HNUE JOURNAL OF SCIENCE DOI: 10.18173/2354-1059.2022-0028
Natural Sciences 2022, Volume 67, Issue 2, pp. 110-119
This paper is available online at http://stdb.hnue.edu.vn

PARTICULATE MATTER LEVELS AND ELEMENTAL COMPOSITION IN THE SPRING AND TRANSITION PERIOD IN HANOI, VIETNAM

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Abstract. Particulate matter (PM) is a major environmental concern in Vietnam as well as in the world. Samples of $PM_{2.5}$, PM_{10}, and total suspended particle (TSP) were collected on the rooftop of a five-floor building inside Hanoi University of Science and Technology, Hanoi, from January to May 2015. The levels $PM_{2,5}$, $PM_{10,}$ and the metal elements of TSP were determined. $PM_{2,5}$ and PM_{10} had average concentrations of 73 ± 37 and 138 ± 67 μg/m^3, respectively. The concentration of $PM_{2,5}$ and PM_{10} in all samples were higher than the recommended level in the World Health Organization (WHO) guideline (2005) for 24h and annual concentrations of 25 and 50 μg/m^3, respectively. Nineteen elements detected in TSP samples included the higher concentration group in order: Ca > Fe > Na > Al > Mg > K > Zn and in the lower concentration group: Pb > Mn > Ti > Sr > V > Cr > Cd. The potential sources revealed from element components were discussed.

Keywords: $PM_{2.5}$, PM_{10}, TSP, element, Hanoi.

1. Introduction

Particulate matter (PM), especially $PM_{2.5}$ is the most serious air pollution problem in Vietnam as well as in Asia because of its health impact. Not only are the concentrations of PM, specifically $PM_{2.5}$ and PM_{10}, associated with the health problem, but their chemical components are also among the major contributor to the overall health effect of PM. In addition, the information on compositions of PM could also imply its sources.

Received April 20, 2022. Revised June 17, 2022. Accepted June 24, 2022.
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Studies have been done to evaluate levels and compositions of ambient particulate matter in the urban and sub-urban areas in Hanoi [1-7]. Review information about $PM_{2.5}$ levels has been presented in the study by Nguyen *et al.* (2018) [8]. The levels of $PM_{2.5}$ were some folds higher than the recommended level in WHO guidelines in 2005. The PM concentration varied seasonally: high in the dry season and low in rainy seasons.

While most studies on PM in Hanoi have addressed the level of PM, the chemical components of PM, including metals, are still a gap in research, especially in this research period (2015). In this study, the levels of PM and the metal composition in the spring and early summer in Hanoi were determined for a better understanding of PM characteristics and their sources.

2. Content

2.1. Materials and methods

2.1.1. Sampling and gravimetric measurement of $PM_{2.5}$, PM_{10}, and TSP concentration

PM samples were collected at the rooftop of a five-floor building inside Hanoi University of Science and Technology (HUST) (height: 22.5 m, N: 20°00'17.7"; W: 105°50'49.4") (Figure 1). The sampling started at 3 pm and ended after 24 hours.

