Source Apportionment and Risk Estimation of Heavy Metals in PM$_{10}$ at a Southern Vietnam Megacity

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ABSTRACT

Airborne particulate matter (PM) pollution is a global concern, in which partitioned heavy metals (HMs) could impose great risks to residents living in metropolitan areas. In this study, PM$_{10}$ samples were collected in Ho Chi Minh City (HCMC) — a megacity in southern Vietnam — and analyzed for 11 HMs to investigate their concentration profiles, perform source apportionment and estimate their risk factors. Results showed that atmospheric HMs concentration decreased following the order of Al > Fe > Sr > Mn > Pb > Cu > Cr > V > Ni > Sb > As. Traffic activities were likely the major cause of rush-hour peaks for most HMs in which Cr, As, and Cu showed > 20% increases in their relative proportions. For seasonal variation, most HMs showed a dry > rainy pattern as a result of washout by higher rainfall in the rainy season while crustal elements (Al, Sr, Mn) showed a rainy > dry pattern and might be explained by the difference in air mass transport modulating by monsoon activities. The positive-matrix factorization (PMF) model revealed 5 primary sources for HMs, including traffic emission, shipping activity and combustion activity, fugitive dust re-suspension and waste incineration. Combustion activity might enrich As, Sb, Pb levels at HCMC, and As contributed half (50.8%) to the potential ecological risk (PER) in the city. Besides, the current Cr level could impose a carcinogenic effect towards children in HCMC (total carcinogenic index $>10^{-4}$) while Mn might impose intolerable non-carcinogenic risk (hazard index $>1$). This study provides information on local air quality status for scientific and regulatory perspectives as well as helps fill the information gap and update the understanding of air pollution in South and Southeast Asia.

Keywords: Ho Chi Minh City, Heavy metals, Source apportionment, Positive matrix factorization, Risk estimation

1 INTRODUCTION

Airborne particulate matter (PM) pollution is gaining more attention as a primary global issue since it commonly results in the adverse impacts to the public health, especially in metropolitan areas with increasing industrial expansion and traffic emission (Nguyen et al., 2022; Southerland et al., 2022). The adverse health effects of PM pollution are well-documented since it surpasses other air pollutants (Cohen et al., 2017; WHO, 2021). PM also causes poor air quality, low visibility as well as causes direct and indirect effects on radiation force and climate change (Pani et al., 2019, 2020; Nguyen et al., 2020).

Besides, PM composition is oftentimes too complex and its elements impact the human ecosystem in a diverse way, with heavy metals (HMs) being one of the greatest concerns (Dockery, 2009; Nguyen et al., 2021a). Sources of HMs in PM comprise both anthropogenic and natural origins, examples of which include As, Pb, Cr as known carcinogenic HMs derived from industrial and...
anthropogenic sources and Fe, Mn and Si as typical elements found in the Earth’s crust (Mulware, 2013; Ramirez et al., 2018). Despite its low abundance relative to the PM total mass, HMs pollution has attracted more attention due to their public health risks (Kumar et al., 2021). According to the International Agency for Research on Cancer (IARC), HMs can be classified into class I carcinogens (As, Ni, Cd, Cr), class II(B) carcinogens (Pb) and non-carcinogenic contaminants (Cu, Zn and Mn) (IARC, 2017). It is also documented that Pb, As, Ni might act as precursors to cardiovascular diseases (Järup, 2003) while As and Cd promotes diabetes symptoms (Lai et al., 2017). Therefore, most studies found inflammation, cancer, cardiovascular and genetic diseases as common diseases associated with HMs exposure which often result in a higher mortality rate. Non-degradable HMs exposure might either occur via air intrusion indoors via open doors and windows, ventilating system and cracks in structures or might get bio-accumulated via the food chain (Leung, 2015).

Several studies have been conducted worldwide concerning several HMs at a wide range of particle sizes (Sahu and Basti, 2021). For instance, PM\(_{2.5}\) studies have been conducted widely in North America, South America, and Europe (Zajusz-Zubek et al., 2015; Di Vaio et al., 2018; Ramirez et al., 2018; Alves et al., 2021; Li et al., 2021; Oroumiyeh et al., 2022). In these studies, spatiotemporal profiles of PM\(_{10}\)-HMs (i.e., heavy metals in PM\(_{10}\)) in combination with either source apportionment or health risk assessment were described as primary methodologies. Industrial emission, vehicle emission, and secondary aerosol processes were reported as governing mechanisms for PM-HMs pattern, with generally higher HMs concentration found in urban than rural areas (Suvarapu and Baek, 2017). On the other hand, similar studies in Asia were conducted in East Asia such as China, Korea and Taiwan (Hsu et al., 2016; Cheng et al., 2018; Wu et al., 2020; Rai et al., 2021; Wu and Huang, 2021; Yang et al., 2021). Besides, studies in Southeast Asia (SEA) were conducted in Malaysia, Thailand and Philippines (Srithawirat et al., 2016; Elhadis et al., 2017; Hagad and Cayetano, 2019; Othman et al., 2021). Pb and As were common primary targets for HMs studies in Asia, partially owing to the heavy reliance on coal combustion for industrial and household uses as well as high traffic density in these areas (Zhang et al., 2018).

With the continuing industrial expansion in developing Asian countries, air pollution issue still remains a critical concern. In SEA, air pollution issue also primarily targeted PM pollution owing to high dependence of fossil fuel use, prevalence of biomass burning and complex atmospheric chemistry within the region (Lin et al., 2013; Nguyen et al., 2020; Tanimoto et al., 2020). Because these factors impact negatively the human ecosystem in metropolitan structures, assessment of characteristics and sources of PM pollutants seems necessary. Risk evaluation of PM and HMs in SEA have also been recorded for soil, sediment and street dust, but little attention has been paid to airborne particulate (Sahu and Basti, 2021). This highlights the need of conducting more studies on PM-HMs to diagnose the overall pollution situation in SEA.

