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Seasonal variations of metals and metalloids in atmospheric particulate matter (PM2.5) in the urban megacity Hanoi

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Abstract

Fine particulate matter (PM2.5) in the atmosphere is of particular concern due to its adverse effects on human health and its impact on global warming. Southeast Asia is a hot spot for fossil fuel combustion with recurrent release of large plumes spreading over the ocean and neighboring countries. Due to the complex mixture of PM2.5, the atmospheric sources contribution related to local and regional emissions in Hanoi (northern Vietnam) is still ill-constrained. Here, we present a year-round study (November 2019 to December 2020) with measurements of 18 metals and metalloids (MM) and lead isotopes in the PM2.5 fraction to quantify weather-related atmospheric inputs and to assess risk to human health. Anthropogenic inputs from fossil fuel combustion accounted for about 80% in PM2.5. We found high PM2.5-bound MM concentrations often exceeding national and global standards with a low risk of chronic inhalation and carcinogenicity, mainly attributable to Cr. During winter monsoon (northeastern winds), stable weather conditions led to the enrichment of long-range air mass transport of local particulate emissions. During the summer monsoon (southeastern winds), warm and moist winds reduced coal contribution in PM2.5. Our study highlights the need for a strict implementation of policies to control hazardous MM emissions by reducing fossil fuel combustion. On the one hand, reducing coal-related activities could reduce Cr emissions and therefore improve the risks to human health. On the other hand, public policies should encourage conversion to green transport in order to reduce petrol combustion and thus limit global warming.

Keywords: contamination, mercury, lead isotopes, atmospheric transport, fossil fuel combustion

1. Introduction
Atmospheric particulate matter (PM) alters the climate (Fuzzi et al., 2015) and has a negative effect on human health (Janssen et al., 2011; Pope et al., 2011; Xing et al., 2016). Fine particles smaller than 2.5 μm (PM2.5) can penetrate deep into the lungs and cause asthma, lung disease, heart disease and cancer, depending on the amount inhaled and the time of exposure and the susceptibility of the person. Globally, inhalation of atmospheric PM is currently estimated to cause 3.3 million premature deaths per year worldwide, and could double by 2050 (Stanaway et al., 2018; Lelieveld et al., 2020). Atmospheric PM is a complex mixture of various compounds such as organic and elemental carbon, sugars, polycyclic aromatic hydrocarbons, secondary inorganic aerosol (e.g., SO$_4^{2-}$, NH$_4^+$, NO$_3^-$), etc. (Finlayson-Pitts et al., 2020).

Among these compounds, metals and metalloids (MM) are of particular concern for human health (Palleschi et al., 2018; Rafiee et al., 2020; Soetrisno and Delgado-Saborit, 2020). In small amounts, MM are essential to maintain biological functions, but in larger amounts they can damage cellular functions and cause toxicity in certain organs such as kidneys, brain, blood, skin, heart (Mitra et al., 2022). Due to their chemical coordination and oxidation-reduction properties, at high concentrations, MM can compete with each other. One element can bind to protein sites in place of another, causing DNA damage and perturbing protein function and enzyme activity (Balali-Mood et al., 2021; Witkowka et al., 2021; Jaishankar et al., 2014). Among them, As, Cd, Cr are of greatest concern due to their numerous sources of emissions, high toxicity, and persistence in urban areas (Li et al., 2021).

Atmospheric PM is ubiquitous and can originate from natural and anthropogenic sources (Pacyna and Pacyna, 2001; Gieré and Querol, 2010). PM-bound MM can be naturally introduced into the atmosphere through wind erosion of soil or sea surface, volcanic emissions and forest fires, mainly as coarse fraction (> 3-4 μm) and relatively non-solvable (Li et al., 2009; Bacon et al., 2011). By contrast, MM from anthropogenic activities can be introduced into the atmosphere through many pathways such as fossil fuel combustion, mining, ferrous and non-ferrous metal manufacturing, industrial production (e.g., cement, ceramic, glass, fertilizers), road traffic, waste incineration,
domestic heating etc. (Pacyna et al., 2007; Hao et al., 2018). Furthermore, anthropogenic MM tend to be associated with fine particles (Hein et al., 2022) and far exceed natural concentrations in heavily urbanized/industrialized areas (McNeill et al., 2020; Guo et al., 2023).

Atmospheric PM is a global concern and even more so for densely populated Asian countries (Xu et al., 2020; Zhang et al., 2021; Sakunkoo et al., 2022). Vietnam’s capital of Hanoi experienced rapid urbanization over the last decades, resulting in a severe increase in PM2.5 atmospheric load with an average annual concentration greater than 45 µg m$^{-3}$ (Makkoken et al., 2023), well above national (25 µg m$^{-3}$, QCVN 05:2013/BTNMT) and updated global guidelines (5 µg m$^{-3}$; WHO, 2021).

During peak hours, congested traffic significantly increases fine particulate emissions, contributing up to 40% of PM2.5 (Cohen et al., 2010; Quang et al., 2021). Northern Vietnam is heavily industrialized with coal-fired power plants as the main source of energy (Huy and Kim Oanh, 2017; Roy et al., 2021). Furthermore, agricultural burning is widely used in rural and suburban areas (Lasko et al., 2018; Le et al., 2020). In addition, long-range air mass transport from China to northern Vietnam contribute to the increase in PM2.5, with concentrations regularly exceeding 150 µg m$^{-3}$ during the northeast winter monsoon (Ly et al., 2021; Ngoc et al., 2021; Makkoken et al., 2023).

Although PM2.5-bound MM are strongly studied in China (e.g., Liao et al., 2023; Guo et al., 2022; Duan et al., 2021), the latter are poorly documented in Vietnam. In 2020, mean annual concentrations for As, Cd, Cr in PM2.5 were found at 6.2, 1.9, 9.4 ng m$^{-3}$, respectively (Nguyen et al., 2022), exceeding global guidelines for As and Cr (6.0 and 0.25 ng m$^{-3}$, respectively; WHO, 2021). In addition, a strong variability in PM2.5-bound MM can be observed between studies.