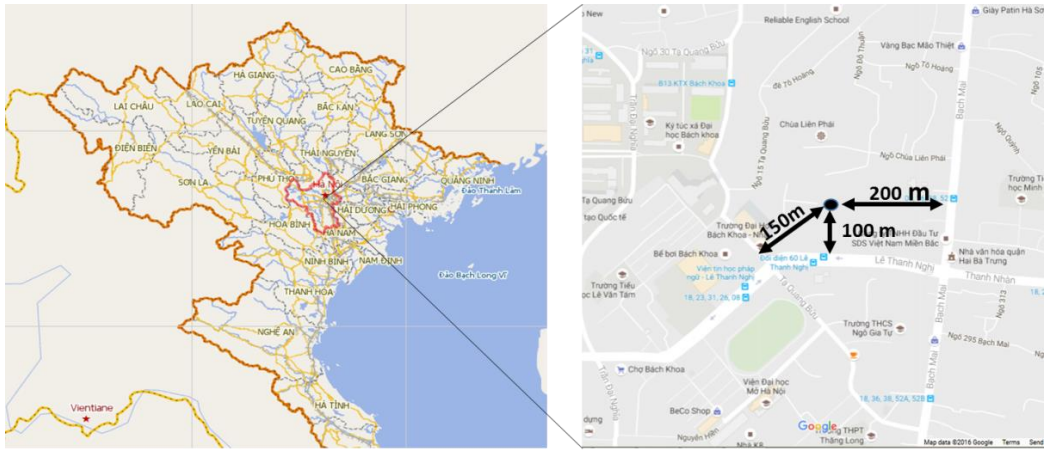

Figure 1. The location and relative distances of the sampling site

Two MiniVol, TM TAS samplers with Airmetrix impactor of the flow rate of 5 L/min was used to collect $PM_{2.5}$ and PM_{10} on a quartz fiber filter (13.8 cm^2 deposition area). A high-volume air sampler - KIMOTO with a flowrate of 60 m^3/h was used to collect TSP on a quartz TSP filter (516 cm^2 area). Details of sampling are presented in Table 1.

PM concentrations were monitored following the research of Co *et al.*, 2014 [3]. Before sampling, the quartz filters were prebaked at 550°C for 5 hours to remove carbonaceous/organic contaminants; afterward, they were kept equilibrated for 24 h at a dedicated temperature (20 ± 5°C) and humidity-controlled (40 ± 10%) weighing room before weighing. The filters were then determined by analytical balance AT261 DeltaRange, Mettler Toledo, Switzerland (precision = 0.01 mg) at HUST. Each pre-weighed filter was kept in a petri-dish and then put in an airtight bag until sampling. After sampling, PM samples were equilibrated again in weighing before post-weighing.

All filters were weighted and recorded three times with a CV value of 0.00 - 0.02 %. A field blank and was determined was subtracted from the net obtained weight of samples. The difference in PM concentration with and without field blank correction was from 3 to 23 %.

2.1.2. Elemental analysis

A quarter of the TSP filter was cut into a small piece of 5×5 mm and put into a Teflon tube followed by adding 5 mL of HNO_3 65%. Metals in the TSP were extracted by microwave-assisted extraction with the digestion program as followed: (1) 20 min of linearly increasing temperature between ambient and 220 ^oC, (2) 25 min of constant temperature 220 ^oC and (3) 20 min of cooling. Afterward, the extract was filtered through a 0.45 µm PTFE filter and added water up to 50 mL. The extracted metals were analyzed by the Inductively coupled plasma mass spectrometry (ICP-MS) technique.

Table 1. Details about sampling volume, date, samples, and meteorological conditions of this research

Sample No.	Start sampling day	Sample volume			Environmental condition				
		$PM_{2,5}$ (L)	*PM_{10} (L)*	*TSP, (m^3)*	*Temp. (^oC)*	*Humidity (%)*	*Wind Direction*	*Wind Velocity (m/s)*	*Pressure (kPa)*
1	14/01/2015	7188	4824	-	20.0	49.0	SW	3.0	101.184
2	21/01/2015	7194	7224	716	22.7	39.1	NW, N	3.5	101.151
3	28/01/2015	7242	7158	722	24.5	63.5	NW, N	6.3	101.195
4	12/02/2015	7176	7200	719	16.4	70.5	NE, N	3.2	101.211
5	01/04/2015	7128	7176	714	30.9	87.1	NE	3.5	101.210
6	07/04/2015	7152	7188	726	20.2	77.9	N	2.9	101.211
7	12/05/2015	7200	7194	721	27.9	64.5	SE	0.3	101.211
8	14/05/2015	7188	7212	717	37.4	56.7	SE	4.3	101.211
9	18/05/2015	7164	7224	714	37.2	56.7	SE	4.26	101.211

Table 1 shows sampling periods, sampling volumes, and environmental conditions including temperature, humidity, wind direction, wind speed, and barometric pressure of each sample. The volume of air was converted to standard conditions (P = 102 kPa, T = 298K).

The following elements were analyzed: K; Na; Ca; Ba; Ni; Pb; Sr; Ti; V; Zn; Fe; Al; Be; Cd; Co; Cr; Cu; Li; As; Se; Sb; Sn; Mg; Mn; Mo; Tl.