As an active economic hub in SEA with a high population and high urbanization rate, air pollution in Vietnam has always been a topic of concern, especially in metropolitan areas. Ho Chi Minh city (HCMC) is a populated city (ca. 9 million) that serves as the largest industrial and economical center in Vietnam (Hien et al., 2019). A preliminary study evaluated the PM-HMs fractionation in HCMC two decades ago (Hien et al., 2001), but the results might not be consistent with the current air pollution status given a much more populated and industrialized scenario. Also, although recent PM pollution assessment in HCMC has been performed on street dust (Dat et al., 2021; Nguyen et al., 2021b), little information was obtained in other fractions. PM\(_{10}\)-HMs investigation, on the other hand, are limited to northern regions like Bac Giang and Hai Phong (Chifflet et al., 2018; Mai et al., 2021). This calls for a need to implement better data coverage for southern region, with HCMC being a typical example.

In this study, PM\(_{2.5}\) samples were collected at an urban roadside site in HCMC to investigate the HMs profile as well as to determine their potential sources. Their perspective temporal variations and associated driving mechanisms were also discussed. Besides, source apportionment of selected HMs was also attempted using Pearson’s correlation coefficient and positive matrix factorization (PMF). In addition, several indices were calculated to investigate the degree of contamination as well as their associating geological, ecological and health risk to children and adults living in HCMC. Results in this study can help shorten the knowledge gap of PM-HMs pollution situation in Vietnam as well as SEA to attain better air quality for the region.
2 METHODOLOGY

2.1 Site Description

PM$_{10}$ samples were collected on a rooftop of the Air Quality Monitoring Station inside the campus of University of Science, HCMC (HCMUS, 10.7626°N, 10.6819°E, 15 m a.g.l., Fig. 1). Regarded as a roadside site in previous studies (Hien et al., 2019; Nguyen et al., 2022), rush-hour influences were detected in HCMC PM$_{2.5}$ diurnal variation with a peak in concentration between 8–10 a.m. Also, an industrial complex within a 60-km radius of HCMC includes a variety of production types and might hinder a multitude of HMs sources. The climate in HCMC was typically tropical while climatic conditions were under the frequent modulation of the East Asia monsoon. NE monsoon prevails during Dec.–Apr. while SW monsoon prevails during May–Sep., showing a distinct rainy and dry season (Le et al., 2019). In 2018, an annual temperature of 29°C and 2440 mm yearly accumulated total rainfall were recorded in HCMC, characterizing for a hot and humid weather.

2.2 PM$_{10}$ Sampling and HMs Analysis

PM$_{10}$ sampling was conducted in a bihourly fashion (at 1 a.m., 3 a.m., 5 a.m. etc.) using inertial filter technology (Hata et al., 2013). A portable high-volume air sampling system (SIBATA HV-500R, Japan) was used for sampling at 500 L min$^{-1}$, in which an impactor was used to achieve a 10 µm cut size for filter samples. A total of 211 samples have been collected in two intensive observation periods (IOPs), sequentially in dry (Jan.–Feb., n = 119) and rainy season (Jul., n = 92) in 2018. Glass-fiber filters (GFF, Ø = 110 mm) were pre-baked (450°C, 8 hours) before sampling to avoid contamination while a pre-filter was installed to remove coarser PM fractions. After sampling, samples were frozen at −20°C prior to analysis.

By following U.S. EPA method 6020B and Method 200.8 revision 5.4, we analyzed Al, V, Mn, Fe, Ni, Cu, Cr, Pb, As, Sr, and Sb in PM$_{10}$ samples. One-fourth of each filter is thoroughly digested using a mixture of concentrated HNO$_3$:HCl = 1:2 (v/v) in a Teflon vessel immersed in an ultrasonic bath. A heat ramp to 180°C in 330 s was applied and held for 45 minutes by a microwave-assisted
digestion system, then samples were cooled to 50°C. Next, the leachate is filtered through a 0.45-µm PTFE syringe and analyzed by ICP-MS (model 7700x, Agilent, USA). SRM 1684a was employed for checking method accuracy which yielded recovery rates within 85–115% for selected HMs. Reagent blanks were used to monitor analysis performance while mean value of filter blanks (n = 4, Table S1) were used to deduct for selected PM10-HMs analyzed concentration prior to calculating atmospheric concentration. Further information on ICP-MS instrumentation and analysis can be referred to Dat et al. (2021).

2.3 Positive-matrix Factorization

In this study, PMF model was employed to quantify the contribution of PM10-HMs at HCMC. PMF is a receptor model utilizing mathematical approach to quantify the contribution of different factors to each variable (Paatero and Tapper, 1994; Do et al., 2021). The model decomposes each variable into two matrices: a factor profile (f) and factor contribution (g) to solve the modeled-observation mass balance, following Eqs. (1) and (2):

\[ x_{ij} = \sum_{k=1}^{n} g_{ik} f_{kj} + e_{ij} \]  

\[ Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left( x_{ij} - \sum_{k=1}^{n} g_{ik} f_{kj} \right)^2 / u_{ij} \]

where \( x \) is the matrix of sample \( i \) by variable \( j \) and associating with uncertainty \( u \); \( g \) is the mass contributed by each factor \( k \); \( f \) and \( e \) are the source profile and residual of each sample, respectively.

