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

3

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20

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22 **Abstract**

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

41

42

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

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47 **1. Introduction**

48 Atmospheric particulate matter (PM) alters the climate (Fuzzi et al., 2015) and has a negative  
49 effect on human health (Janssen et al., 2011; Pope et al., 2011; Xing et al., 2016). Fine particles  
50 smaller than 2.5  $\mu\text{m}$  (PM<sub>2.5</sub>) can penetrate deep into the lungs and cause asthma, lung disease,  
51 heart disease and cancer, depending on the amount inhaled and the time of exposure and the  
52 susceptibility of the person. Globally, inhalation of atmospheric PM is currently estimated to cause  
53 3.3 million premature deaths per year worldwide, and could double by 2050 (Stanaway et al., 2018;  
54 Lelieveld et al., 2020). Atmospheric PM is a complex mixture of various compounds such as organic  
55 and elemental carbon, sugars, polycyclic aromatic hydrocarbons, secondary inorganic aerosol (*e.g.*,  
56  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ), *etc.* (Finlayson-Pitts et al., 2020).

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

67 Atmospheric PM is ubiquitous and can originate from natural and anthropogenic sources  
68 (Pacyna and Pacyna, 2001; Gieré and Querol, 2010). PM-bound MM can be naturally introduced into  
69 the atmosphere through wind erosion of soil or sea surface, volcanic emissions and forest fires,  
70 mainly as coarse fraction ( $> 3\text{-}4 \mu\text{m}$ ) and relatively non-solvable (Li et al., 2009; Bacon et al., 2011). By  
71 contrast, MM from anthropogenic activities can be introduced into the atmosphere through many  
72 pathways such as fossil fuel combustion, mining, ferrous and non-ferrous metal manufacturing,  
73 industrial production (*e.g.*, cement, ceramic, glass, fertilizers), road traffic, waste incineration,

74 domestic heating etc. (Pacyna et al., 2007; Hao et al., 2018). Furthermore, anthropogenic MM tend  
75 to be associated with fine particles (Hein et al., 2022) and far exceed natural concentrations in  
76 heavily urbanized/industrialized areas (McNeill et al., 2020; Guo et al., 2023).

77 Atmospheric PM is a global concern and even more so for densely populated Asian countries  
78 (Xu et al., 2020; Zhang et al., 2021; Sakunkoo et al., 2022). Vietnam's capital of Hanoi experienced  
79 rapid urbanization over the last decades, resulting in a severe increase in PM<sub>2.5</sub> atmospheric load  
80 with an average annual concentration greater than 45  $\mu\text{g m}^{-3}$  (Makkoken et al., 2023), well above  
81 national (25  $\mu\text{g m}^{-3}$ , QCVN 05:2013/BTNMT) and updated global guidelines (5  $\mu\text{g m}^{-3}$ ; WHO, 2021).  
82 During peak hours, congested traffic significantly increases fine particulate emissions, contributing up  
83 to 40% of PM<sub>2.5</sub> (Cohen et al., 2010; Quang et al., 2021). Northern Vietnam is heavily industrialized  
84 with coal-fired power plants as the main source of energy (Huy and Kim Oanh, 2017; Roy et al.,  
85 2021). Furthermore, agricultural burning is widely used in rural and suburban areas (Lasko et al.,  
86 2018; Le et al., 2020). In addition, long-range air mass transport from China to northern Vietnam  
87 contribute to the increase in PM<sub>2.5</sub>, with concentrations regularly exceeding 150  $\mu\text{g m}^{-3}$  during the  
88 northeast winter monsoon (Ly et al., 2021; Ngoc et al., 2021; Makkoken et al., 2023).

89 Although PM<sub>2.5</sub>-bound MM are strongly studied in China (e.g., Liao et al., 2023; Zhou et al.,  
90 2023; Guo et al., 2022; Duan et al., 2021), the latter are poorly documented in Vietnam. In 2020,  
91 mean annual concentrations for As, Cd, Cr in PM<sub>2.5</sub> were found at 6.2, 1.9, 9.4  $\text{ng m}^{-3}$ , respectively  
92 (Nguyen et al., 2022), exceeding global guidelines for As and Cr (6.0 and 0.25  $\text{ng m}^{-3}$ , respectively;  
93 WHO, 2021). In addition, a strong variability in PM<sub>2.5</sub>-bound MM can be observed between studies.  
94 In Hanoi, over the same sampling periods (2001 - 2008 and 2002 - 2005), the mean Pb concentration  
95 in PM<sub>2.5</sub> was assessed to 236  $\text{ng m}^{-3}$  (Cohen et al., 2010) and 137  $\text{ng m}^{-3}$  (Hopke et al., 2008),  
96 respectively, namely a difference greater than 50% between the two studies. In addition, maximum  
97 measured values were three times lower in 2001 - 2008 than in 2002 - 2005 (5.4 and 15.0  $\mu\text{g m}^{-3}$ ,  
98 respectively), but these results are well above the WHO guidelines (0.15  $\mu\text{g m}^{-3}$ ; WHO, 2021) for the  
99 two studies.

100 Principal Component Analysis (PCA) is a statistical technique widely used to identify the  
101 sources of MM, but the correlation matrices are poorly weighted and do not allow them to be  
102 quantified. Alternative techniques using Chemical Mass Balance (CMB) or Positive Matrix  
103 Factorization (PMF) are mathematical techniques used to solve systems of linear equations. The CMB  
104 model requires a large number of samples and the identification of sources is based on the chemical  
105 profiles from data obtained mainly in northern America, which may be different for southeast Asia  
106 (Henry et al., 1984, Paatero and Tapper, 1994; Pant and Harrison, 2012). With the PMF model, results  
107 are constrained to provide positive source contributions, and the uncertainty weighted difference  
108 between the observed and predicted species concentration is minimized. However, analyses of large  
109 datasets are often time-consuming and use up all the computer's available memory, which slow  
110 down the programme and can even cause errors (Hopke, 2000). Using PMF model, Cohen et al.  
111 (2010) found that the main sources of PM<sub>2.5</sub> in Hanoi were from traffic (40 ± 10%), industry  
112 (19 ± 8%), and coal (17 ± 7%). The contribution of sources related to local and regional PM<sub>2.5</sub>  
113 emissions is still under debate (Nguyen et al., 2020). In a recent study, Makkonen et al. (2023), found  
114 that PM<sub>2.5</sub> in Hanoi are from local and regional secondary inorganic emissions (18 and 25%,  
115 respectively), biomass burning (19%), dust (17%), traffic (12%) and industry (9%). Given the high  
116 concentrations of PM<sub>2.5</sub> and associated MM already observed, it is important to better define and  
117 assess anthropogenic contributions in order to limit the risk of exposure to human health. (Nguyen et  
118 al., 2022; Vo et al., 2022).

119 Isotopic analyses are commonly used for the identification and quantification of MM sources  
120 (Chifflet et al., 2018). Although the stable radiogenic lead isotopic composition (<sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb)  
121 can be naturally transferred in the environment *via* weathering processes (Stacey and Kramers,  
122 1975), these isotopes are not significantly affected by physico-chemical fractionation processes after  
123 mixing with secondary Pb sources thus providing an efficient tool for determining the origins and  
124 pathways of Pb pollution (Komárek et al., 2008). In order to better assess the impact of  
125 anthropogenic activities on air quality, we are presenting here a year-round study (November 2019

126 to December 2020) with quantitative measurements of 18 MM (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn,  
127 Ni, Pb, Sb, Sn, Ti, U, V and Zn) and lead isotopes analyses ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ) in PM<sub>2.5</sub> collected in  
128 Hanoi. The objectives are i) to identify and quantify the main anthropogenic sources, ii) to study the  
129 impact of weather conditions on MM variability in PM<sub>2.5</sub> and, iii) to assess potential inhalation risks  
130 to human health per MM. Given the energy demand in Southeast Asia and the population density of  
131 Hanoi, the objective of this article is not to conduct an exhaustive study of PM<sub>2.5</sub> sources but to  
132 focus on the impact of fossil fuels combustion on air quality.

133

134

## 135 **2. Materials and Methods**

### 136 *2.1 Study site*

137 Hanoi is a megacity covering an area of 3,359 km<sup>2</sup> with a population of 5.2 million in 2023  
138 ([Makkoken et al., 2023](#)). The city is located in the Red River delta (northern Vietnam) about 100 km  
139 from the Gulf of Tonkin (Fig. 1). The subtropical climate is mainly influenced by the northeast  
140 monsoon in winter (November to March) and the southeast monsoon in summer (May to  
141 September) with two short intermediate seasons in spring and fall ([Ngu and Hieu, 2004](#)). In winter,  
142 the high atmospheric pressure above central China brings cold and calm air masses to northern  
143 Vietnam, the low boundary mixing layer favouring the accumulation of local atmospheric particles  
144 ([Hai and Kim Oanh, 2013](#)). In summer, the high atmospheric pressure moves toward the southern  
145 hemisphere bringing wet and warm air masses to Hanoi ([Hien et al., 2002](#)).

