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JOURNAL OF  
ENVIRONMENTAL  
SCIENCES  
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# Chemical characteristics, oxidative potential, and sources of PM<sub>2.5</sub> in wintertime in Lahore and Peshawar, Pakistan

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## ARTICLE INFO

### Article history:

Received 16 April 2020

Revised 2 September 2020

Accepted 6 September 2020

Available online 1 October 2020

### Keywords:

Air pollution

DTT

Health risk

Oxidative potential

Source apportionment

## ABSTRACT

The chemical characteristics, oxidative potential, and sources of PM<sub>2.5</sub> were analyzed at the urban sites of Lahore and Peshawar, Pakistan in February 2019. Carbonaceous species, water soluble ions, and metal elements were measured to investigate the chemical composition and sources of PM<sub>2.5</sub>. The dithiothreitol (DTT) consumption rate was measured to evaluate the oxidative potential of PM<sub>2.5</sub>. Both cities showed a high exposure risk of PM<sub>2.5</sub> regarding its oxidative potential (DTT<sub>v</sub>). Carbonaceous and some of the elemental species of PM<sub>2.5</sub> correlated well with DTT<sub>v</sub> in both Lahore and Peshawar. Besides, the DTT<sub>v</sub> of PM<sub>2.5</sub> in Lahore showed significant positive correlation with most of the measured water soluble ions, however, ions were DTT-inactive in Peshawar. Due to the higher proportions of carbonaceous species and metal elements, Peshawar showed higher mass-normalized DTT activity of PM<sub>2.5</sub> compared to Lahore although the average PM<sub>2.5</sub> concentration in Peshawar was lower. The high concentrations of toxic metals also posed serious non-carcinogenic and carcinogenic risks to the residents of both cities. Principle component analysis coupled with multiple linear regression was applied to investigate different source contributions to PM<sub>2.5</sub> and its oxidative potential. Mixed sources of traffic and road dust resuspension and coal combustion, direct vehicle emission, and biomass burning and formation of secondary aerosol were identified as the major sources of PM<sub>2.5</sub> in both cities. The findings of this study provide important data for evaluation of the potential health risks of PM<sub>2.5</sub> and for formulation of efficient control strategies in major cities of Pakistan.

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## Introduction

Rapid urbanization and unplanned industrialization in Pakistan have resulted in substantial anthropogenic emissions of

air pollutants that impose significant environmental and public health impacts (Rasheed et al., 2015; Ahmad et al., 2020). Fine particulate matter (PM<sub>2.5</sub>) is a major atmospheric pollutant in Pakistan. Being two ancient megacities in Pakistan, the air pollution status of Lahore and Peshawar have attracted great interests. The mean mass concentration of PM<sub>2.5</sub>

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reported in Lahore ranged between 91–194  $\mu\text{g}\cdot\text{m}^{-3}$  (Stone et al., 2010; Alam et al., 2011; Khanum et al., 2017; Ahmad et al., 2020), and the mean mass concentration of  $\text{PM}_{2.5}$  in Peshawar in November 2016 was 286  $\mu\text{g}\cdot\text{m}^{-3}$  (Zeb et al., 2018). The concentration of  $\text{PM}_{2.5}$  in both Lahore and Peshawar appeared higher than that recorded in several other highly polluted megacities worldwide (Ahmad et al., 2020). The major PM sources in Lahore were emissions from power plants, industries, and vehicles (Parekh et al., 2001), and road dust re-suspension, industrial emissions, vehicle emissions, emissions from brick kiln and domestic combustion sources were included in the major sources of PM in Peshawar (Alam et al., 2015).

The toxicity of particulate matter is determined by both its size and composition. In some cases, researchers have verified that particle composition may contribute more dramatically than particle size (Karlsson et al., 2009; Feng et al., 2019). Several epidemiological studies have documented the increased morbidity and mortality of various diseases due to enhanced  $\text{PM}_{2.5}$  concentration (Cao et al., 2012). One of the commonly proposed theories for how aerosols impact human health is that when inhaled, several types of aerosols with particular composition can generate reactive oxygen species (ROS) in-situ in human body. ROS production creates an imbalance in the body between oxidants and antioxidants and contributes to DNA damage, cell death, and systematic inflammation in human body (Amatullah et al., 2012; Xu et al., 2018).

The oxidative potential (OP) of  $\text{PM}_{2.5}$  has been widely applied to evaluate the oxidation ability of  $\text{PM}_{2.5}$  as well as its health impact (Crobeddu et al., 2017). The oxidative potential of atmospheric particulate matter can be quantified by measuring the dithiothreitol (DTT) consumption rate of particulate matter, with DTT serving as a substitute for cellular reductants (Cho et al., 2005). Generally, the chemical components loaded in  $\text{PM}_{2.5}$  can catalyze the electronic transfer from DTT to oxygen, producing reactive radicals such as superoxide radicals. This cell-free DTT assay enables the evaluation of the exposure-relevant toxicity of  $\text{PM}_{2.5}$  with the advantages of easy controllability and quick result reading (Vreeland et al., 2017). Various studies have reported the significant correlation between DTT and different chemical components of particulate matter in the atmosphere, including humic-like substances, water soluble organic compounds and water soluble transition metals (Verma et al., 2012, 2014; Chirizzi et al., 2017). However, the contributions of respective PM sources to its oxidative potential remain largely unresolved because of the complex interactions among chemicals that are DTT-active.

The objectives of this research were to examine the chemical characteristics and oxidative potential of  $\text{PM}_{2.5}$  in the heavily polluted urban sites of both Lahore and Peshawar, and identify the major sources of  $\text{PM}_{2.5}$  in both cities. The links between specific  $\text{PM}_{2.5}$  components and the DTT activity of  $\text{PM}_{2.5}$  were also investigated. This work is the first in Pakistan that reports the cell-free oxidative potential of  $\text{PM}_{2.5}$  in major cities of Pakistan and investigates the  $\text{PM}_{2.5}$  species responsible for its oxidative potential. The results of this study provide important data and evidence for further evaluation of the potential health risks of  $\text{PM}_{2.5}$  in major cities of Pakistan and formulation of efficient air-pollution control measures.

## 1. Methods and materials

### 1.1. $\text{PM}_{2.5}$ sampling and chemical analysis

The sampling of  $\text{PM}_{2.5}$  was carried out on the roof of a four-story building (around 10–12 m above the ground) in the urban areas of Lahore (31°32'N 74°22'E) and Peshawar (34°01'N 71°35'E), respectively. The 12-hr day and night  $\text{PM}_{2.5}$  samples were collected for a consecutive sampling period of 15 days in February 2019 at each sampling site. In total, 60 samples of  $\text{PM}_{2.5}$  were collected. The concentrations of carbonaceous species, water soluble ions and metal elements were analyzed in the  $\text{PM}_{2.5}$  samples. Details of the  $\text{PM}_{2.5}$  sampling procedure and the measurement procedure of carbonaceous species and water soluble ions are referred to our previous study (Ahmad et al., 2020).