The objective of PMF model is to minimize the sum of the squares of the error-weighted residuals \( Q_{\text{robust}} \) and \( Q_{\text{true}} \) in the Eq. (2), where \( u_{ij} \) is the uncertainty of the measured concentration of each variable. In this study, EPA PMF 5.0 software was used to perform the simulation, with details of calculation of uncertainty can be referred to Anttila et al. (1995).

2.4 Risk Factor Assessment

2.4.1 Degree of contamination

Contamination factor \( C_f \) is used to evaluate HMs contamination in comparison with background values, which is calculated by Eq. (3).

\[ C_f = \frac{C_i}{B_i} \]

where \( C_i \) and \( B_i \) (ng m\(^{-3}\)) are perspective average ambient HMs concentration at HCMC and a designated background site. Since background PM10-HMs data is yet to be determined in HCMC, in this study, background concentrations reported by Querol et al. (2007) were employed to assess the HMs contamination at our site. Besides, pollutant loading index (PLI) can be calculated as the geometric mean of perspective \( C_f \) values (Eq. (4)) then compared with a set of criteria to evaluate the level of contamination of each individual HM (Table S2).

\[ PLI = \sqrt[n]{\prod_{i=1}^{n} C_f} / B_i \]

2.4.2 Geological risk assessment

Enrichment factor (\( E_i \)) is an effective tool to evaluate the magnitude of contamination of certain HMs in reference to natural origins, which was also applied in other sample matrices
EF is calculated by Eq. (5), with Fe being chosen as reference metal to normalize for other HMs:

\[
EF = \frac{\left(\frac{C_i}{C_{Fe}}\right)_{sample}}{\left(\frac{C_i}{C_{Fe}}\right)_{background}}
\]

where \(\frac{C_i}{C_{Fe}}\) ratios (unitless) are calculated for each sample then compared with the corresponding ratio from upper continental crust (Taylor and McLennan, 1995). The calculated EF values are then compared with ranges of criteria shown in Table S2.

Beside, HMs data from a designated background site (Querol et al., 2007) can also reflect the geo-accumulation of the elements in our study by using Eq. (6):

\[
I_{geo} = \log_2 \left( \frac{C_i}{1.5B_i} \right)
\]

where \(C_i\) and \(B_i\) (ng m\(^{-3}\)) are perspective average ambient HMs concentration at HCMC and the background site. A correction factor of 1.5 was employed to account for background variation. A set of seven criteria was chosen to evaluate the calculated \(I_{geo}\) of each HM (Table S2).

### 2.4.3 Ecological risk assessment

The potential ecological risk (PER) index was initially attempted by Hakanson (1980) to diagnose the ecological impact of certain HMs with a toxicity coefficient (\(T_i\)). Besides, the PER value represents the risk factor of multiple metals and was calculated via the ecological index (\(E_i\)), using the Eqs. (7)–(8). The set of criteria to evaluate PER values was also presented in Table S2.

\[
E_i = T_i \times C_i
\]

\[
PER = \sum E_i
\]

### 2.4.4 Health risk assessment

In this study, airborne PM\(_{10}\)-HMs non-carcinogenic and carcinogenic risk were evaluated primarily via inhalation pathway, using EPA standards (U.S. EPA, 2011). Since HCMC has a young population structure, the risks were evaluated for children (< 12 years old) and adults. For urban areas in SEA, the chronic daily intake (CDI) of selected HMs can be evaluated via Eqs. (9)–(10) (Betha et al., 2013; Sah et al., 2019).

\[
CDI = \frac{IR_{inh} \times C_i \times E}{BW}
\]

\[
E = -0.081 + 0.23 \ln(D_p^2) + 0.23 \sqrt{D_p}
\]

with \(C_i\) as the average HMs concentration (mg m\(^{-3}\)), \(IR_{inh}\) as the inhalation rate (7.6 m\(^3\) day\(^{-1}\) for children, 20 m\(^3\) day\(^{-1}\) for adults), \(BW\) as average body weight (10 kg for children, 55 kg for adults) and \(E\) as the deposition fraction of PM\(_{10}\) (at \(D_p = 10 \mu m\), Volckens and Leith, 2003).

The non-carcinogenic feature of selected PM\(_{10}\)-HMs is then evaluated via hazard index (\(HI\), Eq. (11)), where RFD is the HMs reference dose via inhalation (Table S3). A value of \(HI < 1\) suggests a tolerable non-carcinogenic risk for the chosen age group while \(HI > 1\) suggests a possible adverse health risk to human health. Besides, total carcinogenic risk (TCR) of Cr, Ni, As and Pb are evaluated...
via Eq. (12) where SF (kg day$^{-1}$ mg$^{-1}$) is the slope factor for selected HMs (Table S3). A TCR < 10$^{-6}$ suggests an acceptable carcinogenic level of selected PM$_{10}$-HMs for the designated age group while $TCR > 10^{-4}$ indicates a susceptibility to metal poisoning.

$$HI = \frac{CDI}{RfD}$$ (11)

$$TCR = CDI \times SF$$ (12)

### 3 RESULTS AND DISCUSSIONS

#### 3.1 General Characteristics of PM$_{10}$-HMs

Concentrations of HMs associated with PM$_{10}$ in this study as well as other studies are displayed in Table 1. Certain HMs (As, Mn, Ni, Pb, V) shown in our study were lower than WHO recommended guideline values for air pollutants (WHO, 2017), indicating a tolerable HMs pollution level for PM$_{10}$ in HCMC. Average HMs concentration decreased in the following order: Al (5144 ng m$^{-3}$) > Fe (1573 ng m$^{-3}$) > Sr (49.3 ng m$^{-3}$) > Mn (45.5 ng m$^{-3}$) > Pb (44.1 ng m$^{-3}$) > Cu (16.1 ng m$^{-3}$) > Cr (4.4 ng m$^{-3}$) > V (12.7 ng m$^{-3}$) > Ni (6.2 ng m$^{-3}$) > Sb (3.1 ng m$^{-3}$) > As (2.8 ng m$^{-3}$). From this sequence, HMs with natural origins (Al, Fe, Sr) had a higher abundance than other trace HMs while HMs with anthropogenic origins (As, Mn, Ni, Pb, V) had a lower abundance.

