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

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CRediT author statement

To Thi Hien: Conceptualization, Writing – review & editing, Funding acquisition.
Nguyen Doan Thien Chi: Formal analysis, Visualization, Writing - original draft.
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Abstract

Hanoi and Ho Chi Minh City (HCM), the most populous cities in Vietnam, have received increasing global attention because of their poor air pollution status. As part of the recent UK-Vietnam 2-Cities project, the concentrations of trace metals in fine particulate matter have been characterized. 24-hour samples of PM$_2$ were collected at 2 sites in Hanoi and 3 sites in HCM during two 4-week periods in September / October 2018 and March 2019. The soluble fraction of 15 trace metal(loid)s (Fe, Al, Mn, Ti, Zn, V, Cu, Ni, Co, Cd, Pb, Th, Cr, As, and Sb) bound to PM$_2$ were analyzed by ICP-MS. The results show that Zn was the most abundant soluble metal in PM$_2$ in both cities, with very large numbers of road vehicles (e.g. tyre wear) likely contributing in both cities and non-ferrous metal production being a substantial additional source in Hanoi. Fe and Al, derived from crustal sources, were the dominant metals after Zn. Most trace metals concentrations in Hanoi were higher than in HCM, especially toxic metals such as Pb, Cd, Cr and As. V and Ni were the only two metals having higher concentrations in HCM than in Hanoi, likely due to shipping emissions (combustion of heavy fuel oil) that strongly affect the air quality in HCM. Coal-power plants and non-ferrous metal production are likely to be the major sources of trace metals in Hanoi. Health risk assessment shows that a high carcinogenic risk exists for inhalation exposure of soluble trace metals bound to PM$_2$ in both cities.

Keywords: particulate matter, PM$_2$, soluble trace metals, Hanoi, Ho Chi Minh City.
1. Introduction

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

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

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

Fine PM has been investigated because of its potentially harmful effects and the increase of serious haze events in Vietnam, particularly in Hanoi and Ho Chi Minh City (HCM) (Cohen et al., 2010; Hai and Oanh, 2013; Hien et al., 2019). There have been very few studies on trace metal concentrations in PM in Vietnam, most of which have focused on total, rather than soluble, metal fractions (Gataria et al., 2005; Cohen et al., 2010). This study evaluated the levels of the soluble trace metals in fine PM in HCM and Hanoi as part of an air quality research project in these cities. The trace metals studied included those with known toxicity (e.g. zinc
(Zn), vanadium (V), copper (Cu), nickel (Ni), iron (Fe)), as well as elements characteristic of mineral dust aerosols (e.g. aluminium (Al), titanium (Ti), Fe) and anthropogenic emissions from various sources (e.g. cadmium (Cd), lead (Pb), arsenic (As), V, Ni). Our aim was to identify the major characteristics of the PM soluble trace metal load at these two heavily populated and highly polluted cities, and to highlight instances where the observed PM trace metal load might be cause for concern on health grounds.

2. Materials and methods

2.1 Study sites and background information

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

Hanoi, the capital of Vietnam, has a subtropical climate with 4 distinct seasons, although the influence of the prevailing wet/dry seasons remains strong, with northeasterly winds in September / October and southeasterly winds in March. According to the Hanoi Environment and Natural Resource Department (Huu and Ngoc, 2021), Hanoi has a population of about 7 million, with 5 million motorbikes, 500,000 cars, and high levels of construction works due to rapid urbanization. Energy consumption in the city is dominated by the combustion of millions of litres of gasoline each day and 40 million-kilowatt hours electricity. There are approximately fifteen coal-fired power stations within ~200 km of Hanoi, mostly fuelled by anthracite (Duong, 1995). Anthracite has low sulfur content, but generates large amounts of particulate matter emissions (Cohen et al., 2010). In recent years, Hanoi has often been ranked as the most
polluted city in the world. In 2017, Hanoi had only 38 days in which air quality was considered healthy by the World Health Organization (WHO) (Kim, 2019).

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

2.2 Sampling strategy

There were two concurrent campaigns of aerosol sampling in the 2 cities, each campaign lasting for one month (see Table 1). In the first campaign (wet season, 2018), 3 sampling sites were established: HCMC-18, HCMB1-18, and HNC-18. HCMC-19, HCMB2-19, HNC-19, and HNB-19 were the sampling sites in the second campaign (dry season, 2019). High volume samplers (Tisch Environmental) were used for aerosol sampling. A Sierra-type cascade impactor head was applied to separate PM$_2$ (≤ 2 µm aerodynamic diameter) at a flow rate of 0.7 m$^3$ min$^{-1}$ over 24 hours. Sampler flow rates were calibrated every week using a calibration orifice. Before sampling, glass microfiber filters (Whatman, GF/CTM, 20 x 25.4 cm) were treated sequentially with 0.5 M HCl, 0.1 M HCl and ultrapure water (18.2 MΩ cm) (Rickli, 2010). Filters were then dried overnight under HEPA filtered air, wrapped in aluminium foil and baked at 450°C for 4 hours before being stored until sampling.