The measured metals included Li, Al, V, Cr, Mn, Mg, Fe, Cu, Zn, Ga, Cd, Pb, Be, Ti, As, Bi, Sn, Sr, Ba, Tl, Co and Ni. The fourth part of each filter was cut into pieces and digested with a mixture of 10 mL of acid (167.5 mL HCl and 55.5 mL  $\text{HNO}_3$ , diluted to a volume of 1 L with ultrapure water). The digestion was maintained at 200 °C for 20 min using a microwave digestion apparatus. After cooling, the extracted samples were filtered through a Teflon filter of 0.45  $\mu\text{m}$  pore size and diluted with ultrapure water to 40 mL. Inductively coupled plasma-mass spectrometry (iCAP TQ ICP-MS, Thermo Scientific) was then employed to measure the metals in the solution.

Using the same methods as for sample filters, the blank filters were measured to correct background concentrations of carbonaceous species, ions and metals.

### 1.2. Measurement of oxidative potential by DTT consumption rate

A quarter of each sample filter was cut, extracted, and filtered similar to the pre-treatment procedure of water soluble components. A mixture of 3 mL sample extract, 1.2 mL DTT dilute solution (3 mM DTT dissolved in potassium phosphate buffer), and 1.8 mL 0.5 M potassium phosphate buffer of pH 7.4 was incubated at 37 °C using a thermo-mixer. A 200  $\mu\text{L}$  mixture of the reaction solution was mixed with 2.5 mL 0.4 M Tris-HCl solution and 0.3 mL 10 mM 5,5'-dithio-bis(2-nitrobenzoic acid (DTNB) at fixed time intervals of 0, 10, 20, 30, 40, and 50 min, which formed a yellow colored complex, 2-nitro-5-benzoic acid (TNB) with DTT. A spectrophotometer was used to calculate TNB absorbance at wavelengths of 412 nm. A standard solution for DTT consumption rate was prepared by mixing 2.5 mL Tris-HCl solution and 0.3 mL DTNB solution with 200  $\mu\text{L}$  DTT dilute solution. The blank consumption rate of DTT by Milli-Q water was simultaneously measured. The DTT consumption rate was estimated by the slope of the linear regression equation with  $R^2 > 0.98$ . For the correction of the result of  $\text{PM}_{2.5}$  samples, the blank and standard consumption rates were applied. The air-volume normalized DTT consumption rate ( $\text{DTT}_v$ ) was considered to be equivalent to human exposure, and the  $\text{PM}_{2.5}$ -mass normalized ( $\text{DTT}_m$ ) was an indicator of the intrinsic oxidative potential of  $\text{PM}_{2.5}$ .

### 1.3. Calculation of source contributions to $PM_{2.5}$ and its oxidative potential

Principle component analysis coupled with multiple linear regression (PCA/MLR) was applied to investigate different source contributions to  $PM_{2.5}$  and its oxidative potential. Statistically, PCA is a dimension reduction technique that produces a limited number of factors to explain the majority of the data variation within a large data set. PCA was performed by the software package SPSS with concentrations of the measured carbon fractions, ions, and metals as variables for the PCA analysis. The principal components were selected with eigenvalue greater than one, and Varimax was applied for rotation. The MLR analysis was conducted between  $PM_{2.5}$  or DTTv activity (dependent variables) and the measured chemical components (independent variables), which eliminated poorly associated variables and determined the key species responsible for  $PM_{2.5}$  and its oxidative potential. MLR was conducted to calculate the contributions of different sources to  $PM_{2.5}$  and its oxidative potential (i.e., DTTv) by the same procedure described in detail by Guo et al. (2004) and Yang et al. (2005).

## 2. Results and discussion

### 2.1. Mass concentrations of $PM_{2.5}$ and its chemical components

#### 2.1.1. $PM_{2.5}$

Table 1 shows the average and range of  $PM_{2.5}$  mass concentrations and its chemical components in Lahore and Peshawar during the sampling period in February 2019. Lahore (31°32'N 74°22'E) is the second-largest city of Pakistan, with an estimated population of 9.01 million, around 1986 industries and 2.7 million motor vehicles. The metropolitan area of Lahore has been expanded from 332 km<sup>2</sup> to around 1000 km<sup>2</sup> due to the rapid urbanization. Vehicle and industrial emissions are the major sources of air pollution in the city (Stone et al., 2010). Lahore is about 217 m above the sea level. The climate of Lahore is hot semi-arid, with monsoon seasons and warm dry winters. Peshawar (34°01'N 71°35'E) is the capital of Khyber Pakhtunkhwa (KP) province, with an estimated population of 3.6–4 million and a total area of approximately 1257 km<sup>2</sup>. Peshawar is also Pakistan's industrial city, and is considered one of the major steel centers of Pakistan (Alam et al., 2011). The elevation of Peshawar from the sea level is about 539 m. The climate of Peshawar is semi-arid.

As shown in Table 1, the concentration of  $PM_{2.5}$  in Lahore and Peshawar varied from 184 to 898  $\mu\text{g}/\text{m}^3$  and 147 to 852  $\mu\text{g}/\text{m}^3$  with an average of  $522 \pm 222$  and  $370 \pm 176$   $\mu\text{g}/\text{m}^3$ , respectively. In Lahore and Peshawar, the concentration of  $PM_{2.5}$  in the current study were significantly higher than those reported in the previous studies conducted in Pakistan and India (Alam et al., 2015; Das et al., 2015; Shahid et al., 2016; Kumar et al., 2018; Mukherjee and Agrawal, 2018; Zeb et al., 2018; Sahu et al., 2019). Furthermore, the  $PM_{2.5}$  concentration in Lahore in February of 2019 in this study with an average of  $522 \pm 222$   $\mu\text{g}/\text{m}^3$  was much higher than that in July of 2018 in our previous study with an average of  $170 \pm 54.0$   $\mu\text{g}/\text{m}^3$

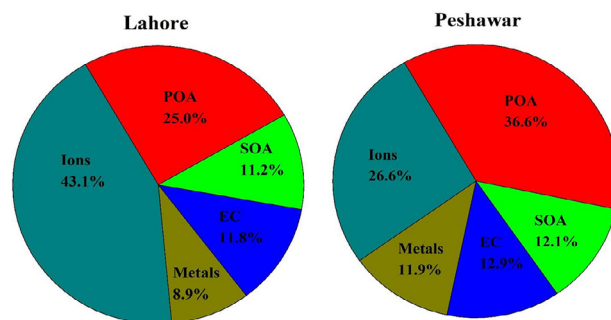


Fig. 1 – Percentages of the  $PM_{2.5}$  identified components in Lahore and Peshawar during the sampling period in February 2019.