2.2. Repeatability and recovery of the analysis method

The blank filters were spiked with a multi-metal standard to check the recovery and the triple samples were analyzed to check the precision. The relative standard deviation for triple samples was in the range of 0.0 - 2.0 %. The recoveries of analysis for elements were in the range of 100 ± 25% (required by TCVN 8246:2009) (Table 2).

Table 2. Reliability of the recovery efficiencies of elements

Elements	Prepared concentration, (µg/L)	Measured concentration (µg/L)				Relative standard deviation (%) (n=3)	Ratio (%)
		Sample No. 1	*Sample No. 2*	*Sample No. 3*	*Average*		
Pb	161	135	137	138	136	1.13	84.7
Cd	3.97	3.15	3.22	3.22	3.19	1.28	80.4
Zn	694	626	640	635	634	1.05	91.3
Fe	9630	7256	7360	7340	7340	1.01	76.2
Co	7.49	6.16	6.30	6.33	6.26	1.44	83.6
Ni	34.6	41.1	40.4	41.6	41.0	1.57	118.7
Al	4360	4280	4280	4290	4290	0.04	98.3
Mn	330	255	260	262	259	1.32	78.4
Mg	10000	11400	11400	11400	11400	0.02	113.6
Cr	198	186	190	187	187	1.16	94.7
As	68.8	52.1	52.5	53.7	52.8	1.64	76.7
Sb	15.81	13.9	14.2	14.0	14.0	1.02	88.7
Sn	14.9	12.4	12.5	12.7	12.5	1.48	84.4
Li	6.97	5.66	5.87	5.84	5.79	1.99	83.0
Ca	67500	61300	61400	61300	61300	0.01	90.9
V	121	99	101	101	100	1.27	83.2
Sr	160	201	194	199	198	1.70	123.5

2.3. Results and discussion

2.3.1. $PM_{2.5}$ and PM_{10} levels

The results of $PM_{2.5}$ and PM_{10} concentrations are presented in Table 3 and Figure 2. PM levels in January and February 2015 (dry season) were very high, except for January 28th due to rain. The average PM_{10} concentration varied from 57 to 285 µg/m^3 with an average of 138 ± 67 µg/m^3. In terms of $PM_{2.5}$, the variation range and average concentration were 39-170 µg/m^3, and 73 ± 37 µg/m^3, respectively. During the investigated period, 02 out of 09 PM_{10} concentrations and 06 out of 09 $PM_{2.5}$ concentrations exceeded the 24h-required levels in national ambient air quality standard QCVN 05:2013/BTNMT (150 µg/m^3 for PM_{10} and 50 µg/m^3 for $PM_{2.5}$). Compared to WHO guidelines (2005), all PM_{10} and $PM_{2.5}$ concentrations were higher than the recommended values (50 µg/m^3 for PM_{10} and 25 µg/m^3 for $PM_{2.5}$).

Table 3. Average, min and max concentrations of 24h $PM_{2,5}$, PM_{10}, ($\mu g/m^3$) (n = 9)

Type of sample	Average concentration (n = 9)	Standard deviation	Min	Max
PM_{10}	138	67	57	285
$PM_{2,5}$	73	37	39	170

High levels of PM at the beginning of the year and lower levels down to the middle of the year were reported in Hanoi in previous studies [3, 6, 9]. In the present study, the concentrations of PM were also higher in January and lower in April, and May (seasonal transition time).

The $PM_{2.5}/PM_{10}$ ratio averaged at 0.55 and ranged from 0.35 to 0.68 (Figure 2). This result showed the significant contribution of fine particles ($PM_{2.5}$) to PM_{10}. Those ratios are in the same range as the previous study in Hanoi [10].