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

2.3 Trace metals analysis

In this study, we analyzed the soluble fraction of fifteen trace metal(loid)s associated with PM$_2$: Fe, Al, manganese (Mn), Ti, Zn, V, Cu, Ni, cobalt (Co), Cd, Pb, thorium (Th), chromium (Cr),
As and antimony (Sb). All post-collection sample handling and soluble metals extraction procedures were conducted under a laminar flow hood in a trace metal clean laboratory.

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

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

Results from field blank determinations and limits of detection for each element are shown in Table 2. Limits of detection (LOD) were defined following Chance et al. (2015), either from the analytical LOD derived from the calibration curve, or as the procedural LOD (3 × standard
deviation of the field blank samples). All the lab blank samples had concentrations below the analytical LOD. Soluble Th concentrations were below the LOD in all samples and are not discussed further. Concentrations below the LOD were also observed for V (21% of values), Cu, Ni, Pb and As (all ≤ 5% of values). Where sample concentrations were below the LOD, they were substituted with 75% of the relevant LOD (e.g. in Fig. 3 & 4). Field blanks for each of the 7 sampling periods were subtracted from their respective sample concentrations, unless the field blank was below the analytical LOD (i.e. for Fe, Ni, Co, Pb: see Table 2) in which case there was no blank subtraction.

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

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

2.4. Backward trajectories and Concentration Weighted Trajectory

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

\[
\ln(C_{ij}) = \frac{1}{\sum_{k=1}^{N} \tau_{ijk}} \sum_{k=1}^{N} \ln(C_k) \tau_{ij}
\]  

(1)

Where \(i\) and \(j\) are the parameters of a grid cell, \(k\) is the index of trajectory, \(N\) is the total number of trajectories, \(C_k\) is the pollutant concentrations measured upon arrival of trajectory \(k\), and \(\tau_{ijk}\) the residence time of trajectory \(k\) in grid cell \((i, j)\). The higher the value of \(C_{ij}\), the higher the concentrations at the receptor site when air parcels passed over grid cell \((i, j)\) (Carslaw, 2014). CWT analysis was conducted using the Openair package in R software.
2.5 Health risk assessment of soluble trace metals inhalation

We undertook the health risk assessment of soluble metals in PM$_2.5$ by calculating the Hazard Index (HI) for non-carcinogenic risk and total carcinogenic risk (TCR) following Environmental Protection Agency Guidance (EPA, 2009). According to the International Agency for Research on Cancer (IARC): As, Cd, and Cr (VI) belong to Group 1 of cancer hazard agents, Pb and Co are classified as probably carcinogenic (Group 2A), nickel is in Group 2B of carcinogens, and Mn compounds are classed as pollutants of potential interest (IARC, 2014). In this study, the health risk assessment was conducted for Mn, Ni, Co, Cd, Pb, Cr (we assume all Cr was present as Cr (VI) in order to assess the maximum potential risk from this element), and As. The HI of the selected metals was calculated based on Reference Concentration RfC (mg m$^{-3}$). The TCR values were evaluated based on Inhalation Unit Risk IUR ($\mu$g m$^{-3}$)$^{-1}$. The RfC and IUR values of those metals were cited from Environmental Protection Agency. The exposure concentrations of selected metals were calculated using the equation below:

$$EC_i = \frac{CA_i \times ET \times EF \times ED}{AT}$$  \hspace{1cm} (2)

where:

- $EC_i$ = exposure concentration of the trace metal $i$ (μg m$^{-3}$)
- $CA_i$ = concentration of the trace metal $i$ in air (μg m$^{-3}$)
- $ET$ = exposure time – 8 hours/day
- $EF$ = exposure frequency – 365 days/year
- $ED$ = exposure duration – 40 years for adults
- $AT$ = averaging time (75-year lifetime x 365 days/year x 24 hours/day) (75 years, the average life expectancy of the Vietnam population in 2018, World Bank Group, https://data.worldbank.org/indicator/SP.DYN.LE00.IN?locations=VN&view=chart)