(Ahmad et al., 2020). Biomass burning, construction activities, road dust re-suspension, industrial and vehicular emissions, two-stroke vehicles, small-scale brick kiln industry, and municipal solid waste burning are the possible sources of  $PM_{2.5}$  in both cities (Khan et al., 2008; Shivani et al., 2018). Compared to the much lower concentration in summer (Ahmad et al., 2020), the  $PM_{2.5}$  pollution in the winter season was probably attributable to the low inversion layer and high atmospheric stability, therefore the pollutants were trapped near the surface (Bisht et al., 2015). The concentration of  $PM_{2.5}$  differed greatly in different days, due to the impact of weather conditions. The concentration of  $PM_{2.5}$  differed between the cities being analyzed, with significantly higher concentration in Lahore as compared to Peshawar.

#### 2.1.2. Carbonaceous species

Carbonaceous species were the dominant species in  $PM_{2.5}$  in both Lahore and Peshawar during the sampling period. Table 1 depicts the mass concentrations of the carbonaceous components including organic carbon (OC), elemental carbon (EC), secondary organic carbon (SOC), and water-soluble organic carbon (WSOC). Based on the OC and EC mass concentrations, the mass concentration of secondary organic aerosols (SOA) was estimated by  $SOA = (OC - EC \times (OC/EC)_{\min}) \times 1.6$  using the traditional OC/EC minimum ratio method (Strader et al., 1999; Wu et al., 2009), and the mass concentration of primary organic aerosols (POA) was thereafter calculated by  $POA = OC \times 1.6 - SOA$ . Fig. 1 shows the percentages of POA, SOA, EC, ions and metals in the identified mass of  $PM_{2.5}$  in Lahore and Peshawar. The average concentrations of OC and EC were 50.7  $\mu\text{g}/\text{m}^3$  and 26.5  $\mu\text{g}/\text{m}^3$  respectively in Lahore, and 42.1  $\mu\text{g}/\text{m}^3$  and 17.8  $\mu\text{g}/\text{m}^3$  respectively in Peshawar. There was a strong correlation between OC and EC with a correlation coefficient of 0.93 in Lahore and 0.94 in Peshawar, suggesting that both OC and EC were emitted from the same major sources in both cities. The high concentrations of carbonaceous particles in major cities of Pakistan resulted from the extensive use of diesel engines and unrefined coal in various industrial units (Alam et al., 2015). The increased combustion of coal and burning of biomass as well as the unfavorable weather conditions in winter may have aggravated the OC and EC pollution in winter. The carbonaceous species contributed higher to the mass of  $PM_{2.5}$  in Peshawar

**Table 1 – The statistical data of the concentrations of measured species in PM<sub>2.5</sub> and the measured DTT<sub>v</sub> (nmol/(min·m<sup>3</sup>)) and DTT<sub>m</sub> (pmol/(min·μg)), and correlation coefficient (R) of PM<sub>2.5</sub> and its species with DTT<sub>v</sub>.**

	Mean±SD	Lahore Range	R	Mean±SD	Peshawar Range	R
<i>PM<sub>2.5</sub>, carbonaceous species and ions (μg/m<sup>3</sup>)</i>						
PM <sub>2.5</sub>	522 ± 222	184–898	0.48**	370 ± 176	147–852	0.64**
OC	50.7 ± 30.5	11.9–110	0.60**	42.1 ± 18.9	11.7–82.7	0.59**
EC	26.5 ± 18.0	4.5–64.9	0.60**	17.8 ± 9.1	4.1–33.3	0.50**
WSOC	35.2 ± 14.9	14.7–69.9	0.46*	22.9 ± 9.2	8.2–41.5	0.60**
SOC	15.7 ± 11.3	0.0–43.7	0.43*	10.5 ± 6.4	0.0–25.0	0.50**
NO <sub>3</sub> <sup>−</sup>	20.6 ± 11.7	4.3–47.4	0.39*	8.4 ± 5.5	1.5–25.4	0.28
SO <sub>4</sub> <sup>2−</sup>	24.2 ± 12.3	5.9–58.9	0.27	7.3 ± 3.3	2.8–15.4	0.20
Cl <sup>−</sup>	27.3 ± 18.8	1.5–73.1	0.29	6.9 ± 4.0	1.1–16.2	0.27
Na <sup>+</sup>	1.3 ± 0.6	0.3–2.9	0.44*	1.3 ± 0.8	0.3–3.5	0.10
NH <sub>4</sub> <sup>+</sup>	14.7 ± 8.2	1.3–30.3	0.38*	2.1 ± 1.3	0.5–5.9	0.34
K <sup>+</sup>	4.9 ± 2.5	0.7–10.5	0.40*	1.9 ± 1.1	0.6–4.4	0.23
Mg <sup>2+</sup>	0.6 ± 0.2	0.2–1.3	0.51**	0.6 ± 0.3	0.2–1.2	0.08
Ca <sup>2+</sup>	3.2 ± 1.7	0.8–8.5	0.50**	8.1 ± 3.1	1.6–15.1	0.13
<i>Metals (ng·m<sup>−3</sup>)</i>						
Li	2.4 ± 2.9	BDL–10.0	0.39*	2.8 ± 3.3	BDL–13.0	0.74**
Mg	1170 ± 853	429–3810	0.41*	2080 ± 1220	441–6110	0.72**
Al	2280 ± 2130	483–9250	0.41*	3910 ± 2820	542–14000	0.74**
Ti	94.6 ± 88.4	14.8–378	0.42*	154 ± 115	13.1–560	0.74**
V	5.5 ± 7.6	BDL–26.4	0.39*	4.2 ± 6.2	BDL–25.2	0.75**
Cr	66.5 ± 55.3	14.7–252	−0.04	155 ± 150	12–574	0.01
Mn	170 ± 116	53–446	0.40*	125 ± 75	15–356	0.66**
Fe	4490 ± 4710	1000–19700	0.44*	4380 ± 2760	743–12900	0.69**
Ni	28.7 ± 26.5	3.9–118	−0.03	72.0 ± 73.1	1.7–281	0.02
Cu	174 ± 129	44–539	0.47**	26.7 ± 16.4	5.4–80.7	0.64**
Zn	7290 ± 6050	573–24700	0.12	4720 ± 5260	152–21700	0.14
As	17.6 ± 19.1	1.5–67.1	0.31	0.0 ± 1.1	BDL–3.3	0.68**
Sr	37.7 ± 23.2	12.9–113	0.43*	78.5 ± 45.8	14.1–217	0.77**
Cd	64.0 ± 77.0	4.8–414	0.11	22.7 ± 22.1	0.2–92.1	0.24
Sn	92.8 ± 74.3	12.3–262	0.26	30.1 ± 29.1	BDL–122	0.28
Ba	69.7 ± 42.0	23.3–188	0.35	52.6 ± 27.3	16.4–137	0.71**
Pb	3810 ± 5610	178–18100	0.16	563 ± 512	32–2090	0.21
Bi	11.8 ± 11.6	BDL–32.0	0.09	3.9 ± 11.4	BDL–23.7	0.18
DTT <sub>v</sub>	8.9 ± 3.8	1.5–14.7		9.3 ± 3.9	2.0–21.7	
DTT <sub>m</sub>	18.9 ± 10.5	4.9–44.1		27.7 ± 12.1	7.1–63.4	

