PM$_{2.5}$ mass concentration and associated water-soluble ionic species in a sub-urban coastal area of Kuala Terengganu, Southern South China Sea (Malaysia) (PM$_{2.5}$ dan spesies ion berkaitan di kawasan bandar pesisir pantai, Kuala Terengganu, perairan selatan laut China selatan (Malaysia))

Norhayati Mohd Tahir*, Meikee Koh & Suaimi Suratman

Abstract

PM$_{2.5}$ mass concentration and associated water-soluble ionic species in a sub-urban coastal area of Kuala Terengganu, Malaysia were investigated intermittently from year 2006 to 2009. A total of 78 weekly PM$_{2.5}$ samples were analyzed. The mass concentration of PM$_{2.5}$ exhibited annual, seasonal and diurnal variations. Temporal distributions of rainfall, sporadic haze episodes and local air flow (sea breeze circulation) were factors controlling PM$_{2.5}$ mass variations in the study area. Although the PM$_{2.5}$ concentrations were increased during haze episodes in 2006 (August and October) and 2007 (October), their concentrations however, were still within the international guidelines. The average concentration of individual ions was in decreasing trend: SO$_4^{2-}$ > NH$_4^+$ > K$^+$ > Na$^+$ > NO$_3^-$ > Cl$^-$ > Ca$^{2+}$. The concentrations of SO$_4^{2-}$ and NH$_4^+$ accounted for > 70% of the water-soluble aerosol mass. More than 80% of ionic species associated with PM$_{2.5}$ are from non-marine sources. Major processes affecting the ionic composition of PM$_{2.5}$ are biomass burning, crustal loading and sea spray. Air quality mitigation strategies should focus on anthropogenic activities emitting SO$_2$, which promotes aerosol SO$_4^{2-}$ formation.

Keywords: Aerosols; fine particles; source apportionment, trans-boundary haze episode; water-soluble ionic species

Suggestion: It is recommended to further elaborate on the impact of anthropogenic activities on air quality and the role of sea breeze circulation. This could include a more detailed discussion on the implications of these findings for air quality management and policies in the study area.

Introduction

Airborne particulate matter (APM) is known to influence the environmental processes and human health. Among APM of different sizes, particulate matter with aerodynamic diameter <2.50 μm (PM$_{2.5}$) is of considerable concern as it poses great risk to health and long-term exposure to PM$_{2.5}$ is found to be associated with non-accidental mortality (Dockery et al. 1993; Pope III et al. 2002; Samet et al. 2000). Furthermore, the measurement of PM$_{2.5}$ is thought to be a better approach to assess the impact of anthropogenic activities on air quality because coarse particles are highly affected by natural sources such as sea spray and wind-blown dust (Almeida et al. 2005). The awareness on the impact of APM to human has led to intensive studies on ambient aerosols, focusing on the chemical composition and source apportionment (Fang et al. 2002; Park & Kim 2004).

In Malaysia, there is a general lack of studies on APM chemistry, particularly in sub-urban coastal areas such as Kuala Terengganu. During dry season (June to October), southeasterly seasonal wind often facilitates the northward advection of smoke-haze emitted from biomass burning (occur naturally and/or set intentionally) in Sumatra, Indonesia to Kuala Terengganu, east coast of Peninsular Malaysia (Anwar et al. 2010; Juneng et al. 2009). Though affected by seasonal smoke-haze episodes, specific studies
on Kuala Terengganu air quality are still limited. Two recent studies has been reported but the focus has been on the total particulate matter (Mohd Tahir et al. 2009) and PM$_{10}$ (Mohd Tahir et al. 2008). In view of the gaps, this study seeks to investigate the temporal distribution and ionic composition of PM$_{2.5}$ at Kuala Terengganu coast. The results will provide baseline information for future research as the environmental condition in Kuala Terengganu becomes more complex with progressive urbanization. The understanding on PM$_{2.5}$ will also help to improvise abatement strategies for improving air quality in Kuala Terengganu.

METHODS

PM$_{2.5}$ samplings were conducted intermittently for four sequential years, 2006 to 2009, at Kuala Terengganu Meteorology Station (KTMS) (Figure 1) using low-volume air sampler (Casella APM 950). KTMS is located on an open flat ground; approximately 1.0 km from the coast and 0.10 km from the airport. The study site has low traffic and relatively low population density within 2.0 km radius. There is no important industrial operation within KTMS vicinity.