146 Hanoi is surrounded by many suburban industrial activities (*e.g.*, Thang Long industrial Park  
147 in the North, Saidong industrial zone in the East, Ngoc Hoi industrial zone in the South) and several  
148 highly industrialized provinces in northern Vietnam (Thai Nguyen, Quang Ninh, Bac Ninh, and Hung  
149 Yen) ([Hien et al., 2020](#)). Approximately 10 coal-fired power plants are located within 200 km of Hanoi  
150 and emit large amounts of PM into the atmosphere  
151 (<https://globalenergymonitor.org/projects/global-coal-plant-tracker/tracker/>). In addition, the

152 vehicle traffic increases sharply together with the expansion of urban and industrial activities. In  
153 2019, more than 6.6 million vehicles were registered in Hanoi (0.7 million cars and 5.8 million  
154 motorcycles) causing serious congestion problems on some roads during peak hours (Huu and Ngoc,  
155 2021).

156

## 157 *2.2 Sampling*

158 PM2.5 were collected on the roof top of the University of Science and Technology of Hanoi  
159 (USTH; 21.0489°N, 105.8011°E) using a Staplex High Volume Air sampler. The sampling was  
160 conducted from November 2019 to December 2020 (14 months) with quartz fiber filters (Staplex  
161 Type TFAQ810 of 20x25 cm). PM2.5 samples (n = 27) were collected weekly over 24-hour periods (1  
162 sample per week), except during the lockdown in April 2020 due to COVID-19 pandemic  
163 (corresponding to 4 “missing” samples as of 31/03/2020, 07/04/2020, 14/04/2020 and 21/04/2020).  
164 The average air volume filtered –calculated using the recorded air flow and the sampling time– was  
165  $1803 \pm 81 \text{ m}^3 \text{ filter}^{-1}$ . Filters were pre-combusted (550°C, 12h) before sampling to prevent organic  
166 matter and mercury residue (US EPA 2013). Field blanks were handled identically to the PM2.5  
167 sampling, but were run on the Staplex sampler for only 1 min (Pekney and Davidson, 2005). The  
168 quartz filters were kept frozen in clean aluminium foils and plastic bags until laboratory analyses.

169

## 170 *2.3 Weather conditions*

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

176 For each sampling period, the NOAA’s Hybrid Single-Particle Lagrangian Integrated Trajectory  
177 model (NOAA HYSPLIT; Stein et al., 2015; Rolph et al., 2017) was used to draw 24 h backward air



178 mass trajectories based on weather data in the Global Data Assimilation System (GDAS) archive  
179 starting at 8 am (01:00 UTC) with a temporal resolution of 1 hour at the sampling site and the height  
180 of 500 m (Fig. S1). However, the accuracy of an individual trajectory is limited by various  
181 uncertainties, leading to coarse approximation of air mass origin (Draxler et al., 2022). Large numbers  
182 of trajectories were statistically used to identify homogeneous groups of transport pathways.  
183 Weather conditions (wind roses and trajectory frequencies) grouped by seasonal variations (winter  
184 and summer monsoon, intermediate spring and fall) are presented in Fig. 2 using the HYSPLIT model  
185 available online (<https://www.ready.noaa.gov/HYSPLIT.php>).

186

## 187 *2.4 Laboratory analyses*

### 188 *2.4.1 Metals and metalloids (MM)*

189 Sample processing was carried out in a clean laboratory (ISO 5) at the MIO (Aix Marseille  
190 University), using bi-distilled (HCl and HNO<sub>3</sub>) and commercial grade (HF; Optima grade, Fisher  
191 Chemical) acids as well as ultrapure water (Milli-Q Integral 3, Millipore). The perfluoroalkoxy vials  
192 (PFA vials, Savillex) were pre-cleaned in two acid baths (HCl 10%, 90°C, 24 h and HNO<sub>3</sub> 10%, 90°C,  
193 24 h). The analytical tubes (metal-free centrifuge tubes, VWR) were pre-cleaned in HCl (10%)  
194 overnight at room temperature. PFA vials and analytical tubes were thoroughly rinsed then dried  
195 under a laminar flow hood (ISO 1) before using. Sub-samples (47 mm punch diameter) were digested  
196 in PFA vials in a mixture of pure acids (HNO<sub>3</sub>, 2 mL; HCl, 2 mL; HF, 1 mL), heated at 120°C during 24 h,  
197 evaporated to near dryness, and re-dissolved into 3 mL of HNO<sub>3</sub> (2% v/v). The digested samples were  
198 then diluted in analytical tubes using HNO<sub>3</sub> (2% v/v) before running MM analyses (modified method  
199 3050B; US EPA, 1996).

200 MM (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, Ti, U, V and Zn) analyses were  
201 performed using an inductively-coupled plasma mass spectrometer (ICP-MS NexION 300; Perkin  
202 Elmer) at the LA-ICP-MS platform (CEREGE, Aix Marseille University). Indium was used as internal  
203 standard to correct for instrumental mass bias. The digestion procedure was assessed using two

204 certified samples, from marine sediments (MESS4, National Research Council of Canada), and from  
205 atmospheric PM (NIST1649b, National Institute of Standard and Technology, USA). Our  
206 determinations of MM concentrations in certified samples were within the satisfactory target  
207 recovery of  $100 \pm 15\%$  (Chen and Ma, 2001). All MM concentrations in PM<sub>2.5</sub> were blank corrected.  
208 The latter had values below 1% for most MM, except for Al, Cr, Ni and U, which had values of  
209 approximately 3%. Quality control details are presented in Table S1.

210

#### 211 2.4.2 Mercury

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

218

#### 219 2.4.3 Lead isotopes

220 Lead isotopic analyses ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ) were performed using a multi collector inductively  
221 coupled plasma mass spectrometer (MC-ICP-MS; Nu Instrument) at the I3 platform (IPREM,  
222 University of Pau and Pays de l'Adour). All sample preparations were carried out in clean laboratories  
223 (MIO, Aix Marseille University). Acids used were either bi-distilled (HCl and HNO<sub>3</sub>) or commercial  
224 (HBr; Optima, Fisher Chemical). In order to minimise matrix effects during analysis, Pb was extracted  
225 from digested samples (see section 2.4.1) and purified by an ion exchange resin (Dowex 1X8, 100-200  
226 mesh, Acros Organics) according to a conventional protocol (Monna et al., 1997; Ortega et al., 2012).  
227 The purified Pb samples were introduced into the MC-ICP-MS as dry aerosol (*via* an APEX nebulizer  
228 attached to a SPIRO membrane; ESI) at  $50 \mu\text{g L}^{-1}$ . An internal Tl isotopic standard (NIST997; National  
229 Institute of Standard and Technology, USA) was added at  $12.5 \mu\text{g L}^{-1}$  to all samples to correct mass

230 fractionation effects. In addition, a standard bracketing method was applied to correct the  
231 instrumental drift with a Pb isotopic standard (NIST981; National Institute of Standard and  
232 Technology, USA). Blank and Pb standard (NIST981) were run several times per analytical batch for  
233 the quality control procedure. The averages of the measured  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios  
234 ( $n = 70$ ) in these standards were  $0.9144 \pm 0.0002$  and  $2.1662 \pm 0.0011$ , respectively, matching with  
235 the respective reference values of  $0.9146 \pm 0.0003$  and  $2.1681 \pm 0.0008$ .

236

## 237 *2.5 Data processing*

### 238 *2.5.1 Reconstructed mass*

239 PM2.5 was estimated using mass reconstruction equations (Querol et al., 2001; Putaud et al.,  
240 2010; Chow et al., 2015). Briefly, the concentration of PM2.5 is expressed as the sum of its  
241 representative chemical components, including: inorganic major ions ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ); organic  
242 carbon (OC); elementary carbon (EC, also known as black carbon or BC); geological minerals (Al, Ca,  
243 Fe, K, Mg, Mn, Ti, P); sea salts ( $\text{Na}^+$ ) and other elements (Cu, Ni, Pb, V, Zn). Chemical analyses were  
244 performed at the Air-O-Sol analytical platform (IGE, Grenoble Alpes University). Details of the PM2.5  
245 mass reconstruction are presented in supplementary information.

246

### 247 *2.5.2 Sources apportionment of Pb*

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

$$252 \left( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_{\text{PM2.5}} = x_1 \left( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_1 + x_2 \left( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_2 + x_3 \left( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_3 \quad (1)$$

$$253 \left( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_{\text{PM2.5}} = x_1 \left( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_1 + x_2 \left( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_2 + x_3 \left( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_3 \quad (2)$$

$$254 x_1 + x_2 + x_3 = 1 \quad (3)$$

255 where the numbers in subscript (1, 2 and 3) represent sources, and x their relative contribution.