SD: standard deviation; R: correlation coefficient  
 \* :  $p < 0.05$   
 \*\* :  $p < 0.01$ ; BDL: below detection limit.

than in Lahore. Peshawar is one of the major steel centers of Pakistan (Alam et al., 2011). A large amount of carbonaceous species from the extensive emissions of steel mills probably contributed highly to the PM<sub>2.5</sub> pollution in Peshawar.

The SOC contribution to OC was 16% and 13% in Lahore and Peshawar, respectively, while the SOC/OC ratio in winter could be higher than 50% in other urban areas such as Beijing (Yu et al., 2019a). Besides, the wintertime SOC/OC ratio in Lahore in this study was also much lower than the summertime value of 47% in our previous study (Ahmad et al., 2020). While the secondary formation processes contributed significantly to OC during the summertime of Lahore (Ahmad et al., 2020), the vast majority of OC in winter was again evidenced to originate from the primary emissions in both cities. Because SOC is closely related to WSOC, WSOC can be used as a marker of SOA formation (Kim et al., 2011). As shown in Table 1, the mean concentration of WSOC in Lahore and Peshawar were 35.2 and 22.9 μg/m<sup>3</sup> respectively, over two times of that of SOC in both

cities. In comparison, the mean concentration of WSOC in Lahore was 10.7 μg/m<sup>3</sup> and 42.6% higher than that of SOC during the summertime of Lahore (Ahmad et al., 2020). Compared to the summertime, the primary emissions dominated in WSOC pollution in winter. In addition to biomass burning, other primary sources such as exhaust emissions from vehicles and residual oil combustion residual can also lead to WSOC pollution (Zhang et al., 2007; Kaul et al., 2014; Vodicka et al., 2015).

### 2.1.3. Water soluble ions

The mean concentrations of water-soluble cations and anions in Lahore and Peshawar are listed in Table 1. In general, water-soluble ions in Lahore were dominated by Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, NO<sub>3</sub><sup>−</sup>, and NH<sub>4</sub><sup>+</sup>, and in Peshawar by NO<sub>3</sub><sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, Cl<sup>−</sup>, and Ca<sup>+</sup>. Total water-soluble ions accounted for about 43.1% in Lahore and 26.6% in Peshawar to the identified mass of PM<sub>2.5</sub> (Fig. 1). The SO<sub>2</sub> and NO<sub>x</sub> atmospheric reactions primarily produced the atmospheric particulate SO<sub>4</sub><sup>2−</sup> and NO<sub>3</sub><sup>−</sup>. Coal combustion



is usually the main source of  $\text{SO}_2$ , while  $\text{NO}_x$  is commonly released by the combustion processes of vehicles and coal power plants (Chen et al., 2014). The higher contribution of secondary ionic species ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ ) to the mass of  $\text{PM}_{2.5}$  in Lahore indicated higher contribution of secondary inorganic formation to  $\text{PM}_{2.5}$  pollution in Lahore (Wu et al., 2016). The higher  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations in Lahore also showed its acidic nature of  $\text{PM}_{2.5}$  (Satsangi et al., 2013). Peshawar showed higher  $\text{Ca}^{2+}$  concentration in  $\text{PM}_{2.5}$ , which may be due to the drier weather conditions that contribute to the soil particles or dust re-suspension (Liu et al., 2018). The construction of the Bus Rapid Transit (BRT) in Peshawar city and the stone crushing machines installed on the border with Peshawar in Khyber district also contributed to the higher concentration of  $\text{Ca}^{2+}$  in Peshawar.  $\text{Cl}^-$  shows a high concentration in marine salt particles and can also be emitted from the coal and biomass combustion (Duan et al., 2006). In Lahore and Peshawar, the average mass ratio of  $\text{Cl}^-/\text{Na}^+$  was much greater than that of seawater (1.797) (Arhami et al., 2018), suggesting the major contribution of combustion processes.  $\text{K}^+$  is a good tracer of biomass burning (Ding et al., 2012; Pachon et al., 2013). In both cities, biomass combustion for cooking and heating in winter was widespread, which resulted in the high loading of  $\text{K}^+$ .

#### 2.1.4. Metal elements

The mean concentrations with standard deviation of metal elements are listed in Table 1. The metals such as Al, Pb, Zn, Fe, and Mg showed high proportions, accounting up to 95% of the measured elements. Metals such as Li, V, Cr, Mn, Cu, Cd, Ti, As, Bi, Sn, Sr, Ba, and Ni showed lower concentrations, and metals including Ga, Be, Co and Tl were below detection limit and not listed in Table 1. The average concentrations of the major metals Al, Pb, Zn, Fe, and Mg reported in the current study were significantly higher than in previous studies in Lahore (Schneidmesser et al., 2010), Karachi (Mansha et al., 2012), and Peshawar (Alam et al., 2015; Zeb et al., 2018). In Lahore and Peshawar, metals contributed 8.9% and 11.9% respectively to the identified mass of  $\text{PM}_{2.5}$  (Fig. 1). Among the major metal elements, Al mostly comes from wind-blown soil dust and re-suspension of road dust. Pb is emitted from battery units, and also emitted from paint, alloy, plastics and rubber industries (Haritash and Kaushik, 2007), which are very common on large and small scales in both studied cities. The fuel combustion in vehicles of both cities may also emit high concentration of Pb that causes health problems in human as well as animals (Mansha et al., 2012). The high concentration of Zn in both cities is largely caused by the tyre wear and burning of fuels in cars, buses, trucks, motorcycles, and rickshaws, etc. (Klimaszewska et al., 2007). The incessant uses of motorcycles and motorbikes in both cities highly emit Zn by the combustion of lubrication oil (Begum et al., 2013). Fe is a good tracer of steel industry or steel metallurgy, and steel mills are located in both cities (Mouli et al., 2006).

