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Soluble trace metals associated with atmospheric fine particulate matter in the two most populous cities in Vietnam

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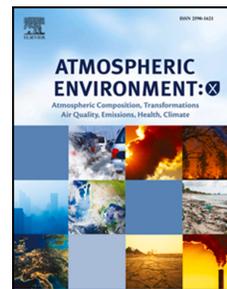
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1 **SOLUBLE TRACE METALS ASSOCIATED WITH ATMOSPHERIC FINE**
2 **PARTICULATE MATTER IN THE TWO MOST POPULOUS CITIES IN VIETNAM**

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18 **To Thi Hien:** Conceptualization, Writing – review & editing, Funding acquisition.

19 **Nguyen Doan Thien Chi:** Formal analysis, Visualization, Writing - original draft.

20 **Duong Huu Huy:** Investigation. **Hoang Anh Le:** Resources. **David E. Oram:**

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22 **Forster:** Writing – review & editing. **Graham P. Mills:** Investigation. **Alex R.**

23 **Baker:** Conceptualization, Methodology, Resources, Visualization, Writing - review

24 & editing.

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16 **Abstract**

17 Hanoi and Ho Chi Minh City (HCM), the most populous cities in Vietnam, have received
18 increasing global attention because of their poor air pollution status. As part of the recent UK-
19 Vietnam 2-Cities project, the concentrations of trace metals in fine particulate matter have been
20 characterized. 24-hour samples of PM₂ were collected at 2 sites in Hanoi and 3 sites in HCM
21 during two 4-week periods in September / October 2018 and March 2019. The soluble fraction
22 of 15 trace metal(oid)s (Fe, Al, Mn, Ti, Zn, V, Cu, Ni, Co, Cd, Pb, Th, Cr, As, and Sb) bound
23 to PM₂ were analyzed by ICP-MS. The results show that Zn was the most abundant soluble
24 metal in PM₂ in both cities, with very large numbers of road vehicles (e.g. tyre wear) likely
25 contributing in both cities and non-ferrous metal production being a substantial additional
26 source in Hanoi. Fe and Al, derived from crustal sources, were the dominant metals after Zn.
27 Most trace metals concentrations in Hanoi were higher than in HCM, especially toxic metals
28 such as Pb, Cd, Cr and As. V and Ni were the only two metals having higher concentrations in
29 HCM than in Hanoi, likely due to shipping emissions (combustion of heavy fuel oil) that
30 strongly affect the air quality in HCM. Coal-power plants and non-ferrous metal production
31 are likely to be the major sources of trace metals in Hanoi. Health risk assessment shows that
32 a high carcinogenic risk exists for inhalation exposure of soluble trace metals bound to PM₂ in
33 both cities.

34 *Keywords: particulate matter, PM₂, soluble trace metals, Hanoi, Ho Chi Minh City.*

35

36 1. Introduction

37 Aerosol fine particulate matter (PM) affects the Earth's climate (Adams et al., 2001) and can
38 have negative impacts on ecology (Clark et al., 2013) and human health (Dockery, 2001;
39 Dominici et al., 2006). The environmental and social impacts of PM are dependent to varying
40 extents on its inorganic and organic composition and the size of the particles. Many hazardous
41 components derived from anthropogenic activities are concentrated mainly on fine particles
42 (Hien et al., 2007; Hu et al., 2014; Li et al., 2015) and particles smaller than 2.5 μm (PM_{2.5})
43 are of particular concern because they are able to penetrate deep into the lungs.

44 PM soluble components have been shown to be released within minutes in simulated lung
45 interstitial environment solution (Palleschi et al., 2018) and to affect the energy metabolism,
46 protein synthesis, and chromatin modification of human cells (Oeder et al., 2015). Trace metals
47 in PM are known to have negative health effects (Okuda et al., 2008; Qi et al., 2016), such as
48 impacts on human attention, executive function, mental flexibility and cognitive efficiency
49 (Jiang et al., 2014; Rafiee et al., 2020; Soetrisno and Delgado-Saborit, 2020), lung damage
50 (Palleschi et al., 2018) and cancer (IARC, 2014; Wang et al., 2015; Galon-Negru et al., 2019).
51 The toxicity of trace metals in PM has been shown to be largely due to the soluble fraction of
52 the metals (Adamson et al., 1999).

53 The trace metals in PM may be derived from natural and anthropogenic sources (Pacyna and
54 Pacyna, 2001; Zhang et al., 2015). Natural sources of trace metals are dominated by the
55 generation of mineral dust through the wind erosion of soils in arid regions. Artificial sources
56 include metallurgical industries, fossil fuel use, and transport activities. The size distribution
57 and soluble fractions of metals in PM vary considerably between natural and anthropogenic
58 sources. Many crustal elements occur predominantly in larger size fractions and have relatively
59 low solubility, while anthropogenic metals tend to be associated with finer particles and have
60 high soluble fractions (Mahowald et al., 2018; Baker et al., 2020).

61 Fine PM has been investigated because of its potentially harmful effects and the increase of
62 serious haze events in Vietnam, particularly in Hanoi and Ho Chi Minh City (HCM) (Cohen et
63 al., 2010; Hai and Oanh, 2013; Hien et al., 2019). There have been very few studies on trace
64 metal concentrations in PM in Vietnam, most of which have focused on total, rather than
65 soluble, metal fractions (Gataria et al., 2005; Cohen et al., 2010). This study evaluated the
66 levels of the soluble trace metals in fine PM in HCM and Hanoi as part of an air quality research
67 project in these cities. The trace metals studied included those with known toxicity (e.g. zinc

68 (Zn), vanadium (V), copper (Cu), nickel (Ni), iron (Fe)), as well as elements characteristic of
69 mineral dust aerosols (e.g. aluminium (Al), titanium (Ti), Fe) and anthropogenic emissions
70 from various sources (e.g. cadmium (Cd), lead (Pb), arsenic (As), V, Ni). Our aim was to
71 identify the major characteristics of the PM soluble trace metal load at these two heavily
72 populated and highly polluted cities, and to highlight instances where the observed PM trace
73 metal load might be cause for concern on health grounds.

74 **2. Materials and methods**

75 **2.1 Study sites and background information**

76 In HCM there are two distinct seasons. The wet season, which generally lasts from May to
77 November, is dominated by southwesterly winds and heavy rainfall (typically around 1900 mm
78 each year). The dry season lasts from December to April, with winds predominantly from the
79 northeast and southeast. The annual average temperature is 27.1°C, with the highest and lowest
80 average temperatures in April and December being 28.9°C and 26°C, respectively. In 2017, the
81 population in HCM was 8.7 million people with a density of 5876 people per km². Road traffic
82 is very intense, with 6.2 million motorbikes (>93% of which have 4-stroke engines) being the
83 most popular means of transportation. Cars, fuelled by petrol (75%) and diesel (25%) (Dung et
84 al., 2015), are increasingly circulating in the city, reaching six hundred thousand units by 2016
85 (Huu and Ngoc, 2021). The city's buses are fuelled by diesel (75%) and compressed natural
86 gas (25%), and heavy trucks using diesel fuel operate mainly at night from 10:00 PM to 6:00
87 AM. Natural gas is the main fuel in household cooking and in restaurants, while honeycomb
88 charcoal, wood charcoal, and kerosene are also widely used. These are the main sources of air
89 pollution in HCM, besides several industrial parks, enterprises, and production facilities.

90 Hanoi, the capital of Vietnam, has a subtropical climate with 4 distinct seasons, although the
91 influence of the prevailing wet/dry seasons remains strong, with northeasterly winds in
92 September / October and southeasterly winds in March. According to the Hanoi Environment
93 and Natural Resource Department (Huu and Ngoc, 2021), Hanoi has a population of about 7
94 million, with 5 million motorbikes, 500,000 cars, and high levels of construction works due to
95 rapid urbanization. Energy consumption in the city is dominated by the combustion of millions
96 of litres of gasoline each day and 40 million-kilowatt hours electricity. There are approximately
97 fifteen coal-fired power stations within ~200 km of Hanoi, mostly fuelled by anthracite
98 (Duong, 1995). Anthracite has low sulfur content, but generates large amounts of particulate
99 matter emissions (Cohen et al., 2010). In recent years, Hanoi has often been ranked as the most

100 polluted city in the world. In 2017, Hanoi had only 38 days in which air quality was considered
101 healthy by the World Health Organization (WHO) (Kim, 2019).

102 As part of a joint UK-Vietnam project investigating present day air quality and air pollution
103 sources in HCM and Hanoi, rooftop sampling sites were set up in both cities (**Fig. 1, Table 1**).
104 In HCM, three sites were selected: the urban central site (HCMC), the south-western
105 “background” site (HCMB1) and the north-eastern “background” site (HCMB2). In Hanoi, two
106 sampling sites were established: an urban central site (HNC), and eastern background site
107 (HNB). The background sites were ~15 km from the urban sites and were chosen as
108 representative of air arriving into each city (i.e. upwind of the urban sites) under typical flow
109 conditions in each season.

110 **2.2 Sampling strategy**

111 There were two concurrent campaigns of aerosol sampling in the 2 cities, each campaign lasting
112 for one month (see Table 1). In the first campaign (wet season, 2018), 3 sampling sites were
113 established: HCMC-18, HCMB1-18, and HNC-18. HCMC-19, HCMB2-19, HNC-19, and
114 HNB-19 were the sampling sites in the second campaign (dry season, 2019). High volume
115 samplers (Tisch Environmental) were used for aerosol sampling. A Sierra-type cascade
116 impactor head was applied to separate PM₂ ($\leq 2 \mu\text{m}$ aerodynamic diameter) at a flow rate of
117 $0.7 \text{ m}^3 \text{ min}^{-1}$ over 24 hours. Sampler flow rates were calibrated every week using a calibration
118 orifice. Before sampling, glass microfiber filters (Whatman, GF/CTM, 20 x 25.4 cm) were
119 treated sequentially with 0.5 M HCl, 0.1 M HCl and ultrapure water (18.2 M Ω cm) (Rickli,
120 2010). Filters were then dried overnight under HEPA filtered air, wrapped in aluminium foil
121 and baked at 450°C for 4 hours before being stored until sampling.