256

### 257 2.5.3 Health risk assessment

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

264 The inhalation exposure concentration (EC,  $\mu\text{g m}^{-3}$ ) was expressed as follows (US EPA, 2009):

$$265 \quad EC_i = \frac{C_i^{95\%} \times ET \times EF \times ED}{AT_n} \quad (4)$$

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

271 The mean concentration of a metal or metalloid in sample ( $C_i^{95\%}$ ) is considered as the  
272 reasonable maximum exposure and was calculated as follows (Zhang et al., 2021):

$$273 \quad C_i^{95\%} = \exp\left(\overline{\ln C_i} + 0.5 \times S_{\ln C_i}^2 + \frac{S_{\ln C_i} \times H_{0.95}}{\sqrt{n-1}}\right) \quad (5)$$

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

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

$$279 \quad HQ_i^{inh} = \frac{EC_i}{RfC_i \times 1000} \quad (6)$$

280 
$$CR_i^{inh} = EC_i \times IUR_i \quad (7)$$

281 where  $RfC_i$  and  $IUR_i$  are the reference concentration and the inhalation unit risk for a metal or  
282 metalloid  $i$ , respectively.  $HQ_i > 1$  indicates a potential chronic effect through inhalation of a metal or  
283 metalloid  $i$ .  $CR_i$  indicates the probability that a person will develop cancer by inhaling certain MM  
284 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  
285 ( $10^{-3} \leq CR < 10^{-1}$ ), very high ( $CR \geq 10^{-1}$ ) (Hu et al., 2012; Roy et al., 2019; Behrooz et al., 2021). To  
286 assess the risk of exposure to multiple MM, the cumulative HI and TCR indexes were calculated as  
287 the sum of individual  $HQ_i$  and  $CR_i$ , respectively. Updated reference values ( $RfC_i$  and  $IUR_i$ ) can be found  
288 on the Office of Environmental Health Hazard Assessment website (<https://dtsc.ca.gov>; OEHHA,  
289 2019) or in Zhang et al. (2021) and shown in Table S2.

290

### 291 *2.6 Multivariate statistical analyses*

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

299

300

## 301 **3. Results**

### 302 *3.1 Temporal variations of PM2.5 and MM concentrations*

303 PM2.5 concentrations varied from 8.3 to 148  $\mu\text{g m}^{-3}$  during the sampling period (November  
304 2019 to December 2020) (Fig. 3; Table S3). High concentrations were observed mainly during the  
305 winter monsoon, dominated by east and northeast winds. Conversely, low PM2.5 concentrations

306 were observed during the summer monsoon, dominated by southeast or southwest winds. This  
307 monitoring was consistent with recent studies of PM<sub>2.5</sub> levels in Hanoi (Ngoc et al., 2021, Ly et al.,  
308 2021; Bui et al., 2022; Voung et al., 2023). The average annual concentration ( $40.2 \pm 26.3 \mu\text{g m}^{-3}$ ) was  
309 1.6 and 8.0 times higher than the national standard ( $25 \mu\text{g m}^{-3}$ ; QCVN 05:2013/BTNMT) and the  
310 World Health Organization guidelines ( $5 \mu\text{g m}^{-3}$ ; WHO, 2021), respectively. For the 24-hour exposure  
311 to PM<sub>2.5</sub>, 31.6% and 89.5% of the samples had concentrations above the national standard ( $50 \mu\text{g m}^{-3}$ ;  
312 QCVN 05:2013/BTNMT) and the WHO guidelines ( $15 \mu\text{g m}^{-3}$ ; WHO, 2021), respectively. Although  
313 very low precipitation (near  $0 \text{ mm d}^{-1}$ ) was recorded in winter and spring, a large increase in  
314 precipitation was observed from summer onwards, reaching a maximum of  $135 \text{ mm d}^{-1}$  in October  
315 2020. Wind speed was variable ( $2.81 \pm 0.85 \text{ m s}^{-1}$ ) during the sampling period but the lowest values  
316 were recorded in winter.

317 Statistical data (average, minimum and maximum) for PM<sub>2.5</sub>-bound MM concentrations over  
318 the sampling period are presented in Table 1 and detailed values per sample in Table S4. PM<sub>2.5</sub>-  
319 bound MM average concentrations varied over several orders of magnitude, with Al, Fe and Zn being  
320 the most abundant (higher than  $300 \text{ ng m}^{-3}$ ), followed by Cu, Mn, Pb and Ti (between 30 and  $60 \text{ ng m}^{-3}$ ;  
321 As, Cd, Cr, Ni Sb, Sn and V (between 1 and  $5 \text{ ng m}^{-3}$ ), and other MM (Ag, Co, Hg and U) at less than  
322  $0.3 \text{ ng m}^{-3}$ . These results are in good agreement with previous studies in Hanoi (Nguyen et al., 2022;  
323 Bui et al., 2022; Vuong et al., 2023). No information was found to compare these values with the  
324 recommendations of national or global health organizations. However, for PM<sub>10</sub> (atmospheric  
325 particulate matter  $< 10\mu\text{m}$  in aerodynamic diameter), the European Community and the WHO  
326 recommend limiting annual exposure to Pb, Ni, As, Cd and Cr<sup>VI</sup> to 150, 20, 6, 5, and  $0.25 \text{ ng m}^{-3}$ ,  
327 respectively (Directives 2008/50/EC; 2004/107/EC; WHO, 2021). In the present study, some targeted  
328 MM (Pb, As, Cd and Cr) had 24-hour maximum concentrations above the annual exposure guidelines.

329

330 *3.2 Principal Component Analysis and clustering*

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

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

355

356 *3.3 Lead isotopes*

357 The complex mixture of particles does not allow for accurate quantification of anthropogenic  
358 sources using statistical studies alone. Due to quantum theory, isotopes are powerful tools for  
359 tracing Pb sources and atmospheric transport pathways. Although the isotopic composition of stable  
360 radiogenic lead ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ) is naturally transferred in the environment (Bollhöfer and  
361 Rosman 2000), this composition may vary after mixing with secondary sources emitted by  
362 anthropogenic activities (Zheng et al., 2004; Komárek et al., 2008). Despite the phase-out of leaded  
363 gasoline in southeast Asia over the past two decades, anthropogenic Pb inputs are still large enough  
364 to accurately quantify its sources of emissions (Mukai et al., 2001a; Bing-Quan et al., 2001; Yao et al.,  
365 2015). Lead isotopic ratios in PM<sub>2.5</sub> collected during the sampling period ranged from 0.8005 to  
366 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  
367 consistent with those found locally in the Tay Ho urban lake in Hanoi (Kikuchi et al., 2010) or with  
368 PM<sub>10</sub> collected in Haiphong (Chifflet et al., 2018) showing the good relevance of the results.

369

370

## 371 4. Discussion

### 372 4.1 Sources identification

373 Atmospheric particles are highly dynamic and reactive compounds whose chemical  
374 composition is attributed to a wide range of natural and anthropogenic sources (Laskin et al., 2019).  
375 Because PM-bound MM depend primarily on soil composition, raw material use, and primary energy  
376 sources (from oil and coal combustion), elemental ratios are widely used to identify emission sources  
377 (e.g., Okuda et al., 2004; Hopke and Cohen, 2011). For example, V/Ni is well-known as an indicator of  
378 oil combustion (Pacyna and Pacyna, 2001). Previous studies have reported typical V/Ni ratios in heavy  
379 oil combustion for ship engines (with values between 3 – 4, Mazzei et al., 2008), in oil combustion for  
380 household heating (2.4; Lee et al., 2000) or in road traffic (1.49; Thorpe and Harrison, 2008). In  
381 addition, low V/Ni ratios (0.5) have also been reported in Chinese megacities (Beijing, Changchun and  
382 Chengdu) and attributed to PM from traffic and/or coal mining activities (Xu et al., 2020). Finally,



383 V/Ni ratios of 0.55 and 0.15 have also been found in Vietnamese coal and diesel, respectively (Chifflet  
384 et al., 2018). In this study, the V/Ni ratios in PM<sub>2.5</sub> ranged from 0.7 to 2.8, showing the mixing of  
385 various sources (probably from fossil fuel combustion). A specific trend (V/Ni = 0.15,  $r^2 = 0.98$ ,  $n = 3$ )  
386 was also observed in the spring under easterly winds with V/Ni highlighting the impact of road traffic  
387 in the samples (Fig. 5a).