In Hanoi, over the same sampling periods (2001 - 2008 and 2002 - 2005), the mean Pb concentration in PM2.5 was assessed to 236 ng m$^{-3}$ (Cohen et al., 2010) and 137 ng m$^{-3}$ (Hopke et al., 2008), respectively, namely a difference greater than 50% between the two studies. In addition, maximum measured values were three times lower in 2001 - 2008 than in 2002 - 2005 (5.4 and 15.0 µg m$^{-3}$, respectively), but these results are well above the WHO guidelines (0.15 µg m$^{-3}$; WHO, 2021) for the two studies.
Principal Component Analysis (PCA) is a statistical technique widely used to identify the sources of PM, but the correlation matrices are poorly weighted and do not allow them to be quantified. Alternative techniques using Chemical Mass Balance (CMB) or Positive Matrix Factorization (PMF) are mathematical techniques used to solve systems of linear equations. The CMB model requires a large number of samples and the identification of sources is based on the chemical profiles from data obtained mainly in northern America, which may be different for southeast Asia (Henry et al., 1984, Paatero and Tapper, 1994; Pant and Harrison, 2012). With the PMF model, results are constrained to provide positive source contributions, and the uncertainty weighted difference between the observed and predicted species concentration is minimized. However, analyses of large datasets are often time-consuming and use up all the computer’s available memory, which slows down the programme and can even cause errors (Hopke, 2000). Using PMF model, Cohen et al. (2010) found that the main sources of PM2.5 in Hanoi were from traffic (40 ± 10%), industry (19 ± 8%), and coal (17 ± 7%). The contribution of sources related to local and regional PM2.5 emissions is still under debate (Nguyen et al., 2020). In a recent study, Makkonen et al. (2023), found that PM2.5 in Hanoi are from local and regional secondary inorganic emissions (18 and 25%, respectively), biomass burning (19%), dust (17%), traffic (12%) and industry (9%). Given the high concentrations of PM2.5 and associated MM already observed, it is important to better define and assess anthropogenic contributions in order to limit the risk of exposure to human health. (Nguyen et al., 2022; Vo et al., 2022).

Isotopic analyses are commonly used for the identification and quantification of MM sources (Chifflet et al., 2018). Although the stable radiogenic lead isotopic composition ($^{206}$Pb, $^{207}$Pb and $^{208}$Pb) can be naturally transferred in the environment via weathering processes (Stacey and Kramers, 1975), these isotopes are not significantly affected by physico-chemical fractionation processes after mixing with secondary Pb sources thus providing an efficient tool for determining the origins and pathways of Pb pollution (Komárek et al., 2008). In order to better assess the impact of anthropogenic activities on air quality, we are presenting here a year-round study (November 2019...
to December 2020) with quantitative measurements of 18 MM (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Sn, Ti, U, V and Zn) and lead isotopes analyses ($^{206}$Pb, $^{207}$Pb and $^{208}$Pb) in PM2.5 collected in Hanoi. The objectives are i) to identify and quantify the main anthropogenic sources, ii) to study the impact of weather conditions on MM variability in PM2.5 and, iii) to assess potential inhalation risks to human health per MM. Given the energy demand in Southeast Asia and the population density of Hanoi, the objective of this article is not to conduct an exhaustive study of PM2.5 sources but to focus on the impact of fossil fuels combustion on air quality.

2. Materials and Methods

2.1 Study site

Hanoi is a megacity covering an area of 3,359 km² with a population of 5.2 million in 2023 (Makkonen et al., 2023). The city is located in the Red River delta (northern Vietnam) about 100 km from the Gulf of Tonkin (Fig. 1). The subtropical climate is mainly influenced by the northeast monsoon in winter (November to March) and the southeast monsoon in summer (May to September) with two short intermediate seasons in spring and fall (Ngu and Hieu, 2004). In winter, the high atmospheric pressure above central China brings cold and calm air masses to northern Vietnam, the low boundary mixing layer favouring the accumulation of local atmospheric particles (Hai and Kim Oanh, 2013). In summer, the high atmospheric pressure moves toward the southern hemisphere bringing wet and warm air masses to Hanoi (Hien et al., 2002).

Hanoi is surrounded by many suburban industrial activities (e.g., Thang Long industrial Park in the North, Saidong industrial zone in the East, Ngoc Hoi industrial zone in the South) and several highly industrialized provinces in northern Vietnam (Thai Nguyen, Quang Ninh, Bac Ninh, and Hung Yen) (Hien et al., 2020). Approximately 10 coal-fired power plants are located within 200 km of Hanoi and emit large amounts of PM into the atmosphere (https://globalenergymonitor.org/projects/global-coal-plant-tracker/tracker/). In addition, the
vehicle traffic increases sharply together with the expansion of urban and industrial activities. In 2019, more than 6.6 million vehicles were registered in Hanoi (0.7 million cars and 5.8 million motorcycles) causing serious congestion problems on some roads during peak hours (Huu and Ngoc, 2021).

2.2 Sampling

PM2.5 were collected on the roof top of the University of Science and Technology of Hanoi (USTH; 21.0489°N, 105.8011°E) using a Staplex High Volume Air sampler. The sampling was conducted from November 2019 to December 2020 (14 months) with quartz fiber filters (Staplex Type TFAQ810 of 20x25 cm). PM2.5 samples (n = 27) were collected weekly over 24-hour periods (1 sample per week), except during the lockdown in April 2020 due to COVID-19 pandemic (corresponding to 4 “missing” samples as of 31/03/2020, 07/04/2020, 14/04/2020 and 21/04/2020). The average air volume filtered –calculated using the recorded air flow and the sampling time– was 1803 ± 81 m³ filter⁻¹. Filters were pre-combusted (550°C, 12h) before sampling to prevent organic matter and mercury residue (US EPA 2013). Field blanks were handled identically to the PM2.5 sampling, but were run on the Staplex sampler for only 1 min (Pekney and Davidson, 2005). The quartz filters were kept frozen in clean aluminium foils and plastic bags until laboratory analyses.

2.3 Weather conditions

During the study, weather data (wind speed and direction) were downloaded from the National Oceanic and Atmospheric Administration (NOAA, USA) station at Noibai International Airport (21.2212°N, 105.8072°E), 12 m above ground level. The NOAA station was located 23 km North of the USTH. Local precipitation was downloaded online (https://www.historique-meteo.net/asi-sud-est/vietnam/2020/05/).

For each sampling period, the NOAA’s Hybrid Single-Particle Lagrangian Integrated Trajectory model (NOAA HYPLIT; Stein et al., 2015; Rolph et al., 2017) was used to draw 24 h backward air
mass trajectories based on weather data in the Global Data Assimilation System (GDAS) archive starting at 8 am (01:00 UTC) with a temporal resolution of 1 hour at the sampling site and the height of 500 m (Fig. S1). However, the accuracy of an individual trajectory is limited by various uncertainties, leading to coarse approximation of air mass origin (Draxler et al., 2022). Large numbers of trajectories were statistically used to identify homogeneous groups of transport pathways.

Weather conditions (wind roses and trajectory frequencies) grouped by seasonal variations (winter and summer monsoon, intermediate spring and fall) are presented in Fig. 2 using the HYSPLIT model available online (https://www.ready.noaa.gov/HYSPLIT.php).

2.4 Laboratory analyses

2.4.1 Metals and metalloids (MM)

Sample processing was carried out in a clean laboratory (ISO 5) at the MIO (Aix Marseille University), using bi-distilled (HCl and HNO₃) and commercial grade (HF; Optima grade, Fisher Chemical) acids as well as ultrapure water (Milli-Q Integral 3, Millipore). The perfluoroalkoxy vials (PFA vials, Savillex) were pre-cleaned in two acid baths (HCl 10%, 90°C, 24 h and HNO₃ 10%, 90°C, 24 h). The analytical tubes (metal-free centrifuge tubes, VWR) were pre-cleaned in HCl (10%) overnight at room temperature. PFA vials and analytical tubes were thoroughly rinsed then dried under a laminar flow hood (ISO 1) before using. Sub-samples (47 mm punch diameter) were digested in PFA vials in a mixture of pure acids (HNO₃, 2 mL; HCl, 2 mL; HF, 1 mL), heated at 120°C during 24 h, evaporated to near dryness, and re-dissolved into 3 mL of HNO₃ (2% v/v). The digested samples were then diluted in analytical tubes using HNO₃ (2% v/v) before running MM analyses (modified method 3050B; US EPA, 1996).