Table 1. HMs concentration (ng m$^{-3}$) in PM$_{10}$ from different sites worldwide.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Country</th>
<th>Al</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>As</th>
<th>Sr</th>
<th>Sb</th>
<th>Pb</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Ho Chi Minh</td>
<td>Vietnam</td>
<td>5144</td>
<td>12.7</td>
<td>14.4</td>
<td>45.5</td>
<td>1573</td>
<td>6.2</td>
<td>16.1</td>
<td>2.8</td>
<td>49.3</td>
<td>3.1</td>
<td>44.1</td>
</tr>
<tr>
<td>Ho Chi Minh</td>
<td>Vietnam</td>
<td>2678</td>
<td>19.8</td>
<td>11.3</td>
<td>66</td>
<td>1483</td>
<td>-</td>
<td>4.3</td>
<td>6.1</td>
<td>3.8</td>
<td>152</td>
<td>152</td>
</tr>
<tr>
<td>Bac Giang</td>
<td>Vietnam</td>
<td>-</td>
<td>8.55</td>
<td>31.8</td>
<td>110</td>
<td>-</td>
<td>12.2</td>
<td>40.9</td>
<td>8.7</td>
<td>-</td>
<td>121</td>
<td>Mai et al., 2021</td>
</tr>
<tr>
<td>Hai Phong</td>
<td>Vietnam</td>
<td>1543</td>
<td>10.6</td>
<td>7.8</td>
<td>44.6</td>
<td>828</td>
<td>4.7</td>
<td>48.2</td>
<td>63.7</td>
<td>5.5</td>
<td>56</td>
<td>Chifflet et al., 2018</td>
</tr>
<tr>
<td>Ontario</td>
<td>Canada</td>
<td>52.7</td>
<td>0.79</td>
<td>0.87</td>
<td>3.97</td>
<td>91</td>
<td>0.73</td>
<td>7.97</td>
<td>0.61</td>
<td>1.06</td>
<td>0.31</td>
<td>3.37</td>
</tr>
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<td>Bogota</td>
<td>Colombia</td>
<td>720</td>
<td>1.50</td>
<td>2.92</td>
<td>-</td>
<td>480</td>
<td>1.69</td>
<td>51.7</td>
<td>0.53</td>
<td>4.62</td>
<td>4.74</td>
<td>24.8</td>
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<tr>
<td>Arequipa</td>
<td>Peru</td>
<td>-</td>
<td>21.3</td>
<td>20.2</td>
<td>900</td>
<td>3.0</td>
<td>17.1</td>
<td>13.4</td>
<td>12.8</td>
<td>-</td>
<td>4.6</td>
<td>Li et al., 2021</td>
</tr>
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<td>Los Angeles</td>
<td>United States</td>
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<td>1.1</td>
<td>4.8</td>
<td>361.6</td>
<td>0.6</td>
<td>12.1</td>
<td>-</td>
<td>3.1</td>
<td>2.2</td>
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</tr>
<tr>
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<td>44.1</td>
<td>1322</td>
<td>14.0</td>
<td>21.0</td>
<td>2.03</td>
<td>-</td>
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<td>11.5</td>
<td>2.87</td>
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<td>8.35</td>
<td>-</td>
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<td>1.57</td>
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<td>Xiamen</td>
<td>China</td>
<td>610</td>
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<td>11.2</td>
<td>25.6</td>
<td>750</td>
<td>8.49</td>
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<td>1.89</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Chengdu</td>
<td>China</td>
<td>-</td>
<td>9.2</td>
<td>41.4</td>
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<td>-</td>
<td>15.5</td>
<td>172.9</td>
<td>17.5</td>
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<td>-</td>
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<td>20.1</td>
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<td>9.8</td>
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<td>Central region</td>
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<td>950</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>2</td>
<td>13</td>
<td>3</td>
<td>290</td>
<td>-</td>
<td>-</td>
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Who guideline levels:

<table>
<thead>
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<th>HMs (ng m$^{-3}$)</th>
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<td>WHO guideline levels:</td>
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<tr>
<td>1000</td>
</tr>
<tr>
<td>150</td>
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<td>25</td>
</tr>
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<td>6.6</td>
</tr>
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<td>500</td>
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</table>

WHO, 2017
Since emission ratios for PM-HMs could vary between a factor of 2–10, absolute HM concentrations might not help pinpoint their origins as good as elemental ratios (Nriagu and Pacyna, 1988). In several studies, ratios of Fe/Al and V/Ni are commonly regarded as indicators for remobilized crustal dust and oil combustion sources (Viana et al., 2009; Zhang et al., 2014). In our study, an Fe/Al ratio of 0.31 was obtained and approached the Fe/Al ratio of 0.48 in the upper continental layer (Taylor and McLennan, 1995). This ratio was also lower than urban areas with huge local anthropogenic influences such as Bangkok (2.41, Kayee et al., 2020) and central Taiwan (1.03–2.66, Wu and Huang, 2021), implying the crustal origins for Al and Fe at our sites. Besides, a V/Ni ratio of 2.05 observed in HCMC was higher than that of Bangkok (1.76, Kayee et al., 2020), lower than Hai Phong (2.4, Chifflet et al., 2018) but remained within the range of road traffic sources (1.49–2.4, Thorpe and Harrison, 2008). A Cu/Sb ratio of 5.2 in HCMC also resembled those of brake lining wear (6, Thorpe and Harrison, 2008) and further reinforced the impact of traffic sources on PM$_{10}$ at our sampling site.