388 Coal combustion, industrial smelting and waste incineration are important  
389 sources of Cd and Pb in atmospheric particles (Pacyna and Pacyna, 2001; Sun et  
390 al., 2010; Tang et al., 2013; Sun et al., 2014). Generally, Cd/Pb ratios in  
391 urban/industrial cities in Asia have values close to 0.033 in Taiwan (Chen et al.,  
392 2015), 0.030 in Taipei (Hsu et al., 2005), 0.025 in Beijing and Changchun and  
393 0.049 in Chengdu (Xu et al., 2020). In Europe, same ratios (0.029) have also been  
394 observed in the steel industry (Oravisjarvi et al., 2003) and higher values (0.08)  
395 have been found in municipal waste incinerators (Font et al., 2015). Conversely,  
396 lower Cd/Pb ratios have been found in natural Asian soils (0.017; Hsu et al., 2005)  
397 or rural European villages (0.013; Font et al., 2015). In this study, the Cd/Pb ratios in  
398 PM<sub>2.5</sub> showed two trends with values close to 0.032 ( $r^2 = 0.96$ ;  $n = 48$ ) or close to 0.012 ( $r^2 = 0.99$ ;  
399  $n = 8$ ) (Fig. 5b). Although the highest trend appears to be independent of weather conditions, the  
400 lowest trend was observed with southeasterly winds and rainy days. These results could indicate a  
401 dominant emission of PM<sub>2.5</sub> from local urban/industrial activities throughout the year and a  
402 predominance of natural inputs of PM<sub>2.5</sub> in specific weather conditions. In addition, high Cd/Pb ratio  
403 (0.088) was also observed during a specific event (18/02/2020) probably related to waste  
404 incineration emissions.

405 Sb is mainly derived from anthropogenic sources, in particular emissions from brake pad  
406 wear (Varrica et al., 2013) as well as, more broadly, from industrial activities and fossil fuel  
407 combustion (Pacyna and Pacyna, 2001; Tian et al., 2014). A specific Sb/Cd ratio of 5.0 has been  
408 attributed to road brake pad wear (Thorpe and Harrison, 2008) A lower Sb/Cd ratio can also be found

409 in Chinese and Vietnamese coal but the value varies by geographical area. Indeed, a Sb/Cd ratio of  
410 1.2 was found in the Liupanshui coal mine (Guizhou, southwest China; [Zhuang et al., 2000](#)) and an  
411 average of 0.9 (n = 1,123) was proposed for the whole country ([Dai et al., 2012](#)). However, coal mines  
412 in northern Vietnam are rich in organic sulphur and enriched with Sb thus increasing the Sb/Cd ratio  
413 ([Li et al., 2023](#)). For example, a Sb/Cd ratio of 3.0 was found in the Coc Sau coal mine ([Chifflet et al.,](#)  
414 [2018](#)). In this study, high variability in Sb/Cd ratios was observed in PM<sub>2.5</sub>, indicating a possible mix  
415 of different anthropogenic sources (Fig. 5c). Three trends were observed during the sampling period  
416 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  
417 ( $r^2 = 0.92$ ; n = 11). Although the weakest trends are observed by east and northeast winds  
418 (Sb/Cd = 1.3) or northeast and southeast winds (Sb/Cd = 2.6), the highest trend (Sb/Cd = 4.3) does  
419 not appear to be influenced by wind direction. These results seem to confirm the predominance of  
420 regional and local PM<sub>2.5</sub> emissions from coal activities mixed with local PM<sub>2.5</sub> emissions from road  
421 traffic..

422 Rapid urbanisation and industrialisation in southeast Asia, as well as long-range  
423 transboundary transport of atmospheric PM, make it difficult to assess the presence of natural  
424 sources in this region. In general, natural particles are emitted by wind erosion of soils in arid regions.  
425 MM concentrations from pristine soil in Vietnam are missing. However, soil dust appears to be the  
426 dominant source of Al and Ti in Hanoi ([Hein et al., 2022](#)) and a significant Al/Ti ratio of 14.5 ( $r^2 = 0.98$ ;  
427 n = 54) is observed in this study (Fig. 5d). Same Al/Ti ratio (14.3) was also found in PM<sub>2.5</sub> collected  
428 during sand dust storms in northern Chinese megacities ([Xu et al., 2004a](#); [Shen et al., 2007](#)) showing  
429 a possible long-range transport of atmospheric PM. In Seoul (North Korea), the variation in the Al/Ti  
430 ratio was closely related to atmospheric transport of particles from the Gobi Desert through China  
431 and Mongolia (Al/Ti = 23.5) or particles emitted locally by soil resuspension (Al/Ti = 15.2) ([Kim et al.,](#)  
432 [2003](#)). In addition, an average Al/Ti of 25 was proposed for the upper continental crust ([Wedepohl,](#)  
433 [1995](#)). These results show the likely mix between natural dust and urban dust in this study.

434

## 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, PM<sub>2.5</sub> 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.

460 2018). In addition, heavy precipitation during the intermediate fall periods further decreases PM2.5  
461 (and bound MM) due to the scavenging effects (Wang et al. 2018).

462

#### 463 4.2.2 Temporal variation of sources

464 The predominant origin of Pb in PM2.5 was further evidenced by the plotting of Pb isotopic  
465 ratios ( $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{207}\text{Pb}/^{206}\text{Pb}$ ) from different anthropogenic sources (urban traffic and unleaded  
466 gasoline, urban/industrial activities and coal mining) of neighbouring countries (*i.e.*, China, India,  
467 Indonesia, Taiwan, Thailand) (Fig. 6, Table S8). Lead in atmospheric particles has been extensively  
468 studied in Asian countries over the last two decades and has shown specific isotopic variations  
469 depending on the emission source (Bing-Quan et al., 2001; Bollhöfer and Rosman, 2001; Mukai et al.,  
470 2001a,b; Zhu et al., 2001; Zheng et al., 2004; Yao et al., 2015; Zhao et al., 2015; Bi et al., 2017). Here,  
471 the mixing between three sources is represented by a triangle whose end-members define the Pb  
472 isotopic ratios in sources S1, S2 and S3. The end-member S1, less radiogenic than other  
473 anthropogenic samples, could represent the geochemical background derived from the Earth's crust  
474 (Bollhöfer and Rosman, 2001; Li et al., 2001). However, due to the high heterogeneity of Asian soils  
475 and the intensity of anthropogenic activities, the measurement of the geochemical background is  
476 uncertain. It is highly probable that natural dusts from long-range transport are contaminated by  
477 deposition of anthropogenic emissions (Table 2). The Pb isotopic composition in S1 was compared to  
478 ceramic or metals assemblies from neolithic archaeological site in southeast Asian (Pryce et al., 2014).  
479 The relics had Pb isotopic signatures close to S1, thus confirming the latter as a natural background.  
480 Therefore, Pb isotopic composition in 'natural' soil (S1) were assessed by calculating the intercept  
481 between the "coal line" and the "oil line". The Pb isotopic ratios in S2 were associated with those of  
482 the Coc Sau coal mine (northern Vietnam; Chifflet et al., 2018) which merges with other Chinese coal  
483 mines (the solid green circles specifically representing the southern mines). Finally, the end-member  
484 S3 was associated with values from vehicle exhaust emissions in the megacity of Bangkok (Thailand,  
485 Bing-Quan et al., 2001) which also merges with those from Chinese unleaded gasoline (Yao et al.,

486 [2015](#)) and Russian oil fields ([Mukai et al., 2001b](#)). The orange linear trend is defined with Pb isotopic  
487 ratios measured in samples from anthropogenic petroleum-related activities labelled S3 'oil', here  
488 after.

489 The contributions of the three Pb sources in PM<sub>2.5</sub> was calculated using a linear mixing  
490 model (Fig. 7, Table S9). A low contribution of 'natural' soil ( $14 \pm 11\%$ ) and high PM<sub>2.5</sub> concentrations  
491 ( $54 \pm 30 \mu\text{g m}^{-3}$ ) were observed during the northeast winter monsoon. Conversely, the contribution  
492 of 'natural' soil increased sharply (up to 83% on 07/07/2020) with a decrease in PM<sub>2.5</sub>  
493 concentrations ( $26 \pm 11 \mu\text{g m}^{-3}$ ) during the southeast summer monsoon. In winter, this contribution  
494 can be attributed to Asian dust storms, which transport fine soil dust from eastern (or inland) China  
495 to northern Vietnam before reaching Hanoi. Locally, the dry climate favours the resuspension of  
496 street dust and fine particles from vehicle exhaust ([Hein et al., 2002](#)). In addition, during this period,  
497 air masses with low vertical mixing favour PM<sub>2.5</sub> enrichment ([Ngoc et al., 2021](#)), thus decreasing the  
498 natural contribution of PM<sub>2.5</sub> from long-range transport. Conversely, during the summer monsoon,  
499 the increase in natural contribution of PM<sub>2.5</sub> can be attributed to both mixing with a cleaner marine  
500 airflow and scavenging of local anthropogenic emissions due to a wet climate. The 'oil' contribution  
501 (encompassing any use) in PM<sub>2.5</sub> remained stable over the sampling period ( $48 \pm 13\%$  during the  
502 northeast winter monsoon and  $42 \pm 17\%$  during the southeast summer monsoon), although the year  
503 2020 is marked by the traffic restrictions imposed by COVID-19 and a possible reduction in fuel  
504 consumption in many motorists (*e.g.*, vehicles, buses, trucks *etc.*). In China, almost one third of the  
505 cities were in lockdown for several weeks in January and February 2020, resulting in improved local  
506 air quality ([He et al., 2020](#); [Yuan et al., 2021](#)). Therefore, during this period (winter monsoon), Hanoi  
507 may have been less impacted by transboundary oil emissions. In addition, during the summer  
508 monsoon, South China Sea winds are expected to decrease the anthropogenic contribution of  
509 atmospheric particles in Hanoi (*via* dilution and wet scavenging) which does not seem to be the case  
510 for the 'oil' contribution which remains stable over the year. These observations suggest that 'oil'  
511 contribution in PM<sub>2.5</sub> was mainly of local origin, not influenced by long-range transport from China