Non-carcinogenic health risk is assessed by:

$$HQ_i = \frac{EC_i}{RfC_i \times 1000}$$  \hspace{1cm} (3)

$$HI = \sum HQ_i$$  \hspace{1cm} (4)

where:
RfC<sub>i</sub> = reference concentration for the element i – inhalation toxicity value (mg m<sup>-3</sup>)

HQ<sub>i</sub> = Hazard Quotient of element i (unitless)

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

\[ R_i = EC_i \times IUR_i \]  \hspace{1cm} (5)

\[ TCR = \sum R_i \]  \hspace{1cm} (6)

where:

IUR<sub>i</sub> = Inhalation Unit Risk of the carcinogenic element i (µg m<sup>-3</sup>)<sup>-1</sup>

R<sub>i</sub> = carcinogenic risk of the element i (unitless)

3. Results

3.1 Air mass origins

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

3.2 Trace metals levels in PM<sub>2</sub>

Overall, by mass concentration, Zn, Fe, Pb and Al were the most abundant soluble metals in PM<sub>2</sub> in both cities (Table 4). Fe and Al in airborne particulate matter originate primarily from soils, while anthropogenic activities are the dominant sources of Zn and Pb to the atmosphere. Previous studies have also found Zn to be the most abundant metal in fine particles in Hanoi (Gataria et al., 2005; Cohen et al., 2010; McNeill et al., 2020).

The daily concentrations of selected trace metals (Fe, V, Mn, Zn, Cr, Cd, Pb, As & Sb) in PM<sub>2</sub> in the central sites in HCM and Hanoi during the two sampling periods are illustrated in Figures 3 and 4, respectively, and equivalent plots for the background sites can be found in Figure S1. The results obtained at HCM and Hanoi indicate that there were substantial differences in the concentrations of the trace metals studied at the regional level (e.g. Zn, Pb and Cd were substantially higher in Hanoi than in HCM) and over time, both seasonally (e.g. As in HCM) and on a daily basis (Table 4, Fig. 3 & 4). These patterns indicate that a variety of sources influence trace metals in PM<sub>2</sub> at the two cities, as discussed below.
4 Discussion

4.1 Comparison with other cities

Table 5 shows the concentrations of soluble trace metals in airborne particulate matter at various global locations together with the method used to extract the soluble components in each study. Direct comparison between the results from the different studies shown in Table 5 is not straightforward because of the different aerosol size fractions collected (e.g. PM$_{10}$ may contain higher concentrations of a given trace metal than PM$_{2.5}$, depending on the element’s particle size distribution) and because the solubility of trace metals is pH dependent. Thus the more aggressive extraction method employed by McNeill et al., (2020) is likely to recover a larger fraction of aerosol trace metals than the method employed in this work, with even lower recoveries for methods using deionized water (Heal et al., 2005; Jiang et al., 2014; Wang et al., 2015; Galon-Negru et al., 2019). The soluble fraction recovered by a given method is also influenced by aerosol particle size distribution. Crustal elements (e.g. Fe and Al) are predominantly present in the coarse mode and have relatively low solubility while Zn is found in fine mode particles with high solubility (Witt et al., 2010; Li et al., 2015).

Previous studies have reported Zn, Fe, Al and Pb as the most abundant soluble trace metals in aerosols in Hanoi and other locations in East Asia (Table 5). In contrast, the soluble trace metal concentrations reported for European cities (Edinburgh and Iasi) were substantially lower than in East Asia with lower proportions of the anthropogenic elements Zn and Pb (compare PM$_{10}$ at Beijing and Edinburgh and PM$_{2.5}$ at Hong Kong and Iasi).

4.2 Seasonal differences

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

Differences in concentration between air mass types in each season may also contribute to these changes in overall concentration. For example, the As concentrations in the air mass types at
HCM in October were 0.56 ± 0.27 ng m$^{-3}$, 0.96 ± 0.51 ng m$^{-3}$, 0.52 ± 0.24 ng m$^{-3}$ and 1.60 ± 0.99 ng m$^{-3}$ for the SW, S, E and NE air mass types respectively, while in March As concentrations were 0.30 ± 0.13 ng m$^{-3}$, 0.30 ± 0.13 ng m$^{-3}$ and 0.44 ± 0.39 ng m$^{-3}$ for the SE, E and NE air mass types respectively. Concentrations of As in the NE air mass type were significantly lower in March than in October. Thus, the overall change in As concentrations between sampling periods appears to be due to a combination of greater boundary height in March (contributing to lower concentrations in E and NE arrivals) and lower As concentrations in SE (March) compared to SW and S (October) arrivals.