On the other hand, the PM$_{10}$-HMs pattern in our study slightly differed from other sites in northern Vietnam. For instance, higher crustal HMs levels (Al, Fe, Sr) were observed in HCMC than Hai Phong and Bac Giang (Chifflet et al., 2018; Mai et al., 2021). Road dust re-suspension and the impact of construction activity nearby might account for higher crustal HMs level, given that our site is a roadside site (Nguyen et al., 2022). On the other hand, HMs such as Cu, As, Pb, and Sb showed comparatively lower concentrations, implying that industrial activities and emission sources are much more intense in northern Vietnam. Exceptionally, As abundance in Bac Giang and Hai Phong were 3.1 and 22.8-times higher than that of HCMC. Studies have considered As as a tracer for coal combustion especially in industrial sectors (Cheng et al., 2018; Zhang et al., 2018; Wu et al., 2020) which could imply more coal-burning activities (e.g., industrial zone or coal fire power plans) observed in northern Vietnam than southern regions. Besides, we also attempted to compare the HCMC PM$_{10}$-HMs with results shown in a previous study (Hien et al., 2001). From Table 1, it can be seen that reported HMs concentration in our study were generally higher (92% for Al and 274% for Cu) than two decades ago, with exceptions of As and Pb. The results might indicate the impact of urbanization on elevated PM$_{10}$-HMs levels whereas lower Pb concentrations could result from the effort to ban leaded gasoline since the 2000s. In conclusion, despite relatively moderate HMs levels observed in comparison with other studies worldwide, the PM$_{10}$-HMs pattern in HCMC reflected the influences of anthropogenic activities (e.g., construction and traffic emission) as a result of the rapid urbanization over the last two decades.

### 3.2 Temporal Variation of PM$_{10}$-HMs

By utilizing a 2-hour sampling window, we were able to examine both of HMs diurnal and seasonal variations (Figs. 2 and 3). A few types of diurnal variations were observed for the 11 chosen HMs (Fig. 2). For instance, rush-hour peaks (i.e., 10 a.m.) were visible for most HMs (including Cr, Mn, Fe, Ni, Cu, and As, Fig. 2(a)), showing enhancements of 18–52% from their perspective means. By using real-time air pollutants data, Hien et al. (2001) described a similar rush-hour peak of PM$_{2.5}$ at HCMUS to be associated with both primary local emission and secondary aerosol formation. Therefore, the diurnal patterns of these HMs could be a result of peak-hour emission followed by subsequent dilution by increased turbulence at noon. On the other hand, Al, Pb and Sb showed reversed diurnal patterns (Fig. 2(b)), with higher nighttime (6 p.m.–7 a.m.) than daytime (7 a.m.–6 p.m.) concentrations. Such a pattern could be either a result of planetary boundary height (PBL) modulation or increased emission rates at nighttime (Maletto et al., 2003; Chandra et al., 2017). The reduction of PBL height during soil and dust re-suspension process could elevate mineral elements (Al, Sr) concentration (Ramirez et al., 2018; Rai et al., 2021) which was also observed in studies surrounding Tibetan Plateau where fugitive dust might influence crustal elements concentration and PM$_{10}$ pattern (Tripathee et al., 2014; Guo et al., 2017). Besides, statistically insignificant daytime-nighttime differences between V ($p = 0.056$) and Sr ($p = 0.58$) concentration showed their lack of a diurnal cycle (Fig. 2(c)). Therefore, the influences of mixed origins or other sources that differ from the rest of HMs might control V and Sr patterns. Overall, a variety of diurnal patterns of PM$_{10}$-HMs at HCMC was observed in response to the possible contributions of local emission and PBL modulation.

In order to clarify for the effect of the rush-hour to HMs pattern at HCMC, the relative
Fig. 2. Diurnal variation of selected HMs in PM$_{10}$ in HCMC with (a) a rush-hour peak, (b) night > day pattern and (c) unclear pattern.

Fig. 3. Diurnal variation of the relative contributions of selected PM$_{10}$-HMs (except Al, Fe).

contribution of each HM was plotted against total concentration in each time stamp (Fig. 3). Al and Fe was excluded to avoid mass compensation over other HMs. From Fig. 3, a change in HMs proportions was observed at rush-hour peak (i.e., 10 a.m.), with > 20% increase in the relative contributions of Cr (30.6%), As (24.8%), and Cu (20%) when compared to their daily average contributions (Fig. 3). These HMs are often assigned with non-exhaust vehicle emissions and combustion activity (Hsu et al., 2016; Ramirez et al., 2018), suggesting the impact of rush-hour vehicular emission in spiking their abundance. Other HMs showed slighter increases (14.0% for Sb and 10.0% for Pb), which are HMs with nighttime > daytime diurnal variation.
For seasonal variations, HMs concentrations during dry and rainy season were shown in Fig. 4. Mann-Whitney U test (i.e., a non-parametric test for testing the difference between two groups of variables) showed significant seasonal variations ($p < 0.05$) for selected HMs, with magnitudes of $1.2–4.5$ times between the two seasons’ concentration. A rainy > dry seasonal pattern was observed for crustal elements (Al, Mn, and Sr) while a dry > rainy pattern was seen for others (Fig. 4). Such a contrast in seasonal variations of crustal elements versus industrial and anthropogenic elements was also described in other studies. For instance, in Delhi, India (Chandra et al., 2017), the contrasting seasonal cycles of crustal elements (Fe, Mn) and anthropogenic HMs (Cu, Zn, Pb, Cd) was attributed to Indian monsoon activity that exerts a change in influencing sources to receptor site as well as washout effect from precipitation. Monsoon activity also alters wind field and meteorological conditions which in turn alters HMs characteristics at Tibetan Plateau and Malaysia (Guo et al., 2017; Othman et al., 2021). HCMC is also under the effect of Indian monsoon, in which clear seasonal variations in rainfall, relative humidity (RH), PBL height were recorded during the two IOPs (Table S4). Higher rainfall in rainy season could promote PM washout by precipitation, which in turn reduced PM$_{10}$-HMs concentration and resulted in a rainy < dry pattern for most of selected HMs. For crustal HMs that showed an opposed seasonal pattern, the seasonal difference in transport pattern and air mass origins could be a primary contributor. Five-day backward trajectories (BWTs) simulated by HYSPLIT 4 (GDAS meteorological data, $1° \times 1°$ resolution at $200$ m a.g.l.) showed different BWTs patterns between two seasons (Fig. S1), in which the different in topography, geology and emission sources distribution between S–SW and N–NE sectors might contribute to the observed crustal HMs seasonal cycles. To sum up, washout by rainfall and the seasonal difference in air mass transport pattern could govern the seasonal variations for the PM$_{10}$-HMs at HCMC.

### 3.3 Source Apportionment of PM$_{10}$-HMs in HCMC

#### 3.3.1 Correlation analysis

The inter-element Pearson’s correlation of PM$_{10}$-HMs in HCMC are shown in Table S5. Statistically significant ($p < 0.05$) correlations are observed for almost all HMs pairs, showing their possible mutual origins. However, general weak-to-moderate correlations ($0 < |r| < 0.7$) were detected among PM$_{10}$-HMs, in which lower $r$ values (i.e., As, Ni) might imply the influence of mixed sources rather than one origin. From Table S5, all HMs can be classified into two sub-groups of influencing sources: natural (i.e., Al, Sr, Mn) and anthropogenic (traffic, combustion and industrial) in which members showed their mutual positive correlations and negative correlations with the other...
group. For instance, positive correlations ($r = 0.56–0.93$) were found between Al and Mn, Sr while negative correlations were found for other Al-related correlations ($r = 0.13–0.54$). This pattern suggests two major groups of sources influencing PM$_{10}$-HMs at HCMC and can be further explained by the use of PMF model.

### 3.3.2 PMF analysis
A solution of 5 factors was selected as the adequate fit (i.e., $Q_{\text{robust}} = Q_{\text{true}} = 2.9$) to our dataset in which modeled-observation agreement was generally favored for all selected HMs ($R^2 = 0.85–1.00$), showing the model capability. The summary of 5 PMF factors is displayed in Table 2, with information on their perspective HMs contribution displayed in Fig. 5 and their temporal variation presented in Fig. S2. We attributed these factors to combustion, construction and industrial activity (shipping, metal smelting), waste incineration, traffic and non-exhaust vehicle emission; which is similar to other urban areas in Taiwan and Portugal (Hsu et al., 2016; Alves et al., 2021).

Table 2. Pollution sources and their contributors derived by PMF for PM$_{10}$-HMs in HCMC.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Assigned pollution source</th>
<th>Primary HMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oil combustion, shipping industry</td>
<td>V</td>
</tr>
<tr>
<td>2</td>
<td>Coal combustion, non-exhaust vehicle emissions</td>
<td>Sb, As</td>
</tr>
<tr>
<td>3</td>
<td>Natural dust re-suspension, construction</td>
<td>Al, Sr, Mn</td>
</tr>
<tr>
<td>4</td>
<td>Metal smelting industry, traffic emission</td>
<td>Cu, Cr, Fe, Ni</td>
</tr>
<tr>
<td>5</td>
<td>Waste incineration plants</td>
<td>Pb</td>
</tr>
</tbody>
</table>

![Fig. 5. Source profiles of 5 PM$_{10}$-HMs factors in HCMC extracted by PMF model.](Image)
V is the primary component for Factor 1, which represents a secondary pollutant of stationary anthropogenic emissions such as fossil fuel or oil combustion. Oil combustion is also commonly used in oil-fired power plants, shipping industry or aluminum smelters (Hsu et al., 2016). In HCMC, Nha Rong Wharf and Cat Lai Port are commercial trading ports with a large density of shipping activities and both situate 5–15 km afar from HCMUS. Furthermore, Cat Lai acts a major transshipment port in HCMC with a high volume of container trucks operating at a high frequency. These heavy trucks might consume large diesel oil quantities and contribute as V emission source. 

For Factor 2, the primary contributors are Sb and As, suggesting the definite influence from non-exhaust vehicle emission and coal burning. Arsenic is primarily released during combustion at high temperatures, then subsequently condensed to soot particles and released in coal fly ash (Zhang et al., 2018). Therefore, As is commonly used as a coal-burning tracer that is related to coal-fired power plants, incinerator sources or combustion engines (Biegalski and Hopke, 2004; Hsu et al., 2016). Besides, Sb has been associated with non-exhaust vehicle emissions such as brake and tire wear processes as well as road dust re-suspension (Amato et al., 2014). However, As and Sb are both considered markers for coal combustion in some studies (Hsu et al., 2016; Wu and Huang, 2021). In HCMC, the rush-hour peak was observed for As diurnal variation but not for Sb (Fig. 2), showing the influence of more than one source to Sb pattern. Coal combustion from residential sectors could also emit great Sb quantities which could arise from family use and food stalls surrounding the campus (Tian et al., 2012).

Crustal elements including Al, Sr and Mn are main elements for Factor 3, showing the impact of dust re-suspension and/or construction activity. Similar findings were found for road dust HMs in HCMC and PM\textsubscript{10}-HMs in Hai Phong (Chifflet et al., 2018; Dat et al., 2021), showing the localized influences for airborne Al, Sr, Mn in Vietnam. Soil-like elements (Al, Sr) in urban areas are emitted from either fugitive dust re-suspension, construction activities or either deteriorated pavement (Hsu et al., 2016; Ramirez et al., 2018). Furthermore, Mn in PM\textsubscript{10} could re-suspend from brake wear, steel manufacturing facility or even gasoline and diesel engines (Cui et al., 2019), which are traffic-related and industrial-related sectors. Since Mn exhibited the rush-hour peak in its diurnal pattern (Fig. 2(a)), there is a possible influence of traffic and industrial sectors to PM\textsubscript{10}Mn. On the other hand, cement production activities are prominent to the south-southwest which could transport soil-like elements to PM\textsubscript{10} nearby HCMUS. Therefore, higher crustal abundances in PM\textsubscript{10} were found in July (Fig. S2) when S–SW wind is predominant. Recent urbanization movement has also led to the emergence of more construction sites within the vicinity and could spike up crustal HMs concentration. Moreover, heavy automobiles commute in early morning might also facilitate road dust re-suspension, producing high crustal-like HMs concentration.

Factor 4 had contributions from Cu, Cr, Ni, Fe, which are typically attributed to traffic activity and metal smelting industry. Cu is regarded as a tracer for non-exhaust vehicle emission (Cui et al., 2019; Rai et al., 2021), which is used in lubricants to improve friction stability and emits during brake abrasion (Querol et al., 2007; Amato et al., 2014). A strong Cu-Sb correlation (r = 0.75) was observed and indicated traffic emission as one major PM\textsubscript{10} contributor. Sources of Cu also include non-ferrous metallurgical industry, metal processing and refinery industry (Ramirez et al., 2018; Men et al., 2018), which is shown via moderate correlations with Ni (r = 0.56) and Cr (r = 0.52). While some studies indicated Ni and Cr origins from break and tire wear and fuel combustion, few also pointed our their origins in metallurgical industry (Hsu et al., 2016; Zhao et al., 2019). In HCMC, small-scale metallurgy and manual steel-iron reproduction are typical for the surrounding industrial zones and might contribute to the Factor 4 HMs. Therefore, this factor could illustrate the effect of traffic activity and metal smelting industry on PM\textsubscript{10} pattern in HCMC.

Finally, Pb is the sole contributor for Factor 5 in the chosen PMF solution. Derived Pb in PM\textsubscript{10} is often associated with fossil fuel burning, solid waste incineration and industrial activities including metallurgy, steel, ceramics and glass production (Zhao et al., 2019). Since insignificant (p > 0.05) correlations between Pb and Factor 4 HMs (i.e., Cu, Cr, Ni) were obtained (Table S5), metal smelting industry is not considered a PM\textsubscript{10}-Pb source. Furthermore, the use of Pb in gasoline has been banned in Vietnam since 2000, suggesting that fossil fuel combustion as a possible PM\textsubscript{10}-Pb source rather than vehicle emission (Hien et al., 2001). Some waste incineration plants located to the west of HCMUS operate on an all-day basis (e.g., Vietstar, Tam Sinh Nghia...). Therefore, upcoming studies with a focus on the Pb characteristics and isotopic ratios at these point sources would be essential to confirm our hypothesis. In short, PMF model was
successful in illustrating the potential PM\(_{10}\)–HMs sources at HCMC, showing an emphasis on sources of traffic emission, industrial activities, dust re-suspension and combustion activities.

### 3.4 Risk Factors Assessment for PM\(_{10}\)–HMs

#### 3.4.1 Geological indices

Table S6 shows the EF values of PM\(_{10}\)–HMs present in this study. According to Table S2, a wide range of enrichment levels was obtained for HMs in our study. Crustal elements (Al, Sr, Mn) showed a minor-to-moderate enrichment (1 < EF < 5) which shared similar levels to upper continental crust (Taylor and McLennan, 1995). On the other hand, As (40.4), Pb (52.4) and Sb (338.7) are HMs with largest EF values, showing the impact of severe combustion activity and traffic emission in HCMC to airborne particulate HMs. Such a finding contrasts those found by Dat et al. (2021) for road dust, and highlight the more favorable HMs accumulation on airborne particles (Suvarapu and Baek, 2017). It was also true for remaining HMs (V, Cr, Ni, Cu) which showed a moderate severe to severe enrichment level (5 < EF < 25).

However, upon comparing with the PM\(_{10}\)–HMs level from urban background sites (Querol et al., 2007), a slightly different pattern was obtained in I\(_{geo}\) values (Table S6). It can be seen that crustal elements such as Sr (2.0) and Al (2.7) were classified as moderate and moderate-to-severe contaminated, showing the possible influence of construction activity to relatively higher crustal PM\(_{10}\)–HMs concentration. Besides, Cr, Fe, and As were defined as slightly contaminated (I\(_{geo}\) < 1) while the rest are uncontaminated (I\(_{geo}\) < 0). It can then be concluded that geochemical content of these PM\(_{10}\)–HMs was comparable to the reference urban sites.