## 2.2. DTT activity of $\text{PM}_{2.5}$

### 2.2.1. Averages and diurnal variations of DTT

As shown in Table 1, the average values of the volume-normalized ( $\text{DTT}_v$ ) and mass-normalized ( $\text{DTT}_m$ ) DTT activ-

ity of  $\text{PM}_{2.5}$  were  $8.9 \text{ nmol}/(\text{min}\cdot\text{m}^3)$  and  $18.9 \text{ pmol}/(\text{min}\cdot\mu\text{g})$  in Lahore, and  $9.3 \text{ nmol}/(\text{min}\cdot\text{m}^3)$  and  $27.7 \text{ pmol}/(\text{min}\cdot\mu\text{g})$  in Peshawar, respectively. The inherent oxidative potential of PM is assessed by its mass normalized DTT activity while the evaluation of inhalation and population exposure risk of PM regarding its oxidative potential is measured by its volume normalized DTT activity. The much higher  $\text{DTT}_m$  in Peshawar than in Lahore indicated the greater oxidative potential of  $\text{PM}_{2.5}$  in Peshawar on the chemical basis. For comparison with the current study, the average  $\text{DTT}_v$  for the fine particulate matter in two Indian cities, i.e., Bangalore ( $0.79 \pm 0.13 \text{ nmol DTT}/(\text{min}\cdot\text{m}^3)$ , Vreeland et al., 2016), and Patiala ( $3.8 \pm 1.4 \text{ nmol DTT}/(\text{min}\cdot\text{m}^3)$ , Patel and Rastogi, 2018), were significantly lower, while that in Beijing ( $12.6 \pm 6.82 \text{ nmol DTT}/(\text{min}\cdot\text{m}^3)$ , Yu et al., 2019b) was higher. However, the average  $\text{DTT}_m$  in both cities were lower than that in Beijing ( $0.13 \pm 0.10 \text{ nmol}/(\text{min}\cdot\mu\text{g})$ , Yu et al., 2019b), Patiala ( $27 \pm 8 \text{ pmol}/(\text{min}\cdot\mu\text{g})$ , Patel and Rastogi, 2018), and Bangalore ( $107 \pm 25 \text{ pmol}/(\text{min}\cdot\mu\text{g})$ , Vreeland et al., 2016).

The high concentration of  $\text{PM}_{2.5}$  over the two cities highly contributed to the high level of  $\text{DTT}_v$ . The diurnal variations of  $\text{PM}_{2.5}$  and  $\text{DTT}_v$  in the winter season in Lahore and Peshawar were plotted and shown in Fig. 2. At daytime, the concentration of  $\text{PM}_{2.5}$  in Lahore and Peshawar were significantly higher than at nighttime, suggesting significant sources of  $\text{PM}_{2.5}$  that existed during the daytime. Compared to  $\text{PM}_{2.5}$ , the day-night differences of  $\text{DTT}_v$  in the two cities were less significant with slightly higher values in the daytime. Moreover, the  $\text{DTT}_v$  of  $\text{PM}_{2.5}$  in Peshawar was even higher than that in Lahore while the situation of mass concentrations of  $\text{PM}_{2.5}$  was on the contrary, suggesting that changes in  $\text{PM}_{2.5}$  composition also contributed to the variations of  $\text{DTT}_v$ .

### 2.2.2. Correlations of $\text{DTT}_v$ with $\text{PM}_{2.5}$ and its chemical components

The chemical composition of  $\text{PM}_{2.5}$  cannot be ignored when relating the risk factors of PM mass with various disease mortality and morbidity (Patel and Rastogi, 2018). Table 1 shows the correlation coefficients of  $\text{DTT}_v$  with  $\text{PM}_{2.5}$  and its chemical components in both Lahore and Peshawar during the sampling period. The measured  $\text{DTT}_v$  is considered to be a product of organics, metals, inorganics, and other unidentified chemical species of  $\text{PM}_{2.5}$ , and our study was based on chemical species that are generally linked with the oxidative potential of  $\text{PM}_{2.5}$ .

As shown in Table 1, carbonaceous species and some of the elemental and metallic species of  $\text{PM}_{2.5}$  in both Lahore and Peshawar correlated well with the volume-normalized DTT activity. In addition to carbonaceous species (OC, EC, WSOC, SOC), the  $\text{DTT}_v$  of  $\text{PM}_{2.5}$  in Lahore showed significant positive correlation with most of the measured water soluble ions such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^+$  and some of the measured metal elements such as Cu, Fe, Mn, Sr, Mg, Al, Ti, V, while the  $\text{DTT}_v$  of  $\text{PM}_{2.5}$  in Peshawar showed significant positive correlation with most of the measured metal elements but weak correlation with the measured water soluble ions. Moreover, the  $\text{DTT}_v$  of  $\text{PM}_{2.5}$  in Peshawar showed stronger positive correlation with the measured metal elements than in Lahore. Similar strong positive correlations between DTT activity and OC, EC, and water-soluble transition metals have