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

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

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

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

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

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

The CWT plots indicate that sources in northeast Vietnam and southeast China, and possibly also in Hainan, make strong contributions to the concentrations of soluble trace metals
observed in Hanoi (Fig. 6). However, V and Ni (not shown) appear to have distributions consistent with sources in the seas around Vietnam (Gulf of Tonkin and South China Sea: Fig. 5 & 6).

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

4.3.1 Contribution from soil dust

Al, Fe, Ti, and Mn are major components of the upper continental crust (Rudnick and Gao, 2014). In HCM, these elements (and the less abundant crustal component Co) were strongly correlated with one another (all relationships p < 0.01) implying that soil dust is their dominant source in PM$_2$ in this city. Long range transport from desert regions in northern China has been reported to make substantial contributions to the soil dust content at Hanoi (Hien et al., 2004). Soil dust appears to be the dominant source of Al, Fe and Ti at Hanoi, with the Fe - Al and Ti - Al relationships there being very similar to those in HCM (Fig. 7c & d). Both Mn and Co appear to be enriched with respect to Al in several samples in Hanoi, especially in the NE and E air mass types (Fig. 7a & b). This suggests that anthropogenic sources in northeast Vietnam and southern China contribute substantially to Mn and Co concentrations at Hanoi.

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

4.3.2 Influence of heavy fuel oil combustion

V and Ni were unusual among the metals studied here in that their concentrations were higher in HCM than in Hanoi (Table 4). Combustion of heavy fuel oil (HFO), predominantly by shipping, has been shown to be a strong source of these elements to the atmosphere (Becagli et al., 2012) (Viana et al., 2009). The significant correlation between V and Ni in HCM and
Hanoi (p<0.001 in both cases, Figure S6), and the association of both elements with maritime air mass back trajectories (e.g. Fig. 8) indicate that shipping is the dominant source of V and Ni in both cities. Even in Hanoi, concentrations of V and Ni were significantly higher (p < 0.05) in the strongly maritime-influenced SE air mass type than in the terrestrially-influenced NE and E types in March. Cohen et al., noted that HFO was used in barges for river and canal freight in Hanoi, so there may also be a local source of V and Ni there (Cohen et al., 2010).

There are a total of 320 ports operating along the coast of Vietnam, with the 34 seaports around HCM accounting for more than 60 percent of the total amount of trade of all Vietnamese ports. The study of Ho et al., (2019) applied a combination of bottom-up and top-down methods for calculating atmospheric emissions in HCM and found that the seaports contributed up to 5% and 15% of total TSP (total suspended particulate matter) and SO2 emissions, respectively (Ho et al., 2019). Thus the combustion of HFO by shipping emits not only V and Ni but also various pollutants including PM, inorganic and organic compounds and affects air quality in HCM (Becagli et al., 2012; Oeder et al., 2015).

### 4.3.3 Local and regional sources of Zn

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

### 4.3.4 Coal-fired power plants and air quality in Vietnam

Coal combustion is associated with emissions of several trace metals including Mn, Cr, Cd, As and Pb (Pacyna and Pacyna, 2001; McNeill et al., 2020). There are more than 20 coal power plants running in the north of Vietnam, and only 3 power plants in the south of the country. There are also a large number of coal power plants in the southeastern provinces of China...
(Guizhou, Guangxi, Hunan) and along the eastern coast of China. Cohen et al., identified long
range transport from power plants in China (especially in Guangxi, Hunan and Hubei
provinces) as the most prominent sources of PM associated with coal combustion at Hanoi.
Since the study of Cohen et al., power generation from coal-fired plants in Vietnam and China
has increased substantially (https://globalenergymonitor.org/projects/global-coal-plant-
tracker/) and these facilities are likely to contribute to poor air quality in Hanoi and HCM for
some time.

4.4 Health risk exposure of PM$_2$ soluble metals

The WHO recommends guideline annual average concentration limits for Pb and Cd in air of
500 and 5 ng m$^{-3}$, respectively (WHO, 2000). Although Cd concentrations at Hanoi exceeded
the 5 ng m$^{-3}$ threshold on two occasions, the average concentrations of the soluble fraction of
these two toxic metals in Hanoi and HCM were below the WHO guideline. Arsenic and Cr in
the +6 oxidation state (Cr (VI)) are human carcinogens (causing lung cancer), for which the
WHO has not defined any safe level of inhalation exposure. Their 1:100,000 lifetime excess
risk levels are 6.6 and 0.25 ng m$^{-3}$, respectively (WHO, 2000). PM$_2$ soluble As concentrations
exceeded 6.6 ng m$^{-3}$ on 6 occasions during sampling in Hanoi and concentrations in HCM also
approached this value in October (Fig. 3). Considering that As is also present in coarser aerosol
particles (McNeill et al., 2020) and that only a fraction of As is likely to be released by the
leaching procedure used, it seems likely that the 6.6 ng m$^{-3}$ threshold was exceeded on many
more occasions in both cities. Mean soluble Cr concentrations were above the lifetime excess
risk level for Cr (VI) in both cities, suggesting that further research into the redox speciation
of Cr in PM in Vietnamese cities might be advisable.