MM (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Ti, U, V and Zn) analyses were performed using an inductively-coupled plasma mass spectrometer (ICP-MS NexION 300; Perkin Elmer) at the LA-ICP-MS platform (CEREGE, Aix Marseille University). Indium was used as internal standard to correct for instrumental mass bias. The digestion procedure was assessed using two
certified samples, from marine sediments (MESS4, National Research Council of Canada), and from atmospheric PM (NIST1649b, National Institute of Standard and Technology, USA). Our determinations of MM concentrations in certified samples were within the satisfactory target recovery of 100 ± 15% (Chen and Ma, 2001). All MM concentrations in PM2.5 were blank corrected. The latter had values below 1% for most MM, except for Al, Cr, Ni and U, which had values of approximatively 3%. Quality control details are presented in Table S1.

2.4.2 Mercury

For total Hg determination, sub-samples (47 mm punch diameter) were analysed by atomic absorption spectrometry after thermal calcination (AMA-254, Leco). The method detection limit, estimated as three times the standard deviation of blank samples, was 20 pg. The certified reference material (MESS4, National Research Council of Canada) was run several times per analytical batch and systematically before starting the measurements to check the accuracy of the measurements. The measured values were always within ± 5% of the recommended values.

2.4.3 Lead isotopes

Lead isotopic analyses (206Pb, 207Pb, 208Pb) were performed using a multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS; Nu Instrument) at the I3 platform (IPREM, University of Pau and Pays de l’Adour). All sample preparations were carried out in clean laboratories (MIO, Aix Marseille University). Acids used were either bi-distilled (HCl and HNO3) or commercial (HBr; Optima, Fisher Chemical). In order to minimise matrix effects during analysis, Pb was extracted from digested samples (see section 2.4.1) and purified by an ion exchange resin (Dowex 1X8, 100-200 mesh, Acros Organics) according to a conventional protocol (Monna et al., 1997; Ortega et al., 2012). The purified Pb samples were introduced into the MC-ICP-MS as dry aerosol (via an APEX nebulizer attached to a SPIRO membrane; ESI) at 50 µg L⁻¹. An internal TI isotopic standard (NIST997; National Institute of Standard and Technology, USA) was added at 12.5 µg L⁻¹ to all samples to correct mass
fractionation effects. In addition, a standard bracketing method was applied to correct the instrumental drift with a Pb isotopic standard (NIST981; National Institute of Standard and Technology, USA). Blank and Pb standard (NIST981) were run several times per analytical batch for the quality control procedure. The averages of the measured $^{207}\text{Pb} / ^{206}\text{Pb}$ and $^{208}\text{Pb} / ^{206}\text{Pb}$ ratios ($n = 70$) in these standards were $0.9144 \pm 0.0002$ and $2.1662 \pm 0.0011$, respectively, matching with the respective reference values of $0.9146 \pm 0.0003$ and $2.1681 \pm 0.0008$.

2.5 Data processing

2.5.1 Reconstructed mass

PM2.5 was estimated using mass reconstruction equations (Querol et al., 2001; Putaud et al., 2010; Chow et al., 2015). Briefly, the concentration of PM2.5 is expressed as the sum of its representative chemical components, including: inorganic major ions ($\text{NH}_4^+$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$); organic carbon (OC); elementary carbon (EC, also known as black carbon or BC); geological minerals (Al, Ca, Fe, K, Mg, Mn, Ti, P); sea salts ($\text{Na}^+$) and other elements (Cu, Ni, Pb, V, Zn). Chemical analyses were performed at the Air-O-Sol analytical platform (IGE, Grenoble Alpes University). Details of the PM2.5 mass reconstruction are presented in supplementary information.

2.5.2 Sources apportionment of Pb

In Vietnam, Pb could come mainly from natural (soil) and anthropogenic (fossil fuel combustion) sources. Therefore, the contribution of each source could be assessed using Pb isotopic ratios ($^{207}\text{Pb} / ^{206}\text{Pb}$ and $^{208}\text{Pb} / ^{206}\text{Pb}$) with the following linear mixing model (Monna et al., 1997; Chifflet et al., 2018):

$$\left( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_{\text{PM2.5}} = x_1 \left( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_1 + x_2 \left( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_2 + x_3 \left( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_3 \quad (1)$$

$$\left( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_{\text{PM2.5}} = x_1 \left( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_1 + x_2 \left( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_2 + x_3 \left( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_3 \quad (2)$$

$$x_1 + x_2 + x_3 = 1 \quad (3)$$
where the numbers in subscript (1, 2 and 3) represent sources, and x their relative contribution.

2.5.3 Health risk assessment

Health risk assessment provides indexes of adverse health effects for a specific group of population over a specific period (US EPA, 2005). It can be expressed as hazard quotient to assess the non-carcinogenic risk (HQ) and carcinogenic risk (CR). Some MM involved in carcinogenic processes were classified by the International Agency for Research on Cancer (IARC, 2023) as hazardous carcinogens (Group 1: As, Cd, and Cr^{VI}), probably carcinogens (Group 2A: Pb and Co^{0II}), carcinogens (Group 2B: Ni, Ti, and V), pollutants of potential interest (Group 3: Hg^{0}, Mn, Co^{III}, and Cr^{0III}).

The inhalation exposure concentration (EC, µg m^{-3}) was expressed as follows (US EPA, 2009):

\[ EC_i = \frac{C_{i95\%} \times ET \times EF \times ED}{AT_n} \]  

where \( C_{i95\%} \) is the mean concentration (95% upper confidence limit) of a metal or metalloid in PM2.5 (µg m^{-3}); ET is the exposure time (24 h d^{-1}); EF is the exposure frequency (365 d yr^{-1}); ED is the exposure duration (yr); and AT_n is the averaging time (= ED \times 365 \times 24 \times 1 \text{ yr} \times 70 \text{ yr} \times 365 \text{ d yr}^{-1} \times 24 \text{ h} \text{ for non-carcinogens and carcinogens, respectively}). The reference values (ET, EF, ED and AT_n) are from the EPA Integrated Risk Assessment System (EPA IRIS) website (https://epa.gov/iris).

The mean concentration of a metal or metalloid in sample (\( C_{i95\%} \)) is considered as the reasonable maximum exposure and was calculated as follows (Zhang et al., 2021):

\[ C_{i95\%} = \exp \left( \overline{\ln C_i} + 0.5 \times S_{\ln C_i}^2 + \frac{S_{\ln C_i} \times H_{0.95}}{\sqrt{n-1}} \right) \]  

where \( \overline{\ln C_i} \) and \( S_{\ln C_i} \) are the arithmetic mean and standard deviation of the log-transformed \( C_i \), respectively; \( n \) is the number of samples. Statistical \( H_{0.95} \) values that depend on \( S_{\ln C_i} \), \( n \), and the confidence level (0.05) are taken from Gilbert (1987).