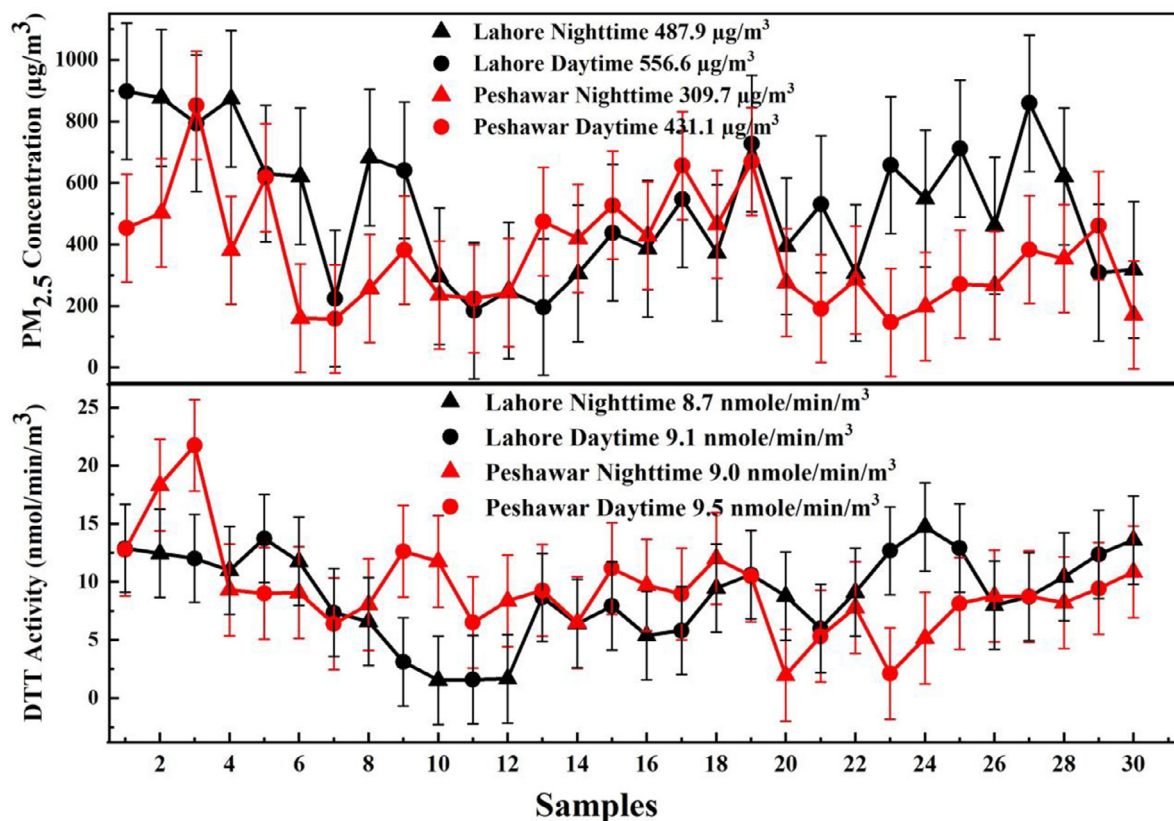


Fig. 2 – The diurnal variations of  $PM_{2.5}$  and its volume-normalized DTT activity in Lahore and Peshawar during the sampling period in February 2019.

also been reported in some previous studies under different environments (Verma et al., 2012, 2014; Chirizzi et al., 2017), whereas other earlier studies have shown that inorganic ions are DTT inactive (Ntziachristos et al., 2007; Verma et al., 2012). Contributions from different combustion sources such as coal combustion, industrial activities, biomass burning, and vehicle emission, as well as secondary oxidation of  $PM_{2.5}$  in the atmosphere have been attributed to the significant correlations of DTTv with metallic and carbonaceous species. (Verma et al., 2014). The ionic species  $Mg^{2+}$  and  $Ca^{2+}$  showed strong correlations with DTTv in Lahore, which indicated the existence of a dust related oxidation risk.

In summary, the results of the correlation analysis showed that the carbonaceous species of  $PM_{2.5}$  were DTT active in both cities, while the inorganic ions and metals showed different behaviors. In Lahore certain ions were involved in DTT activity whereas in Peshawar inorganic ions did not show DTT activity. The OP activity of PM could result from the generation of ROS by the synergistic or antagonistic interactions between different chemical species, which cannot be entirely explained through the correlation analysis with specific components (Xiong et al., 2017). Nevertheless, based on the correlation analysis and the higher mass-normalized DTT activity in Peshawar compared to Lahore, it is inferred that the DTT activity of PM could be highly attributable to the interactions between organic species and metal species while water soluble ions are less involved in the ROS generation process.

### 2.3. Sources of $PM_{2.5}$ and its oxidative potential

#### 2.3.1. Source identification by PCA analysis

In Lahore and Peshawar, principal component analysis (PCA) and multiple linear regression (MLR) were performed to determine the sources of  $PM_{2.5}$  and their contributions to  $PM_{2.5}$  and its oxidative potential. The results of the principal component analysis in both cities are outlined in Table 2. Varimax rotated factor analysis, based on the factor loading, was used to identify the principal components. In both cities three factors were identified as the major sources of  $PM_{2.5}$ , including mixed sources, direct vehicle emission, and biomass burning and secondary aerosol formation. The three factors accounted for approximately 56.3%, 11.5% and 10.3% of the total variance in Lahore and 53.7%, 9.9%, and 16.4% of the total variance in Peshawar, respectively.

The species displaying a high loading in each factor are marked in bold in Table 2. In Lahore, Factor 1 of the PCA result was highly loaded with Li, Mg, Al, Ti, V, Mn, Fe, Sr, Ba and  $Ca^{2+}$ . Al, Ti, Fe, Sr, Ba and  $Ca^{2+}$  have been used as markers of dust resuspension. In particular, Al, Ba and Fe are brake wear markers, and can serve as traffic re-suspension indicators (Srimuruganandam and Nagendra 2012; Yao et al., 2016). Besides, Mn and Fe are closely associated with coal combustion in different industrial activities (Kulshrestha et al., 2009). Therefore, Factor 1 represents mixed sources of traffic and road dust resuspension and coal combustion. Factor 2 was

Table 2 – Principal component analysis of PM<sub>2.5</sub> in Lahore and Peshawar.

	Lahore			Peshawar		
	Mixed sources <sup>a</sup>	Direct vehicle emission	Biomass burning & SAF <sup>b</sup>	Mixed sources <sup>a</sup>	Biomass burning & SAF <sup>b</sup>	Direct vehicle emission
OC	0.595	0.564	0.436	<u>0.864</u>	0.240	0.272
EC	0.467	<u>0.612</u>	0.374	<u>0.766</u>	0.325	0.420
WSOC	0.484	0.598	0.489	<u>0.794</u>	0.337	0.208
SOC	<u>0.624</u>	0.237	0.392	<u>0.613</u>	–0.109	–0.254
NO <sub>3</sub> <sup>–</sup>	0.549	0.299	0.666	0.296	<u>0.861</u>	0.179
SO <sub>4</sub> <sup>2–</sup>	0.357	0.196	<u>0.734</u>	0.080	<u>0.917</u>	0.041
Cl <sup>–</sup>	0.029	0.005	<u>0.897</u>	0.207	<u>0.908</u>	–0.026
Na <sup>+</sup>	0.491	0.123	<u>0.783</u>	0.004	<u>0.922</u>	–0.070
NH <sub>4</sub> <sup>+</sup>	0.262	0.100	<u>0.863</u>	0.340	<u>0.604</u>	0.162
K <sup>+</sup>	0.228	0.068	<u>0.939</u>	0.215	<u>0.949</u>	–0.020
Mg <sup>2+</sup>	0.481	0.112	<u>0.722</u>	0.022	<u>0.909</u>	0.179
Ca <sup>2+</sup>	<u>0.686</u>	0.029	0.072	0.182	<u>0.708</u>	0.109
Li	<u>0.866</u>	0.349	0.191	<u>0.903</u>	0.235	0.232
Mg	<u>0.956</u>	0.122	0.169	<u>0.966</u>	0.141	0.134
Al	<u>0.957</u>	0.135	0.154	<u>0.969</u>	0.128	0.110
Ti	<u>0.956</u>	0.139	0.177	<u>0.968</u>	0.126	0.108
V	<u>0.795</u>	0.416	0.269	<u>0.966</u>	0.141	0.140
Cr	0.066	0.378	–0.407	0.136	0.255	0.248
Mn	<u>0.702</u>	0.612	0.275	<u>0.870</u>	0.129	0.447
Fe	<u>0.868</u>	0.233	0.242	<u>0.937</u>	0.178	0.197
Ni	0.098	0.383	–0.410	0.160	0.258	0.245
Cu	0.573	<u>0.616</u>	0.251	<u>0.803</u>	0.157	0.512
Zn	0.147	<u>0.847</u>	0.218	0.142	0.112	<u>0.948</u>
As	0.514	<u>0.742</u>	0.095	<u>0.893</u>	0.153	0.291
Sr	<u>0.937</u>	0.158	0.192	<u>0.945</u>	0.172	0.143
Cd	0.015	<u>0.857</u>	–0.089	0.252	0.057	<u>0.911</u>
Sn	0.333	<u>0.908</u>	0.138	0.310	0.037	<u>0.921</u>
Ba	<u>0.836</u>	0.364	0.212	<u>0.897</u>	0.167	0.317
Pb	0.133	<u>0.877</u>	0.015	0.293	0.119	<u>0.874</u>
Bi	0.164	0.510	0.104	0.020	0.360	0.257
% of Variance	56.3	11.5	10.3	53.7	16.4	9.9
Cumulative %	56.3	67.8	78.1	53.7	70.1	80.0