The calculated Hazard Index (HI) and total carcinogenic risk (TCR) for Mn, Ni, Co, Cd, Pb,
Cr and As in PM$_2$ at all study sites are shown in Table 6. The HI values at all sites in both
HCM and Hanoi were below the critical level of 1 (EPA, 1989) suggesting that there is no
chronic influence of inhalation of those metals in PM$_2$. Nonetheless, all TCR values are much
higher than the carcinogenic benchmark level of 1 × 10$^{-6}$ (EPA, 1989) indicating high cancer
risk for respiration in the two cities. The TCR value in HCM was 1.9 times lower than in Hanoi.
The largest contributions to the TCR value in HCM was from Cr and As, accounting for 84% and
10%, respectively. Cr and As also dominated TCR values in Hanoi (67% and 25% of TCR).
Previous studies have also found soluble As and Cr (VI) to be the largest carcinogenic risks
elements in PM$_{2.5}$ (Galon-Negru et al., 2019; Kogianni et al., 2020). It should be noted however
that our TCR values over-estimate the contribution from Cr, since only a fraction of soluble Cr
is in the form of Cr (VI).

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

4. Conclusions

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

Acknowledgement

This research was funded by the RCUK (Research Councils UK)-NAFOSTED (Vietnam
National Foundation for Science and Technology Development) Newton Fund Research
Partnership under grant number NE/P014771/1. We would like to thank the Le Hong Phong
Political School, Vietnam National University of Agriculture and Binh Chanh High School for
use of their facilities. We thank Matthew Bradnam and Nat Brown for interesting discussions
and Nguyen Tan Thanh, Ho Truong Nam Hai, Phan Le Nhat Duat, Tran Anh Ngan, and Tran
Ngoc Chau Tram for assistance with sample collection. We acknowledge the NOAA Air
Resources Laboratory for the provision of the HYSPLIT model and David Carslaw for
providing the Openair package used in this study.

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Table captions

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

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

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

**Table 4**: Summary statistics (mean ± standard deviation and range concentrations, ng m$^{-3}$) of the soluble trace metals in PM$_2$ in Ho Chi Minh City (HCM) and Hanoi during the September / October 2018 and March 2019 sampling campaigns (including urban and background sites, where available).

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

**Table 6**: Non-carcinogenic and carcinogenic risks (mean ± SD) for target soluble trace metals (Mn, Ni, Co, Cd, Pb, Cr and As) in PM$_2$ in HCM and Hanoi.
**Table 1:** Detail descriptions of the PM sampling sites in HCM and in Hanoi.

<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
<th>Height above ground level</th>
<th>Sampling Dates</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCMC</td>
<td>10.7625°N 106.6823°E</td>
<td>~ 50 m</td>
<td>19 Sept – 19 Oct 2018</td>
<td>Urban</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 Mar – 2 Apr 2019</td>
<td></td>
</tr>
<tr>
<td>HCMB1</td>
<td>10.6627°N 106.5779°E</td>
<td>~ 15 m</td>
<td>19 Sept – 19 Oct 2018</td>
<td>Background</td>
</tr>
<tr>
<td>HCMB2</td>
<td>10.8769°N 106.7975°E</td>
<td>~ 20 m</td>
<td>5 Mar – 3 Apr 2019</td>
<td>Background</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 Mar – 1 Apr 2019</td>
<td></td>
</tr>
<tr>
<td>HNB</td>
<td>21.00098°N 105.9318°E</td>
<td>~ 10 m</td>
<td>4 Mar – 1 Apr 2019</td>
<td>Background</td>
</tr>
</tbody>
</table>
Table 2: Field blank contributions (ng / filter) and limits of detection (calculated for a typical air sample volume of 1000 m$^3$; ng m$^{-3}$) for each element. Values given are the ranges observed for the 7 sampling periods at HCM and Hanoi.