The non-carcinogenic (HQ) and carcinogenic (CR) risks associated with chemical inhalation exposure were calculated as follows (US EPA, 2009):

\[ HQ_i^{nh} = \frac{EC_i}{RfC_i \times 1000} \]

where \( RfC_i \) is the reference concentration of metal or metalloid (µg m^{-3}).
where \( RfC_i \) and \( IUR_i \) are the reference concentration and the inhalation unit risk for a metal or metalloid \( i \), respectively. \( HQ_i > 1 \) indicates a potential chronic effect through inhalation of a metal or metalloid \( i \). \( CR_i \) indicates the probability that a person will develop cancer by inhaling certain MM with varying risk of very low \((CR \leq 10^{-6})\), low \((10^{-6} \leq CR < 10^{-4})\), moderate \((10^{-4} \leq CR < 10^{-3})\), high \((10^{-3} \leq CR < 10^{-1})\), very high \((CR \geq 10^{-1})\) (Hu et al., 2012; Roy et al., 2019; Behrooz et al., 2021). To assess the risk of exposure to multiple MM, the cumulative HI and TCR indexes were calculated as the sum of individual \( HQ_i \) and \( CR_i \), respectively. Updated reference values \((RfC_i \) and \( IUR_i \)) can be found on the Office of Environmental Health Hazard Assessment website (https://dtsc.ca.gov; OEHHA, 2019) or in Zhang et al. (2021) and shown in Table S2.

### 2.6 Multivariate statistical analyses

Statistical analyses were performed using XLstat software package version 2022.2.1 (Addinsoft 2023, Boston, USA, https://www.xlstat.com). First, the normality and homoscedasticity of data were tested. Then, Principal Component Analysis (PCA) and Hierarchical Cluster Analyses (HCA) were applied to explain the temporal variability of MM in PM2.5. The Pearson correlation matrix was used to examine the relationships between concentrations of the various MM. The Ward’s method with Euclidean distances was used to assess similarity or dissimilarity between samples. All statistical tests were performed with a probability (p) < 0.05.

### 3. Results

#### 3.1 Temporal variations of PM2.5 and MM concentrations

PM2.5 concentrations varied from 8.3 to 148 \( \mu g \) m\(^{-3} \) during the sampling period (November 2019 to December 2020) (Fig. 3; Table S3). High concentrations were observed mainly during the winter monsoon, dominated by east and northeast winds. Conversely, low PM2.5 concentrations...
were observed during the summer monsoon, dominated by southeast or southwest winds. This monitoring was consistent with recent studies of PM2.5 levels in Hanoi (Ngoc et al., 2021; Ly et al., 2021; Bui et al., 2022; Voung et al., 2023). The average annual concentration (40.2 ± 26.3 µg m⁻³) was 1.6 and 8.0 times higher than the national standard (25 µg m⁻³; QCVN 05:2013/BTNMT) and the World Health Organization guidelines (5 µg m⁻³; WHO, 2021), respectively. For the 24-hour exposure to PM2.5, 31.6% and 89.5% of the samples had concentrations above the national standard (50 µg m⁻³; QCVN 05:2013/BTNMT) and the WHO guidelines (15 µg m⁻³; WHO, 2021), respectively. Although very low precipitation (near 0 mm d⁻¹) was recorded in winter and spring, a large increase in precipitation was observed from summer onwards, reaching a maximum of 135 mm d⁻¹ in October 2020. Wind speed was variable (2.81 ± 0.85 m s⁻¹) during the sampling period but the lowest values were recorded in winter.

Statistical data (average, minimum and maximum) for PM2.5-bound MM concentrations over the sampling period are presented in Table 1 and detailed values per sample in Table S4. PM2.5-bound MM average concentrations varied over several orders of magnitude, with Al, Fe and Zn being the most abundant (higher than 300 ng m⁻³), followed by Cu, Mn, Pb and Ti (between 30 and 60 ng m⁻³), As, Cd, Cr, Ni Sb, Sn and V (between 1 and 5 ng m⁻³), and other MM (Ag, Co, Hg and U) at less than 0.3 ng m⁻³. These results are in good agreement with previous studies in Hanoi (Nguyen et al., 2022; Bui et al., 2022; Voung et al., 2023). No information was found to compare these values with the recommendations of national or global health organizations. However, for PM10 (atmospheric particulate matter < 10µm in aerodynamic diameter), the European Community and the WHO recommend limiting annual exposure to Pb, Ni, As, Cd and CrVI to 150, 20, 6, 5, and 0.25 ng m⁻³, respectively (Directives 2008/50/EC; 2004/107/EC; WHO, 2021). In the present study, some targeted MM (Pb, As, Cd and Cr) had 24-hour maximum concentrations above the annual exposure guidelines.

3.2 Principal Component Analysis and clustering
The Pearson correlation matrix and Ward’s Euclidean distances were examined to highlight
the links between PM2.5-bound MM and weather data (wind speed, precipitation and wind direction
as qualitative values). High and significant correlations ($r > 0.6$ and $p < 0.05$, $n = 57$) were observed
between all variables except Ag, Cu and Precipitation (Table S5). Although wet deposition is
considered a major process for removing particulate-bound MM, transfer mechanisms depend on
particle size and metal solubility (Pan and Wang 2014; Jaffrezo and Colin, 1988). PM10 is more
readily recovered than PM2.5 (Cheng et al., 2021; Zhou et al., 2021) and only the soluble fraction of
MM is cleaned from particles (Vithanage et al., 2022). These considerations may explain the lack of
correlation between PM2.5-bound MM and precipitation. In addition, the 24-hour sampling
conducted on 10/12/2019 and 12/05/2020 made high contribution (26 and 40%, respectively) to
factors loadings focusing multivariate statistical analyses on these two specific events instead of the
overall study. These two events were characterized by maximum concentrations of PM2.5, Al, Ti, Fe,
Co, Pb and Hg on 10/12/2019 and, a low concentration of PM2.5 associated with high concentrations
of Ni and Cr on 12/05/2020.

To better assess the impact of seasonal variations PM2.5-bound MM, multivariate statistical
analyses were reviewed without these two samples, and by redefining some variables (wind speed
and direction, precipitation, Ag and Cu) as illustrative parameters (Fig. 4). The original variables were
reduced to two factors (F1 and F2) explaining 65% of the total variance with eigenvalues > 1. F1 had a
high positive loading for all MM and negative loading for weather data (wind speed and
precipitation). F2 had a high positive loading for Al, Cr, Co, Fe, Ni, Ti, U, and V and a negative loading
for As, Cd, Hg, Mn, Pb, Sb, Sn and Zn. The scatter plot corresponding to samples showed two clusters
(C1 and C2) clearly distributed along F1 axis with a positive barycentre for C2 and a negative
barycentre for C1. Although PM2.5 in C1 could have originated from different air mass trajectories,
PM2.5 in C2 all originated from northerly or north-easterly winds (Table S6).