<sup>a</sup> mixed sources: traffic and road dust resuspension and coal combustion.

<sup>b</sup> SAF: secondary aerosol formation.

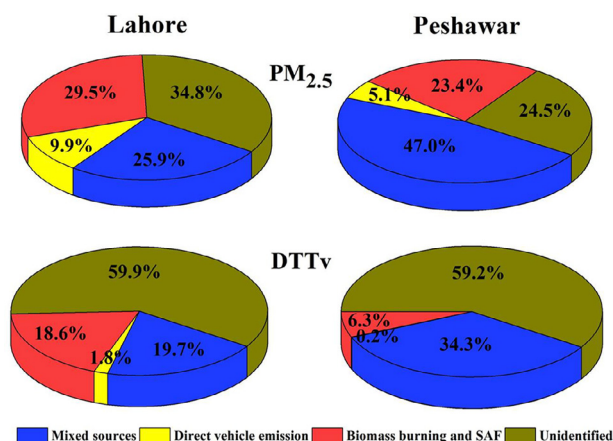
highly loaded with Sn, Pb, Zn, Cd, Cu, As, and EC. Pb, Zn, Cd and EC have been used as markers of vehicle emissions (Khare and Baruah, 2010). Zn is emitted from two stroke engines as a gasoline additive and as tyre wear (Kothai et al. 2008), Pb from gasoline additives and brake pads (Pant and Harrison 2012), and EC from incomplete combustion of fuels (Ahmad et al., 2020). Therefore, Factor 2 was identified as direct vehicle emission. Factor 3 was dominated by K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>–</sup>, SO<sub>4</sub><sup>2–</sup>, and NO<sub>3</sub><sup>–</sup>. K<sup>+</sup> and Cl<sup>–</sup> are strong tracers for biomass and wood burning, while SO<sub>4</sub><sup>2–</sup>, NO<sub>3</sub><sup>–</sup>, and NH<sub>4</sub><sup>+</sup> correspond to secondary aerosols formation (Pant and Harrison, 2012). Therefore, Factor 3 was identified as biomass burning and secondary aerosol formation. The sources of PM<sub>2.5</sub> in Peshawar were identified in the same way as in Lahore. It should be noted that Factor 1 (mixed sources) in Peshawar showed much higher loadings of carbonaceous species than in Lahore, suggesting different emission characteristics of the mixed sources.

### 2.3.2. Source contributions to PM<sub>2.5</sub> and DTT<sub>v</sub>

Multiple linear regression analysis was performed using PM<sub>2.5</sub> and DTT<sub>v</sub> as dependent variables and the absolute principal component score (APCS) calculated by PCA as independent

variables to estimate the source contributions to PM<sub>2.5</sub> and its oxidative potential in Lahore and Peshawar (Guo et al., 2004; Yang et al., 2005). As shown in Fig. 3, the mixed sources of traffic and road dust resuspension and coal combustion, the combined sources of biomass burning and secondary aerosol formation, and direct vehicle emission contributed to 25.9, 29.5 and 9.9% of PM<sub>2.5</sub> in Lahore and 47.0, 23.4, and 5.1% of PM<sub>2.5</sub> in Peshawar. The mixed sources with coal combustion included shows a higher contribution percentage in Peshawar, while direct vehicle emission shows a higher contribution percentage in Lahore.

Fig. 3 also shows the relative contributions of different sources to the oxidative potential (DTT<sub>v</sub>) of PM<sub>2.5</sub> in the two cities. However, compared to PM<sub>2.5</sub>, the sources of DTT remained largely unexplained (59.9% in Lahore and 59.2% in Peshawar unexplained). Meanwhile, according to the multiple linear regression results shown in Table 3, the regression coefficients (R<sup>2</sup>) of the models for DTT<sub>v</sub> were much lower those for PM<sub>2.5</sub>, making the source contribution results less reliable for DTT<sub>v</sub> than for PM<sub>2.5</sub>. As mentioned in Section 3.2.2, the DTT activity of PM<sub>2.5</sub> could be a result from ROS generation by synergistic or antagonistic relationships between different chem-



**Fig. 3 – Relative contributions of different sources to PM<sub>2.5</sub> and its oxidative potential (DTTv) in Lahore and Peshawar during the sampling period in February 2019.**

**Table 3 – Multiple linear regression analysis results using PM<sub>2.5</sub> and DTTv as the dependent variables and the mass concentrations of PM<sub>2.5</sub> chemical components as the independent variables.**

PM <sub>2.5</sub> in Lahore	B	Std. error	t	Sig.	R <sup>2</sup>
Constant	182	35.7	5.08	0.00	0.85
Mixed Sources	121	16.7	7.22	0.00	
Vehicle Emission	128	16.7	7.67	0.00	
Biomass Burning and SAF	104	16.7	6.23	0.00	
<b>PM<sub>2.5</sub> in Peshawar</b>					
Constant	90.7	17.3	5.23	0.00	0.95
Mixed Sources	159	7.42	21.5	0.00	
Biomass Burning and SAF	49.4	7.42	6.66	0.00	
Vehicle Emission	39.9	7.42	5.38	0.00	
<b>DTTv in Lahore</b>					
Constant	5.33	1.36	3.94	0.00	0.27
Mixed Sources	1.58	0.64	2.48	0.02	
Vehicle Emission	0.40	0.64	0.62	0.54	
Biomass Burning and SAF	1.12	0.64	1.76	0.09	
<b>DTTv in Peshawar</b>					
Constant	5.49	1.21	4.54	0.00	0.55
Mixed Sources	2.91	0.52	5.63	0.00	
Biomass Burning and SAF	0.34	0.52	0.65	0.52	
Vehicle Emission	0.03	0.52	0.06	0.96	