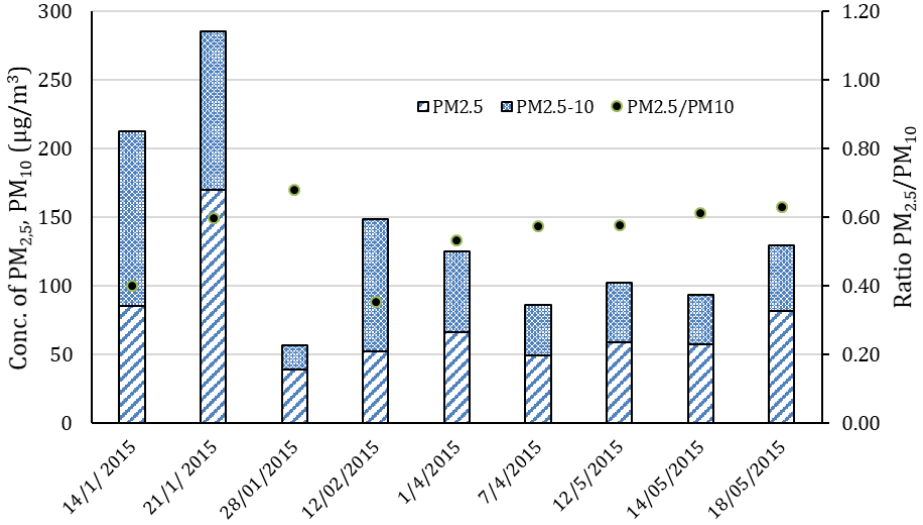

Figure 2. $PM_{2.5}$, PM_{10}, and their ratios

Figure 2 shows that the $PM_{2.5}$ to PM_{10} ratio was highest on January 28, 2015 (0.68) during the strengthening northeast monsoon, leading to a sudden increase in $PM_{2.5}$ concentration in the air.

2.3.2. Element levels

There were 19 metal elements determined in TSP with a recovery rate within 100 ± 25% (meet the requirement of TCVN 8246: 2009), including K, Na, Ca, Ba, Ni, Pb, Sr, Ti, V, Zn, Fe, Al, Cd, Cr, As, Se, Sn, Mg, Mn, Mo. The most abundant metals were Ca, Na, Fe, Zn, Al, Mg, K, Ba (Figure 3a). Most of these elements are naturally abundant in the crust of the earth. The low concentration group were Pb, Mn, Ti, Sr, Cr, V, Mo, Cd, Co, Li, Mn (Figure 3b).

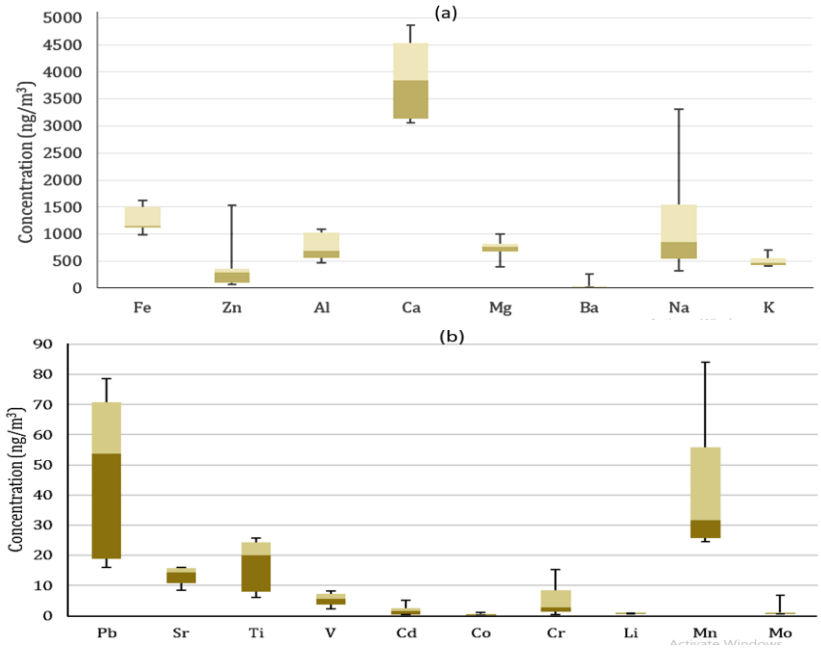

Figure 3. Elemental composition in the TSP samples (whisker graph shows values of 25%, 75%, min, and max) a) high concentration group, b) Low concentration group (n = 8)

Figure 4 shows the percentage of each element in TSP. High concentrations of Ca were probably mainly due to the suspended dust from roads, exhaust of vehicles, and construction sites in the city [11]. High Na-concentrations were likely contributed by the sea-salt aerosol sources during transition time. Fe, Zn, Pb, Al, Mg might have been generated from road dust, exhaust from diesel engines, fuel consumption, construction sites, and metallurgical industry areas around Hanoi.