122 In total 89 samples were collected in the first campaign and 112 samples in the second
123 campaign (2 samples were eliminated because of bad quality). Field blanks were conducted at
124 the end of the sampling periods at each site by deploying unused filters in the collectors for 24
125 hours without operating the pumps. After collection, filters were folded in half, wrapped in
126 aluminium foil, sealed in zip-lock plastic bags, stored frozen for storage, and transported under
127 dry ice to the University of East Anglia, UK for chemical analysis.

128 **2.3 Trace metals analysis**

129 In this study, we analyzed the soluble fraction of fifteen trace metal(oid)s associated with PM₂:
130 Fe, Al, manganese (Mn), Ti, Zn, V, Cu, Ni, cobalt (Co), Cd, Pb, thorium (Th), chromium (Cr),

131 As and antimony (Sb). All post-collection sample handling and soluble metals extraction
132 procedures were conducted under a laminar flow hood in a trace metal clean laboratory.

133 An eighth of the filter sample was cut with ceramic bladed scissors into small pieces for
134 chemical extraction. The samples were mechanically shaken for 30 minutes with 25 mL 0.01M
135 nitric acid (TraceSELECT™, for trace analysis, ≥69.0%, Honeywell Fluka™) at pH 2, after
136 which the extracted solutions were passed through 0.2 µm cellulose acetate filters (minisart
137 Sartorius). This leaching solution was chosen to represent the readily soluble component of
138 trace metals in the sampled aerosol PM. However, a relatively dilute nitric acid solution cannot
139 be expected to reproduce the complex and heterogeneous conditions that solubilize trace metals
140 in the lungs (Boisa et al., 2014; Wiseman, 2015). Lab blank samples were run in parallel with
141 each batch of sample extractions. Calibration solutions were prepared by dilution of single
142 element SPEX CertiPrep stock solutions in 0.01 M nitric acid. Iridium was chosen as an internal
143 standard for trace metals analysis because this element was not detected in preliminary scans
144 of the samples. 1 mL of iridium (100 ppb) was added to 9 mL of samples, calibration standards
145 and Certified Reference Materials (CRMs) before analysis by inductively coupled plasma -
146 mass spectrometry ICP-MS (Thermo Scientific, iCAP-TQ). Fe, V and As were determined in
147 triple quad mode as their MO⁺ ions, after reaction with O₂ in a collision cell. All other elements
148 were determined as M⁺ in single quad mode. Samples were introduced into the instrument using
149 a micromist nebulizer at a flow rate of 1.08 mL min⁻¹. Instrument RF power was 1.55kW.
150 Polypropylene centrifuge tubes used for extractions and storage of filtered extracts were
151 pretreated by soaking in 1.54 M HNO₃ for at least 48 hours, rinsed with ultrapure water and
152 dried.

153 Measurement accuracy was assessed by analyzing the solution-phase CRMs TMRain-04
154 (simulated rainwater), TM27.3 and TMDA-64.2 (both modified lake waters) (Environment
155 Canada) alongside the samples. The percentage recoveries for these CRMs were in the ranges
156 97 - 100% (Fe), 89 - 100% (Al), 85 - 92% (Mn), 89 - 129% (Ti), 86 - 89% (Zn), 83 - 97% (V),
157 76 - 95% (Cu), 72 - 92% (Ni), 94 - 100% (Co), 87 - 103% (Cd), 91 - 96% (Pb), 91 - 102% (Cr),
158 84 - 102% (As) and 92 - 101% (Sb). Reported concentrations have not been adjusted to take
159 account of CRM recoveries.

160 Results from field blank determinations and limits of detection for each element are shown in
161 **Table 2**. Limits of detection (LOD) were defined following Chance et al. (2015), either from
162 the analytical LOD derived from the calibration curve, or as the procedural LOD (3 × standard

163 deviation of the field blank samples). All the lab blank samples had concentrations below the
 164 analytical LOD. Soluble Th concentrations were below the LOD in all samples and are not
 165 discussed further. Concentrations below the LOD were also observed for V (21% of values),
 166 Cu, Ni, Pb and As (all $\leq 5\%$ of values). Where sample concentrations were below the LOD,
 167 they were substituted with 75% of the relevant LOD (e.g. in **Fig. 3 & 4**). Field blanks for each
 168 of the 7 sampling periods were subtracted from their respective sample concentrations, unless
 169 the field blank was below the analytical LOD (i.e. for Fe, Ni, Co, Pb: see **Table 2**) in which
 170 case there was no blank subtraction.

171 At the HCMB1 site, one sample was found to have a concentration of Al that exceeded any
 172 other measurement of Al in the dataset by a factor of 6, while all other trace metal
 173 concentrations for this sample were well within the range of values for the dataset. This Al
 174 value was judged to be caused by contamination and has been excluded from the data presented
 175 here.

176 Significance testing of the dataset was performed using parametric tests (one- and two-sided t-
 177 tests, one-way ANOVA) and their non-parametric equivalents (Mann-Whitney U and Kruskal
 178 Wallis tests) using the SciPy package in python. For simplicity, only the results of the
 179 parametric tests are reported here, although the non-parametric tests gave very similar results.

180 **2.4. Backward trajectories and Concentration Weighted Trajectory**

181 To identify the main source of trace metals to both cities, backward trajectory analysis at the
 182 two central sites using the Hysplit model (NOAA) was conducted in an R environment (SplitR
 183 package). 120-hour backward trajectory arrivals were calculated every 3 hours at the two
 184 central sampling sites (HCMC and HNC) at an arrival height of 50 m. The approach of
 185 concentration weighted trajectory (CWT) analysis was used to understand the potential source
 186 of individual trace elements in this study. The logarithmic mean concentration of a pollutant
 187 species (or CWT) was calculated as follows:

$$188 \quad \ln(C_{ij}) = \frac{1}{\sum_{k=1}^N \tau_{ijk}} \sum_{k=1}^N \ln(C_k) \tau_{ij} \quad (1)$$

189 Where i and j are the parameters of a grid cell, k is the index of trajectory, N is the total number
 190 of trajectories, C_k is the pollutant concentrations measured upon arrival of
 191 trajectory k , and τ_{ijk} the residence time of trajectory k in grid cell (i, j) . The higher the value of
 192 C_{ij} , the higher the concentrations at the receptor site when air parcels passed over grid cell $(i,$
 193 $j)$ (Carslaw, 2014). CWT analysis was conducted using the Openair package in R software.

194 2.5 Health risk assessment of soluble trace metals inhalation

195 We undertook the health risk assessment of soluble metals in PM₂ by calculating the Hazard
 196 Index (HI) for non-carcinogenic risk and total carcinogenic risk (TCR) following
 197 Environmental Protection Agency Guidance (EPA, 2009). According to the International
 198 Agency for Research on Cancer (IARC): As, Cd, and Cr (VI) belong to Group 1 of cancer
 199 hazard agents, Pb and Co are classified as probably carcinogenic (Group 2A), nickel is in Group
 200 2B of carcinogens, and Mn compounds are classed as pollutants of potential interest (IARC,
 201 2014). In this study, the health risk assessment was conducted for Mn, Ni, Co, Cd, Pb, Cr (we
 202 assume all Cr was present as Cr (VI) in order to assess the maximum potential risk from this
 203 element), and As. The HI of the selected metals was calculated based on Reference
 204 Concentration RfC (mg m⁻³). The TCR values were evaluated based on Inhalation Unit Risk
 205 IUR (µg m⁻³)⁻¹. The RfC and IUR values of those metals were cited from Environmental
 206 Protection Agency. The exposure concentrations of selected metals were calculated using the
 207 equation below:

$$208 \quad EC_i = \frac{CA_i \times ET \times EF \times ED}{AT} \quad (2)$$

209 where:

210 EC_i = exposure concentration of the trace metal i (µg m⁻³)

211 CA_i = concentration of the trace metal i in air (µg m⁻³)

212 ET = exposure time – 8 hours/day

213 EF = exposure frequency – 365 days/year

214 ED = exposure duration – 40 years for adults

215 AT = averaging time (75-year lifetime x 365 days/year x 24 hours/day) (75 years, the average
 216 life expectancy of the Vietnam population in 2018, World Bank Group,
 217 <https://data.worldbank.org/indicator/SP.DYN.LE00.IN?locations=VN&view=chart>)

218 Non-carcinogenic health risk is assessed by:

$$219 \quad HQ_i = \frac{EC_i}{RfC_i \times 1000} \quad (3)$$

$$220 \quad HI = \sum HQ_i \quad (4)$$

221 where:

222 RfC_i = reference concentration for the element i – inhalation toxicity value (mg m^{-3})

223 HQ_i = Hazard Quotient of element i (unitless)

224 The cancer risk of soluble trace metals via the inhalation pathway is estimated with:

$$225 \quad R_i = EC_i \times IUR_i \quad (5)$$

$$226 \quad TCR = \sum R_i \quad (6)$$

227 where:

228 IUR_i = Inhalation Unit Risk of the carcinogenic element i ($\mu\text{g m}^{-3}$)⁻¹

229 R_i = carcinogenic risk of the element i (unitless)

230

231 3. Results

232 3.1 Air mass origins

233 Air mass arrivals at the HCMC and HNC sites during the two sampling campaigns are
 234 illustrated in **Figure 2**. Cluster analysis (Openair) divided the trajectories recorded at each site
 235 into several air mass types. These types and their percentage occurrences during each campaign
 236 are described in **Table 3**.

237 3.2 Trace metals levels in $PM_{2.5}$

238 Overall, by mass concentration, Zn, Fe, Pb and Al were the most abundant soluble metals in
 239 $PM_{2.5}$ in both cities (**Table 4**). Fe and Al in airborne particulate matter originate primarily from
 240 soils, while anthropogenic activities are the dominant sources of Zn and Pb to the atmosphere.
 241 Previous studies have also found Zn to be the most abundant metal in fine particles in Hanoi
 242 (Gataria et al., 2005; Cohen et al., 2010; McNeill et al., 2020).