Real time mass concentration of PM$_{2.5}$ was monitored and recorded at 30 min interval using integrated data logger. The air sampler was operated 24 h continually, except during sample collection, at a flow rate of 17 L min$^{-1}$. The PM$_{2.5}$ was collected on pre-weighed Teflon filter of 47 mm diameter and with 0.2 μm pore size (Whatman). Mass of retained PM$_{2.5}$ was determined using a gravimetric method. For water-soluble ionic species determination, the exposed filter was cut, added with 10 mL of de-ionized water in a centrifuge tube and subjected to ultrasonic extraction (15 min interval) for an hour at <27°C. All extracts were analyzed using ion chromatography technique (Dionex Model DX-120). The results reported in this study are corrected with blank filter papers. Secondary data such as monthly total rainfall and wind speed during the study period were obtained from the Malaysia Meteorological Department (MMD).

Prevailing environmental features at KTMS in each sampling year are summarized in Table 1.

![Figure 1. Location of Kuala Terengganu Meteorological Station (KTMS)](image)

<table>
<thead>
<tr>
<th>Year</th>
<th>Environmental features at KTMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>KTMS area was affected by smoke-haze due to large-scale Indonesian forest fire. El Nino phenomenon caused reduction of rainfall in wet season</td>
</tr>
<tr>
<td>2007</td>
<td>No major haze episode was being reported. Manifest of El Nino phenomenon extended the dry season and this is shown in Figure 2</td>
</tr>
<tr>
<td>2008</td>
<td>No major smoke-haze episode was being reported. Rainfall was significantly increased in November and December</td>
</tr>
<tr>
<td>2009</td>
<td>No major smoke-haze episode was being reported. Rainfall was high throughout the sampling period</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

ANNUAL VARIATIONS OF PM$_{2.5}$ MASS CONCENTRATION

In general, PM$_{2.5}$ mass concentrations were higher in the years 2006 and 2007 compared with 2008 and 2009 (Figure 2). The annual 24 h mean concentrations of PM$_{2.5}$ at KTMS were 9.50±4.00, 8.00±2.50, 5.30±1.00 and 5.40±1.50 μg m$^{-3}$, respectively, for 2006 to 2009. The annual mean value is calculated based on the available monthly 24 h average data. Generally, the PM$_{2.5}$ concentrations in KTMS showed amplification during haze episodes in 2006 and 2007, however, the values recorded were still within the 24 h exposure limits set by the World Health Organization (WHO 2008) and the United States Environmental Protection Agency (USEPA 2010) at 25 and 35 μg m$^{-3}$, respectively.

Higher PM$_{2.5}$ mass concentration in 2006 and 2007 could be attributed to the reduction of rainfall and sporadic haze episodes. El Nino phenomenon that hit Southeast Asia in 2006 reduced the amount of rainfall and conduced long dry season (Tangang et al. 2010). The dry season prolongs APM residence time and consequently resulted in higher PM$_{2.5}$ mass concentration. In August and October 2006, in conjunction with the strong manifest of El Nino, KTMS area was severely affected by smoke-haze transported from Indonesian forest fire. El Nino appeared to persist in 2007 as evidenced by relatively low rainfall, even in the wet season (November-December). Though no major haze episode was being reported in 2007, the dry season allowed accumulation of low intensity haze transported from Indonesia, causing seasonal PM$_{2.5}$ maximal to occur in between June and October. This seasonal amplification of PM$_{2.5}$ level is also observed in other sampling years. Local wind-blown dust could not be ruled out in contributing PM$_{2.5}$ as large-scale sea reclamation and construction activities commenced around KTMS since 2007. Open burning of solid wastes, particularly garden refuse, could be another crucial contributing factor since it is widely practiced by the local community.

Compared with 2006 and 2007, the average PM$_{2.5}$ mass concentration at KTMS during 2008 and 2009 were lowered by >30%. The overall reduction of PM$_{2.5}$ mass concentration is ascribed to the significant increased of rainfall in November to December of 2008 and throughout 2009 sampling period. The rainfall events enhance air particulate removal from the atmosphere (Khare & Baruah 2010; Kocak et al. 2007). Other key factor could be the decreased of biomass burning in Indonesia, owing to stringent law enforcement after the smoke-haze havoc in October 2006.