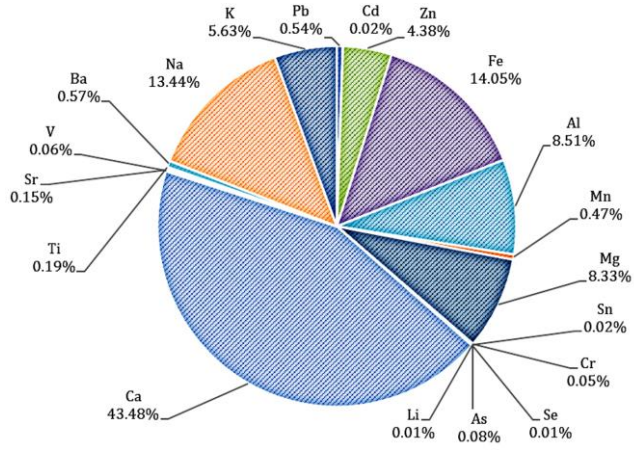

Figure 4. Percentage (%) of the elements on the total number of elements identified in the TSP samples measured from January to May 2015 at HUST (n = 8)

The levels of Pb were significantly lower than in previous studies, reflecting the efficiency of a policy of phasing out leaded gasoline in Hanoi. According to Hopke et al., (2006) [12] in previous years most the lead in the developing world comes from motorcycle gasoline. The average Pb concentration at 48 ± 24 ng/m^3 is within the hign range of data in Vietnam (total Pb in fine and coarse dust is about ~30-700 ng/m^3) in the study of urban air quality in Asia. The average Zn concentration in this study was 390 ± 445 ng/m^3, which is within the high range of data in the study of Hopke *et al*. (2006) [12] (The total Zn concentration in fine and rough dust is about ~ 30-600 ng/m^3). Two-stroke diesel engines are one of the main sources of Zn emissions. Zinc dialkyl dithiophosphate, an additive in diesel as a lubricant, is emitted from the engine exhaust when oil is burnt. Other significant sources of Zn emissions are battery factories, metal processing factories [12], *etc*.

The concentrations of the elements determined in the TSP samples in this study and previous studies are shown in Table 4. The concentrations of elements in the TSP samples in this study and previous studies have the same range. It is noted that those samples were collected from different places and periods, therefore the comparison is relative.

Table 4. The concentrations of the elements determined in the TSP samples, (n=8) ng/m^3

Position	**An Thinh, near power plant**	**Hanoi**		**Ho Chi Minh City**		**Hanoi**		**Rural, Northeast of Hanoi**		**Hanoi**	
Time	11/2001-2/2002	9/2009-9/2010		11/1997-8/1998		2001 - 2008		5-10/2000		1-5/2015	
No. of samples	n = 31	n = 42				n = 780		n = 84		n = 8	
Research	Lewerissa et al, 2007 [11]	Okuda et al, 2013 [4]		Hien P.D. et al, 1999 [12]		Cohen et al, 2010b [6]		Gatari et al, 2006 [13]		This research	
PM type	-	PM_{10}		TSP		$PM_{2,5}$		$PM_{2,5}$		TSP	
Element	C*, ng/m^3	C, ng/m^3	SD	C, ng/m^3	SD	C, ng/m^3	SD	C, ng/m^3	SD	C, ng/m^3	SD
Pb	38000	134	75	163	113	236	0.36	83	82	48	24
Cd	-	-	-	-	-		-	-	-	2	2
Zn	61000	683	581	203	100	487	0.65	100	100	390	445
Fe	280000	2611	991	3078	1054	394	0.29	320	380	1250	216
Al	-	2332	705	2760	1461	224	0.22	-	-	756	227
Mn	21000	138	71	37.8	11.6	61	0.063	24	28	41	20
Mg	-	-	-	640	242	-	-	-	-	740	160
Cr	1400	8.3	3.8	9.4	3.3	5	0.005	3.4	3.6	4	5
As	-	-	-	-	-	-	-	-	-	7	5
Sn	-	-	-	-	-	-	-	-	-	1	1
Li	-	-	-	-	-	-	-	-	-	2	2