<table>
<thead>
<tr>
<th>Element</th>
<th>Blank</th>
<th>Limit of Detection</th>
<th>Element</th>
<th>Blank</th>
<th>Limit of Detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>&lt; 1500</td>
<td>1.5 – 2.3</td>
<td>Co</td>
<td>&lt; 3.5</td>
<td>0.003</td>
</tr>
<tr>
<td>Al</td>
<td>14100 – 16600</td>
<td>5.0 – 10.7</td>
<td>Cd</td>
<td>0.7 – 3.1</td>
<td>0.001 – 0.009</td>
</tr>
<tr>
<td>Mn</td>
<td>17 – 47</td>
<td>0.04 – 0.22</td>
<td>Pb</td>
<td>&lt; 539</td>
<td>0.5 – 0.8</td>
</tr>
<tr>
<td>Ti</td>
<td>9 – 16</td>
<td>0.005 – 0.032</td>
<td>Th</td>
<td>&lt; 7</td>
<td>0.07 – 0.20</td>
</tr>
<tr>
<td>Zn</td>
<td>15700 – 37000</td>
<td>10 – 34</td>
<td>Cr</td>
<td>23 – 46</td>
<td>0.002 – 0.031</td>
</tr>
<tr>
<td>V</td>
<td>3.6 – 4.6</td>
<td>0.002 – 0.54</td>
<td>As</td>
<td>4 – 11</td>
<td>0.002 – 0.070</td>
</tr>
<tr>
<td>Cu</td>
<td>76 – 775</td>
<td>0.01 – 0.80</td>
<td>Sb</td>
<td>2.4 – 6.1</td>
<td>0.002 – 0.017</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt; 25 – 106</td>
<td>0.01 – 0.28</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3: Summary of the characteristics of the air mass clusters identified at HCMC and Hanoi during the two field campaigns and the percentage contributions of each air mass type during each sampling campaign.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>% 2018</th>
<th>% 2019</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCMC – Sept/Oct 2018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SW</td>
<td>18.8</td>
<td></td>
<td>Peninsular Malaya &amp; Indonesia</td>
</tr>
<tr>
<td>S</td>
<td>20.3</td>
<td></td>
<td>Southern South China Sea</td>
</tr>
<tr>
<td>E</td>
<td>11.7</td>
<td></td>
<td>Philippines</td>
</tr>
<tr>
<td>NE</td>
<td>49.2</td>
<td></td>
<td>Southern China / Taiwan</td>
</tr>
<tr>
<td></td>
<td>HCMC – Mar 2019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SE</td>
<td>28.8</td>
<td></td>
<td>Southeasterly arrivals from southern South China Sea / Philippines</td>
</tr>
<tr>
<td>S</td>
<td>35.6</td>
<td></td>
<td>Easterly arrivals from Philippines</td>
</tr>
<tr>
<td>NE</td>
<td>35.6</td>
<td></td>
<td>Taiwan / northern Philippines</td>
</tr>
<tr>
<td>SE</td>
<td>22.4</td>
<td>37.5</td>
<td>Gulf of Tonkin / Marine</td>
</tr>
<tr>
<td>E</td>
<td>25.0</td>
<td>30.8</td>
<td>Coastal and inland China</td>
</tr>
<tr>
<td>NE</td>
<td>52.6</td>
<td>31.7</td>
<td>Inland China</td>
</tr>
</tbody>
</table>
Table 4: Summary statistics (mean ± standard deviation and range concentrations, ng m$^{-3}$) of the soluble trace metals in PM$_2$ in Ho Chi Minh City (HCM) and Hanoi during the September / October 2018 and March 2019 sampling campaigns (including urban and background sites, where available).