243 The daily concentrations of selected trace metals (Fe, V, Mn, Zn, Cr, Cd, Pb, As & Sb) in $PM_{2.5}$
 244 in the central sites in HCM and Hanoi during the two sampling periods are illustrated in **Figures**
 245 **3 and 4**, respectively, and equivalent plots for the background sites can be found in **Figure S1**.
 246 The results obtained at HCM and Hanoi indicate that there were substantial differences in the
 247 concentrations of the trace metals studied at the regional level (e.g. Zn, Pb and Cd were
 248 substantially higher in Hanoi than in HCM) and over time, both seasonally (e.g. As in HCM)
 249 and on a daily basis (**Table 4, Fig. 3 & 4**). These patterns indicate that a variety of sources
 250 influence trace metals in $PM_{2.5}$ at the two cities, as discussed below.

251 4 Discussion

252 4.1 Comparison with other cities

253 **Table 5** shows the concentrations of soluble trace metals in airborne particulate matter at
254 various global locations together with the method used to extract the soluble components in
255 each study. Direct comparison between the results from the different studies shown in **Table 5**
256 is not straightforward because of the different aerosol size fractions collected (e.g. PM₁₀ may
257 contain higher concentrations of a given trace metal than PM₂, depending on the element's
258 particle size distribution) and because the solubility of trace metals is pH dependent. Thus the
259 more aggressive extraction method employed by McNeill et al., (2020) is likely to recover a
260 larger fraction of aerosol trace metals than the method employed in this work, with even lower
261 recoveries for methods using deionized water (Heal et al., 2005; Jiang et al., 2014; Wang et al.,
262 2015; Galon-Negru et al., 2019). The soluble fraction recovered by a given method is also
263 influenced by aerosol particle size distribution. Crustal elements (e.g. Fe and Al) are
264 predominantly present in the coarse mode and have relatively low solubility while Zn is found
265 in fine mode particles with high solubility (Witt et al., 2010; Li et al., 2015).

266 Previous studies have reported Zn, Fe, Al and Pb as the most abundant soluble trace metals in
267 aerosols in Hanoi and other locations in East Asia (**Table 5**). In contrast, the soluble trace metal
268 concentrations reported for European cities (Edinburgh and Iasi) were substantially lower than
269 in East Asia with lower proportions of the anthropogenic elements Zn and Pb (compare PM₁₀
270 at Beijing and Edinburgh and PM_{2.5} at Hong Kong and Iasi).

271 4.2 Seasonal differences

272 In HCM there were substantial differences between the concentrations of several trace metals
273 observed in the October and March sampling periods (**Fig. 3, Table 4**). For Cr, Zn, Cd, Pb, As
274 and Sb concentrations were significantly lower (one-tailed t-test, $p < 0.05$) in March than
275 October. These decreased concentrations may be partly due to changes in boundary layer height
276 between the two seasons. (Boundary layer in HCM was ~ two-fold higher in March than
277 October (**Table S2**), implying a halving of atmospheric concentrations if emissions remained
278 constant). This result was consistent with that of CO and most VOCs which were also measured
279 during the campaigns (Hien et al., 2022). Average PM_{2.5} mass concentrations at HCMC were
280 also ~30% lower in March than October (Table S2).

281 Differences in concentration between air mass types in each season may also contribute to these
282 changes in overall concentration. For example, the As concentrations in the air mass types at

283 HCM in October were $0.56 \pm 0.27 \text{ ng m}^{-3}$, $0.96 \pm 0.51 \text{ ng m}^{-3}$, $0.52 \pm 0.24 \text{ ng m}^{-3}$ and $1.60 \pm$
284 0.99 ng m^{-3} for the SW, S, E and NE air mass types respectively, while in March As
285 concentrations were $0.30 \pm 0.13 \text{ ng m}^{-3}$, $0.30 \pm 0.13 \text{ ng m}^{-3}$ and $0.44 \pm 0.39 \text{ ng m}^{-3}$ for the SE,
286 E and NE air mass types respectively. Concentrations of As in the NE air mass type were
287 significantly lower in March than in October. Thus, the overall change in As concentrations
288 between sampling periods appears to be due to a combination of greater boundary height in
289 March (contributing to lower concentrations in E and NE arrivals) and lower As concentrations
290 in SE (March) compared to SW and S (October) arrivals.

291 Similar patterns in air mass type concentrations, with significant difference between the NE
292 type in the two seasons were also observed for Cd and Pb, and these three elements also showed
293 the largest overall decrease in concentration between the two seasons (by factors of 2.1 to 3.5).
294 For Co, Ti, Ni and V, concentrations were significantly higher (one-tailed t-test, $p < 0.05$)
295 during the March dry season and Co and Ti concentrations were also significantly higher in the
296 E and NE air mass types in March than in October. Drier conditions (**Table S2**) can be expected
297 to lead to higher aerosol concentrations in general, due to decreased rates of particle rain-out.
298 In some cases, soluble metal concentrations may be enhanced by atmospheric processing of
299 aerosol during transport, independently of total metal concentration changes (Baker and Croot,
300 2010). We did not measure total metal concentrations and are therefore not able to assess the
301 fractional solubility (the ratio of soluble to total concentrations) of the trace metals at HCM or
302 Hanoi, or changes in this parameter during transport. However, solubility enhancement is
303 probably less significant for anthropogenic metals whose fractional solubilities are inherently
304 high (e.g. Zn, Cd, Pb (Chance et al., 2015; Mahowald et al., 2018; Shelley et al., 2018)), or for
305 metals whose solubility appears to be insensitive to atmospheric processing (e.g. Mn, Co
306 (Baker et al., 2020)). The concentrations of the low solubility crustal metals (Fe, Al, Ti (Baker
307 et al., 2020)) may be influenced by atmospheric processing.

308 There were fewer significant differences between seasons at Hanoi, and all these concentrations
309 differed by less than a factor of 2. Concentrations of Al, Co, Cr and V were significantly higher,
310 and Mn, Zn and Pb significantly lower, respectively, in March than in October. Seasonal
311 differences in atmospheric transport were less marked at Hanoi than at HCM, with a general
312 shift in the prevailing wind to the southeast in March (**Fig. 2**).

313 **4.3 Local vs Regional Sources of Trace Metals**

314 Although the background sampling sites were established with the intention of characterizing
315 the aerosol arriving at each city, variations in atmospheric circulation meant that there were
316 extended periods during each campaign when the background and urban sites were not within
317 the same air flow. Conditions under which the two sites were connected may have occurred at
318 HCM in October 2018 for the SW air mass type (background site upwind of urban site) and
319 NE air mass type (urban site upwind of background site) and for the NE type at HCM and E
320 type at Hanoi in March 2019 (both background site upwind). Wind data collected at the central
321 sites indicate that the central and background sites were within the same airflow for less than
322 10% of each campaign (**Figure S2**). Both air mass back trajectories (**Fig. 2c**) and local wind
323 data (**Fig. S2a**) indicate that atmospheric circulation at HCM in Sept / Oct 2018 was not typical
324 of wet season conditions in that city.

325 Very few of the trace metals had significantly different (t-test, $p < 0.05$) concentrations at the
326 background and urban sites, with only Pb at HCM in October (NE air mass type) and Co and
327 Zn at Hanoi in March having higher concentrations at the downwind site (by factors of 1.5, 1.9
328 and 2.6 respectively). This suggests that in most cases, regional sources are at least as important
329 as local sources of trace metals in the two cities. Potential local and regional sources of Zn at
330 Hanoi are discussed below.

331 Almost all trace metals showed no statistical difference in concentrations between weekends
332 and weekdays (t-test, $p < 0.05$) at all sampling locations. Exceptions were found for Zn at the
333 HCM background site in March 2019 (HCMB2, lower at weekends (t-test, $p = 0.038$)), and at
334 HNB site in March 2019, lower at weekend for Al (t-test, $p = 0.016$), Cu (t-test, $p = 0.013$), and
335 Cr (t-test, $p = 0.007$). Weekend effects can indicate the relative importance of local sources
336 (e.g. due to decreased industrial activity or commuting), so that the small number of significant
337 differences identified here may also point towards regional trace metal sources being
338 significant at HCM and Hanoi.

339 Concentration Weighted Trajectory (CWT) plots for several soluble trace metals in the two
340 cities are shown in **Figures 5 and 6**. For HCM, **Figure 5** indicates that many of the soluble
341 metals (e.g. Fe, Mn, Pb, Cr, Sb) are associated with transport from the coastal regions of
342 Vietnam, both to the northeast and southwest of the city. The dominant sources of Cd and As
343 at HCM appear to be associated with transport from the northeast (**Fig. 5**).

344 The CWT plots indicate that sources in northeast Vietnam and southeast China, and possibly
345 also in Hainan, make strong contributions to the concentrations of soluble trace metals

346 observed in Hanoi (**Fig. 6**). However, V and Ni (not shown) appear to have distributions
347 consistent with sources in the seas around Vietnam (Gulf of Tonkin and South China Sea: **Fig.**
348 **5 & 6**).

349 The influences of potential sources of trace metals from industrial activities (e.g. mining, non-
350 ferrous metal refining), coal-fired power plants and maritime activities in Vietnam and southern
351 China are discussed below.

352 **4.3.1 Contribution from soil dust**

353 Al, Fe, Ti, and Mn are major components of the upper continental crust (Rudnick and Gao,
354 2014). In HCM, these elements (and the less abundant crustal component Co) were strongly
355 correlated with one another (all relationships $p < 0.01$) implying that soil dust is their dominant
356 source in PM₂ in this city. Long range transport from desert regions in northern China has been
357 reported to make substantial contributions to the soil dust content of fine PM at Hanoi (Hien et
358 al., 2004). Soil dust appears to be the dominant source of Al, Fe and Ti at Hanoi, with the Fe -
359 Al and Ti - Al relationships there being very similar to those in HCM (**Fig. 7c & d**). Both Mn
360 and Co appear to be enriched with respect to Al in several samples in Hanoi, especially in the
361 NE and E air mass types (**Fig. 7a & b**). This suggests that anthropogenic sources in northeast
362 Vietnam and southern China contribute substantially to Mn and Co concentrations at Hanoi.

363 Mining of titanium deposits (placers) occurs along the central coastal region of Vietnam, with
364 $> 2 \times 10^5$ tonnes yr⁻¹ of ore extracted in 2018 and 2019 (Tolcin and Gambogi, 2021). These
365 activities may contribute to the concentration of crustal metals in both cities. At Hanoi, the SE
366 air type may carry dust generated by placer extraction in Ha Tinh, Quang Tri and Thua Thien
367 – Hue provinces, while mining in Binh Dinh and Binh Thuan provinces may contribute crustal
368 material to NE air masses observed at HCM. If these mining activities do contribute to the
369 mineral dust loading at Hanoi and HCM, there is little evidence of enrichment of Ti in the air
370 mass types identified above (**Fig. 7d**). This may be due to the very low solubility of Ti in
371 mineral dust aerosols (Baker et al., 2020), since the soluble Ti data reported here are likely to
372 be only a very small fraction of the total Ti present in the samples.

373 **4.3.2 Influence of heavy fuel oil combustion**

374 V and Ni were unusual among the metals studied here in that their concentrations were higher
375 in HCM than in Hanoi (**Table 4**). Combustion of heavy fuel oil (HFO), predominantly by
376 shipping, has been shown to be a strong source of these elements to the atmosphere (Becagli
377 et al., 2012) (Viana et al., 2009). The significant correlation between V and Ni in HCM and

378 Hanoi ($p < 0.001$ in both cases, **Figure S6**), and the association of both elements with maritime
379 air mass back trajectories (e.g. **Fig. 8**) indicate that shipping is the dominant source of V and
380 Ni in both cities. Even in Hanoi, concentrations of V and Ni were significantly higher ($p <$
381 0.05) in the strongly maritime-influenced SE air mass type than in the terrestrially-influenced
382 NE and E types in March. Cohen et al., noted that HFO was used in barges for river and canal
383 freight in Hanoi, so there may also be a local source of V and Ni there (Cohen et al., 2010).

384 There are a total of 320 ports operating along the coast of Vietnam, with the 34 seaports around
385 HCM accounting for more than 60 percent of the total amount of trade of all Vietnamese ports.
386 The study of Ho et al., (2019) applied a combination of bottom-up and top-down methods for
387 calculating atmospheric emissions in HCM and found that the seaports contributed up to 5%
388 and 15% of total TSP (total suspended particulate matter) and SO_2 emissions, respectively (Ho
389 et al., 2019). Thus the combustion of HFO by shipping emits not only V and Ni but also various
390 pollutants including PM, inorganic and organic compounds and affects air quality in HCM
391 (Becagli et al., 2012; Oeder et al., 2015).

392 **4.3.3 Local and regional sources of Zn**

393 In common with other cities in East Asia (**Table 5**), Zn concentrations were high in both HCM
394 and Hanoi. Tyre wear from high levels of traffic likely contribute to the high Zn concentrations
395 in both cities (Duan and Tan, 2013). Large numbers of two-stroke engine-powered motorcycles
396 in use ($\sim 450 \times 10^3$ in HCM (Dung et al., 2015)) may also contribute, due to combustion of Zn-
397 enriched lubricating oil in these engines. In Hanoi, additional sources of Zn appear to be
398 associated with atmospheric transport from southeast China (**Fig. 6**). These may well be
399 associated with Zn smelting activities in Guangxi and Hunan provinces (Zhang et al., 2011).
400 Smelters in China accounted for $\sim 45\%$ of global Zn production ($\sim 6.2 \times 10^6$ tonnes) in 2019
401 (Tolcin, 2021). Zn and Pb refining facilities are often co-located and As and Cd are produced
402 as a by-product of Zn smelting (Pacyna and Pacyna, 2001; Shiel et al., 2010). Thus, the similar
403 CWT profiles of Zn, Pb, As and Cd may all be indicative of nonferrous metal processing
404 emissions, especially since these processes have been identified as the largest global sources
405 of As, Cd, Cu and Zn to the atmosphere (Pacyna and Pacyna, 2001).

406 **4.3.4 Coal-fired power plants and air quality in Vietnam**

407 Coal combustion is associated with emissions of several trace metals including Mn, Cr, Cd, As
408 and Pb (Pacyna and Pacyna, 2001; McNeill et al., 2020). There are more than 20 coal power
409 plants running in the north of Vietnam, and only 3 power plants in the south of the country.
410 There are also a large number of coal power plants in the southeastern provinces of China

411 (Guizhou, Guangxi, Hunan) and along the eastern coast of China. Cohen et al., identified long
412 range transport from power plants in China (especially in Guangxi, Hunan and Hubei
413 provinces) as the most prominent sources of PM associated with coal combustion at Hanoi.
414 Since the study of Cohen et al., power generation from coal-fired plants in Vietnam and China
415 has increased substantially (<https://globalenergymonitor.org/projects/global-coal-plant-tracker/>)
416 and these facilities are likely to contribute to poor air quality in Hanoi and HCM for
417 some time.

418 **4.4 Health risk exposure of PM₂ soluble metals**

419 The WHO recommends guideline annual average concentration limits for Pb and Cd in air of
420 500 and 5 ng m⁻³, respectively (WHO, 2000). Although Cd concentrations at Hanoi exceeded
421 the 5 ng m⁻³ threshold on two occasions, the average concentrations of the soluble fraction of
422 these two toxic metals in Hanoi and HCM were below the WHO guideline. Arsenic and Cr in
423 the +6 oxidation state (Cr (VI)) are human carcinogens (causing lung cancer), for which the
424 WHO has not defined any safe level of inhalation exposure. Their 1:100,000 lifetime excess
425 risk levels are 6.6 and 0.25 ng m⁻³, respectively (WHO, 2000). PM₂ soluble As concentrations
426 exceeded 6.6 ng m⁻³ on 6 occasions during sampling in Hanoi and concentrations in HCM also
427 approached this value in October (**Fig. 3**). Considering that As is also present in coarser aerosol
428 particles (McNeill et al., 2020) and that only a fraction of As is likely to be released by the
429 leaching procedure used, it seems likely that the 6.6 ng m⁻³ threshold was exceeded on many
430 more occasions in both cities. Mean soluble Cr concentrations were above the lifetime excess
431 risk level for Cr (VI) in both cities, suggesting that further research into the redox speciation
432 of Cr in PM in Vietnamese cities might be advisable.

433 The calculated Hazard Index (HI) and total carcinogenic risk (TCR) for Mn, Ni, Co, Cd, Pb,
434 Cr and As in PM₂ at all study sites are shown in **Table 6**. The HI values at all sites in both
435 HCM and Hanoi were below the critical level of 1 (EPA, 1989) suggesting that there is no
436 chronic influence of inhalation of those metals in PM₂. Nonetheless, all TCR values are much
437 higher than the carcinogenic benchmark level of 1×10^{-6} (EPA, 1989) indicating high cancer
438 risk for respiration in the two cities. The TCR value in HCM was 1.9 times lower than in Hanoi.
439 The largest contributions to the TCR value in HCM was from Cr and As, accounting for 84%
440 and 10%, respectively. Cr and As also dominated TCR values in Hanoi (67% and 25% of TCR).
441 Previous studies have also found soluble As and Cr (VI) to be the largest carcinogenic risks
442 elements in PM_{2.5} (Galon-Negru et al., 2019; Kogianni et al., 2020). It should be noted however

443 that our TCR values over-estimate the contribution from Cr, since only a fraction of soluble Cr
444 is in the form of Cr (VI).

445 Relatively few studies have assessed health risk exposure from soluble trace metals in fine
446 atmospheric PM. The TCR values calculated for HCM and Hanoi (**Table 6**) are comparable to
447 a value of 7.12×10^{-6} reported for Iasi, Romania (Galon-Negru et al., 2019), but lower than
448 Nanjing, China (Sun et al., 2014) (45.9×10^{-6}).

449 **4. Conclusions**

450 This study is the first evaluation of the concentrations of soluble trace metals in fine PM in
451 both Hanoi and HCM, the largest cities in Vietnam. The soluble fraction of metals provides the
452 base information necessary for understanding the health risk for populations. We suggest
453 shipping activities strongly affect air quality in HCM, while coal power plants and nonferrous
454 metal refining are emission sources of soluble trace metals in fine particulate matter in Hanoi.
455 Zn was found to be the most abundant soluble metal in both cities, with the very high numbers
456 of vehicles in use being a significant source. The health risk assessment reflects a high
457 carcinogenic risk of inhalation soluble trace metals in fine PM in both cities in Vietnam.

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632 **Table captions**

633 **Table 1:** Detail descriptions of the PM sampling sites in HCM and in Hanoi.

634 **Table 2:** Field blank contributions (ng / filter) and limits of detection (calculated for a typical
635 air sample volume of 1000 m³; ng m⁻³) for each element. Values given are the ranges
636 observed for the 7 sampling periods at HCM and Hanoi.

637 **Table 3:** Summary of the characteristics of the air mass clusters identified at HCMC and Hanoi
638 during the two field campaigns and the percentage contributions of each air mass type during
639 each sampling campaign.

640 **Table 4:** Summary statistics (mean \pm standard deviation and range concentrations, ng m⁻³) of
641 the soluble trace metals in PM₂ in Ho Chi Minh City (HCM) and Hanoi during the September
642 / October 2018 and March 2019 sampling campaigns (including urban and background sites,
643 where available).

644 **Table 5:** Comparison of mean soluble trace metals concentrations (ng m⁻³) in aerosols at
645 different cities.

646 **Table 6:** Non-carcinogenic and carcinogenic risks (mean \pm SD) for target soluble trace
647 metals (Mn, Ni, Co, Cd, Pb, Cr and As) in PM₂ in HCM and Hanoi.

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654 **Table 1:** Detail descriptions of the PM sampling sites in HCM and in Hanoi.