DIURNAL VARIATIONS OF PM$_{2.5}$ MASS CONCENTRATION

Diurnal variations of PM$_{2.5}$ mass concentration were recorded in the study period. Diurnal pattern and PM$_{2.5}$ mass concentration in non-haze and haze episodes were found to be distinct (Figure 3). In non-haze episode, the PM$_{2.5}$ mass concentration showed gradual increment at local time 07:00 to 09:00 (land to sea breeze) and 19:00 to 21:00 (sea to land breeze), respectively. During land breeze (00:00 to 06:00), low wind speed (~1.40 -1.50 m s$^{-1}$) limited the dispersion of APM and hence PM$_{2.5}$ mass concentration fluctuated within a narrow range of 5.00 to 6.00 μg m$^{-3}$. As sea breeze sets in (10:00 to 17:00), mass concentration of PM$_{2.5}$ decreased by approximately 50% to a minimum value of 2.60 μg m$^{-3}$. Higher wind speed (~1.70-2.60 m s$^{-1}$) during sea breeze could have blown away land air to inner land and therefore enhanced the dispersion of PM$_{2.5}$. In addition,
sea breeze may bring cleaner marine air landward and thus reduced the PM$_{2.5}$ mass concentration (Pillai et al. 2002).

On the contrary, in haze episode, higher wind speed during sea breeze (11:00-16:00) appeared to transport more PM$_{2.5}$ to KTMS. Such observation may indicate the recirculation of PM$_{2.5}$ back to the land after it was being transported out to the sea during land breeze (Baumgardner et al. 2006; Eleftheriadis et al. 1998). The PM$_{2.5}$ level in haze episode was approximately ten times higher than in non-haze. High PM$_{2.5}$ mass concentration and prevailing southeasterly wind could signify long-range transport of smoke-haze from Indonesian forest fire to KTMS.

**GENERAL AEROSOL CHEMISTRY**

Major water-soluble ionic species identified in PM$_{2.5}$ were SO$_4^{2-}$, NH$_4^+$, K$^+$, Na$^+$, NO$_3^-$, Cl$^-$ and Ca$^{2+}$. Table 2 presents the concentrations of ionic species associated with PM$_{2.5}$ collected throughout the sampling period and their relative weight percentage.

The concentrations of major ionic species were in decreasing trend of SO$_4^{2-}$ > NH$_4^+$ > K$^+$ > Na$^+$ > NO$_3^-$ > Cl$^-$ > Ca$^{2+}$. Among the ionic species, SO$_4^{2-}$ and NH$_4^+$ accounted for > 70% of the water-soluble aerosol mass, suggesting these secondary aerosols are important components in the formation of PM$_{2.5}$. High SO$_4^{2-}$ concentration (~60%) may enhance the acidity of PM$_{2.5}$ if there were no sufficient cations to neutralize SO$_4^{2-}$. Significant correlations of SO$_4^{2-}$-NH$_4^+$ ($r=0.70$) and SO$_4^{2-}$-Ca$^{2+}$ ($r=0.65$) indicates that NH$_4^+$ and Ca$^{2+}$ are important for SO$_4^{2-}$ neutralization. Hence, SO$_4^{2-}$ could exist as ammonium salt and gypsum. Letovice [$(\text{NH}_4)_2\text{H}_2\text{SO}_4$] or solution with corresponding ions is the dominant species of SO$_4^{2-}$ since NH$_4^+$ / SO$_4^{2-}$ molar ratio (1.60) is above the theoretical value of 1.50 (Hernandez-Mena et al. 2010; Seinfeld & Pandis 1998).

The molar ratio suggests that substantial fraction of SO$_4^{2-}$ is neutralized by NH$_4^+$. This result is reasonable since SO$_4^{2-}$ and NH$_4^+$ are dominant species in PM$_{2.5}$.

The impact of marine sources on ionic composition of PM$_{2.5}$ is estimated by comparing mass ratio of ionic component (X) and Na$^+$ ([X] / [Na$^+$]) to the ratio in seawater (Table 3). Na$^+$ is used as tracer for estimating the contribution of marine sources, assuming all Na$^+$ to be of marine origin. The ionic ratio may overestimate NSS components as Na$^+$ could be originating from other sources such as soil dust. However, the ratio is still adequate for providing useful guidelines.