Ca	500000	11482	4367	3360	2835	459	0.42	440	510	3860	652
V	5200	15	6	7.6	4.5	-	-	4.8	4.2	5	2
Sr	2300	-	-	-	-	3	0.003	1.9	2	13	3
Ti	31000	260	101	266	106	31	0.027	31	34	17	7
Mo	-	-	-	-	-	-	-	-	-	2	2
Ba	-	-	-	33	11	-	-	-	-	51	81
Na	-	-	-	836	317	123	0.03	-	-	1190	899
K	690000	1678	667	915	425	974	0.63	1200	900	500	92

2.2.3. Analysis of correlation matrices between elements

The correlation between the pairs of Mg and Na was quite high (R^2 = 0.81), indicating a common source of these two metals in the atmosphere.

In term of the main metals present in the crust of the earth, namely Fe, Al, Ca, Ti, Sr, while high correlations were observed for Al-Ti (R^2 = 0.89) and Ca-Sr (R^2 = 0.87), Fe-Al, Fe-Ca, Fe-Ti, and Fe-I were insignificant correlated. Such findings indicated a contribution of anthropogenic sources for Fe in TSP. The possible sources might be from industrial activities involving mechanical processes, i.e. mechanical processing workshops.

According to Gatari *et al.* (2006) [13], the ratio between Mn and V can be used to distinguish between coal-burning and oil-burning emissions. Such a ratio is less than 1 indicating the oil-burning source and greater than 1 indicating the coal-burning source. In our study, the average ratio of Mn/V was 8, which implied a significant contribution of coal-burning emissions to the presence of Mn and V in TSP.

Table 5. Correlation matrix for elements identified in the TSP sample, January to May measurements (N = 8)

	Pb	*Zn*	*Fe*	*Al*	*Mn*	*Ca*	*V*	*Sr*	*Ti*	*K*
Pb	1.00									
Zn	0.58	1.00								
Fe	0.34	-0.05	1.00							
Al	-0.32	-0.14	-0.15	1.00						
Mn	0.49	0.04	0.84	-0.48	1.00					
Ca	-0.64	-0.47	0.01	0.35	-0.45	1.00				
V	-0.06	0.48	-0.79	-0.04	-0.71	-0.09	1.00			
Sr	-0.68	-0.58	-0.32	0.31	-0.66	0.87	0.13	1.00		
Ti	0.00	0.10	0.09	0.89	-0.21	0.14	-0.11	-0.05	1.00	
K	-0.80	-0.54	-0.20	0.69	-0.49	0.55	0.00	0.63	0.42	1.00

3. Conclusions

Nine samples of TSP, PM_{10}, and $PM_{2.5}$ were collected during the spring and early summer period of 2015 on the rooftop of a fifth-floor building in HUST. Concentrations of PM_{10}, and $PM_{2.5}$ were determined, and element compositions of TSP were analyzed.

The levels of $PM_{2.5}$ and PM_{10} were high with an average of 73 and 138 $\mu g/m^3$, respectively. There were 2 out of 9 PM_{10} samples and 3 out of 9 $PM_{2.5}$ samples have higher concentrations than the limited value in QCVN 05:2013/BTNMT. All observed $PM_{2.5}$ and PM_{10} concentrations exceeded the WHO recommendation (PM_{10} -50 $\mu g/m^3$; $PM_{2.5}$ - 25 $\mu g/m^3$). The concentrations of PM were lower in April (seasonal change), compared with samples in the dry season in January and February.

Nineteen metallic elements were analyzed and detected in the TSP sample, including Na; Ca; Ba; Ni; Pb; Sr; Ti; V; Zn; Fe; Al; Cd; Cr; As; Se; Sn; Mg; Mn; Mo. Levels of elements in the higher concentration group were Ca>Fe>Na>Al>Mg>K>Zn and in the lower concentration group were Pb>Mn>Ti>Sr>V>Cr>Cd. The results from correlation evaluation between elements initially explained the sources of metals in TSP.

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