Site	Location	Height above ground level	Sampling Dates	Description
HCMC	10.7625°N 106.6823°E	~ 50 m	19 Sept – 19 Oct 2018 4 Mar – 2 Apr 2019	Urban
HCMB1	10.6627°N 106.5779°E	~ 15 m	19 Sept – 19 Oct 2018	Background
HCMB2	10.8769°N 106.7975°E	~ 20 m	5 Mar – 3 Apr 2019	Background
HNC	21.0068°N 105.8178°E	~ 30 m	24 Sept – 23 Oct 2018 4 Mar – 1 Apr 2019	Urban
HNB	21.00098°N 105.9318°E	~ 10 m	4 Mar – 1 Apr 2019	Background

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657 **Table 2:** Field blank contributions (ng / filter) and limits of detection (calculated for a typical
 658 air sample volume of 1000 m³; ng m⁻³) for each element. Values given are the ranges
 659 observed for the 7 sampling periods at HCM and Hanoi.

Element	Blank	Limit of Detection	Element	Blank	Limit of Detection
Fe	< 1500	1.5 – 2.3	Co	< 3.5	0.003
Al	14100 – 16600	5.0 – 10.7	Cd	0.7 – 3.1	0.001 – 0.009
Mn	17 – 47	0.04 – 0.22	Pb	< 539	0.5 – 0.8
Ti	9 – 16	0.005 – 0.032	Th	< 7	0.07 – 0.20
Zn	15700 – 37000	10 – 34	Cr	23 – 46	0.002 – 0.031
V	3.6 – 4.6	0.002 – 0.54	As	4 – 11	0.002 – 0.070
Cu	76 – 775	0.01 – 0.80	Sb	2.4 – 6.1	0.002 – 0.017
Ni	< 25 – 106	0.01 – 0.28			

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662 **Table 3:** Summary of the characteristics of the air mass clusters identified at HCMC and Hanoi
 663 during the two field campaigns and the percentage contributions of each air mass type during
 664 each sampling campaign.

Cluster	% 2018	% 2019	Description
HCMC – Sept/Oct 2018			
SW	18.8		Peninsular Malaya & Indonesia
S	20.3		Southern South China Sea
E	11.7		Philippines
NE	49.2		Southern China / Taiwan
HCMC – Mar 2019			
SE		28.8	Southeasterly arrivals from southern South China Sea / Philippines
S		35.6	Easterly arrivals from Philippines
NE		35.6	Taiwan / northern Philippines
Hanoi – Sept/Oct 2018 & Mar 2019			
SE	22.4	37.5	Gulf of Tonkin / Marine
E	25.0	30.8	Coastal and inland China
NE	52.6	31.7	Inland China

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667 **Table 4:** Summary statistics (mean \pm standard deviation and range concentrations, ng m⁻³) of
 668 the soluble trace metals in PM₂ in Ho Chi Minh City (HCM) and Hanoi during the September
 669 / October 2018 and March 2019 sampling campaigns (including urban and background sites,
 670 where available).

Element	September / October 2018			
	HCM (n=60)		Hanoi (n=29)	
	mean \pm st. dev.	range	mean \pm st. dev.	range
Fe	44.6 \pm 13.8	19.0 - 95.2	51.7 \pm 17.2	22.8 - 82.2
Al	28.0 \pm 10.7	8.9 - 67.5	37.2 \pm 15.3	11.8 - 70.6
Mn	5.44 \pm 2.25	2.45 - 13.3	16.1 \pm 9.4	3.9 - 40.3
Ti	0.40 \pm 0.14	0.17 - 0.89	0.60 \pm 0.22	0.24 - 1.00
Zn	231 \pm 159	21 - 1490	592 \pm 646	39 - 2780
V	2.29 \pm 1.31	0.53 - 5.94	1.03 \pm 0.39	<0.82 - 1.80
Cu	5.22 \pm 5.67	1.25 - 43.3	4.24 \pm 2.31	1.50 - 11.8
Ni	0.70 \pm 0.37	0.13 - 1.63	0.60 \pm 0.23	0.17 - 0.97
Co	0.054 \pm 0.018	0.028 - 0.101	0.081 \pm 0.022	0.036 - 0.115
Cd	0.59 \pm 0.48	0.11 - 2.98	1.69 \pm 1.33	0.30 - 5.55
Pb	29.0 \pm 40.9	4.4 - 280	56.0 \pm 35.5	7.2 - 152
Cr	0.37 \pm 0.22	0.09 - 1.28	0.40 \pm 0.12	0.20 - 0.62
As	1.12 \pm 0.86	0.26 - 4.32	3.76 \pm 2.53	1.20 - 10.7
Sb	1.39 \pm 1.33	0.24 - 7.30	1.34 \pm 0.68	0.39 - 3.02

Element	March 2019			
	HCM (n=56)		Hanoi (n=56)	
	mean \pm st. dev.	range	mean \pm st. dev.	range
Fe	47.0 \pm 14.4	23.3 - 96.2	60.9 \pm 27.5	16.9 - 155
Al	38.7 \pm 14.9	12.7 - 82.2	50.4 \pm 28.2	13.7 - 147
Mn	5.06 \pm 2.38	1.66 - 12.0	11.9 \pm 7.7	2.7 - 45.0
Ti	0.56 \pm 0.17	0.25 - 1.17	0.68 \pm 0.38	0.11 - 1.87
Zn	142 \pm 135	3.5 - 469	363 \pm 446	36 - 2100
V	3.53 \pm 1.54	1.37 - 7.88	1.73 \pm 0.91	<0.82 - 3.70
Cu	3.66 \pm 3.06	0.64 - 12.6	6.78 \pm 9.78	<2.1 - 60.5
Ni	1.13 \pm 0.47	0.40 - 2.97	0.67 \pm 0.29	0.14 - 1.34
Co	0.071 \pm 0.030	0.028 - 0.169	0.106 \pm 0.050	0.022 - 0.219
Cd	0.28 \pm 0.18	0.05 - 0.82	1.60 \pm 1.34	0.33 - 7.62
Pb	9.6 \pm 7.4	1.5 - 28.1	56.0 \pm 84.6	5.5 - 432
Cr	0.27 \pm 0.09	0.12 - 0.79	0.51 \pm 0.23	0.19 - 1.21
As	0.32 \pm 0.15	0.13 - 0.79	3.35 \pm 2.42	1.05 - 17.3
Sb	0.87 \pm 1.30	0.09 - 8.70	1.45 \pm 0.75	0.34 - 3.98

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673 **Table 5:** Comparison of mean soluble trace metals concentrations (ng m^{-3}) in aerosols at
 674 different cities.

	HCM*	Hanoi*	Hanoi , (McNeill et al., 2020)	Beijing, China (Wang et al., 2015)	Kowloon Tong, Hong Kong (Jiang et al., 2014)	Edinburgh, UK (Heal et al., 2005)	Iasi, Romania (Galon- Negru et al., 2019)
Aerosol size	PM ₂	PM ₂	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Extraction solution	0.01M HNO ₃	0.01M HNO ₃	0.8M HNO ₃	Deionised water	Deionised water	Deionised water	Deionised water
Fe	45.7	57.8	282	N.A	400	183	69.9
Al	33.2	45.9	N.A	N.A	215	N.A	72.5
Mn	5.26	13.3	80.1	32.7	32.2	1.16	9.9
Ti	0.48	0.65	5.21	N.A	N.A	3.7	N.A
Zn	189	441	1180	145	350	5.05	29.5
V	2.89	1.49	2.10	2.3	8.3	0.73	0.44
Cu	4.47	5.91	14.1	15.5	53.5	2.25	9.71
Ni	0.91	0.64	N.A	N.A	4.7	0.97	20.5
Co	0.06	0.10	N.A	N.A	N.A	N.A	0.07
Cd	0.44	1.63	4.25	2.5	2.7	0.25	0.29
Pb	19.6	56.0	141	98.2	131	5.64	2
Cr	0.32	0.47	2.28	1.9	4.7	0.22	2.14
As	0.73	3.49	N.A	12.1	N.A	0.24	6.59
Sb	1.14	1.41	N.A	N.A	N.A	N.A	N.A

*: This study

N.A: not available

675

676 **Table 6:** Non-carcinogenic and carcinogenic risks (mean \pm SD) for target soluble trace
 677 metals (Mn, Ni, Co, Cd, Pb, Cr and As) in PM₂ in HCM and Hanoi.

Sites	HCM		Hanoi		HCM		Hanoi	
	Sep-Oct 2018	Mar 2019	Sep-Oct 2018	Mar 2019	Sep-Oct 2018	Mar 2019	Sep-Oct 2018	Mar 2019
HI	0.05 \pm 0.02	0.03 \pm 0.02	0.15 \pm 0.08	0.12 \pm 0.07	0.04 \pm 0.02	0.13 \pm 0.08	0.04 \pm 0.02	0.13 \pm 0.08
TCR ($\times 10^{-6}$)	7.24 \pm 3.96	4.82 \pm 1.67	10.33 \pm 4.05	11.8 \pm 5.04	6.07 \pm 3.29	11.3 \pm 4.75	6.07 \pm 3.29	11.3 \pm 4.75

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679 **Figure captions**

680 **Fig. 1:** The sampling sites in the two cities.

681 **Fig. 2:** 5-day airmass back trajectories for the central sampling sites in a) Sept / Oct 2018 &
682 b) Mar 2019 at Hanoi and c) Sept / Oct 2018 & d) Mar 2019 at Ho Chi Minh City.

683 Trajectories at 09:00 and 21:00 UTC on each sampling day are plotted.

684 **Fig. 3:** Daily variation of selected trace metals in PM₂ at HCMC in a) Sept-Oct 2018 and b)
685 Mar 2019. Values below the limit of detection are indicated by inverted triangles.

686 **Fig. 4:** Daily variation of selected trace metals in PM₂ at HNC in a) Sept-Oct 2018 and b)
687 Mar 2019. Values below the limit of detection are indicated by inverted triangles.

688 **Fig. 5:** CWT plots for selected trace metals in HCM. Concentration data from the central site
689 during both campaigns were combined with 5-day air mass backward trajectories at the central
690 sampling site (HCMC, black dot) for CWT analysis.