| Element | September / October 2018 | | | March 2019 | | |
|---------|------------------------|--------|------------------------|------------------------|
|         | HCM (n=60)             | Hanoi (n=29) | | HCM (n=56)             | Hanoi (n=56) | |
|         | mean ± st. dev. | range | mean ± st. dev. | range | mean ± st. dev. | range |
| Fe      | 44.6 ± 13.8 | 19.0-95.2 | 51.7 ± 17.2 | 22.8-82.2 | 47.0 ± 14.4 | 23.3-96.2 | 60.9 ± 27.5 | 16.9-155 |
| Al      | 28.0 ± 10.7 | 8.9-67.5 | 37.2 ± 15.3 | 11.8-70.6 | 38.7 ± 14.9 | 12.7-82.2 | 50.4 ± 28.2 | 13.7-147 |
| Mn      | 5.44 ± 2.25 | 2.45-13.3 | 16.1 ± 9.4 | 3.9-40.3 | 5.06 ± 2.38 | 1.66-12.0 | 11.9 ± 7.7 | 2.7-45.0 |
| Ti      | 0.40 ± 0.14 | 0.17-0.89 | 0.60 ± 0.22 | 0.24-1.00 | 0.56 ± 0.17 | 0.25-1.17 | 0.68 ± 0.38 | 0.11-1.87 |
| Zn      | 231 ± 159 | 21-1490 | 592 ± 646 | 39-2780 | 142 ± 135 | 3.5-469 | 363 ± 446 | 36-2100 |
| V       | 2.29 ± 1.31 | 0.53-5.94 | 1.03 ± 0.39 | <0.82-1.80 | 3.53 ± 1.54 | 1.37-7.88 | 1.73 ± 0.91 | <0.82-3.70 |
| Cu      | 5.22 ± 5.67 | 1.25-43.3 | 4.24 ± 2.31 | 1.50-11.8 | 1.12 ± 0.86 | 0.26-4.32 | 3.76 ± 2.53 | 1.20-10.7 |
| Ni      | 0.70 ± 0.37 | 0.13-1.63 | 0.60 ± 0.23 | 0.17-0.97 | 0.054 ± 0.018 | 0.028-0.101 | 0.081 ± 0.022 | 0.036-0.115 |
| Co      | 0.59 ± 0.48 | 0.11-2.98 | 1.69 ± 1.33 | 0.30-5.55 | 29.0 ± 40.9 | 4.4-280 | 56.0 ± 35.5 | 7.2-152 |
| Cd      | 0.37 ± 0.22 | 0.09-1.28 | 0.40 ± 0.12 | 0.20-0.62 | 0.70 ± 0.37 | 0.13-1.63 | 0.60 ± 0.23 | 0.17-0.97 |
| Pb      | 0.37 ± 0.22 | 0.09-1.28 | 0.40 ± 0.12 | 0.20-0.62 | 0.70 ± 0.37 | 0.13-1.63 | 0.60 ± 0.23 | 0.17-0.97 |
| Cr      | 0.37 ± 0.22 | 0.09-1.28 | 0.40 ± 0.12 | 0.20-0.62 | 0.70 ± 0.37 | 0.13-1.63 | 0.60 ± 0.23 | 0.17-0.97 |
| As      | 1.12 ± 0.86 | 0.26-4.32 | 3.76 ± 2.53 | 1.20-10.7 | 0.054 ± 0.018 | 0.028-0.101 | 0.081 ± 0.022 | 0.036-0.115 |
| Sb      | 1.39 ± 1.33 | 0.24-7.30 | 1.34 ± 0.68 | 0.39-3.02 | 1.39 ± 1.33 | 0.24-7.30 | 1.34 ± 0.68 | 0.39-3.02 |

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

<table>
<thead>
<tr>
<th>Aerosol size</th>
<th>Extraction solution</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>Ti</th>
<th>Zn</th>
<th>V</th>
<th>Cu</th>
<th>Ni</th>
<th>Co</th>
<th>Cd</th>
<th>Pb</th>
<th>Cr</th>
<th>As</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>0.01M HNO$_3$</td>
<td>45.7</td>
<td>33.2</td>
<td>5.26</td>
<td>0.48</td>
<td>189</td>
<td>2.89</td>
<td>4.47</td>
<td>0.91</td>
<td>0.06</td>
<td>0.44</td>
<td>19.6</td>
<td>0.32</td>
<td>0.73</td>
<td>1.14</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>0.01M HNO$_3$</td>
<td>57.8</td>
<td>45.9</td>
<td>13.3</td>
<td>0.65</td>
<td>441</td>
<td>1.49</td>
<td>5.91</td>
<td>0.64</td>
<td>0.10</td>
<td>1.63</td>
<td>56.0</td>
<td>0.47</td>
<td>3.49</td>
<td>1.41</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>0.8M HNO$_3$</td>
<td>282</td>
<td>N.A</td>
<td>80.1</td>
<td>5.21</td>
<td>1180</td>
<td>2.10</td>
<td>14.1</td>
<td>N.A</td>
<td>N.A</td>
<td>N.A</td>
<td>141</td>
<td>4.25</td>
<td>N.A</td>
<td>N.A</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>Deionised water</td>
<td>N.A</td>
<td>N.A</td>
<td>32.7</td>
<td>N.A</td>
<td>145</td>
<td>2.3</td>
<td>15.5</td>
<td>N.A</td>
<td>N.A</td>
<td>N.A</td>
<td>2.5</td>
<td>2.5</td>
<td>N.A</td>
<td>N.A</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>Deionised water</td>
<td>400</td>
<td>215</td>
<td>32.2</td>
<td>3.7</td>
<td>350</td>
<td>8.3</td>
<td>53.5</td>
<td>4.7</td>
<td>4.7</td>
<td>N.A</td>
<td>98.2</td>
<td>4.7</td>
<td>12.1</td>
<td>N.A</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>Deionised water</td>
<td>183</td>
<td>N.A</td>
<td>3.2</td>
<td>N.A</td>
<td>5.05</td>
<td>0.73</td>
<td>2.25</td>
<td>0.97</td>
<td>0.97</td>
<td>N.A</td>
<td>131</td>
<td>0.22</td>
<td>0.24</td>
<td>N.A</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>Deionised water</td>
<td>69.9</td>
<td>N.A</td>
<td>1.16</td>
<td>N.A</td>
<td>29.5</td>
<td>0.44</td>
<td>9.71</td>
<td>20.5</td>
<td>20.5</td>
<td>N.A</td>
<td>5.64</td>
<td>2.14</td>
<td>6.59</td>
<td>N.A</td>
</tr>
</tbody>
</table>