Nonetheless, when the potential background variation and exponential nature of PM\(_{10}\)–HMs were taken into account, PLI values (Table S6) showed that all crustal elements (Al, Sr, Mn, Fe) were classified as heavily polluted (PLI > 3). Besides, Cr (2.6) and As (2.3) were found to be moderately polluted while V (1.1) and Ni (1.3) levels were lowly polluted, leaving other HMs categorized as unpoluted (PLI < 1). As a whole, the pollution loading status decreases through the following sequence: crustal > combustion > traffic, which differs from those of road dust in HCMC (Dat et al., 2021). However, it should be reminded that the use of PM\(_{10}\)–HMs data from a HCMC background site should be encouraged to further complement the findings in this study.

#### 3.4.2 Ecological indices

Fig. 6 illustrates the ecological risk indices (E\(_i\)) of certain HMs (Cr, Mn, Ni, Cu, As, Pb) with a specific toxicity coefficient. From Fig. 6(a), As (29.0 ± 22.3) was the only HM that showed a moderate E\(_i\) level, while other HMs showed a low level of ecological risk (i.e., E < 15). Therefore, it can be inferred that combustion activities in HCMC impose a negative effect to the surrounding ecological areas. Besides, when the cumulative effect of the whole dataset is considered, all chosen HMs showed PER > 200 which is classified as “high” risk category. However, the relative contribution of As remains largest (50.8%, Fig. 6(b)), confirming the predominant ecological threat of coal combustion.

Since HCMC topography is susceptible for recurrent flooding, a complex canal system for rainwater drainage and water supply runs throughout the city. Therefore, PM washout by rainfall might introduce HMs into the waterways especially during rainy season. Given the high PER values of PM\(_{10}\)–HMs, such HMs deposition would impose a great threat to human ecology in HCMC. Therefore, a broader assessment of airborne particulate HMs at a better spatial resolution deems necessary to complement the findings in this study.

#### 3.4.3 Health risk assessment

The average HI indices for children and adults of selected PM\(_{10}\)–HMs in this study are described in Fig. 7(a), showing the decreasing order of HIMn > HI\(_{Cr}\) > HI\(_{Pb}\) > HI\(_{As}\) > HI\(_V\) > HI\(_{Cu}\) > HI\(_Ni\). Except for Mn with HI > 1, other PM\(_{10}\)–HMs showed a tolerable non-carcinogenic level in HCMC. Besides, calculated HI values were higher in children than adults, agreeing with PM\(_{10}\) studies in Italy and road dust in Vietnam (Di Vaio et al., 2018; Dat et al., 2021) and showing that children are generally more sensitive towards HMs poisoning. Besides Mn (85.8%), contribution from Cr (13.5%) into total non-carcinogenic risk also emphasizes the potential risk of traffic activities towards HCMC citizens. As inhalation is a more dominant exposure pathway, it is suggestive that traffic activities...
should be controlled to lessen the carcinogenic impact on HCMC citizens. Similar findings were found for road dust in our study area (Dat et al., 2021) and Indonesia (Betha et al., 2013), emphasizing the importance of traffic non-carcinogenic risk in urban areas.

On the other hand, carcinogenic risk (TCR) evaluation result of certain HMs is displayed in Fig. 7(b). Although children is more seriously exposed to carcinogenic HMs (TCRchildren > TCRadults), it is noticeable that Cr exposure among children reached the “poisoning” level (TCR > 10^{-4}) while other HMs showed acceptable risk (10^{-6} < TCR < 10^{-4}) or tolerable (TCR < 10^{-6}) carcinogenic risk (U.S. EPA, 1996). It is then proposed that children in HCMC should be cautious about potential health risks and effort should be made by local authorities to raise the HMs regulation level.

4 CONCLUSION

Two intensive sampling periods were conducted in this study as an initial step for characterizing sources and risks of 11 PM10-HMs in HCMC, Vietnam. Among the investigated HMs, Al and Fe were the most abundant HMs while Sb and As were those with the least abundances. Although urbanization has boosted PM10-HMs levels over the last two decades, they remain moderate in comparison with other studies worldwide. Most notably, a significant decline in PM10 Pb concentration was obtained from the effort to ban leaded gasoline in HCMC. Most HMs (Cr, Mn, Fe, Ni, Cu, As) showed a rush-hour peak (i.e., 10 a.m.) due to the effect of traffic emission in which Cr, As, Cu showed > 20% increases in their relative proportions. Crustal HMs (Al, Mn, Sr) showed a rainy > dry pattern which might correspond to the seasonal change in air mass transport pattern while others showed a dry > rainy pattern in correspondence to possible PM washout by rainfall. PMF results revealed 5 potential PM10 primary sources including shipping activity (V), coal combustion (As, Sb), dust resuspension and construction (Al, Sr, Mn), traffic emission (Cr, Cu, Ni, Fe) and waste incineration (Pb) at our sampling site. High EF values of As, Pb, Sb (40.4–338.7) showed great HMs enrichment by combustion activity while a sequence of crustal > combustion > traffic contamination level was indicated by PLI index. In addition, As was the only HM that showed a moderate ecological index (Ec = 29.0) and contributed 50.8% to the overall potential ecological risk (PER) at HCMC. Among selected HMs, Cr exhibited a carcinogenic effect towards children (TCR > 10^{-4}) while Mn showed non-carcinogenic effect of traffic activities (HI > 1) towards HCMC residents. Results presented in this study shall provide necessary information to implement upcoming studies regarding more PM fractions and more airborne pollutants to fully understand the air pollution status in HCMC and update local environmental regulations.
Fig. 7. (a) Hazard index (HI) and (b) total carcinogenic risk (TCR) of selected PM$_{10}$-HMs in HCMC.

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SUPPLEMENTARY MATERIAL

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