), organic carbon (OC) and elemental carbon (EC), and trace elements (TEs). The median concentrations of chemical composition found in PM_{2.5} samples, calculated as mass per volume of air are in Figure 2.

In terms of mass concentration, EC was the most abundant species in primary PM_{2.5}, and potassium ion ranked second (Figure 2A). EC is emitted directly from incomplete combustion (Andrew Gray and Cass, 1998). Previous studies showed that potassium ion was originated from biomass combustion (Amato and Hopke, 2012; Lee *et al.*, 2008; Pachon *et al.*, 2013; Pio *et al.*, 2008). Zinc ranked third in primary PM_{2.5}. Zinc may be an indicator element related to traffic source (Almeida *et al.*, 2020) and marker element of tier wear (Wählén *et al.*, 2006). Sodium ion ranked fourth and several studies suggested

that sodium ion was mainly associated with sea salt spray (Kumar *et al.*, 2006; Li *et al.*, 2016; Nava *et al.*, 2020). Ions and elements were found less than 200 ng/m³ including calcium, chloride, magnesium, fluoride, boron, iron, and aluminum. Other elements were in trace level, less than 15 ng/m³.

On a mass concentration basis, OC dominated the secondary PM_{2.5} follow by sulfate, ammonium, and nitrate, respectively. OC is comprised of primary and secondary organic carbon and generated from fuel combustions (Contini *et al.*, 2018; Huang *et al.*, 2018). Sulfate and nitrate ions deposited in PM_{2.5} originate from atmospheric precursors (Tao *et al.*, 2017) including sulfur dioxide (SO₂) and oxide of nitrogen (NO_x). Ammonium ion originates from ammonia precursor mainly emitted by agricultural sector (Ehrnsperger and Klemm, 2021). Level of atmospheric ammonia play a key role in aerosol formation.