*: This study
N.A: not available
Table 6: Non-carcinogenic and carcinogenic risks (mean ± SD) for target soluble trace metals (Mn, Ni, Co, Cd, Pb, Cr and As) in PM$_2$ in HCM and Hanoi.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HI</td>
<td>0.05 ± 0.02</td>
<td>0.03 ± 0.02</td>
<td>0.15 ± 0.08</td>
<td>0.12 ± 0.07</td>
<td>0.04 ± 0.02</td>
<td>0.13 ± 0.08</td>
</tr>
<tr>
<td>TCR (x10$^{-6}$)</td>
<td>7.24 ± 3.96</td>
<td>4.82 ± 1.67</td>
<td>10.33 ± 4.05</td>
<td>11.8 ± 5.04</td>
<td>6.07 ± 3.29</td>
<td>11.3 ± 4.75</td>
</tr>
</tbody>
</table>
Figure captions

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

Fig. 2: 5-day airmass back trajectories for the central sampling sites in a) Sept / Oct 2018 & b) Mar 2019 at Hanoi and c) Sept / Oct 2018 & d) Mar 2019 at Ho Chi Minh City. Trajectories at 09:00 and 21:00 UTC on each sampling day are plotted.

Fig. 3: Daily variation of selected trace metals in PM$_2$ at HCMC in a) Sept-Oct 2018 and b) Mar 2019. Values below the limit of detection are indicated by inverted triangles.

Fig. 4: Daily variation of selected trace metals in PM$_2$ at HNC in a) Sept-Oct 2018 and b) Mar 2019. Values below the limit of detection are indicated by inverted triangles.

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

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

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

Fig. 8: Hysplit 72-hour backward trajectories arriving at 09:00 UTC, coloured according to soluble vanadium concentration in PM$_2$ in a) the first campaign, b) second campaign) in HCM, and c) first campaign, and d) second campaign in Hanoi.
Fig. 2: The sampling sites in the two cities.
Fig. 2: 5-day airmass back trajectories for the central sampling sites in a) Sept / Oct 2018 & b) Mar 2019 at Hanoi and c) Sept / Oct 2018 & d) Mar 2019 at Ho Chi Minh City. Trajectories at 09:00 and 21:00 UTC on each sampling day are plotted.
**Fig. 3**: Daily variation of selected trace metals in PM$_2$ at HCMC in a) Sept-Oct 2018 and b) Mar 2019. Values below the limit of detection are indicated by inverted triangles.
Fig. 4: Daily variation of selected trace metals in PM$_2$ at HNC in a) Sept-Oct 2018 and b) Mar 2019. Values below the limit of detection are indicated by inverted triangles.
**Fig. 5**: CWT plots for selected trace metals in HCM. Concentration data from the central site during both campaigns were combined with 5-day air mass backward trajectories at the central sampling site (HCMC, black dot) for CWT analysis.
Fig. 6: CWT plots for selected trace metals in Hanoi, using concentration data and 5-day air mass back trajectories for the HNC site (black dot).
Fig. 7: Relationships between a) Mn, b) Co, c) Fe and d) Ti and Al for the sampling sites in HCM (grey circles) and HN (coded by air mass type) in 2018 and 2019. Panels also show the regression and correlation coefficient between each soluble metal and Al at HCM (grey dashed line, all relationships p < 0.01).
Fig. 8: Hysplit 72-hour backward trajectories arriving at 09:00 UTC, coloured according to soluble vanadium concentration in PM$_2$ in a) the first campaign, b) second campaign) in HCM, and c) first campaign, and d) second campaign in Hanoi.
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: