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RESEARCH ARTICLE

Physiochemical characteristics and oxidative potential of ambient air particulate matter (PM_{10}) during dust and non-dust storm events: a case study in Tehran, Iran

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Abstract

In the present study, we investigated the characteristics of metal(loid)s, polycyclic aromatic hydrocarbons (PAHs) and oxidative potential (OP) in PM_{10} during dust and non-dust days in a rural and an urban area in Tehran. Water-soluble ions, metal(loid)s, PAHs, and OP were measured using ion chromatography (IC), inductively coupled plasma optical emission spectrometer (ICP-OES) and gas chromatography/mass spectrometry (GC-MS), and dithiothreitol (DTT) assay respectively. The results showed that the average concentrations of ambient PM_{10} were 284 ± 90.4 and 123 ± 31.4 μg m^{-3} on dusty and regular days in urban areas respectively, and were 258 ± 48.3 and 124 ± 41.4 μg m^{-3} on dusty and regular days in rural areas, respectively; these values were 95% above the World Health Organization (WHO) guideline level. The crustal elements Na^+, Mg^{2+}, Ca^{2+}, Al, Si, Fe and Ti were the dominant for PM_{10} on dusty days, and NO^-_3 and SO_4^{2-} were dominant for PM_{10} on regular days. The average ± SD concentrations of total PAHs were 34.3 ± 22.5 and 55.1 ± 28.3 ng m^{-3} on dusty and regular days, respectively, with the maximum value occurring on inversion days. The average OP was 8.90 ± 7.15 and 1.41 ± 0.35 and was 11.4 ± 3.97 and 19.9 ± 8.67 (nmol min^{-1} μg $PM_{10}{}^{-1}$) for water and methanol extracts on dusty and regular days, respectively, with the lowest value occurring on dusty days. The OP was highly associated with Cu and Mn. Briefly; the results of this study demonstrate that OP is mass independent and consequence a promising proxy for PM mass.

Keywords Particulate matter · Dust storm · Chemical characteristics · Oxidative potential · DTT assay · Tehran

Introduction

Particulate matter (PM) are most usually classified according to their size as $PM_{2.5}$ (with an aerodynamic diameter less than 2.5 μm) and PM_{10} (with an aerodynamic diameter less than 10 μm). $PM_{2.5}$ is often produced from combustion processes and formation as secondary particles [1]. PM_{10} is generated by mechanical activities and road dust as well as from natural resources such as pollen and volcanoes [2, 3]. A dust storm is a meteorological phenomenon and usually occur when the wind speed exceeds the threshold value at which particles are removed from the soil [4, 5]. During these events, which can

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last for several days, the PM_{10} concentrations are nearly 2–3 times higher than that of regular days [6, 7]. Hence, dust events play an important role in PM_{10} pollution [7–9].

Numerous epidemiological studies have shown effects of PM on mortality and morbidity [10–15]. In most such investigations, these effects have been associated with the mass concentration of PM, but a major part of this mass is biologically inactivated [16, 17]. Although the current standards of PM are based on particle mass alone, but PM toxicity is more complicated and is based on a combination of PM characteristics, including the number, size, surface area, and chemical compounds [18]. Based on various toxicological studies, the formation of reactive oxygen species (ROS) including hydroxyl radicals ($OH^{\circ -}$), superoxide anion ($O_2^{-\circ}$), hydrogen peroxide (HOOH), and oxygen radicals can react with membrane lipids, nucleic acids, proteins, and enzymes and cause cell damage [19–21]. Oxidative stress which is the imbalance between ROS generation and antioxidant defenses, is caused when ROS or other oxidants overcome the body's natural defense system [22].

Several studies have determined that the oxidative potential (OP) may be more integrative health base measurement rather than the mass concentration of PM alone [23–25]. The ability of PM to oxidize its target molecules is called its OP, and this indicator has shown a stronger association between the biological responses of the body and exposure to PM [10, 26]. The OP of PM may be caused by organic compounds, metals, and other active chemical compounds [15, 16]. Therefore, the OP can be used as a quantitative probe to evaluate the capacity of PM to catalyze the formation of ROS that cause oxidative stress [10, 17].

Various approaches, cellular and acellular assays, exist for measuring the OP of PM. The acellular assay requires fewer controlled environments and determines the OP faster than the cellular assay does [27] . There are various acellular assays used to study the OP of PM, each of which has a different sensitivity to redox active chemical compounds, but there is no theoretical agreement on the most appropriate method. The Electron spin resonance (ESR) method measures the ability of the particle to generate hydroxyl radicals in the presence of H_2O_2 when using spin trap such as 5,5-dimethylpyrroline-N-oxide (DMPO). Another technique is to measure the ability of PM to reduce antioxidants such as ascorbic acid (AA), glutathione (GSH), and uric acid. The Dichlorofluorescein (DCFH) assay, in which the oxidation of DCFH to fluorescent compound (DCF) is measured in the presence of horseradish peroxidase (HRP) [28–30]. DTT is one of the most widely used methods and can be considered a technique for measuring a particle's capacity for ROS generation. The DTT method measures the redox activity of a sample based on the potential of PM to catalyze the electron transfer between DTT and O_2. The reaction rate is usually called the DTT activity and is determined through measuring the DTT consumption over time, which is proportional to the ROS generation potential of PM [31–35]. Cho et al. [36] showed that the DTT method can be a proper measure of redox activity in by determining the formation of superoxide radical in the first step of ROS formation. Li et al. [37] demonstrated that DTT consumption by PM is directly related to their potential to create stress proteins in the cell. Nevertheless, DTT is not a respiratory tract lining fluid (RTLF) but can be considered as a substitute for glutathione as an oxidizing compound in similar biological conditions in the potassium phosphate buffer [28, 38].

PM has become a critical pollutant in Tehran [39]. Based on the most recent report by WHO [40] in May 2016, Tehran ranked 331st in terms of PM_{10} among the 2972 cities studied According to the WHO report on PM pollutants in different cities, more than 80% of the world's population is exposed to air pollution above the standard limits. In Tehran, PM is due mostly to the combustion of motor vehicles, brake abrasion, tire wear and the operation of industrial units [41]. It should be noted that during the recent years, the entry of dust from the western borders of the country has been added to the sources of this pollutant. To the best of our knowledge, there are no studies on the OP of PM in Tehran using the DTT assay. Thus, the main aims of the present study were to determine the redox activity of PM_{10} during dusty and non-dusty (inversion) days; to specify the relationship between different physicochemical characteristics of PM and OP; and to compare the OP of PM between urban and rural areas.

Material and methods

Site locations

In the present study, two sampling locations were selected to collect PM with different physicochemical characteristics (Fig. 1). The urban area (35° 42′ 71″ N, 51° 23′ 19″ E) was 8 m from a local two-way street and 70 m away from a major 4-lane street in Tehran [42]. The number of motor vehicles passing the major 4-lane street was 2.6–3.8 thousands vehicles per day, 80% of which were light-duty; the rest were heavy-duty vehicles. The PM released at this sampling point was mainly influenced by vehicles. The rural area (35° 38′ 10″ N, 51° 12′ 77″ E) was located in the upwind of southwestern of Tehran, where the PM originated mainly from natural sources. The samplers placed on the rooftop at 10 m and 5 m above the ground for urban and rural respectively.

Sampling protocol

Sampling was conducted from April 21 to June 7, 2016, and September 24 to November 15, 2016, for spring and autumn, respectively. PM_{10} samples were simultaneously collected using high volume samplers (Graseby-Andersen) operating at flow rate

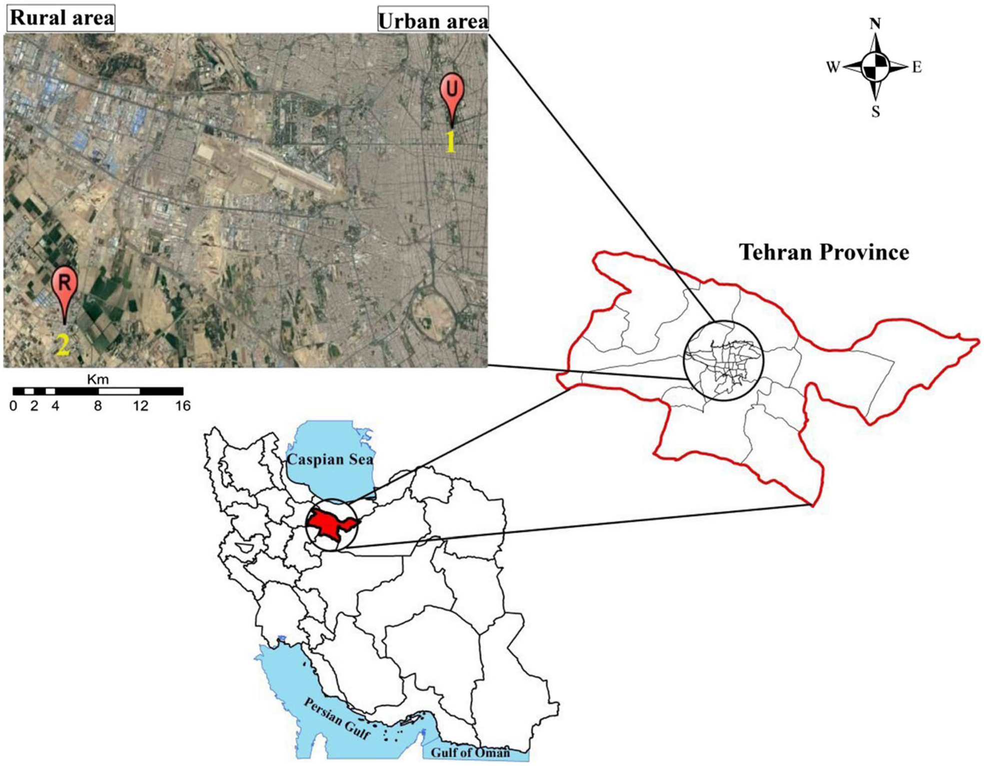


Fig. 1 Location of the study area to show the sampling sites

1.3 ± 0.11 m^3 min^{-1} on fiberglass filters (20.3 cm × 25.4 cm) at two sampling locations for 24 h. The total number of samples collected was 44 and 42 at the urban and rural locations, respectively. The meteorological data including the temperature, wind speed and wind direction were obtained from local meteorological monitoring stations near the sampling locations.

Identification of dusty day

To determine the PM_{10} concentrations associated with desert dust storms, a two-step approach based on Guidance to Member States on PM_{10} Monitoring and Inter-Comparisons With the Reference Method [43] and some studies [3, 8, 44] was used:

1. Days with average daily concentrations above the 90th percentile; in the present study, values greater than 200 and 195 μg m^{-3} at urban and rural locations, respectively, were selected [8].
2. After selecting days based on the above criteria, days with a $PM_{2.5}/PM_{10}$ ratio less than 0.3 were considered. Because based on the results of others studies [6, 41, 45] the coarse PM are usually of natural origin and fine PM are usually of anthropogenic origin, thus, the presence of a low $PM_{2.5}/PM_{10}$ ratio indicates natural PM sources. To calculate the $PM_{2.5}/PM_{10}$ ratio, we used data from stations that were close to the study locations.

Inversion days were determined according to the National Meteorological Organization.

Gravimetric analysis of PM_{10}

To reduce organic background, fiberglass filters were baked at 550 °C for at least 5 h prior to sampling. To determine the mass concentration of PM_{10}, the filters were stored at 22–24 °C with a relative humidity of 40–45% for 48 h before and after sampling and were then weighted using a microbalance (Mettler-Toledo Inc.) with a sensitivity of 0.002 mg. The samples were covered with aluminum foil and frozen at −20 °C until extraction.

Chemical analyses

Water-soluble ion analysis

First, 10 cm^2 of each filter was placed into a sterile polypropylene centrifuge tube, and 20 ml of double deionized water (specific resistance ≥18 Ω cm) was added. Then, the samples were sonicated at 40 KHz for 60 min in a water bath ultrasonic cleaner (Elmasonic). During sonication, the bath temperature was monitored to avoid exceeding 27 °C. Hence, to maintain the temperature at an acceptable level during sonication, ice cubes were added to the bath. To complete the particle extraction, the samples were shaken for 60 min. At the end, the resulting solution was filtered using the 0.22 μm syringe filter

(Schleicher & Schuell) and kept at 4 °C in the refrigerator until analysis. The water-soluble ions measured in this study were sodium (Na^+), ammonium (NH_4^+), potassium (K), magnesium (Mg^{2+}), calcium (Ca^{2+}), chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-) and sulfate (SO_4^{2-}), and were analyzed by Ion Chromatography (Metrohm 850 Professional IC,Switzerland at a flow rate of 0.7 ml min^{-1}) [6].

Metal (loid)s analysis

One tenth of each filter was placed in digestion vessels and an extraction solution containing 0.1 ml of HF, 3 ml of HNO_3 and 1 ml of $HCLO_4$ was added [46]. Then, the samples were digested using a microwave (ETHOS-1600, Milestone, Italy). The sample vessels irradiated at 1500 W and 130^{oC} for 23 min. Then, the digested sample volume was increased to 15 ml using pure deionized water (specific resistance ≥18 Ω cm), and passed through a 0.45 μm syringe filter (Schleicher & Schuell). Finally, the end solutions were analyzed using ICP-OES to determine the concentrations of metals, including Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Si, Sn, Sr, Li, Ti, V, Zn and Mo.

PAHs analysis

To extract and determine the amount of PAHs, one fifth of each filter was placed in a 20-ml vial. Then, 10 ml of methanol/dichloromethane mixture (1:1 *v*/v) was added to each sample and stirred for 2 min. The vials were sonicated at 130 KHz for 30 min in a water bath ultrasonic cleaner (Elmasonic). Then, the methanol/dichloromethane mixture was filtered through 22 μm PTFE filters (Jet Biofil). This aliquot was dried under a gentle stream of nitrogen. After the samples were completely dried, 1 ml of methanol/dichloromethane was added to each vial, transferred to the headspace vials [47], and analyzed by a GC/MS equipped with a fused silica capillary column (DB-5MS). The 16 PAHs species including Naphthalene (Naph), Acenaphthylene (Acy),Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene(Anth), Fluoranthene (Flt), Pyrene (Pyr), Benzo[a]anthracene (BaA),Chrysene (Chr), Benzo[b]fluoroanthene (BbF), Benzo[k]fluoroanthene(BkF), Benzo[a]pyrene (BaP), Dibenzo[a,h]anthracene (DahA), Benzo[ghi]perylene (BghiP), and Indeno[123-cd]pyrene (Ind) were analyzed.

OP analysis

DTT method procedure

To extract for DTT analysis, 10 cm^2 of each filter was placed in 10 ml of deionized water (specific resistance ≥18 Ω cm) and methanol separately in the sterile polypropylene centrifuge tubes and stirred for 5 min. The sample was sonicated at 130 KHz for 30 min in a water bath ultrasonic cleaner (Elmasonic), and then passed through 0.22 μm PTFE filters (Jet Biofil). The extraction efficiency was approximately 73% of PM from the filters. The concentration of the samples with suspended particles was 15–40 μg mL^{-1}. In this study, we followed the method of Cho et al. [33, 36]. First, 3.5 ml of the extracted particles with 1 ml of potassium phosphate buffer (0.1 M) at pH 7.4 treated with Chelex 100 resin (sodium form, Biorad) was placed in the sterilized polypropylene centrifuge tube and 0.5 ml of DTT (100 μM) was added to the mixture. The DTT/phosphate solution mixture was incubated at 37 °C with continuous shaking at 400 rpm at designated time intervals (5, 10, 20, 30, and 40 min).

During the incubation period, the DTT absorption was reduced due to DTT oxidation. After each incubation time (for example, 5 min), 100 μl of the incubated mixture was transferred to another centrifuge tube and 1 ml of 10% trichloroacetic acid (TCA 1% w = v) was added to stop the reaction. Then, 50 μl of 5,50-dithiobis-2-nitrobenzoic acid (DTNB 10 mM) was added to the mixture, stirred properly, and allowed to react for 5 min. Subsequently, 2 ml of Tris-Base (0.08 M with 4 mM EDTA) at pH 8.9 was added. The DTT reaction with DTNB resulted in the formation of the yellow 2-nitro-5-thiobenzoic acid (TNB) solution that was stable for 2 h at room temperature. Finally, the TNB absorption (Abs) level was measured using the UV/VIS spectrophotometer (DR 5000, Hach) at a wavelength of 412 nm. The absorption versus time curve was drawn (Fig. S1, Supplementary material) and the DTT consumption was calculated using the Eq. S1, S2 (see Eq. S1, S2, Supplementary material). Since DTT and TNB are sensitive to light, the tests were performed under an exhaust hood in a dark room and in aluminum-coated vials. DTT activity is expressed based on mass (DTT_m nnmol min^{-1} m^{-3}), and volume (DTTv nmol min^{-1} μg^{-1}). DTT_m shows the inherent characteristics of the PM related to the source and is suitable for comparing the relative OP of the PM from different sources, whereas DTT_v shows the public exposure [48].

Data quality assurance and quality control (QA/QC)

For QA/QC, the laboratory and field blanks, duplicate, and spike samples were analyzed with other samples for each type of chemical analysis. For every 10 samples, a blank filter was used. The recovery efficiencies of 16 PAHs species were 64–104%, 94–106% for the water soluble ions, 65–108% for metal(loid)s and 85–96% for DTT assay. On average, among all of the sample analyses, the mean concentration of the field blank was less than 10% that of the samples. The limit of detection (LOD) was determined to be three times that of the standard deviation of the blank values (Table S1, Supplementary material). Then, the mean blank values were deduced from concentration of the samples that were greater than LOD for all the analyses.

Statistical analyses

The results were expressed in mean ± SD. First, the Shapiro-Wilk test was used to examine the normality of data, and the correlation between OP and the physicochemical characteristics of PM was evaluated by SPSS ver. 20 (IBM Corp.,USA) for each sampling point using spearman's correlation coefficient. Since the distribution of data was not normal, the Kruskal–Wallis test was used to evaluate the difference in particle specifications at two sampling locations, and a statistically significant level was considered when $P_{value} \leq 0.05$.

Results and discussion

PM_{10} mass concentrations

On the basis of the criteria mentioned for selecting dust storm days, 5 days were considered dusty days. Table 1 shows a summary of the average concentration of PM_{10} and the ratios of dust/regular and inversion/regular during the sampling period in the urban and rural areas. Accordingly, the daily average concentration of PM_{10} was 140 and 137 $\mu g\ m^{-3}$, which was 100 and 95% above the WHO guidelines and 60 and 39% above the Environmental Protection Agency (EPA) and Iranian standards (150 $\mu g\ m^{-3}$) in urban and rural areas, respectively. A significant difference was observed based on the concentration of PM_{10} in three different meteorological phenomena: dusty, inversion, and regular days ($P_{value} \leq 0.05$).

As shown in Table 1, on the dusty days, the average PM_{10} mass concentration was 2.31 and 2.08 times greater than concentrations on regular days in the urban and rural areas, respectively. Tehran is surrounded by deserts and the dominant wind in Tehran moves from west and southwest to east and northeast and may have the potential to move the particles from these sources to Tehran. Thus, one of the sources of pollution in Tehran is the dust phenomenon [49]. The average concentration PM_{10} is higher under inversion conditions than on regular days and is 1.79 and 1.31 times greater in urban and rural areas, respectively. This may be due to Tehran's roughness due to its geographical position, i.e., between mountains, as well as the presence of high buildings, which most likely block the winds from the mountains to the plains and, as a result, cause atmospheric stability and the temperature inversion phenomenon during cold weather [41].

PM_{10} chemical components

Water-soluble ions

The average concentrations and standard deviation of water-soluble ions measured for PM_{10} in dusty, inversion and regular days for two sampling sites can be found in Table S2 from Supplementary material. The total concentration of water-soluble ions was 26 and 30% of PM_{10} mass in urban and rural areas, respectively. The ions in PM_{10} for the urban and rural areas were present in the order: $NO_3^- > SO_4^{2-} > Cl^- > Ca^{2+} > NH_4^+ > K^+ > Na^+ > F^- > Mg^{2+}$ for the urban location and $SO_4^{2-+} > NO_3^- > Cl^- > Ca^{2+} > Na^+ > NH_4^+ > K^+ > F^- > Mg^{2+}$ for the rural location. Sulfate and nitrate were dominant ions in PM_{10}. These results are consistent with those of other studies [50, 51]. Nitrate and sulfate ions have no functional groups, for ROS formation, but they may increase the solubility of soluble metals and, thus, their bioavailability in cells, thereby affecting their redox-OP activity by decreasing the pH of the particles [52].

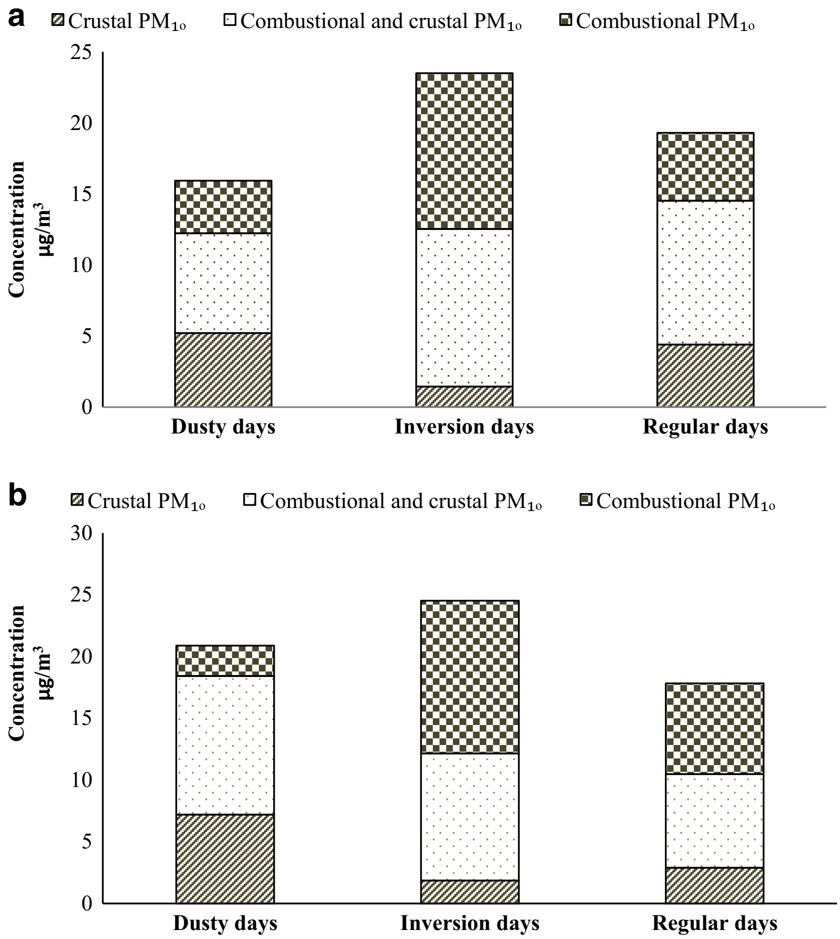
Based on Wang classification [53], three categories were identified in dusty, inversion and regular days: crustal PM_{10} (enriched with Na^+, Mg^{2+}, and Ca^{2+}), combustional and crustal PM_{10} (enriched with K^+, SO_4^{2-}, and Cl^-), and combustional PM_{10} (enriched with NO_3^- and NH_4^+). A statistically significant difference ($P_{value} \leq 0.05$) was found between the concentrations of crustal PM_{10} and combustional PM_{10} in three different meteorological phenomena (dusty, inversion, and regular days). As shown in Fig. 2, regardless of the sampling site, crustal PM_{10} (Na^+,Mg^{2+}, and Ca^{2+}) resulting from resuspended soil dust had a maximum value on dusty days and a minimum value on inversion days because the main source of PM on dusty days was soil compounds. Lough [54] reported that Na^+, $Mg^{2\,+}$ and Ca^{2+} were resuspended compounds. The maximum value of combustional PM_{10} (NO_3^-, NH_4^+), or secondary inorganic aerosols, occurred on inversion days. During stable weather conditions, the low dispersion of pollutants resulted in higher levels of pollutants [47].

The increased concentration of these compounds may have been due to the oxidation of gas-like precursors via NH_4^+

Table 1 The average of PM_{10} mass concentration ($\mu g\ m^{-3}$) and meteorological data (±standard deviation)

Location	PM_{10} concentration($\mu g/m^3$)				Dusty/ Regular	Inversion/ Regular
	Dusty	Inversion	Regular	All days		
Urban	284 ± 90.4	220 ± 17.1	123 ± 31.4	140 ± 54	2.31	1.79
Rural	258.4 ± 48.3	162 ± 15.8	124 ± 41.4	137 ± 54	2.08	1.31

Fig. 2 The contribution of different ion groups to the total ion mass in PM_{10} on dusty, inversion and regular days at urban (**a**) and rural (**b**) locations; crustal PM_{10}: (sum Na^+,Mg^{2+} and Ca^{2+}); combustional and crustal PM_{10}: (sum K^+, SO_4^{2-} and Cl^-); combustion PM_{10}: (sum NO_3^-, NH_4^+)



existing in the atmosphere to form photochemical byproducts. The major form of NH_4^+ is ammonium sulfate and ammonium nitrate, which are formed from gas-like precursors by secondary processes [29, 48, 52].

In accordance with Eq. (1): [41], non-sea-salt sulfates (nss-SO_4^{2-}), regardless of their sampling location, comprised 93% of the total sulfate in PM_{10}, thus reflecting the importance of anthropogenic sources in Tehran air pollution.

$$\text{nss}-SO_4^{2-} = \left[SO_4^{2-}\right]-0.246 \times Na^+ \qquad (1)$$

The NO_3^-/SO_4^{2-} ratio is used as an indicator of the relative importance of moving sources against fixed sources [53]. This ratio had higher values in the urban areas than rural areas (Fig. S2, Supplementary material), thus indicating the significance of mobile sources in Tehran, consistent with the results of Hassanvand et al. [6].

Metal(loid)s

Metals are the one of the critical PM compounds that can lead to the formation of intrinsic ROS The main sources of transition metals are traffic and industrial emissions, which are due to combustion or mechanical processes [19]. The mean (SD) levels of metal(loid)s in urban and rural PM_{10} are summarized in Table S2 (Supplementary material). The relative frequency of metals in the urban and rural areas is as follows: Si > Fe > Al > Ti > Mn > Pb > Ba>Cu > Cr > Zn > Ni > As> Li > V > Mo > Sr > Cd > Co > Sn > Se for urban area and Si > Fe > Al > Zn > Mn > Pb > Cu > Ba> Ti > Cr > Ni > Cd > V > Mo > Co > Sn > Li > As> Sr > Se for rural area. Si, Fe and Al comprised 90 and 80% of the PM_{10} metals in urban and rural areas respectively. As briefly mentioned mainly earth crust elements /metals were detected in previous studies [41, 46, 55]. Additionally, numerous studies have demonstrated that the emission of Cu is from the brake wear, which is mostly from heavy-duty vehicles, and that tire wear is the main source of Zn emission [34, 56]. Some animal husbandry systems use a copper bath for the fungal treatment of cows, which may enter the soil [22].

In the present study, the concentrations of Ni and V were 12.1 and 7.03 ng m^{-3} for urban area and 5.85 and 2.72 ng m^{-3} for rural area. V and Ni are mainly derived from the marine vessels and oil combustion [57]. The IARC [58] has identified Pb, Ni, Cd, and As as carcinogenic for humans (Group 1) [59]. According to the European commission standards for the ambient air limits of Cd (5 ng m^{-3}), Ni (20 ng m^{-3}), As (6 ng m^{-3}) and Pb (500 ng m^{-3}). The values of Pb and Ni were below the limit, but those of Cd and As were above the limit in urban and rural areas, respectively. For As concentration, a significant difference ($P_{value} \leq 0.05$) between urban and rural location was observed. The higher levels of arsenic in the rural areas than the urban ones might be due to the greater use of arsenic-based pesticides since the major part of activity in the studied rural area was in the agricultural lands. Several studies have shown that Sb, S, Cd, Mo, Zn, Pb, and Cu originate from vehicle emissions [29, 60].

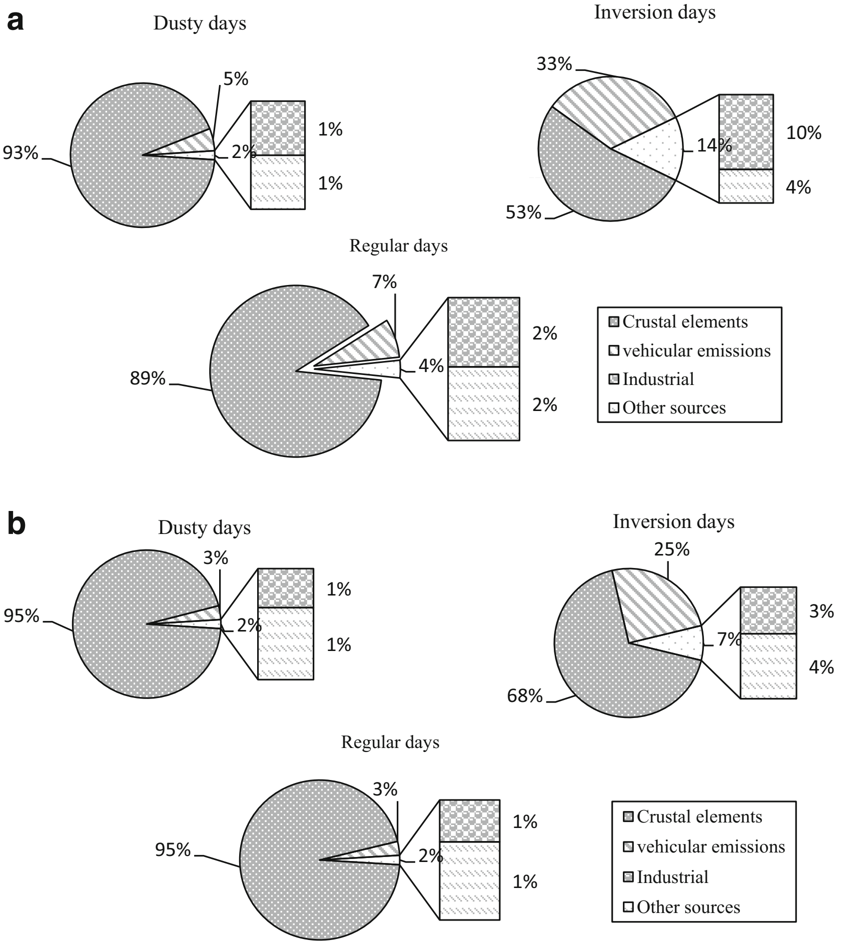
The amount of Pb was less than the national ambient air quality standards in Iran (500 ng m^{-3}). The main reason for this could be the removal of Pb from the consumed fuels in Iran since 2002, which significantly reduced this element in Tehran air [41]. In this study, based on previous studies [34, 41, 61, 62] and the presence of metals, four possible source categories were identified on dusty, inversion, and regular days, crustal elements (Al, Si, Fe,Ti), vehicular emissions (Ba,Mo,Cu,Mn,Zn,As,Cd), industrial (V, Ni, Cr, Pb) and other sources (Li, Se, Sn, Sr, Co).

As shown in Fig. 3, regardless of the sampling site, the concentration of crustal metals was higher on dusty days. Considering the elements with crustal origins, it was found that the sum of these elements was greater in rural areas than in urban ones, which may be due to the limited anthropogenic emissions in the rural areas. The highest values of vehicular and industrial tracer elements occurred on inversion days, especially in urban areas, due to their more stable atmospheric conditions and a lower inversion layer, leading to substantially higher levels of pollutants on inversion days.

PAHs

The statistical summary including the mean and standard deviation of concentrations of PAHs measured at two sampling points are given in Table S2 (Supplementary material). Among the different species, the highest and lowest concentrations were related to Phen and DahA (23.2 and 1.23 ng m^{-3}) and Phen and Acy (4.4 and 1.58 ng m^{-3}), respectively, in urban and rural areas. The results demonstrated that the concentrations of PAHs associated with PM_{10} were lower than the earlier studies in Tehran. The results of Hassanvand [46] concerning the concentration of PAHs compounds associated with PM_{10} on PTFE filters using low volume samplers during one year (2012–2013) in Tehran showed that the

Fig. 3 The contribution of different metals to the total metal mass in PM_{10} on dusty, inversion and regular days at urban location (**a**) and rural location (**b**)



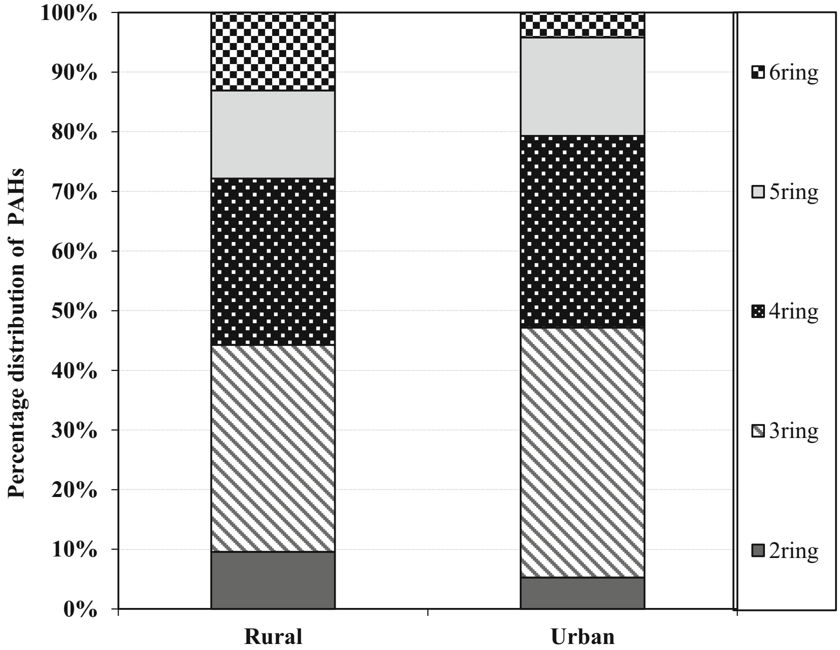


Fig. 4 Ring-wise (two, three, four, five and six-ring) distribution of PAHs in PM$_{10}$ at urban and rural locations

concentration of these compounds varied from 425 to 430 ng m^{-3} at different sampling points. Difference between previously reported PAH concentrations and results from this study may be due to difference in climatic conditions, sampling methods, sampling season and filter type, which can cause a difference in the reported concentrations. Some studies have been shown that fiberglass filters may be absorbing some PAH vapours while PTFE filters are not absorbing those [63, 64].

According to the results, the highest total concentration of PAHs compounds was 127 ng m^{-3} on the inversion days in urban areas, which can be due to the lower inversion layer, leading to a decrease in the distribution of pollutants, including these compounds. Figure 4 shows the percentage of components of PAHs based on the number of aromatic rings including 2-ring PAHs (Nap); 3-ring PAHs (Ace, Acy, Flu, Phen, and Anth);4-ring PAHs (Flt, Pyr, BaA, and Chr); 5-ring PAHs (BbF, BkF, BaP, and DahA); and 6-ring PAHs (BghiP and Ind) [65] in Tehran during the sampling period. As shown in Fig. 4, regardless of the sampling site, more than 50% of the PAHs compounds had 4, 5 and 6 rings with high molecular weight.

The results showed that 3 and 4-ring compounds dominated the PAHs compounds in Tehran whereas 2-ring compounds with low molecular weight had the lowest values and were mostly found in the gas phase [47]. The presence of compounds with high molecular weight such as BkF, BkF, DahA and Ind in PM$_{10}$ was mainly associated with the use of fossil fuels and vehicles. Similar results have been reported in previous studies [46]. The overall mean of the seven carcinogenic PAHs compounds including BaA, Chr, BbF, BkF, BaP, DahA, and Ind was 36.2 ± 16.3 and 7.99 ± 5.64 ng m^{-3} in PM$_{10}$ in urban and rural areas, respectively. Among these seven species of carcinogens, the highest concentration belonged to Chr with means of 11.9 and 2.83 ng m^{-3}, and the lowest belonged to

Table 2 Average of DTT Activity (nmol DTT/m^3, (nmol min^{-1} μgPM$_{10}$$^{-1}$) of PM$_{10}$ (methanol and water extraction) in Dusty, Inversion and regular days at sampling Locations

Location	DTT activity	Dusty days		Inversion days		Regular days		All days	
		Water	Met	Water	Met	Water	Met	Water	Met
Urban area	OP^{DTTm} (nmol min^{-1} μgPM$_{10}$$^{-1}$)	21.31 ± 9.7	12.86.38	20.1 ± 5.43	12.3 ± 3.21	41.5 ± 5.12	27.6 ± 5.31	15.6 ± 4.19	6.73 ± 2.53
	OP^{DTTv} (nmol min^{-1} m^{-3})	4.04 ± 2.63	1.52 ± 0.41	3.86 ± 1.08	1.53 ± 0.36	6.49 ± 1.76	1.79 ± 0.76	3.42 ± 0.89	1.35 ± 0.37
Rural area	OP^{DTTm} (nmol min^{-1} μgPM$_{10}$$^{-1}$)	21.3 ± 10.7	12.1 ± 6.22	22.2 ± 5.70	12.1 ± 4.72	33.1 ± 7.01	21. 6 ± 5.39	10.81 ± 4.39	7.10 ± 1.11
	OP^{DTTv} (nmol min^{-1} m^{-3})	3.23 ± 2.25	1.47 ± 0.38	3.27 ± 0.85	1.44 ± 0.34	3.82 ± 1.05	2.03 ± 0.20	2.71 ± 0.57	1.26 ± 0.36

Met = Methanol

DahA and Ind with means of 1.23 ng m^{-3} and 0.60 ng m^{-3} in urban and rural areas, respectively. The concentration of total PAHs in autumn was higher than in spring ($P_{value} \leq 0.05$) due to the more stable weather conditions. In addition, the lower concentration of PAHs in the warm season is due to the enhanced photochemical degradation of PAHs [66]. Among the different types of PAHs compounds, there is only an annual average national standard of 1 ng m^{-3} for BaP. Because of its carcinogenic potential, BaP is often used as an indicator for assessing exposure to PAHs compounds. In this study, the average concentration of BaP was 6.15 ± 1.75 and 1.45 ± 0.80 ng m^{-3} in the urban and rural area respectively. The percentiles of BaP concentrations in urban and rural locations are given in Fig. S3 (Supplementary material). Accordingly, the BaP concentration exceeded the national standard in 100% of the cases in the urban areas and in 73% of the cases in the rural areas.

Oxidative potential

In Table 2, the OP statistical summary of PM_{10} is given at two sampling locations in three different meteorological phenomena (dusty, inversion, and regular days) with two extraction solvents of water and methanol. As indicated in the Table 2, the amount of OP^{DTTv} was lowest on dusty days ($OP^{DTTv\text{-}water}$ of 1.35 ± 0.4 and 1.26 ± 0.4 nmol min^{-1} m^{-3} in urban and rural locations, respectively). This is most likely because of the high level of soil-based compounds, most of which are not redox active. OP was at its lowest value, despite the increased concentration of PM, which indicates that OP is PM mass independent and an important proxy alongside PM mass in air pollution monitoring [67].

OP^{DTTv} of the PM_{10} was higher on inversion days 1.79 ± 0.76 and 2.03 ± 0.2 nmol min^{-1} m^{-3} at urban and rural locations, respectively than on other days. The higher OP activity in the cold seasons (inversion days) than the warm ones (dusty days) indicated the oxidative activity and formation of secondary organic aerosol during the transport or aging of particles in the atmosphere. The differences in particle OP in different seasons could be associated with changes in PM chemical compounds. Earlier studies have also demonstrated that seasonal variations can change the OP of PM [68].

Table 3 Spearman correlation between DTT activity, and selected species

Species		Urban		Rural	
		DTT activity		DTT activity	
Water soluble ions		R	p	R	p
	Na^+	−.32	.021	−.47	.02
	Cl^-	−.26	.03	−.32	.02
metal(loid)s	Fe	.43	.04	.35	.03
	Cu	.83	.01	.68	.00
	Ni	.51	.04	.47	.03
	V	.64	.02	.68	.02
	Cd	.52	.00	.20	.04
	Mn	.79	.00	.68	.02
PAHs	Ba	.48	.00	.57	.00
	Bap	.61	.01	.38	.01
	Pyr	.36	.04	.32	.04
	Total PAHs	.56	.02	.41	.01

Figure 5 shows the ratio of the OP for urban area to rural area. According to the results of this study, no significant difference was found between the OP in the urban and rural areas ($P_{value} > 0.05$). In the studied rural area, large areas of agricultural lands that may affect the compounds that are redox active due to the use of pesticides. The results of this study (as mention in section 4.2.2) showed that the amount of arsenic in the PM was greater in the rural areas than in the urban environment. The results of this study showed that the choice of extraction solvent affects DTT activity ($p_{value} \leq .05$). Therefore, OP^{DTT} with methanol extract produced greater DTT activity than did that with the water extract. The results of this study are in line with previously reported data [26, 69].

In this study, the relationship between DTT activity and concentration of metals, PAHs, water soluble ions was investigated to determine which affected the DTT activity. Table 3 shows the

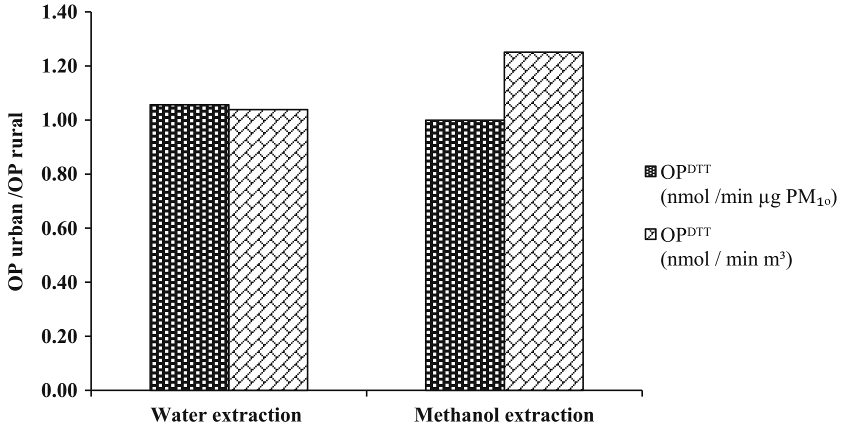


Fig. 5 Ratio of the oxidative potential (OP) for urban area to rural area

correlation coefficient between DTT consumption and concentration of chemical compounds. The results showed a strong relationship between vehicular tracers such as Cu, Mn and OP as well as a moderate relationship among Ba, Cd, Ba, Ni, V, Fe and OP. These results are in line with other studies. [16, 31, 70, 71]. These result indicating vehicular emissions which the main sources of chemical compound of PM in Tehran, may be the important supporters of OP. DTT oxidation is performed by metals via catalytic processes [31]. Cu and Fe can produce $OH^{\circ-}$ via Fenton reactions [19]. The redox active compounds have unconjugated electrons in the d-orbital that can produce free radicals through the redox cycling mechanisms with biological reductants [1]. DTT oxidation by Fe is low, but due to the abundance of Fe, it is usually important in DTT oxidation. Moreover, non-redox active metals such as Zn and Al can affect the OP of metals by exacerbating or lessening free radical production. The mineral compounds were not significantly associated with OP, which was consistent with the study by Hu et al. [29]. Sulfate may have a proxy for the bioavaibility of metals because it can mobilize the dissolved Fe from the surface of the particle by influencing the acidity of the PM [17].

According to Verma method [48] the PM acidity were calculated using the Eq. S3 (see Eq. S3, Supplementary material). Regardless sampling locations, the results showed that PM on inversion days was approximately twice higher acidic compared to regular days, and also the figure for dusty days had the highest acidity value at around 0.5. Thus more acidic conditions during inversion days may be is a leading cause of metal dissolution and consequently high OP of PM_{10}. These results are consistent with previously studies [48, 52, 53]. The inverse relationship between Na^+ and Cl^- and the formation of OH showed that it is a surrogate for other metals. In the case of large amounts of particles such as Na^+ and Cl^-, there was an inverse relationship with OP through a competition with more redox active compounds [16]. PAHs are important as a marker of sources of organic compounds.

A strong correlation was found between DTT activity and BaP concentration and moderate correlation between DTT activity and total PAHs, Pyr. According to the high concentrations of BaP in present study, it may be one of the major participants of OP in Tehran. BaP is a tracer of fuel emission from vehicles, particularly diesel fuel vehicles. Although some compounds of PAHs are not redox active, they may be oxidized to redox active compounds such as quinones and nitro PAHs, which also oxidize DTT [36, 71].

Conclusions

To the best of our knowledge, this is the first study that compares OP of PM_{10} in various meteorological phenomena, including dusty and inversion days in Tehran. In this study, we used DTT assay to measure OP, which may indicate the ability of PM_{10} to produce oxidative stress. The results showed that the mass concentrations of PM_{10} in Tehran were 100 and 95% above the WHO guidelines in urban and rural areas respectively. The crustal tracer elements (Na^+,Mg^{2+}, and Ca^{2+}) had the highest amounts on dusty days and the lowest amounts on inversion days. The total amount of Mo, Zn, Pb, Ba, Ni, V, Cd, Pb and Cu as anthropogenic elements was higher in urban areas than in rural ones. The results show, the highest contribution of PAHs was related to the 3 and 4-ring compounds. The minimum amount of OP (nm DTT μg^{-1} PM_{10}^{-1}) was observed on dusty days. Cu, Ba, Cd, Mn, Ni, V, Fe, total PAHs, Bap and Pyr were significantly related to OP, showing that the main sources of pollution affecting the OP of PM in Tehran are the vehicles. In summary, the results of this study support earlier studies that OP beside PM mass concentration is a good proxy for air quality monitoring. We hope OP measurement in the air quality monitoring networks could be routinely performed.

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