512 or South China Sea. In contrast, coal had a higher contribution in PM<sub>2.5</sub> during the northeast winter  
513 monsoon ( $38 \pm 13\%$ ) than during southeast summer monsoon ( $26 \pm 15\%$ ). Despite the rapid  
514 development of green energy (wind and solar), CO<sub>2</sub> emissions continue to rise in China. In 2020, the  
515 Chinese coal industry emitted 761 Mt CO<sub>2</sub> (*i.e.*, 70% of China's total CO<sub>2</sub> emissions) due to the  
516 growing demand for electricity (IEA, 2020; <https://ourworldindata.org/>). In addition, Vietnam has  
517 also large coal reserves in the north of the country and the share of coal-fired power generation has  
518 increased to 50% by 2020 (<https://ember-climate.org/>). Therefore, the results show a latent local  
519 coal contribution in PM<sub>2.5</sub> (about 26%) enriched by Chinese coal emissions (about +12%) in winter.

520

#### 521 *4.3 Human health risk assessment through exposure to PM<sub>2.5</sub>*

522 In this study, PM<sub>2.5</sub> contain high concentrations of MM, which may constitute a health risk.  
523 Therefore, a comprehensive human health risk assessment can provide useful information for public  
524 policy management. The hazard quotient (HQ<sub>i</sub>) per element could be ranked in the following order:  
525 Cr > Pb > Sb > Zn > Cu > Mn > As > Ti > Cd > V > Ni > Al > Co > Hg > U. The cumulative hazard index  
526 (HI) was less than 1 (*i.e.*, 0.076), suggesting that inhalation of the 15 elements bound to PM<sub>2.5</sub> has no  
527 chronic influence (Table 3). In addition, the total carcinogenic risk (TCR) was estimated at  $1.0 \cdot 10^{-4}$ ,  
528 which suggests that the probability of a person developing cancer by inhalation is low, but would be  
529 mainly imputable to Cr.

530 Other studies on human health risk assessment of PM<sub>2.5</sub> in Hanoi estimated risk values  
531 similar to our results: HI =  $0.13 \pm 0.08$  and TCR =  $1.13 \cdot 10^{-5}$  (Hein et al., 2022), HI = 1.16 and TCR =  $9 \cdot 10^{-6}$   
532 (Nguyen et al., 2022) or HI = 0.006 and TCR =  $5.5 \cdot 10^{-7}$  (Bui et al., 2022). The differences between HI  
533 and TCR values may be explained by the random or incomplete sampling frequency, which were  
534 carried out only in winter 2018-2019, in three seasons winter-spring-fall 2020 or in two seasons  
535 summer-fall 2020, respectively. However, these studies concluded that Cr and As presented a risk of  
536 inhalation exposure. According to the International Agency for Research on Cancer, Cr (Group 1) can  
537 induce harmful human health effects. Coal naturally contains large amounts of Cr (Zhang et al., 2004;

538 [Ketris and Yudovich, 2009; Dai et al., 2012](#)) which are transferred to atmospheric particles during  
539 combustion processes ([Xu et al., 2004b](#)). Consequently, coal mining and combustion could potentially  
540 induce human diseases.

541 Despite risks on human health, Vietnam has significantly increased its use of coal, positioned  
542 as the world's tenth largest producer of coal-fired electricity. In 2022, Vietnamese economy grew by  
543 8% with a very large increase in energy use (<https://ember-climate.org/>). Despite the boom in the  
544 deployment of renewables energies, Vietnam faces several challenges (industrial, economic and  
545 politic) in its effort to become carbon neutral. A "Just Energy Transition Partnership" plan was signed  
546 in 2022 in order to help the country to peak its greenhouse gas emissions by 2030 instead of 2035,  
547 limiting its production of coal energy to 30.2 GW instead of 37 GW, and source 47% of its power from  
548 renewable energy by 2030 (COP27 climate summit; <https://unfccc.int/cop27>). This study highlights  
549 the need for strict regulatory plans to control hazardous MM emissions by reducing coal combustion.  
550 In addition, due to the impact of oil combustion in PM2.5, public policies should encourage  
551 conversion to green transport to limit global warming.

552

553

## 554 **5. Conclusion**

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

558 The annual average PM2.5 concentration ( $40.2 \pm 26.3 \mu\text{g m}^{-3}$ ) was 1.6 and 8.0 times higher  
559 than the national and global standards, respectively. In addition, some PM2.5-bound MM (Pb, As, Cd  
560 and Cr) had 24-hour maximum concentrations above the annual exposure limits. Chemical ratios  
561 (V/Ni, Cd/Pb, Sb/Cd and Al/Ti) presented typical trends indicating the dominance of three emission  
562 sources from road traffic, natural soil, and coal uses (mining, combustion). The source contribution  
563 was assessed using Pb isotopic ratios ( $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{207}\text{Pb}/^{206}\text{Pb}$ ). The oil contribution (encompassing

564 any petroleum-related activities) to PM2.5 remained stable over the sampling period (November  
565 2019 to December 2020) with an annual average of 45%. In contrast, PM2.5 inputs from soil and coal  
566 were impacted by weather conditions. Indeed, 'natural' soil contribution varied between 14 to 83%  
567 depending on the winter and summer monsoons, respectively.. Conversely, coal contribution was  
568 higher in the winter (38%)than in the summer (26%) monsoon. This phenomenon could be due to the  
569 BC emissions (from the incomplete combustion of fossil fuels) coming from both long-range air  
570 transport and local emissions. In addition, the human health risk assessment showed that PM2.5-  
571 bound MM concentrations obtained in this study have no chronic influence although Cr, Pb and Sb  
572 have the highest HQ<sub>i</sub> values. The carcinogenic risk is low but mainly imputable to Cr.

573 In order to discriminate more precisely the black carbon fractions linked to agricultural  
574 burning from those linked to the combustion of fossil fuels, a companion paper will cover the study  
575 of major inorganic ions (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>) and other elements (Ca, K, Mg, P), as well as carbon  
576 speciation (OC, EC, sugars).

577

578

579

## 580 **Supplementary information**

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

582

583

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591

592

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1016 **Tables**

1017 **Table 1.** Variations (Mean, Min and Max) of PM2.5-bound MM concentrations (ng m<sup>-3</sup>) during the sampling period (November 2019 to December 2020).

1018 Mean and standard deviation ( $\sigma$ ) include all samples of this study (n = 57).

|          | <b>Ag</b> | <b>Al</b> | <b>As</b> | <b>Cd</b> | <b>Co</b> | <b>Cr</b> | <b>Cu</b> | <b>Fe</b> | <b>Hg</b> | <b>Mn</b> | <b>Ni</b> | <b>Sb</b> | <b>Sn</b> | <b>Pb</b> | <b>Ti</b> | <b>U</b> | <b>V</b> | <b>Zn</b> |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|----------|-----------|
| 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      |

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1021

1022 **Table 2.** Pb isotopic compositions in estimated natural soil, urban aerosol and relics from China and  
 1023 southeast Asian.

|  |              |             | $^{207}\text{Pb}/^{206}\text{Pb}$ | $^{208}\text{Pb}/^{206}\text{Pb}$ |
|--|--------------|-------------|-----------------------------------|-----------------------------------|
| <i>Estimated natural soil (Bing-Quan et al., 2002)</i>           |              |             |                                   |                                   |
| Northeast China  | min          |             | 0.8673                            | 2.1084                            |
| Northeast China  | max          |             | 0.8511                            | 2.0800                            |
| North China  | min          |             | 0.9615                            | 2.2817                            |
| North China  | max          |             | 0.8621                            | 2.1457                            |
| Indochina  | min          |             | 0.8410                            | 2.0698                            |
| Indochina  | max          |             | 0.8278                            | 2.0613                            |
| <i>Aerosol from urban cities (Bollhöfer and Rosman, 2000)</i>    |              |             |                                   |                                   |
| Vietnam  | Heni         |             | 0.8569                            | 2.1020                            |
| Vietnam  | Huzhimin     |             | 0.8658                            | 2.1039                            |
| Thailand   | Bangkok      |             | 0.8873                            | 2.1331                            |
| Malaysia   | Kuala Lumpur |             | 0.8764                            | 2.1122                            |
| Indonesia  | Bandung      |             | 0.9116                            | 2.1568                            |
| <i>Neolithic relics from southeast Asia (Pryce et al., 2014)</i> |              |             |                                   |                                   |
| Thailand   | Khao SaKaeo  | 400-200 BC  | 0.7695                            | 2.0063                            |
| Thailand   | Non Pa Wai   | 1000-300 BC | 0.7785                            | 1.8921                            |
| Thailand   | Phu Lon      | 1000 BC     | 0.7877                            | 1.9534                            |
| Vietnam  | Lang Nhon    | NA          | 0.7958                            | 2.0531                            |

1024 NA: not available

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1027 **Table 3.** Estimation of human health risk from PM2.5 inhalation in Hanoi: detailed indices ( $HQ_i$  and  
 1028  $CR_i$ ) per element and cumulative indices (HI, TCR).

|       | $HQ_i$                                | $CR_i$                                |
|-------|---------------------------------------|---------------------------------------|
| Ag    | NA                                    | NA                                    |
| Al    | $7.4 \cdot 10^{-5}$                   | NA                                    |
| As    | $2.9 \cdot 10^{-4}$                   | $6.3 \cdot 10^{-6}$                   |
| Cd    | $2.1 \cdot 10^{-4}$                   | $3.0 \cdot 10^{-6}$                   |
| Co    | $2.7 \cdot 10^{-5}$                   | $5.0 \cdot 10^{-7}$                   |
| Cr    | <b><math>3.1 \cdot 10^{-2}</math></b> | <b><math>8.8 \cdot 10^{-5}</math></b> |
| Cu    | $1.5 \cdot 10^{-3}$                   | NA                                    |
| Fe    | NA                                    | NA                                    |
| Hg    | $6.7 \cdot 10^{-6}$                   | NA                                    |
| Mn    | $6.6 \cdot 10^{-4}$                   | NA                                    |
| Ni    | $9.5 \cdot 10^{-5}$                   | $1.2 \cdot 10^{-7}$                   |
| Pb    | <b><math>2.2 \cdot 10^{-2}</math></b> | $3.2 \cdot 10^{-7}$                   |
| Sb    | <b><math>1.8 \cdot 10^{-2}</math></b> | NA                                    |
| Sn    | NA                                    | NA                                    |
| Ti    | $2.8 \cdot 10^{-4}$                   | NA                                    |
| U     | $1.1 \cdot 10^{-6}$                   | NA                                    |
| V     | $1.8 \cdot 10^{-4}$                   | $3.7 \cdot 10^{-6}$                   |
| Zn    | $1.7 \cdot 10^{-3}$                   | NA                                    |
|       | <b>HI</b>                             | <b>TCR</b>                            |
| Total | $7.6 \cdot 10^{-2}$                   | $1.0 \cdot 10^{-4}$                   |

1029 NA: not available

1030

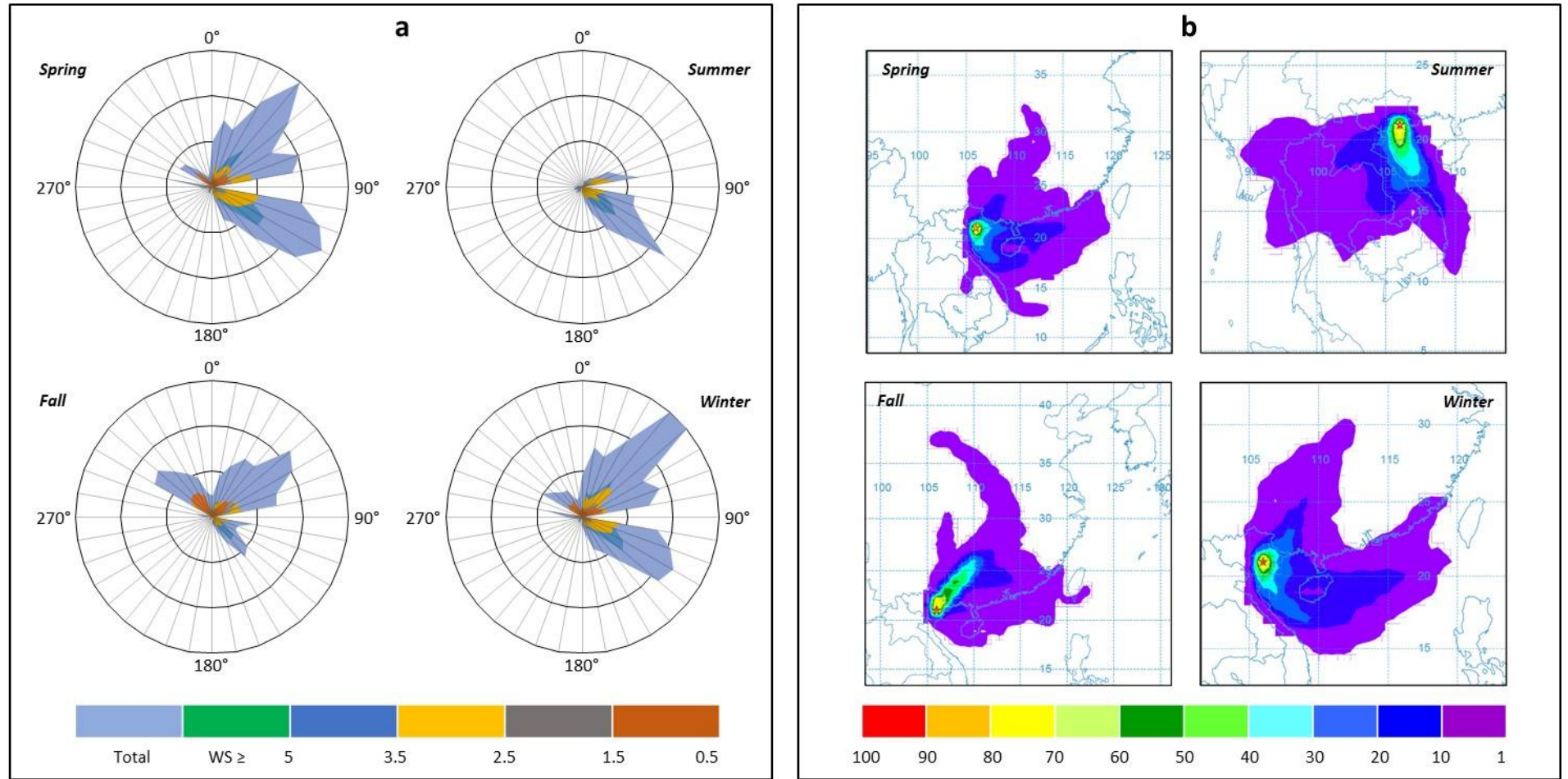


Figure 1: Localisation of sampling site

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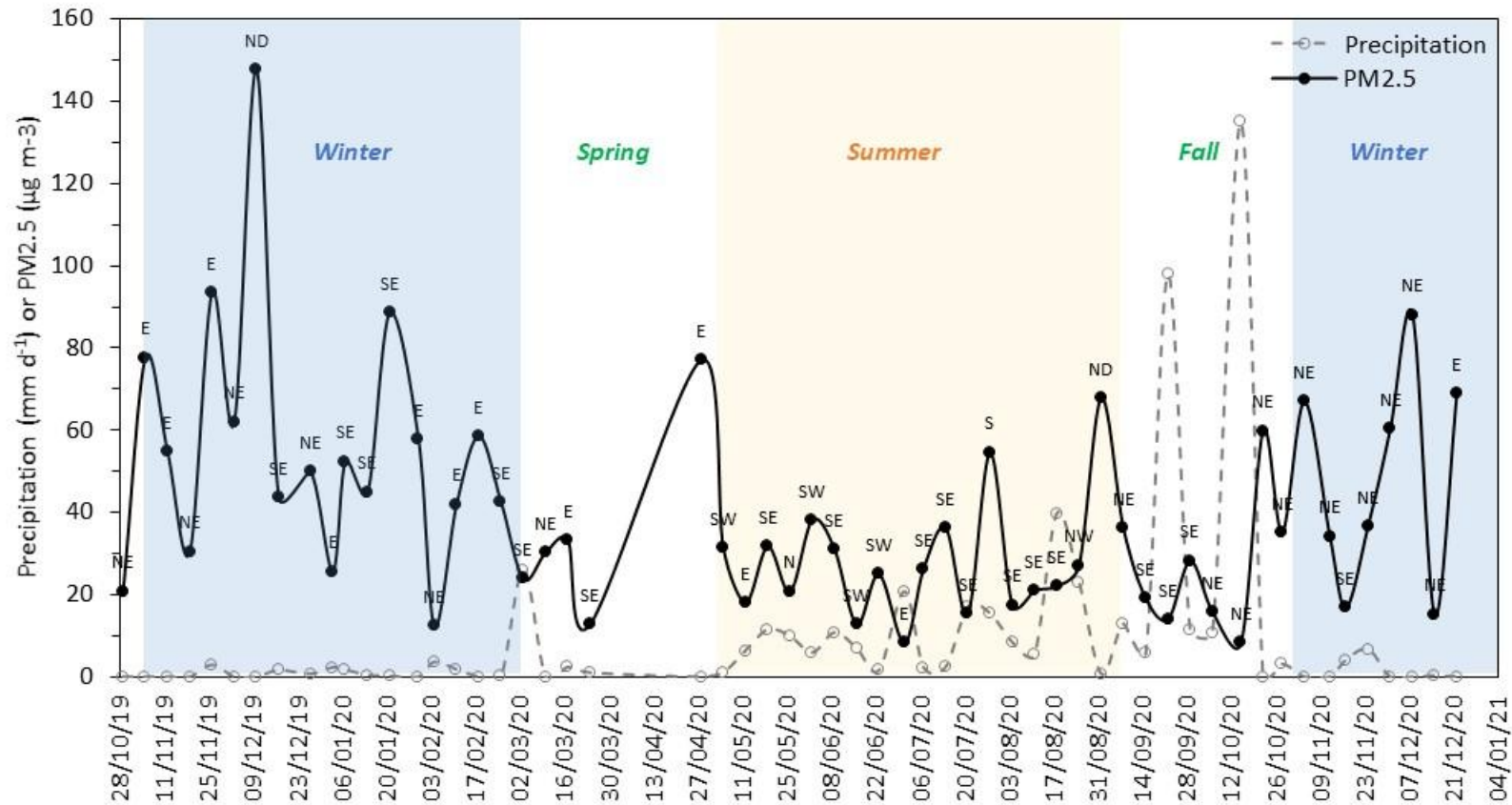


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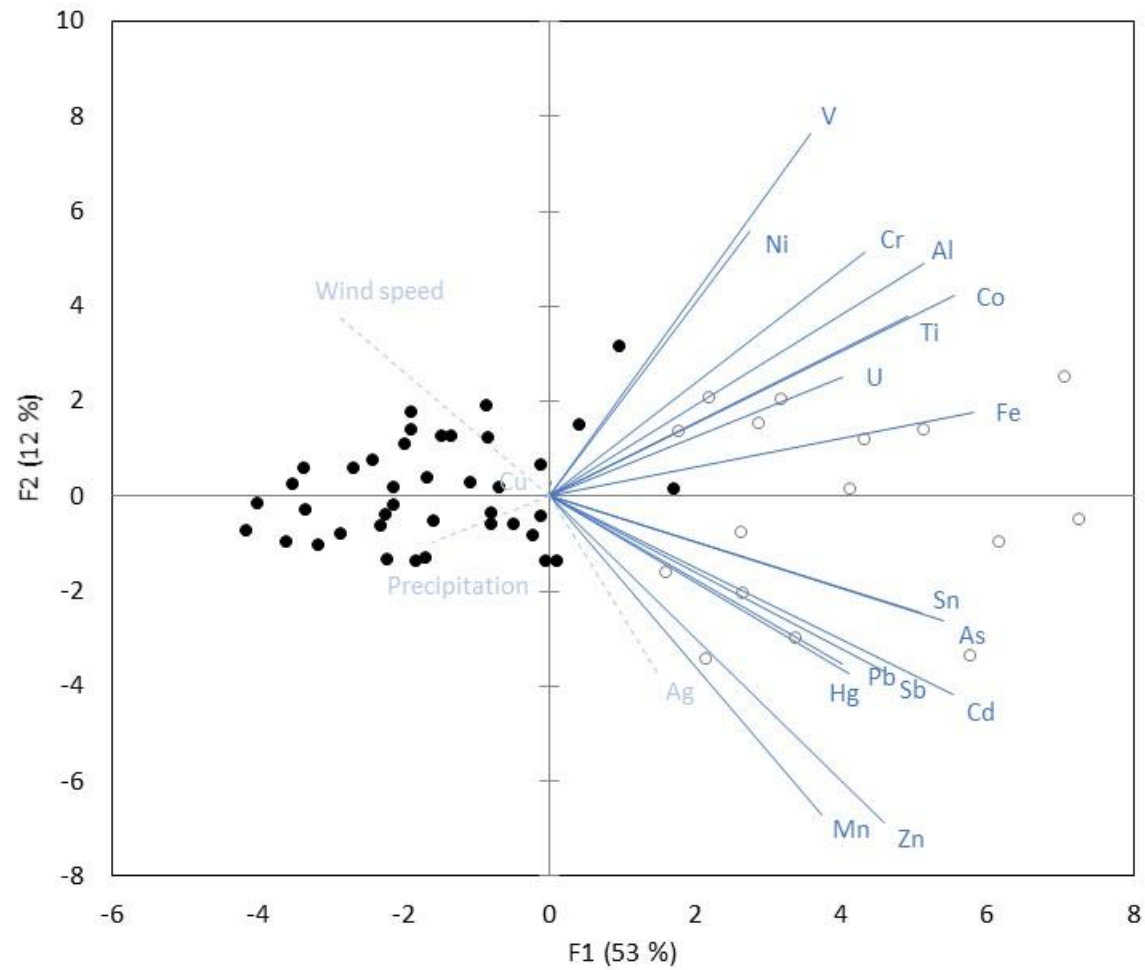
**Figure 2:** Wind roses (a) and trajectory frequencies (b) grouped by seasonal variations during the sampling period. Colour scales of wind speed (WS) and trajectory frequencies are expressed in m s<sup>-1</sup> and %, respectively (NOAA HYSPLIT model, <https://www.ready.noaa.gov/HYSPLIT.php>).



1037

1038 **Figure 3:** Seasonal variations in PM2.5 concentrations (μg m<sup>-3</sup>) and precipitation (mm d<sup>-1</sup>). Abbreviations indicate the wind direction: Northeast (NE), East (E),  
 1039 Southeast (SE), Southwest (SW), Northwest (NW) and not defined (ND)

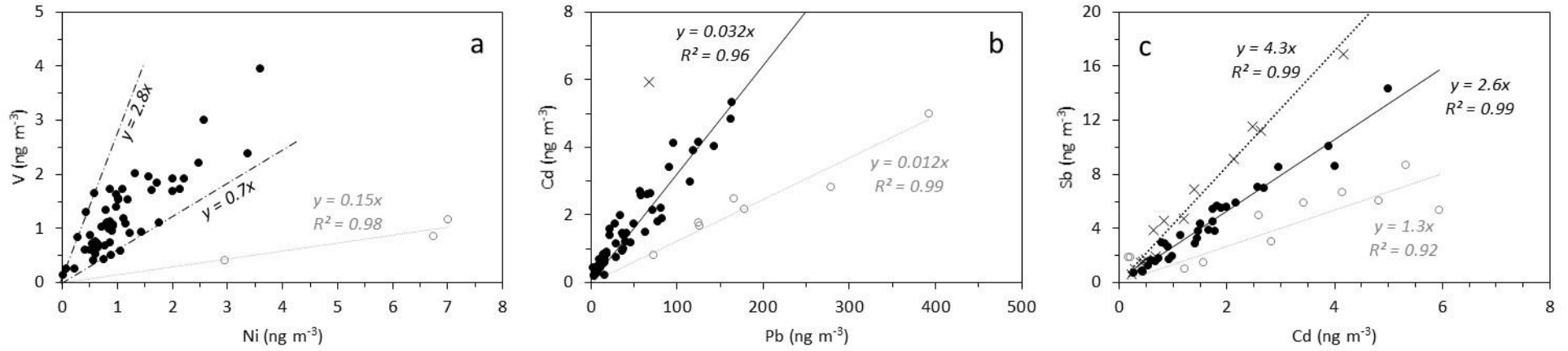
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1042 **Figure 4:** Statistical analyses (PCA-HCA) of MM concentrations in PM<sub>2.5</sub> during the sampling period (November 2019 to December 2020). The contribution  
 1043 of the active and illustrative variables on axes F1 and F2 are presented in solid and dotted lines, respectively. The distribution of samples in clusters C1  
 1044 and C2 are presented in solid and open circles, respectively.



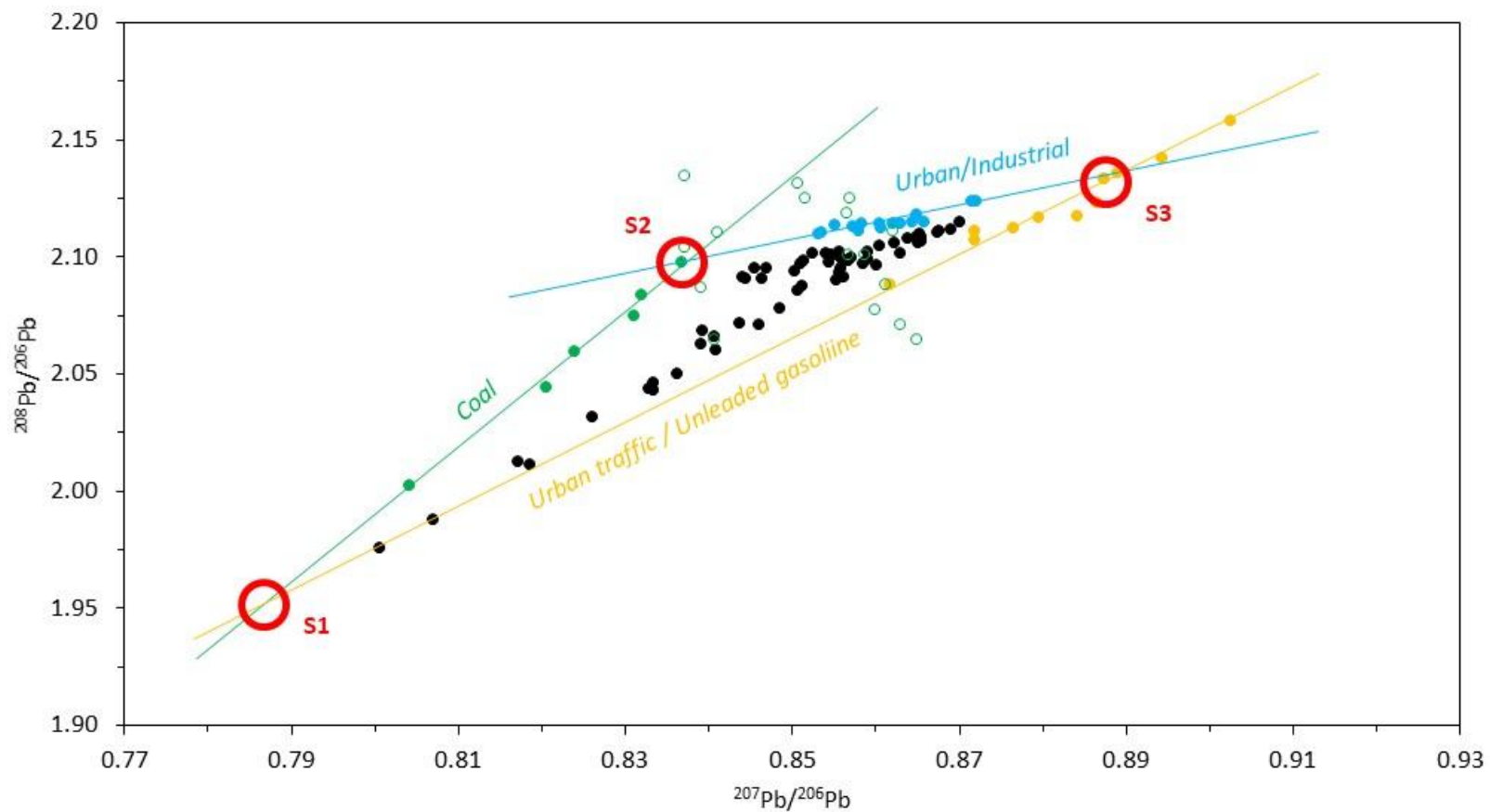


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**Figure 5:** Elementary ratios in PM<sub>2.5</sub> collected during the sampling period (November 2019 to December 2020): a) V/Ni, b) Cd/Pb, c) Sb/Cd and d) Al/Ti

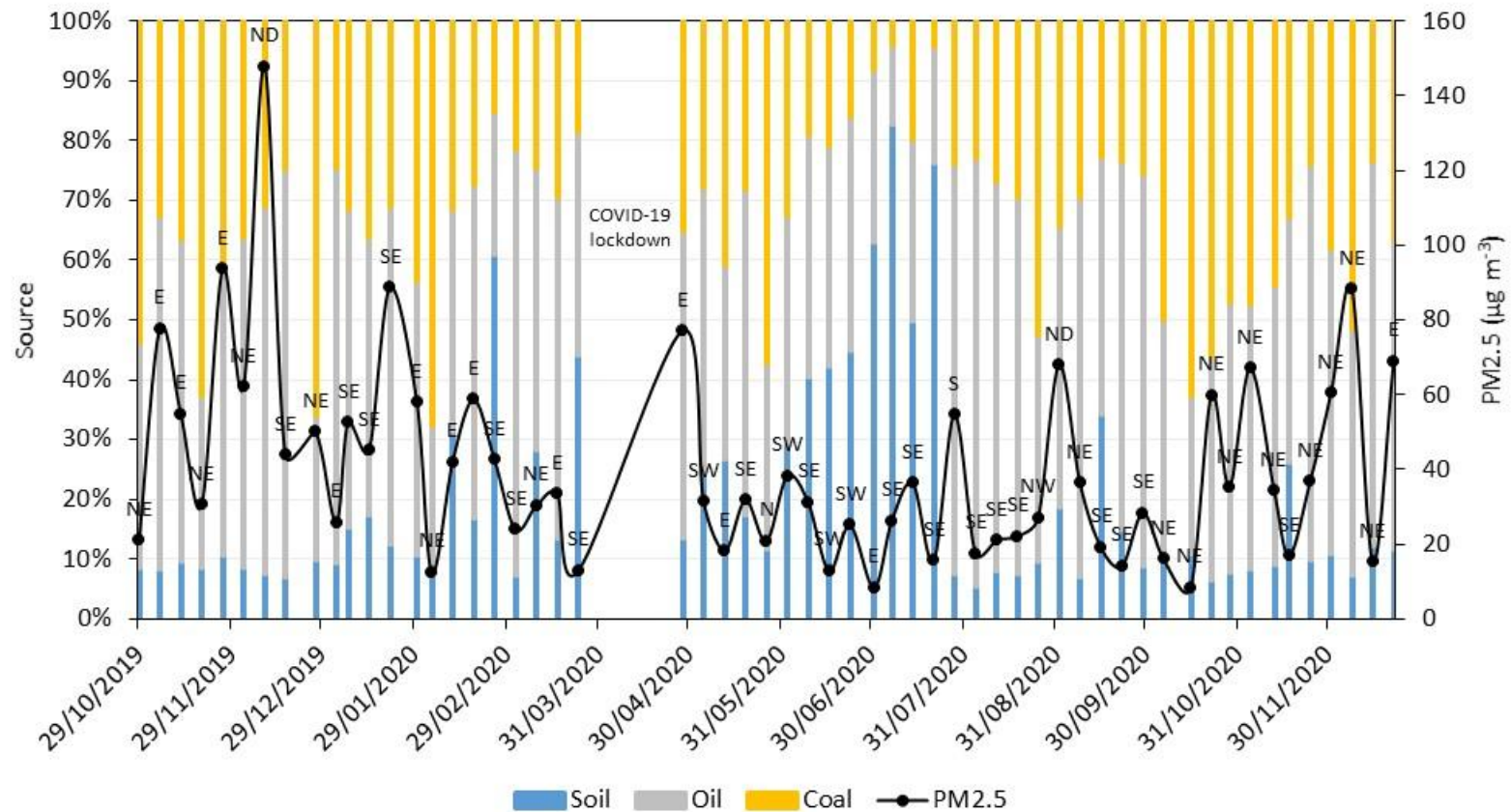
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1049 **Figure 6:** Pb isotopic ratios ( $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{207}\text{Pb}/^{206}\text{Pb}$ ) in PM2.5 collected in Hanoi during the sampling period (in black). The coloured data comes from the  
 1050 literature, in green for Chinese coal mines (solid circles come from southern provinces), in blue for Chinese urban and industrial activities and in  
 1051 orange for petroleum-related activities (e.g., from road traffic in Asian megacities, unleaded Chinese gasoline and Russian oil fields).

1052



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1054 **Figure 7:** Contribution of Pb sources from 'natural' soil, 'oil' and coal to PM2.5 during the sampling period (November 2019 to December 2020).

1055 Abbreviations indicate the wind direction: Northeast (NE), East (E), Southeast (SE), Southwest (SW), Northwest (NW) and not defined (ND)

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