3.3 Lead isotopes
The complex mixture of particles does not allow for accurate quantification of anthropogenic sources using statistical studies alone. Due to quantum theory, isotopes are powerful tools for tracing Pb sources and atmospheric transport pathways. Although the isotopic composition of stable radiogenic lead ($^{206}\text{Pb}$, $^{207}\text{Pb}$ and $^{208}\text{Pb}$) is naturally transferred in the environment (Bollhöfer and Rosman 2000), this composition may vary after mixing with secondary sources emitted by anthropogenic activities (Zheng et al., 2004; Komárek et al., 2008). Despite the phase-out of leaded gasoline in southeast Asia over the past two decades, anthropogenic Pb inputs are still large enough to accurately quantify its sources of emissions (Mukai et al., 2001a; Bing-Quan et al., 2001; Yao et al., 2015). Lead isotopic ratios in PM2.5 collected during the sampling period ranged from 0.8005 to 0.8702 for $^{207}\text{Pb}/^{206}\text{Pb}$ and from 1.9754 to 2.1149 for $^{208}\text{Pb}/^{206}\text{Pb}$ (Table S7). These ratios were consistent with those found locally in the Tay Ho urban lake in Hanoi (Kikuchi et al., 2010) or with PM10 collected in Haiphong (Chifflet et al., 2018) showing the good relevance of the results.

4. Discussion

4.1 Sources identification

Atmospheric particle are highly dynamic and reactive compounds whose chemical composition is attributed to a wide range of natural and anthropogenic sources (Laskin et al., 2019). Because PM-bound MM depend primarily on soil composition, raw material use, and primary energy sources (from oil and coal combustion), elemental ratios are widely used to identify emission sources (e.g., Okuda et al., 2004; Hopke and Cohen, 2011). For example, V/Ni is well-known as indicator oil combustion (Pacyna and Pacyna, 2001). Previous studies have reported typical V/Ni ratios in heavy oil combustion for ship engines (with values between 3 – 4, Mazzei et al., 2008), in oil combustion for household heating (2.4; Lee et al., 2000) or in road traffic (1.49; Thorpe and Harrison, 2008). In addition, low V/Ni ratios (0.5) have also been reported in Chinese megacities (Beijing, Changchun and Chengdu) and attributed to PM from traffic and/or coal mining activities (Xu et al., 2020). Finally,
V/Ni ratios of 0.55 and 0.15 have also been found in Vietnamese coal and diesel, respectively (Chifflet et al., 2018). In this study, the V/Ni ratios in PM2.5 ranged from 0.7 to 2.8, showing the mixing of various sources (probably from fossil fuel combustion). A specific trend (V/Ni = 0.15, \( r^2 = 0.98, n = 3 \)) was also observed in the spring under easterly winds with V/Ni highlighting the impact of road traffic in the samples (Fig. 5a).

Coal combustion, industrial smelting and waste incineration are important sources of Cd and Pb in atmospheric particles (Pacyna and Pacyna, 2001; Sun et al., 2010; Tang et al., 2013; Sun et al., 2014). Generally, Cd/Pb ratios in urban/industrial cities in Asia have values close to 0.033 in Taiwan (Chen et al., 2015), 0.030 in Taipei (Hsu et al., 2005), 0.025 in Beijing and Changchun and 0.049 in Chengdu (Xu et al., 2020). In Europe, same ratios (0.029) have also been observed in the steel industry (Oravisjarvi et al., 2003) and higher values (0.08) have been found in municipal waste incinerators (Font et al., 2015). Conversely, lower Cd/Pb ratios have been found in natural Asian soils (0.017; Hsu et al., 2005) or rural European villages (0.013; Font et al., 2015). In this study, the Cd/Pb ratios in PM2.5 showed two trends with values close to 0.032 (\( r^2 = 0.96; n = 48 \)) or close to 0.012 (\( r^2 = 0.99; n = 8 \)) (Fig. 5b). Although the highest trend appears to be independent of weather conditions, the lowest trend was observed with southeasterly winds and rainy days. These results could indicate a dominant emission of PM2.5 from local urban/industrial activities throughout the year and a predominance of natural inputs of PM2.5 in specific weather conditions. In addition, high Cd/Pb ratio (0.088) was also observed during a specific event (18/02/2020) probably related to waste incineration emissions.

Sb is mainly derived from anthropogenic sources, in particular emissions from brake pad wear (Varrica et al., 2013) as well as, more broadly, from industrial activities and fossil fuel combustion (Pacyna and Pacyna, 2001; Tian et al., 2014). A specific Sb/Cd ratio of 5.0 has been attributed to road brake pad wear (Thorpe and Harrison, 2008) A lower Sb/Cd ratio can also be found
in Chinese and Vietnamese coal but the value varies by geographical area. Indeed, a Sb/Cd ratio of 1.2 was found in the Liupanshui coal mine (Guizhou, southwest China; Zhuang et al., 2000) and an average of 0.9 (n = 1,123) was proposed for the whole country (Dai et al., 2012). However, coal mines in northern Vietnam are rich in organic sulphur and enriched with Sb thus increasing the Sb/Cd ratio (Li et al., 2023). For example, a Sb/Cd ratio of 3.0 was found in the Coc Sau coal mine (Chifflet et al., 2018). In this study, high variability in Sb/Cd ratios was observed in PM2.5, indicating a possible mix of different anthropogenic sources (Fig. 5c). Three trends were observed during the sampling period with Sb/Cd ratios close to 4.3 ($r^2 = 0.99$; n = 32), close to 2.6 ($r^2 = 0.99$; n = 14) or close to 1.3 ($r^2 = 0.92$; n = 11). Although the weakest trends are observed by east and northeast winds (Sb/Cd = 1.3) or northeast and southeast winds (Sb/Cd = 2.6), the highest trend (Sb/Cd = 4.3) does not appear to be influenced by wind direction. These results seem to confirm the predominance of regional and local PM2.5 emissions from coal activities mixed with local PM2.5 emissions from road traffic.

Rapid urbanisation and industrialisation in southeast Asia, as well as long-range transboundary transport of atmospheric PM, make it difficult to assess the presence of natural sources in this region. In general, natural particles are emitted by wind erosion of soils in arid regions. MM concentrations from pristine soil in Vietnam are missing. However, soil dust appears to be the dominant source of Al and Ti in Hanoi (Hein et al., 2022) and a significant Al/Ti ratio of 14.5 ($r^2 = 0.98$; n = 54) is observed in this study (Fig. 5d). Same Al/Ti ratio (14.3) was also found in PM2.5 collected during sand dust storms in northern Chinese megacities (Xu et al., 2004a; Shen et al., 2007) showing a possible long-range transport of atmospheric PM. In Seoul (North Korea), the variation in the Al/Ti ratio was closely related to atmospheric transport of particles from the Gobi Desert through China and Mongolia (Al/Ti = 23.5) or particles emitted locally by soil resuspension (Al/Ti = 15.2) (Kim et al., 2003). In addition, an average Al/Ti of 25 was proposed for the upper continental crust (Wedepohl, 1995). These results show the likely mix between natural dust and urban dust in this study.
4.2 Effect of local and regional air mass transport on source distribution

4.2.1 Impact of weather conditions on MM concentrations

PM typically persists in the atmosphere between a few days and several weeks before being scavenged by dry or wet deposition (Seinfeld 2014). During their lifetime, they may travel long distances between the source of emission and the deposit area, undergoing chemical and physical transformations. Therefore, weather conditions can strongly influence their concentrations and the MM. In this study, the PCA-HCA analyses showed that high MM concentrations in cluster C2 occurred with north or northeast winds during the winter monsoon (Fig. 4). In addition, in C2, PM2.5 concentrations increased as the wind speed decreased (Fig. S2). Such results have already been observed in Hanoi (Hai and Kim Oanh, 2013; Nguyen et al., 2022; Makkoken et al., 2023). This pattern is attributed to recurring temperature inversion events in air layers in winter monsoon, thus limiting the dispersion of PM (Hien et al., 2002; Ly et al. 2021).

In winter, a ridge of high-pressure flows air masses from Siberia to China towards northern Vietnam, bringing cold and dry air, enriched by anthropogenic particles during their long-range transport. However, this is not the only pathway that controls the transport of particles in Hanoi. The height of the boundary layer at the Earth’s surface also plays an important role in vertical mixing. Previous studies have shown that high concentrations of elemental carbon (i.e., black carbon produced by incomplete combustion of fossil fuels) reduces vertical mixing (Wilcox et al., 2016; Hu et al., 2020; Duc et al., 2023). This is because the black carbon emitted in the upper air mass absorbs the sunlight, which heats up faster than the air mass closest to the Earth’s surface (Ding et al., 2016).

As a result, black carbon induces a reduction in turbulent kinetic energy in the surface mixed layer, which promotes its enrichment by local particle emissions (Petäjä et al., 2016). Conversely, during the summer monsoon, winds from the southeastern South China Sea and the sub-tropical western Pacific carry warm, moist, particle-depleted air. High temperatures enhance strong atmospheric convection, thus improving the dispersion of anthropogenic emissions (Hein et al., 2002; Yang et al.
In addition, heavy precipitation during the intermediate fall periods further decreases PM2.5 (and bound MM) due to the scavenging effects (Wang et al. 2018).

4.2.2 Temporal variation of sources

The predominant origin of Pb in PM2.5 was further evidenced by the plotting of Pb isotopic ratios ($^{208}$Pb/$^{206}$Pb vs $^{207}$Pb/$^{206}$Pb) from different anthropogenic sources (urban traffic and unleaded gasoline, urban/industrial activities and coal mining) of neighbouring countries (i.e., China, India, Indonesia, Taiwan, Thailand) (Fig. 6, Table S8). Lead in atmospheric particles has been extensively studied in Asian countries over the last two decades and has shown specific isotopic variations depending on the emission source (Bing-Quan et al., 2001; Bollhöfer and Rosman, 2001; Mukai et al., 2001a,b; Zhu et al., 2001; Zheng et al., 2004; Yao et al., 2015; Zhao et al., 2015: Bi et al., 2017). Here, the mixing between three sources is represented by a triangle whose end-members define the Pb isotopic ratios in sources S1, S2 and S3. The end-member S1, less radiogenic than other anthropogenic samples, could represent the geochemical background derived from the Earth’s crust (Bollhöfer and Rosman, 2001; Li et al., 2001). However, due to the high heterogeneity of Asian soils and the intensity of anthropogenic activities, the measurement of the geochemical background is uncertain. It is highly probable that natural dusts from long-range transport are contaminated by deposition of anthropogenic emissions (Table 2). The Pb isotopic composition in S1 was compared to ceramic or metals assemblies from neolitic archaeological site in southeast Asian (Pryce et al., 2014). The relics had Pb isotopic signatures close to S1, thus confirming the latter as a natural background. Therefore, Pb isotopic composition in ‘natural’ soil (S1) were assessed by calculating the intercept between the “coal line” and the “oil line”. The Pb isotopic ratios in S2 were associated with those of the Coc Sau coal mine (northern Vietnam; Chifflet et al., 2018) which merges with other Chinese coal mines (the solid green circles specifically representing the southern mines). Finally, the end-member S3 was associated with values from vehicle exhaust emissions in the megacity of Bangkok (Thailand, Bing-Quan et al., 2001) which also merges with those from Chinese unleaded gasoline (Yao et al.,
and Russian oil fields (Mukai et al., 2001b). The orange linear trend is defined with Pb isotopic ratios measured in samples from anthropogenic petroleum-related activities labelled S3 'oil', hereafter.

The contributions of the three Pb sources in PM2.5 was calculated using a linear mixing model (Fig. 7, Table S9). A low contribution of 'natural' soil (14 ± 11%) and high PM2.5 concentrations (54 ± 30 µg m⁻³) were observed during the northeast winter monsoon. Conversely, the contribution of 'natural' soil increased sharply (up to 83% on 07/07/2020) with a decrease in PM2.5 concentrations (26 ± 11 µg m⁻³) during the southeast summer monsoon. In winter, this contribution can be attributed to Asian dust storms, which transport fine soil dust from eastern (or inland) China to northern Vietnam before reaching Hanoi. Locally, the dry climate favours the resuspension of street dust and fine particles from vehicle exhaust (Hein et al., 2002). In addition, during this period, air masses with low vertical mixing favour PM2.5 enrichment (Ngoc et al., 2021), thus decreasing the natural contribution of PM2.5 from long-range transport. Conversely, during the summer monsoon, the increase in natural contribution of PM2.5 can be attributed to both mixing with a cleaner marine airflow and scavenging of local anthropogenic emissions due to a wet climate. The 'oil' contribution (encompassing any use) in PM2.5 remained stable over the sampling period (48 ± 13% during the northeast winter monsoon and 42 ± 17% during the southeast summer monsoon), although the year 2020 is marked by the traffic restrictions imposed by COVID-19 and a possible reduction in fuel consumption in many motorists (e.g., vehicles, buses, trucks etc.). In China, almost one third of the cities were in lockdown for several weeks in January and February 2020, resulting in improved local air quality (He et al., 2020; Yuan et al., 2021). Therefore, during this period (winter monsoon), Hanoi may have been less impacted by transboundary oil emissions. In addition, during the summer monsoon, South China Sea winds are expected to decrease the anthropogenic contribution of atmospheric particles in Hanoi (via dilution and wet scavenging) which does not seem to be the case for the 'oil' contribution which remains stable over the year. These observations suggest that 'oil' contribution in PM2.5 was mainly of local origin, not influenced by long-range transport from China.
or South China Sea. In contrast, coal had a higher contribution in PM2.5 during the northeast winter monsoon (38 ± 13%) than during southeast summer monsoon (26 ± 15%). Despite the rapid development of green energy (wind and solar), CO2 emissions continue to rise in China. In 2020, the Chinese coal industry emitted 761 Mt CO2 (i.e, 70% of China's total CO2 emissions) due to the growing demand for electricity (IEA, 2020; https://ourworldindata.org/). In addition, Vietnam has also large coal reserves in the north of the country and the share of coal-fired power generation has increased to 50% by 2020 (https://ember-climate.org/). Therefore, the results show a latent local coal contribution in PM2.5 (about 26%) enriched by Chinese coal emissions (about +12%) in winter.

4.3 Human health risk assessment through exposure to PM2.5

In this study, PM2.5 contain high concentrations of MM, which may constitute a health risk. Therefore, a comprehensive human health risk assessment can provide useful information for public policy management. The hazard quotient (HQ) per element could be ranked in the following order: Cr > Pb > Sb > Zn > Cu > Mn > As > Ti > Cd > V > Ni > Al > Co > Hg > U. The cumulative hazard index (HI) was less than 1 (i.e, 0.076), suggesting that inhalation of the 15 elements bound to PM2.5 has no chronic influence (Table 3). In addition, the total carcinogenic risk (TCR) was estimated at 1.0 × 10−4, which suggests that the probability of a person developing cancer by inhalation is low, but would be mainly imputable to Cr.

Other studies on human health risk assessment of PM2.5 in Hanoi estimated risk values similar to our results: HI = 0.13 ± 0.08 and TCR = 1.13 × 10−5 (Hein et al., 2022), HI = 1.16 and TCR = 9 × 10−7 (Nguyen et al., 2022) or HI = 0.006 and TCR = 5.5 × 10−7 (Bui et al., 2022). The differences between HI and TCR values may be explained by the random or incomplete sampling frequency, which were carried out only in winter 2018-2019, in three seasons winter-spring-fall 2020 or in two seasons summer-fall 2020, respectively. However, these studies concluded that Cr and As presented a risk of inhalation exposure. According to the International Agency for Research on Cancer, Cr (Group 1) can induce harmful human health effects. Coal naturally contains large amounts of Cr (Zhang et al., 2004;
Ketris and Yudovich, 2009; Dai et al., 2012) which are transferred to atmospheric particles during combustion processes (Xu et al., 2004b). Consequently, coal mining and combustion could potentially induce human diseases.

Despite risks on human health, Vietnam has significantly increased its use of coal, positioned as the world’s tenth largest producer of coal-fired electricity. In 2022, Vietnamese economy grew by 8% with a very large increase in energy use (https://ember-climate.org/). Despite the boom in the deployment of renewables energies, Vietnam faces several challenges (industrial, economic and politic) in its effort to become carbon neutral. A "Just Energy Transition Partnership" plan was signed in 2022 in order to help the country to peak its greenhouse gas emissions by 2030 instead of 2035, limiting its production of coal energy to 30.2 GW instead of 37 GW, and source 47% of its power from renewable energy by 2030 (COP27 climate summit; https://unfccc.int/cop27). This study highlights the need for strict regulatory plans to control hazardous MM emissions by reducing coal combustion. In addition, due to the impact of oil combustion in PM2.5, public policies should encourage conversion to green transport to limit global warming.

5. Conclusion

Our study provided a detailed overview of the annual variation in PM2.5 concentrations in Hanoi (northern Vietnam), evaluated Pb anthropogenic sources and examined the impact of weather conditions on inhaled MM concentrations and related toxic risks.

The annual average PM2.5 concentration (40.2 ± 26.3 μg m$^{-3}$) was 1.6 and 8.0 times higher than the national and global standards, respectively. In addition, some PM2.5-bound MM (Pb, As, Cd and Cr) had 24-hour maximum concentrations above the annual exposure limits. Chemical ratios (V/Ni, Cd/Pb, Sb/Cd and Al/Ti) presented typical trends indicating the dominance of three emission sources from road traffic, natural soil, and coal uses (mining, combustion). The source contribution was assessed using Pb isotopic ratios ($^{208}$Pb/$^{206}$Pb vs $^{207}$Pb/$^{206}$Pb). The oil contribution (encompassing
any petroleum-related activities) to PM2.5 remained stable over the sampling period (November 2019 to December 2020) with an annual average of 45%. In contrast, PM2.5 inputs from soil and coal were impacted by weather conditions. Indeed, ‘natural’ soil contribution varied between 14 to 83% depending on the winter and summer monsoons, respectively. Conversely, coal contribution was higher in the winter (38%) than in the summer (26%) monsoon. This phenomenon could be due to the BC emissions (from the incomplete combustion of fossil fuels) coming from both long-range air transport and local emissions. In addition, the human health risk assessment showed that PM2.5-bound MM concentrations obtained in this study have no chronic influence although Cr, Pb and Sb have the highest HQ values. The carcinogenic risk is low but mainly imputable to Cr.

In order to discriminate more precisely the black carbon fractions linked to agricultural burning from those linked to the combustion of fossil fuels, a companion paper will cover the study of major inorganic ions (NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, Na$^+$) and other elements (Ca, K, Mg, P), as well as carbon speciation (OC, EC, sugars).

Supplementary information

The supplementary material related to this article is available online at XXX.

Acknowledgments

The project received financial support from the French (IRD, IRN-SOOT SEA) and Vietnamese (VAST-IMER) research organizations. We thank the MIO “Plateforme Analytique de Chimie des Environnements Marins” (PACEM platform) for laboratory facilities. The authors would like to thank the dedicated efforts of people from Air-o-Sol Platform at IGE for analysing the PM2.5 samples.
authors are deeply grateful for the thorough and constructive corrections and insightful comments of the anonymous reviewers, who have significantly improved the original manuscript.

References


https://doi.org/10.1016/j.jas.2013.08.024.


US EPA, 2013. Reference method for the determination of fine particulate matter as PM 2.5 in the atmosphere. 40 CRF 50.18. Appendix L.


Table 1. Variations (Mean, Min and Max) of PM2.5-bound MM concentrations (ng m$^{-3}$) during the sampling period (November 2019 to December 2020).

Mean and standard deviation ($\sigma$) include all samples of this study ($n = 57$).

|   | Ag | Al | As | Cd | Co | Cr | Cu | Fe | Hg | Mn | Ni | Sb | Sn | Pb | Ti | U | V | Zn |
|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|---|---|----|
| Mean | 0.285 | 349 | 3.97 | 1.82 | 0.153 | 3.31 | 56.8 | 295 | 0.190 | 32.0 | 1.34 | 4.81 | 3.38 | 65.7 | 26.3 | 0.039 | 1.20 | 444 |
| $\sigma$ | 0.467 | 271 | 2.80 | 1.43 | 0.090 | 5.31 | 90.9 | 198 | 0.134 | 43.9 | 1.31 | 3.83 | 2.31 | 71.6 | 19.2 | 0.031 | 0.700 | 545 |
| Min | 0.012 | 15.4 | 0.674 | 0.179 | 0.028 | 0.412 | 2.28 | 70.9 | 0.010 | 2.83 | 0.018 | 0.646 | 0.784 | 3.29 | 4.29 | 0.001 | 0.137 | 22.5 |
| Max | 3.47 | 1427 | 11.2 | 5.95 | 0.477 | 40.5 | 641 | 1033 | 0.576 | 275 | 7.01 | 16.9 | 10.8 | 392 | 98.2 | 0.142 | 3.95 | 2054 |
Table 2. Pb isotopic compositions in estimated natural soil, urban aerosol and relics from China and southeast Asian.