B: regression coefficient; t: t-test value; Sig.: significance level; R: correlation coefficient.

ical species, therefore, the DTT activity of PM<sub>2.5</sub> measured on the basis of the mixed reactions of PM<sub>2.5</sub> would not be precisely described by the sources defined for PM<sub>2.5</sub>. In the explained proportion of the sources of DTTv, the mixed sources of traffic and road dust resuspension and coal combustion were the major sources of the oxidative potential of PM<sub>2.5</sub> in both Lahore and Peshawar while the direct vehicle emission contributed the least to DTTv.

#### 2.4. Potential health risks of PM<sub>2.5</sub> pollution

According to the correlation analysis, it is inferred that the DTT activity of PM could be highly attributable to the interac-

**Table 4 – Carcinogenic and non-carcinogenic risks of heavy metals in PM<sub>2.5</sub> in Lahore and Peshawar during the sampling period in February 2019.**

	Carcinogenic (CR)		Non-Carcinogenic (HQ)	
	Child	Adult	Child	Adult
<b>Lahore</b>				
As	6.50E–06	3.25E–05	3.76E–01	1.13E+00
Cd	9.87E–06	4.94E–05	2.05E+00	6.14E+00
Cr	4.67E–04	2.34E–03	2.12E–01	6.37E–01
Pb	2.61E–05	1.31E–04	NA	NA
Ni	5.90E–07	2.95E–06	1.83E–01	5.50E–01
Mn	NA	NA	1.09E+00	3.26E+00
Total	5.10E–04	2.56E–03	3.91E+00	1.17E+01
<b>Peshawar</b>				
As	1.79E–07	8.60E–07	1.03E–03	3.10E–02
Cd	3.50E–06	1.75E–05	7.25E–01	2.18E+00
Cr	1.09E–03	5.46E–03	4.90E–01	1.49E+00
Pb	3.86E–06	1.93E–05	NA	NA
Ni	1.48E–06	7.40E–06	4.60E–01	1.38E+00
Mn	NA	NA	7.97E–01	2.39E+00
Total	1.10E–03	5.51E–03	2.47E+00	7.47E+00

CR: carcinogenic risk; HQ: hazard quotient; NA: not available.

tions between organic species and metal species while water soluble ions are less involved in the ROS generation process. Several studies have also demonstrated that the oxidative stress of inhalable particulate matter is related to both organic substances and certain metallic elements, such as quinones, Cr and Zn (Verma et al., 2015; Park et al., 2018). Peshawar, being one of the major steel centers of Pakistan, showed higher proportions of carbonaceous species and metal elements than Lahore. Consequently, the mass-normalized DTT activity of PM<sub>2.5</sub> was also higher in Peshawar compared to Lahore although the average PM<sub>2.5</sub> concentration in Peshawar was lower.

In an effort to further reveal the potential health risks of PM<sub>2.5</sub>, the carcinogenic risk (CR) and non-carcinogenic risk (determined by the hazard quotient, HQ) of heavy metals via the inhalation pathway were assessed, and the results are summarized in Table 4. Details of the calculation procedure can be found in the supplementary materials. As shown in Table 4, the non-carcinogenic risks were in the decreasing order of Cd > Mn > As > Cr > Ni for both children and adults in Lahore during the winter season and Mn > Cd > Cr > Ni > As in Peshawar. The non-carcinogenic risk (HQ) of Cd and Mn for both adults and children and the non-carcinogenic risk (HQ) of As in Lahore were greater than the safe level (=1). In contrast, the non-carcinogenic risks of Cd, Cr, Ni, and Mn in Peshawar were higher than the safe level for adults only. For both adults and children, the carcinogenic risks of Cd, As, Pb and Ni were lower than the permissible limit, while the carcinogenic risk of Cr was higher than the permissible limit of ( $1 \times 10^{-4}$ ) in Lahore and Peshawar, indicating that Cr was above the safe level in both cities in winter. In summary, the non-carcinogenic risks posed by Cd and Mn and the carcinogenic risk by Cr posed serious threats to the residents of both Lahore and Peshawar during the winter season via inhalation of fine particulate matter.



### 3. Conclusions

The chemical characteristics, oxidative potential, and sources of  $PM_{2.5}$  were analyzed at the urban sites of Lahore and Peshawar, Pakistan in February 2019. Severe  $PM_{2.5}$  pollution was observed in both cities during the sampling period, which resulted in the high exposure risk of  $PM_{2.5}$  regarding its oxidative potential (DTT<sub>v</sub>). Carbonaceous species were the major species of  $PM_{2.5}$  in both cities. Carbonaceous and some of the metallic species of  $PM_{2.5}$  correlated well with DTT<sub>v</sub> in both Lahore and Peshawar. Besides, the DTT<sub>v</sub> of  $PM_{2.5}$  in Lahore showed significant positive correlation with most of the measured water soluble ions, however, ions were DTT-inactive in Peshawar. Showing higher proportions of carbonaceous species and metal elements, Peshawar showed higher mass-normalized DTT activity of  $PM_{2.5}$  compared to Lahore although the average  $PM_{2.5}$  concentration in Peshawar was lower. The high concentrations of toxic metals also posed serious non-carcinogenic and carcinogenic threats to the residents of both Lahore and Peshawar during the winter season via inhalation of fine particulate matter. Mixed sources of traffic and road dust resuspension and coal combustion, direct vehicle emission, and biomass burning and secondary aerosol formation were identified as the major sources of  $PM_{2.5}$  in both cities. The MLR results of DTT<sub>v</sub> were statistically less reliable compared with  $PM_{2.5}$ . In the explained proportion of the sources of DTT<sub>v</sub>, however, the major sources of the oxidative potential of  $PM_{2.5}$  in both Lahore and Peshawar were mixed sources of traffic and road dust resuspension and coal combustion. Our findings can be used by legislators to formulate efficient strategies to mitigate  $PM_{2.5}$  as well as its adverse health effects in major cities of Pakistan.

### Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 91543110). The first author was grateful to the fellowship granted by China Scholarship Council.

### Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jes.2020.09.014](https://doi.org/10.1016/j.jes.2020.09.014).

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