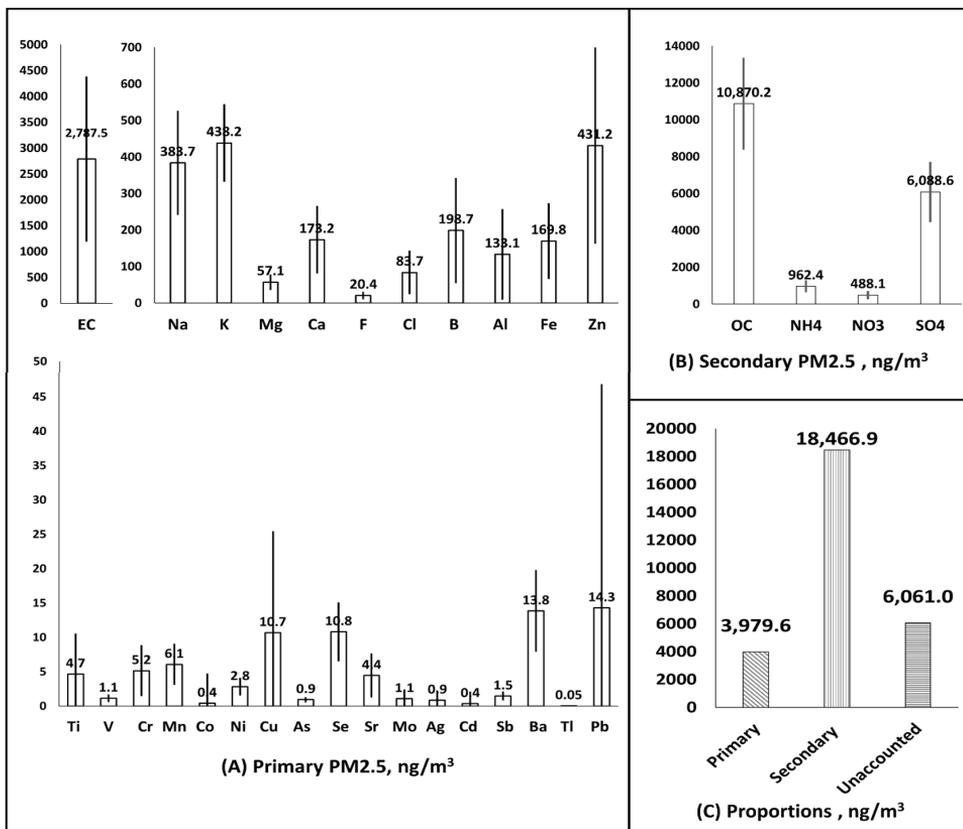


Figure 2. Chemical compositions and classified components in PM_{2.5}

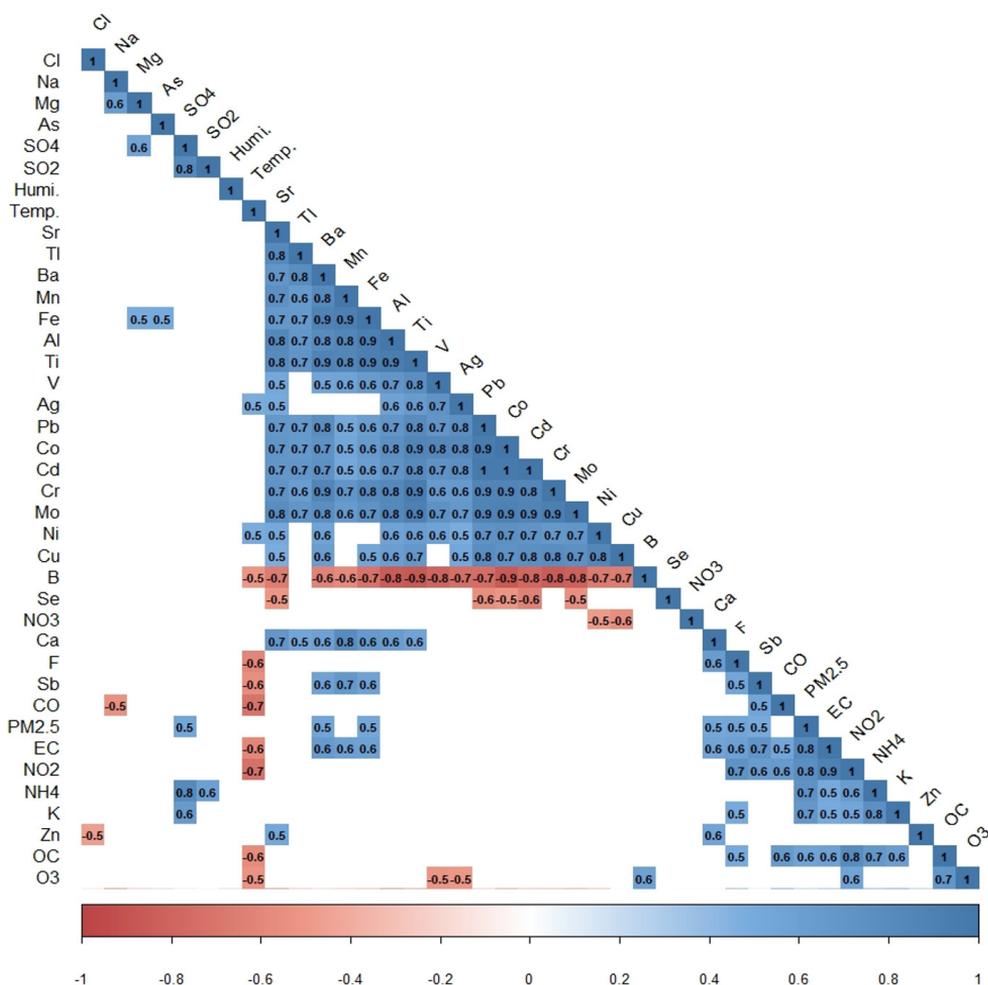


Figure 3. Correlation matrix of chemical composition in log₁₀ scale.

The OC/EC ratio was used to identify the sources of emissions and secondary formation of PM_{2.5} (Appel *et al.*, 1979). The average OC/EC ratio was 4.9 ± 2.0 that may be a part of photochemical reaction of secondary organic particle (Bhowmik *et al.*, 2021; Chow *et al.*, 1976; Liu *et al.*, 2020). Additionally, CO, NO₂, and NH₄⁺ were strongly contributed to the OC concentration in PM_{2.5}. It evidenced that secondary organic component and gas precursor play a significant role in secondary organic carbon concentration. Moreover, negative correlation between OC and surface temperature can be observed in Figure 3. The moderate relationship between OC and EC in PM_{2.5} may possibly indicate that a part of them comes from the same source of emissions. Previous studies provided that the ratio of OC/EC from diesel vehicles ranges

from 0.92 to 2.5 (Mei *et al.*, 2019) and from coal combustion was between 0.3 and 0.7 (Wang *et al.*, 2016). A relatively high in OC/EC ratio may indicated the emissions from biomass combustions (Bhowmik *et al.*, 2021; Wang *et al.*, 2016). Zhang *et al.* (2007) showed that the OC/EC ratio of 7.7 was found in rice, wheat, and corn burning (Zhang *et al.*, 2007). A potassium ion can be used as a source maker from biomass burning (Pachon *et al.*, 2013) but it should be noted that it can have other sources such as sea salt and crustal dust (Duvall *et al.*, 2008). Thus, non-sea-salt potassium was calculated (Lai *et al.*, 2007; Wang *et al.*, 2005; Witkowska *et al.*, 2016) and the contribution of sea-salt potassium was negligible—molar ratio K⁺/Na⁺ was higher than 0.022 (Keene *et al.*, 1986). The positive correlation between OC,

and K was significant ($p < 0.05$) shown in Figure 3, indicating that OC and K had similar source of emissions. The mean OC/ K^+ ratio was 26.2 ± 5.9 suggesting that agricultural combustion partly influenced the OC and K^+ concentration in $PM_{2.5}$ (Andreae, 2019; Bhowmik *et al.*, 2021). The contribution of agricultural burning would be minor due to its near-road locations. Additionally, the concentration of some trace elements (Ba, Mn, Fe) was coincided with EC ($r = 0.6, p < 0.05$). These three elements were found in crust and highly traffic road (Fabretti *et al.*, 2009; Seibert *et al.*, 2020). The result suggested that the source of OC, EC, K in Bangkok during low episode may coincidentally come from both vehicle emissions and solid-biofuel combustion for domestic purpose such as grilling.

Sulfate ion was lower than OC. The results showed strong relationship ($r = 0.8, p < 0.05$) between sulfate ion concentration (ng/m^3) and SO_2 (kg/m^2) in log10 scale (Figure 3). It should be noted that data for SO_2 (kg/m^2) derived from satellite estimate due to lack of actual measurement at the sampling site. The concentration of sulfate ion correlated strongly and positively with ammonium ion ($r = 0.8, p < 0.05$) as shown in Figure 3. It suggested that the neutralization of ammonium ion preferentially reacted with

sulfate ion, forming ammonium sulfate ($[NH_4]_2SO_4$), letovicite ($[NH_4]_3H[SO_4]_2$), or ammonium bisulfate (NH_4HSO_4) (Lee *et al.*, 1993). Nitrate ion concentration was less than $500 ng/m^3$ during this low episode. No correlation of nitrate ion with ammonium ion and nitrate ion with nitrogen oxide precursor can be marked in this study. Nitrate ion would be originated from complex reaction, such as renoxification, heterogeneous reaction, and photochemical reaction (Zhang *et al.*, 2013). Lee *et al.* (2008) explained that relatively high humidity and low temperature were favorable condition for ammonium nitrate formation. In contrast, during the low episode, the sampling area was in summer leading to more volatilization process that may result in low level of nitrate in $PM_{2.5}$. The mean of NO_3^-/SO_4^{2-} mass ratio was 0.08 ± 0.4 , indicating sulfate ion was dominant secondary aerosols in $PM_{2.5}$ during low episode in Bangkok.