Ionic ratio larger than in seawater indicates incorporation of non sea-salt (NSS) constituents in PM$_{2.5}$. The concentrations of NSS-SO$_4^{2-}$, -K$^+$ and -Ca$^{2+}$ are calculated as NSS-X = [X] - [Na$^+$] x (ionic ratio of X in seawater) (Table 3). Lower Cl$^-$ / Na$^+$ ratio could be related to the fractionation of sea-salt (SS) and modification by non-marine constituents. The Cl$^-$ is loss through reaction between NaCl with acidic species such as HNO$_3$, SO$_4$ and H$_2$SO$_4$ (Prodi et al. 2009; Ventakaraman et al. 2002). Higher correlation of Cl$^-$-SO$_4^{2-}$ ($r=0.6$) than Cl$^-$-NO$_3^-$ ($r=0.20$) indicates that SO$_4^{2-}$ has more important role in Cl$^-$ depletion. The NSS constituent calculation suggests that marine sources are main contributors of Cl$^-$ while 87% of Ca$^{2+}$, 97% of both SO$_4^{2-}$ and K$^+$ are from non-marine sources. On the whole, NSS ionic species (including NH$_4^+$ and NO$_3^-$) accounted for 88% of total ions associated with PM$_{2.5}$. Low marine contribution to PM$_{2.5}$ is expected because marine aerosol is typically associated with coarse particles (Almeida et al. 2005).

Correlations of Na$^+$-Cl$^-$ ($r=0.70$) and Ca$^{2+}$-Cl$^-$ ($r=0.60$) suggests that Na and Ca are mainly derived from marine sources. Strong to moderate correlations of Ca$^{2+}$-Na$^+$ ($r=0.70$), Ca$^{2+}$-K$^+$ ($r=0.45$) and Na$^+$-K$^+$ ($r=0.40$) imply the possible of crustal loading to PM$_{2.5}$ (Kumar & Sarin

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**FIGURE 3.** Diurnal variations of PM$_{2.5}$ mass concentrations (in non-haze and haze episodes) and a general wind speed pattern at KTMS.
TABLE 2. Concentrations of ionic species associated with PM$_{2.5}$ and their relative weight percentage

<table>
<thead>
<tr>
<th>Ionic species</th>
<th>Concentrations (ng m$^{-3}$)</th>
<th>Weight percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean$_{n=78}$</td>
<td>Min</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>3804</td>
<td>93.13</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>1119</td>
<td>263.0</td>
</tr>
<tr>
<td>K$^+$</td>
<td>624.4</td>
<td>106.0</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>311.6</td>
<td>4.900</td>
</tr>
<tr>
<td>Ca$_2^{+}$</td>
<td>132.6</td>
<td>2.530</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>158.9</td>
<td>12.40</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>456.3</td>
<td>25.60</td>
</tr>
<tr>
<td>Total average</td>
<td>6607</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3. Ionic ratio and mean concentrations of NSS constituents

<table>
<thead>
<tr>
<th>Ionic species</th>
<th>Ionic ratio</th>
<th>Non sea-salt (NSS)</th>
<th>Mean concentration (ng m$^{-3}$)</th>
<th>Weight percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This study</td>
<td>Seawater</td>
<td>SO$_4^{2-}$</td>
<td>K$^+$</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>8.337</td>
<td>0.2516$^a$</td>
<td>3689</td>
<td>606.1</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.368</td>
<td>0.0400$^a$</td>
<td>K$^+$</td>
<td>606.1</td>
</tr>
<tr>
<td>Ca$_2^{+}$</td>
<td>0.2906</td>
<td>0.0385$^b$</td>
<td>Ca$_2^{+}$</td>
<td>115.0</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.3482</td>
<td>1.800$^b$</td>
<td>Cl$^-$</td>
<td>115.0</td>
</tr>
</tbody>
</table>

$^a$ Karthikeyan & Balasubramaniam 2006
$^b$ Balasubramaniam et al. 2003

2010; Pey et al. 2009; Wang et al. 2005). Meanwhile, high correlations of NH$_4^+$-SO$_4^{2-}$ (r=0.70) and NH$_4^+$-K$^+$ (r=0.60) indicates their common source mainly from biomass burning (regional and/or local emission). The potential of biomass burning in contributing atmospheric SO$_4^{2-}$, NH$_4^+$ and K$^+$ have been widely acknowledged in literatures (Chan et al. 1997; Kang et al. 2004; Sun et al. 2006).

The NO$_3^-$ - SO$_4^{2-}$ correlation (r=0.19) is unexpectedly low in this study possibly because NO$_3^-$ exists mainly in coarse particles while SO$_4^{2-}$ has bimodal (fine and coarse) distribution in aerosol (Kumar & Sarin 2010; Venkataraman et al. 2002). The SO$_4^{2-}$/NO$_3^-$ mass ratio is regularly used as indicator to evaluate the relative importance of mobile (vehicular emission) versus stationary sources (biomass burning, open burning, industrial emission) of SO$_4^{2-}$ and NO$_3^-$ in atmosphere (Arimoto et al. 1996; Hu et al. 2002; Tan et al. 2009). The NSS-SO$_4^{2-}$/NO$_3^-$ mass ratio in this study exhibits considerable variability, with value ranging from 8.00 to 53.0. Nevertheless, the ratio is overwhelmingly higher than in Beijing (1.70) and Shanghai (2.50) where stationary sources of SO$_4^{2-}$ and NO$_3^-$ were found to be dominant over mobile sources (Yao et al. 2002). High NSS-SO$_4^{2-}$/NO$_3^-$ mass ratio at KTMS could indicate that SO$_4^{2-}$ and NO$_3^-$ are predominantly contributed by stationary sources rather than mobile sources. Determination of NSS-SO$_4^{2-}$/NO$_3^-$ mass ratio in coarse APM is essential to give better insight on SO$_4^{2-}$ and NO$_3^-$ source apportionment.