691 **Fig. 6:** CWT plots for selected trace metals in Hanoi, using concentration data and 5-day air
692 mass back trajectories for the HNC site (black dot).

693 **Fig. 7:** Relationships between a) Mn, b) Co, c) Fe and d) Ti and Al for the sampling sites in
694 HCM (grey circles) and HN (coded by air mass type) in 2018 and 2019. Panels also show the
695 regression between and correlation coefficient each soluble metal and Al at HCM (grey dashed
696 line, all relationships $p < 0.01$).

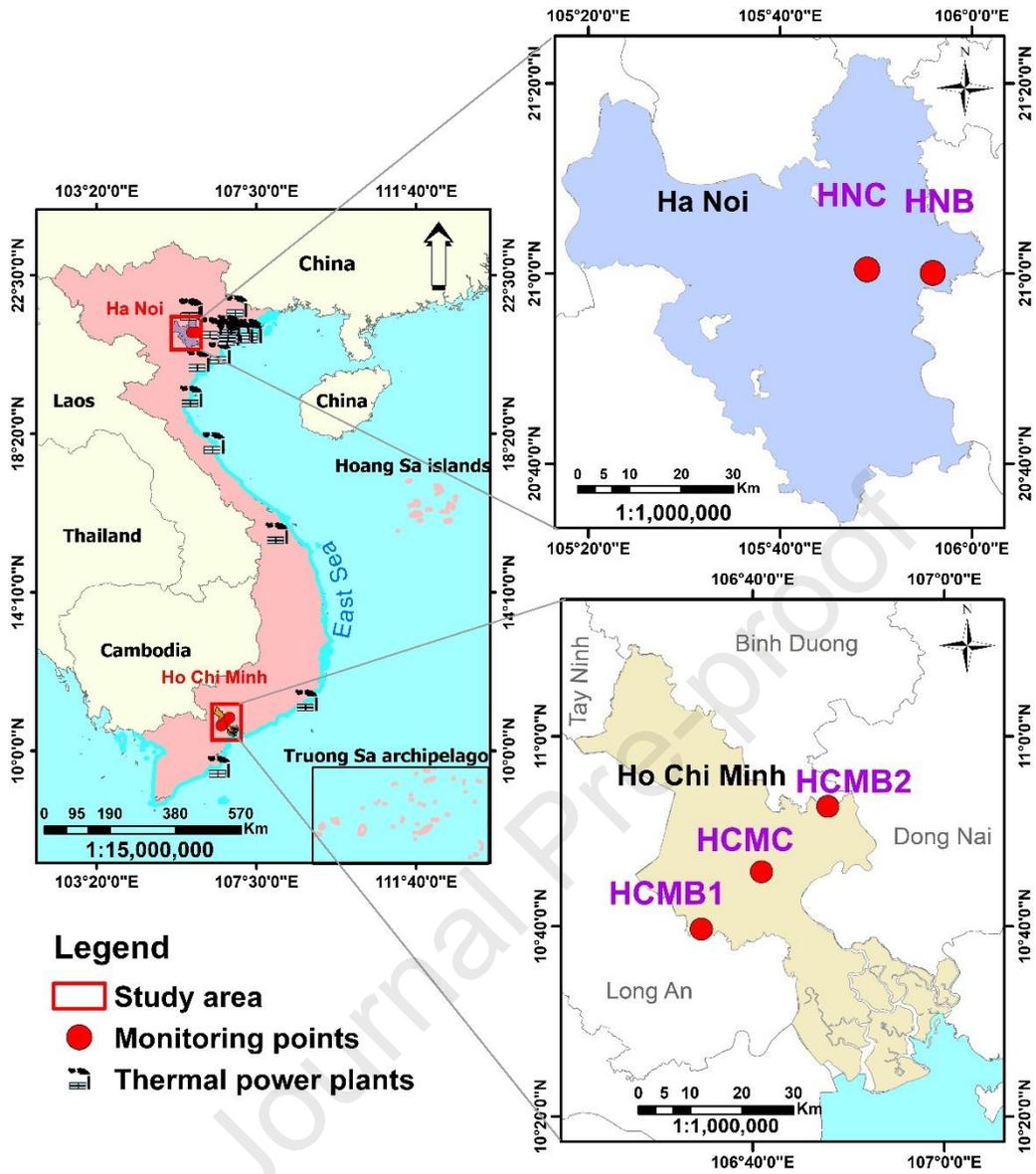
697 **Fig. 8:** Hysplit 72-hour backward trajectories arriving at 09:00 UTC, coloured according to
698 soluble vanadium concentration in PM₂ in a) the first campaign, b) second campaign) in
699 HCM, and c) first campaign, and d) second campaign in Hanoi.

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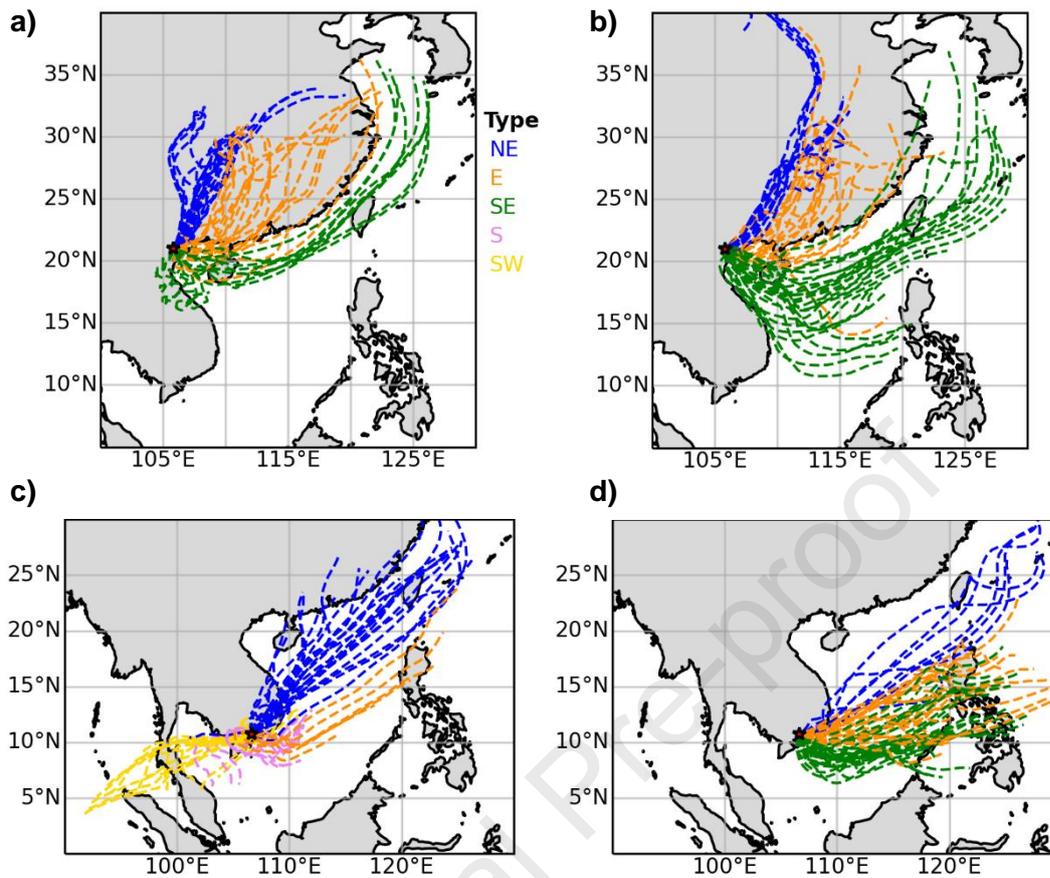


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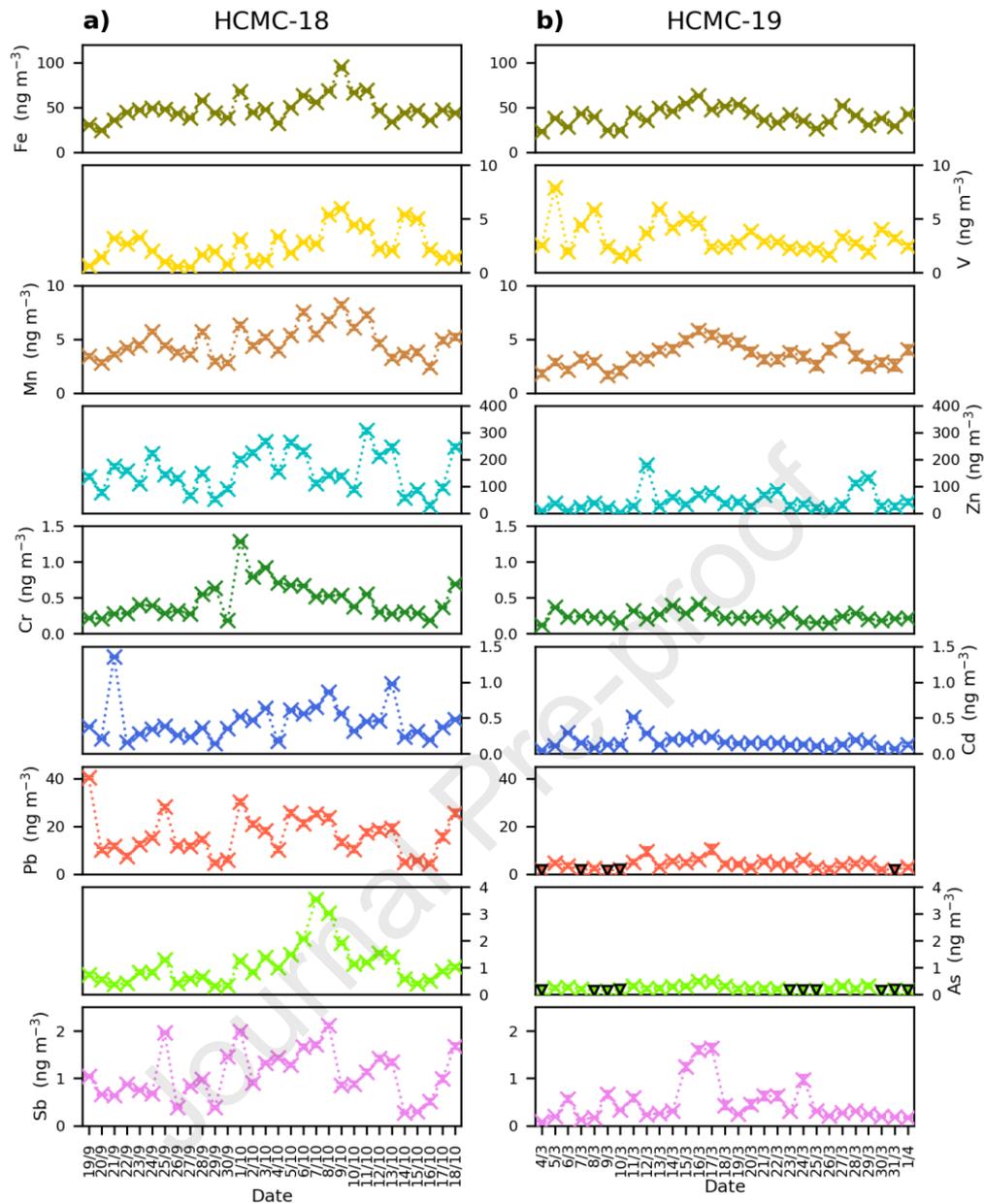
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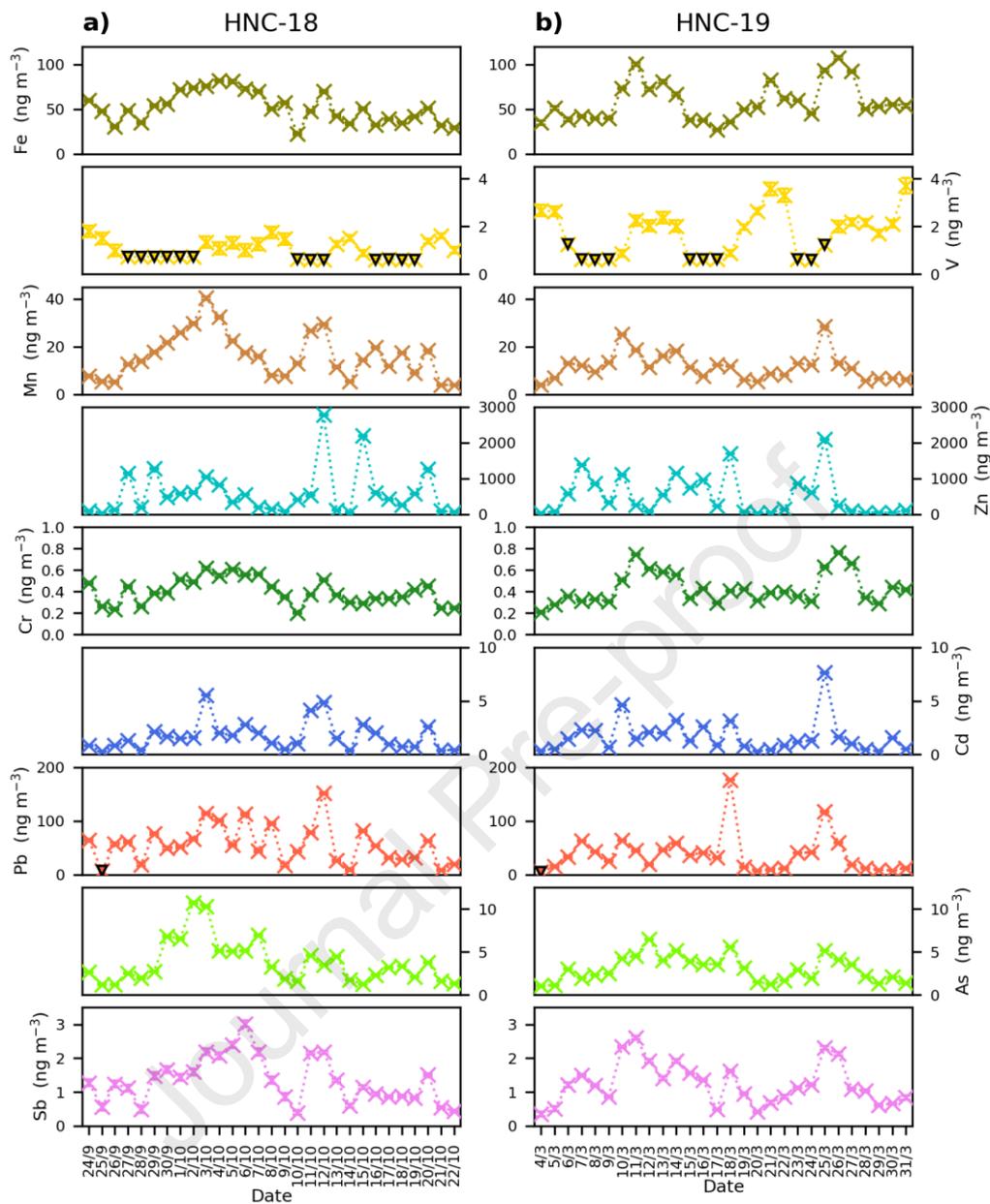
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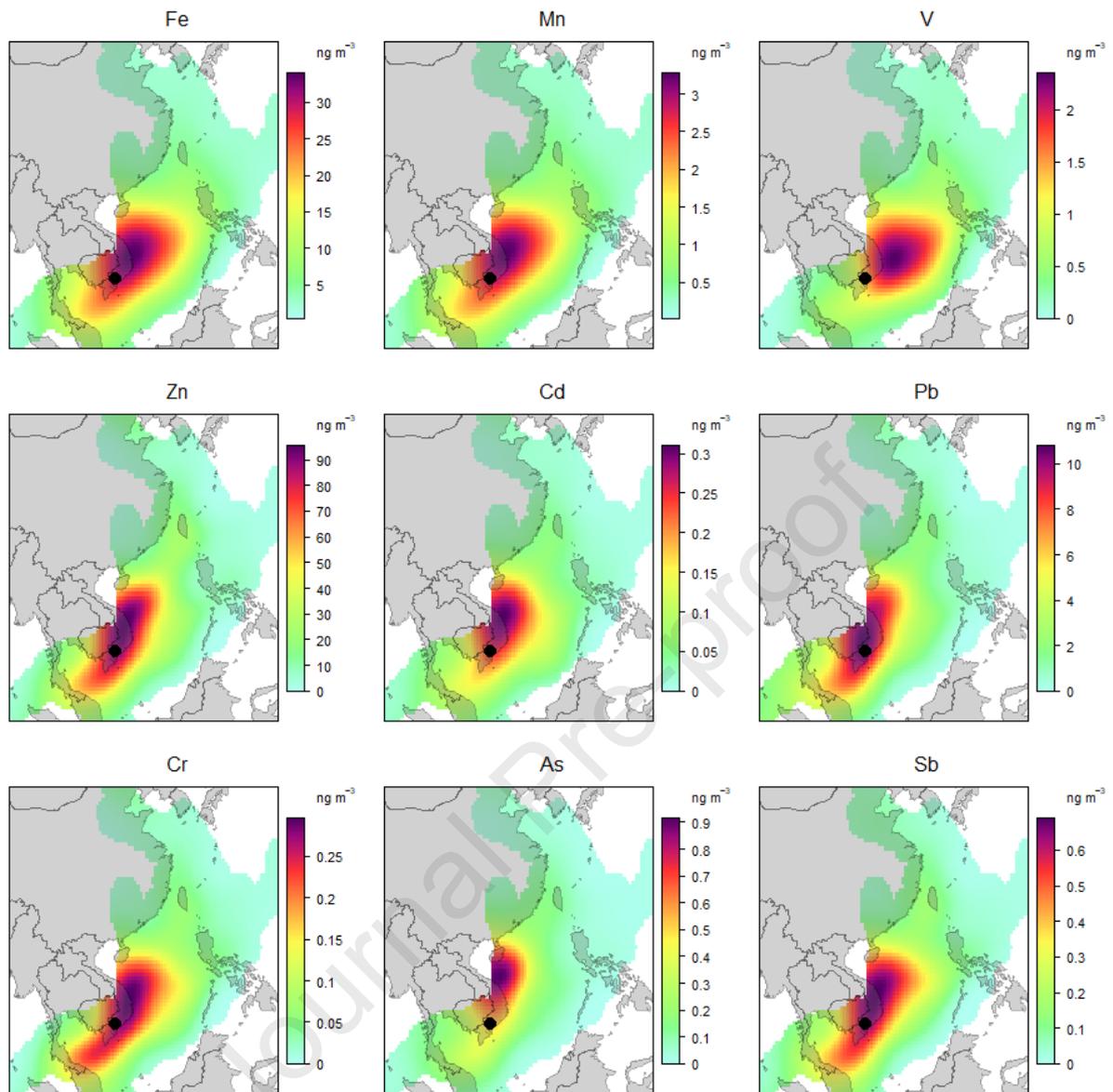
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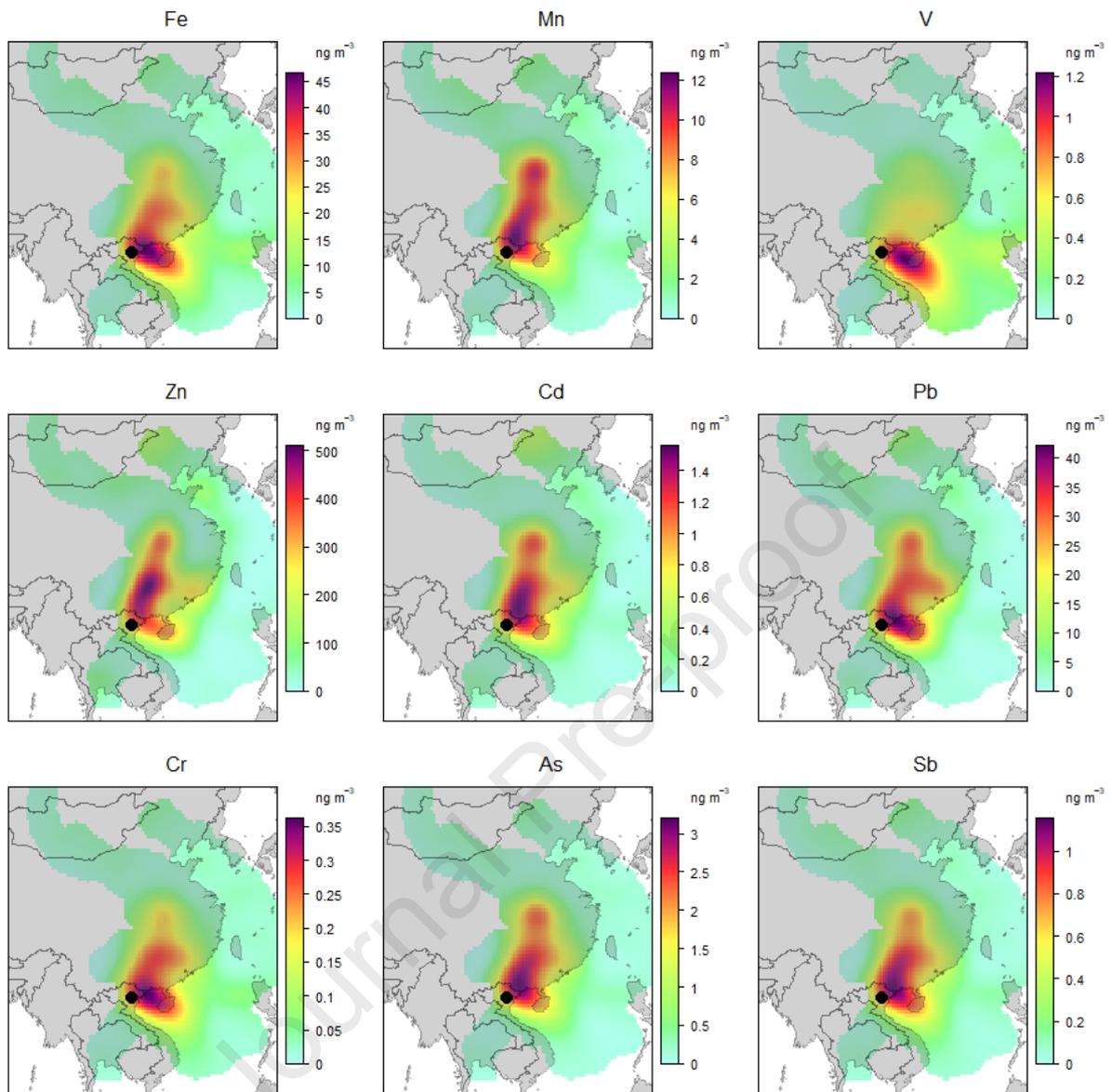


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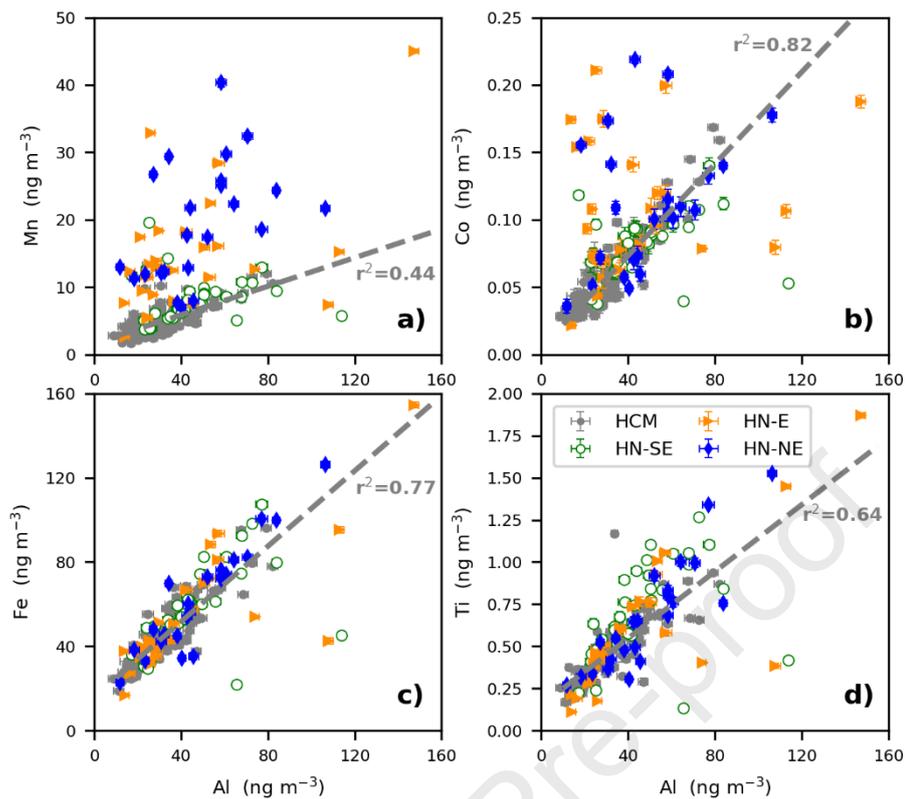


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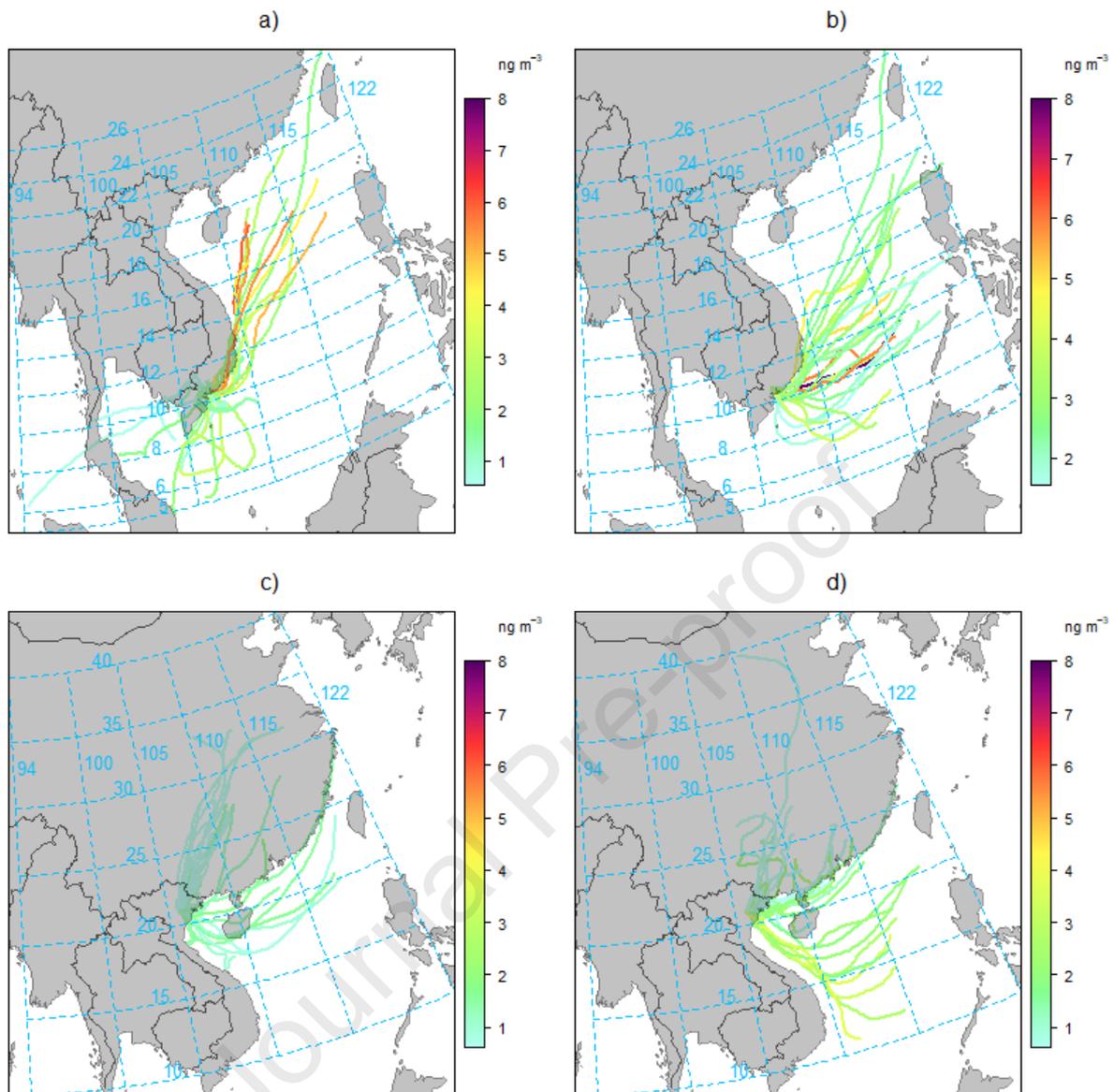
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 733 dashed line, all relationships $p < 0.01$).

734



735

736 **Fig. 8:** Hysplit 72-hour backward trajectories arriving at 09:00 UTC, coloured to
 737 soluble vanadium concentration in PM_{2.5} in a) the first campaign, b) second campaign) in HCM,
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SOLUBLE TRACE METALS ASSOCIATED WITH ATMOSPHERIC FINE PARTICULATE MATTER IN THE TWO MOST POPULOUS CITIES IN VIETNAM

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HIGHLIGHTS

- The first evaluation of the levels of soluble trace metals in fine PM in Hanoi and HCM, the two biggest cities in Vietnam
- Zn was most abundant (motorcycles significant contributor)
- Hanoi > HCM for most metals except V and Ni
- Suggest potential emission sources of soluble trace metal in the two cities. Air quality impacted by ships in HCMC, and coal/metal production in Hanoi.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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