Positive and significant correlation among the minor elements (Sr, Tl, Al, Ti, V, Ag, Pb, Co, Cd, Cr, MO, Ni, and Cu) can be remarked in the present study (Figure 3). It can be pointed out that they would have the same source of emissions. However, the mass contributions of all elements accounted about 3% relative to the mass concentration of $PM_{2.5}$ (Figure 4).

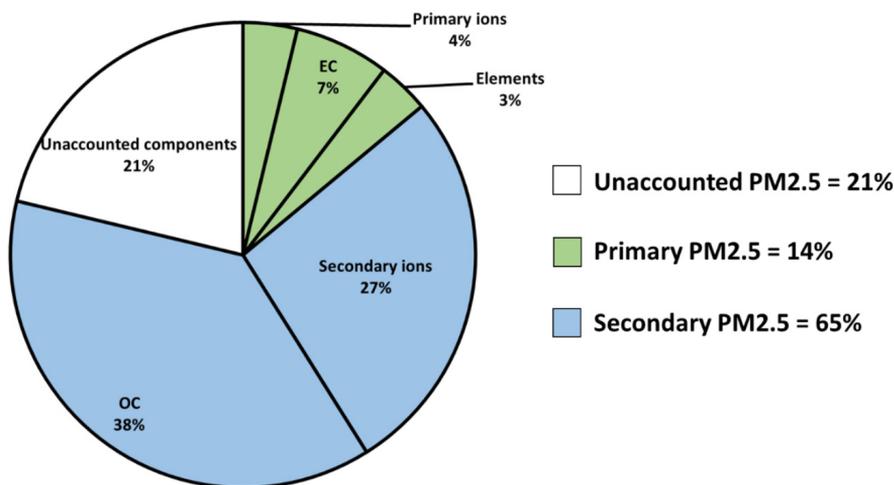


Figure 4. Proportion of aerosol concentration relative to the $PM_{2.5}$ concentration, median basis

The proportion of primary and secondary PM_{2.5} is in Figure 4. The secondary aerosols were constructed from the level of OC, sulfate, nitrate, and ammonium ions, while the primary aerosols were from the levels of other chemical species. The secondary aerosols had higher proportion of PM_{2.5} mass concentration compared to the primary aerosol in Bangkok. Secondary aerosol was about 65% and primary aerosol accounting for 14%. Thus, secondary species in PM_{2.5} accounted about 18.5 µg/m³ during this low episode. The secondary species along accounted more than the recommended WHO guideline.

4. Conclusion

Daily PM_{2.5} concentrations were lower than the national ambient air quality standard, with the average of 29.63 µg/m³, at a near-road location during the strict COVID-19 lockdown in 2020 but all samples exceeded the recommended WHO guideline of 15 µg/m³. Secondary organic ions including sulfate, nitrate, and ammonium ions contributed about 27% of PM_{2.5} mass concentration. Sulfate and sulfur dioxide gaseous precursor were well correlated. The Primary PM_{2.5} was mainly EC and secondary PM_{2.5} was dominated by OC. Secondary PM_{2.5} accounted 67% and primary PM_{2.5} accounting about 14%. The results suggested that vehicle emissions and biomass combustion for domestic purpose were locally contributed to PM_{2.5} concentrations during this unprecedented lockdown in Bangkok. Insight information on chemical species in PM_{2.5} suggested that controlling the level of PM_{2.5} during the non-COVID circumstance would be very challenging and special attention should focus on the control of secondary aerosol.

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