<table>
<thead>
<tr>
<th>Estimated natural soil (Bing-Quan et al., 2002)</th>
<th>207Pb/206Pb</th>
<th>208Pb/206Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northeast China min</td>
<td>0.8673</td>
<td>2.1084</td>
</tr>
<tr>
<td>Northeast China max</td>
<td>0.8511</td>
<td>2.0800</td>
</tr>
<tr>
<td>North China min</td>
<td>0.9615</td>
<td>2.2817</td>
</tr>
<tr>
<td>North China max</td>
<td>0.8621</td>
<td>2.1457</td>
</tr>
<tr>
<td>Indochina min</td>
<td>0.8410</td>
<td>2.0698</td>
</tr>
<tr>
<td>Indochina max</td>
<td>0.8278</td>
<td>2.0613</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aerosol from urban cities (Bollhöfer and Rosman, 2000)</th>
<th>207Pb/206Pb</th>
<th>208Pb/206Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vietnam Heni</td>
<td>0.8569</td>
<td>2.1020</td>
</tr>
<tr>
<td>Vietnam Huzhimin</td>
<td>0.8658</td>
<td>2.1039</td>
</tr>
<tr>
<td>Thailand Bangkok</td>
<td>0.8873</td>
<td>2.1331</td>
</tr>
<tr>
<td>Malaysia Kuala Lummpur</td>
<td>0.8764</td>
<td>2.1122</td>
</tr>
<tr>
<td>Indonesia Bandung</td>
<td>0.9116</td>
<td>2.1568</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Neolithic relics from southeast Asia (Pryce et al., 2014)</th>
<th>207Pb/206Pb</th>
<th>208Pb/206Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thailand Khao SaKaeo 400-200 BC</td>
<td>0.7695</td>
<td>2.0063</td>
</tr>
<tr>
<td>Thailand Non Pa Wai 1000-300 BC</td>
<td>0.7785</td>
<td>1.8921</td>
</tr>
<tr>
<td>Thailand Phu Lon 1000 BC</td>
<td>0.7877</td>
<td>1.9534</td>
</tr>
<tr>
<td>Vietnam Lang Nhon NA</td>
<td>0.7958</td>
<td>2.0531</td>
</tr>
</tbody>
</table>

NA: not available
Table 3. Estimation of human health risk from PM2.5 inhalation in Hanoi: detailed indices ($HQ_i$ and $CR_i$) per element and cumulative indices (HI, TCR).

<table>
<thead>
<tr>
<th>Element</th>
<th>$HQ_i$</th>
<th>$CR_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Al</td>
<td>$7.4 \times 10^{-5}$</td>
<td>NA</td>
</tr>
<tr>
<td>As</td>
<td>$2.9 \times 10^{-4}$</td>
<td>$6.3 \times 10^6$</td>
</tr>
<tr>
<td>Cd</td>
<td>$2.1 \times 10^{-4}$</td>
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</tr>
<tr>
<td>Co</td>
<td>$2.7 \times 10^{-5}$</td>
<td>$5.0 \times 10^7$</td>
</tr>
<tr>
<td>Cr</td>
<td>$3.1 \times 10^2$</td>
<td>$8.8 \times 10^5$</td>
</tr>
<tr>
<td>Cu</td>
<td>$1.5 \times 10^3$</td>
<td>NA</td>
</tr>
<tr>
<td>Fe</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Hg</td>
<td>$6.7 \times 10^{-6}$</td>
<td>NA</td>
</tr>
<tr>
<td>Mn</td>
<td>$6.6 \times 10^{-4}$</td>
<td>NA</td>
</tr>
<tr>
<td>Ni</td>
<td>$9.5 \times 10^{-5}$</td>
<td>$1.2 \times 10^7$</td>
</tr>
<tr>
<td>Pb</td>
<td>$2.2 \times 10^2$</td>
<td>$3.2 \times 10^7$</td>
</tr>
<tr>
<td>Sb</td>
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<td>NA</td>
</tr>
<tr>
<td>Sn</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Ti</td>
<td>$2.8 \times 10^{-4}$</td>
<td>NA</td>
</tr>
<tr>
<td>U</td>
<td>$1.1 \times 10^{-6}$</td>
<td>NA</td>
</tr>
<tr>
<td>V</td>
<td>$1.8 \times 10^{-4}$</td>
<td>$3.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Zn</td>
<td>$1.7 \times 10^{-3}$</td>
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<table>
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<tr>
<th></th>
<th>HI</th>
<th>TCR</th>
</tr>
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<tbody>
<tr>
<td>Total</td>
<td>$7.6 \times 10^{-2}$</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

NA: not available
Figure 1: Localisation of sampling site
Figure 2: Wind roses (a) and trajectory frequencies (b) grouped by seasonal variations during the sampling period. Colour scales of wind speed (WS) and trajectory frequencies are expressed in m s$^{-1}$ and %, respectively (NOAA HYSPLIT model, [https://www.ready.noaa.gov/HYSPLIT.php](https://www.ready.noaa.gov/HYSPLIT.php)).
Figure 3: Seasonal variations in PM2.5 concentrations (µg m$^{-3}$) and precipitation (mm d$^{-1}$). Abbreviations indicate the wind direction: Northeast (NE), East (E), Southeast (SE), Southwest (SW), Northwest (NW) and not defined (ND).
Figure 4: Statistical analyses (PCA-HCA) of MM concentrations in PM2.5 during the sampling period (November 2019 to December 2020). The contribution of the active and illustrative variables on axes F1 and F2 are presented in solid and dotted lines, respectively. The distribution of samples in clusters C1 and C2 are presented in solid and open circles, respectively.
Figure 5: Elementary ratios in PM2.5 collected during the sampling period (November 2019 to December 2020): a) V/Ni, b) Cd/Pb, c) Sb/Cd and d) Al/Ti
Figure 6: Pb isotopic ratios ($^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{207}\text{Pb}/^{206}\text{Pb}$) in PM2.5 collected in Hanoi during the sampling period (in black). The coloured data comes from the literature, in green for Chinese coal mines (solid circles come from southern provinces), in blue for Chinese urban and industrial activities and in orange for petroleum-related activities (e.g., from road traffic in Asian megacities, unleaded Chinese gasoline and Russian oil fields).
Figure 7: Contribution of Pb sources from ‘natural’ soil, ‘oil’ and coal to PM2.5 during the sampling period (November 2019 to December 2020).

Abbreviations indicate the wind direction: Northeast (NE), East (E), Southeast (SE), Southwest (SW), Northwest (NW) and not defined (ND)