As discussed earlier, PM$_{2.5}$ mass concentration shows annual variations due to temporal distributions of rainfall and sporadic haze episodes. These events could also affect the relative weight percentage of NSS ionic species in PM$_{2.5}$ (Figure 4).

Each pie chart represents ionic composition of PM$_{2.5}$ collected under different environmental conditions (Table 1). Compared with 2006, K$^+$ was more important for the formation of PM$_{2.5}$ collected in 2007, 2008 and 2009. In addition to Indonesian biomass burning, this notable variation could be ascribed to crustal input from sea reclamation and construction activities operating around KTMS since 2007. The Ca$_2^{+}$ shared similar variation trend as K$^+$, probably because of the aforementioned sea reclamation and construction activities. Similar results were obtained in the studies conducted in Hong Kong and Singapore (Balasubramaniam et al. 2003; Ka & Tanner 1999). Local air flows, such as land and sea breezes in this study, may facilitate the re-suspension and transportation of dust particles to KTMS.

Long dry season coupled with Indonesian forest fire in 2006 and 2007 has resulted in high SO$_4^{2-}$ composition. This is expected as the peat bog in Indonesia is known for its high sulfur content due to wet and dry deposition of volcanic sulfur (Balasubramaniam et al. 2003; Tangang et al. 2010). In 2008, the weight percentage of SO$_4^{2-}$ appeared to maintain high, probably because rainfall significantly increased only in November and
December, after the peak season of Indonesian forest fire. Therefore, we could expect low intensity haze transported from Indonesian forest fire to KTMS in earlier months and increased the overall weight percentage of SO$_4^{2-}$. High rainfall throughout 2009 sampling subsequently decreased the weight percentage of SO$_4^{2-}$ by 20–25%, suggesting that high rainfall could reduce the amount of smoke-haze transported from Indonesia to KTMS. The contribution of SO$_4^{2-}$ from local sources could be high in view of the fact that PM$_{2.5}$ collected under improved environmental conditions in 2009 (no major smoke-haze emission from Indonesia and high rainfall) still contain 53% of SO$_4^{2-}$. Further verification is needed to confirm this as without measuring the ambient SO$_4$ level at KTMS, we are not able to determine the relative importance of local emission versus long-range transport in contributing SO$_4^{2-}$. Nevertheless, the SO$_4^{2-}$ in PM$_{2.5}$ has to be reduced as it is proven to have direct link with lung cancer and cardiopulmonary mortality (Brook et al. 2004; Pope III et al. 2002). Hence, abatement strategies to improve air quality should focus on activities emitting SO$_2$, a precursor gas which is oxidized to SO$_4^{2-}$ aerosol.

CONCLUSION

The results from this study showed that the variations of PM$_{2.5}$ mass concentration are related to temporal rainfall distributions and sporadic haze episodes. Prolong dry season caused by El Nino phenomenon exacerbates the PM$_{2.5}$ mass concentration in atmosphere. Diurnal variations of PM$_{2.5}$ mass concentration are related to the transition of land and sea breezes. Southeasterly wind facilitates the long-range transport of smoke-haze from Indonesia to KTMS. Annual average concentration of ionic species associated with PM$_{2.5}$ are in decreasing trend of SO$_4^{2-} >$ NH$_4^+ >$ K$^+ >$ Na$^+ >$ NO$_3^->$ Cl$^->$ Ca$^{2+}$. During this study period, contribution of NSS sources to the formation of PM$_{2.5}$ was found to be more important than marine sources. Correlation analysis of combined data set (2006-2009) indicates three major sources of ionic species associated with PM$_{2.5}$ viz. biomass burning, crustal loading and sea spray. It is suggested that strategies to improve air quality in this area should focus on anthropogenic activities emitting SO$_2$, which is conducive to the formation of SO$_4^{2-}$ aerosol.

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