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Oxidative Potential of Ambient Particulate Matter in Beirut during Saharan and Arabian Dust Events

Christopher Lovett¹, Mohammad H. Sowlat¹, Najat A. Saliba², Alan L. Shihadeh^{2,3}, and Constantinos Sioutas^{1,*}

¹Department of Civil and Environmental Engineering, University of Southern California, 3620 South Vermont Avenue, Los Angeles, California, 90089, USA

²Department of Chemistry, American University of Beirut, P.O. Box 11-0236, Riad El Solh, Beirut, 1107 2020, Lebanon

³Dean of the Maroun Semaan Faculty of Engineering Department of Mechanical Engineering, American University of Beirut, P.O. Box 11-0236, Riad El Solh, Beirut, 1107 2020, Lebanon

Abstract

In this study, we examine the oxidative potential of airborne particulate matter (PM) in Beirut, Lebanon, as influenced by dust events originating in the Sahara and Arabian deserts. Segregated fine (< 2.5 μm) and coarse (2.5–10 μm) PM samples collected during dust events, as well as during non-dust periods, were analyzed for chemical composition, and the *in vitro* alveolar macrophage (AM) assay was utilized to determine the oxidative potential of both types of samples. We performed Spearman rank-order correlation analysis between individual chemical components and the oxidative potential of PM to examine the impact of the changes in PM chemical composition due to the occurrence of dust events on overall PM oxidative potential. Our findings revealed that the oxidative potential of Beirut's urban PM during non-dust periods was much higher than during dust episodes for fine PM. Our findings also indicated that tracers of tailpipe emissions (i.e., elemental (EC) and organic carbon (OC)), non-tailpipe emissions (i.e., heavy metals including Cu, Zn, As, Cd, and Pb), and secondary organic aerosols (SOA) (i.e., water-soluble organic carbon, WSOC) were significantly associated with the oxidative potential of PM during dust days and non-dust periods. However, the contribution of desert dust aerosols to Beirut's indigenous PM composition did not exacerbate its oxidative potential, as indicated by the negative correlations between the oxidative potential of PM and the concentrations of crustal elements that were enriched during the dust days. This suggests that aerosols generated during Saharan and Arabian dust events pose no additional health risk to the population due to PM-triggered reactive oxygen species formation. These results significantly contribute to our understanding of the effects of desert dust aerosols on the composition and oxidative potential of PM in several countries throughout the entire Middle East region that are impacted by dust events in the Sahara and Arabian deserts.

*Corresponding author. Tel: 1-213-740-6134; Fax: 1-213-744-1426, sioutas@usc.edu.

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Keywords

Dust Episodes; Sahara and Arabian Deserts; Beirut; Particulate Matter; Oxidative Potential

1. Introduction

Beirut, Lebanon, a major coastal city on the eastern edge of the Mediterranean Sea, is subject to particulate remnants of dust events originating in both the Sahara Desert of North Africa, as well as the Arabian Desert of the Arabian Peninsula. When dust events occur, the resulting airborne particulate matter (PM) from the Sahara travels eastward, making its way over the Mediterranean Sea to Beirut (Athanasopoulou et al., 2016). Aerosols from dust events in the Arabian Desert, however, migrate westward through the urban atmospheres of Saudi Arabia, Jordan and eastern Lebanon before joining with the indigenous Beirut particulate matter (PM) above the city (Jaafar et al., 2014). As a large urban center representative of several large middle-eastern cities throughout the region, particulate air pollution in the urban atmosphere above Beirut arises primarily from vehicle emissions (tailpipe and non-tailpipe), marine emissions and port activity, construction projects, sea salt, and airborne dust composed of crustal material (CM) and metals (Borgie et al., 2016; Daher et al., 2013, 2014; Saliba, et al., 2010; Saliba & Massoud, 2010; Kouyoumdjian et al., 2006).

Particulate matter (PM), especially fine PM (less than 2.5 μm in diameter, or $\text{PM}_{2.5}$), has been associated with several adverse effects on human health, including asthma, lung cancer, coronary heart disease, and heart failure (Li et al., 2003a; Dockery et al., 1993; Shah et al., 2013; Kim et al., 2013; Delfino et al., 2005; Samet et al., 2000; Dominici et al., 2006), as well as central nervous system (CNS) dysfunction resulting from neuroinflammation and subsequently induced cytokine production (Davis et al., 2013; Levesque et al., 2011; MohanKumar et al., 2008; Cheng et al., 2016). These adverse health effects resulting from PM exposure are largely mediated by a cellular inflammatory response that includes production of reactive oxygen species (ROS), a cellular defense mechanism primarily occurring in epithelial cells of the lungs as well as in various neurons and glia of the brain (Li et al., 2003b, 2009a; Prahald, 1999). Oxidative potential, a measure of the potential for PM to induce the formation of ROS and other oxidative species intercellularly, has been linked to specific PM components, some more toxic than others. These PM species and their associated oxidative potential have been attributed to various sources of particulate emissions in several studies (Decesari et al., 2017; Argyropoulos et al., 2016; Mousavi et al., 2018; Shirmohammadi et al., 2018).

In the current study, we examine the influence of desert dust episodes on the oxidative potential of PM indigenous to Beirut, Lebanon, and correlate this redox activity to specific PM species. When dust events of both Saharan and Arabian origin occur, they contribute significantly to the aerosol composition in Beirut's urban atmosphere. The impact of these alterations to PM composition on health effects, as mediated by the oxidative stress and inflammatory response of cells during exposure, has not previously been extensively studied. Using the *in vitro* alveolar macrophage (AM) assay, we first measured the redox activity of PM samples collected during dust events and non-dust periods. This assay involves exposing

alveolar macrophage cells derived from the epithelial lining of the rat lung to PM samples and quantifying the cellular formation of oxidative species during the inflammatory response (Rosenkranz et al., 1992; Landreman et al., 2008; Shafer et al., 2010). Chemical analysis of the components of the PM samples collected during dust events and non-dust periods was also performed, and the relationship between these results and the oxidative potential of the PM samples was examined using Spearman rank-order correlation analysis.

The influence of dust events on particulate matter toxicity is a topic of great interest for the entire Middle Eastern region, extending far beyond the local confines of Beirut, and is heavily debated within the scientific community. Residents of several semi-arid and arid regions of the Middle East have argued that the recommended PM significance thresholds listed in the World Health Organization's *Air Quality Guidelines* (WHO, 2006) cannot be directly applied to their regions because there have been no carefully designed studies evaluating the toxicity of these particles as affected by dust events. Our study is one of the first to examine changes to PM composition and toxicity under these conditions.

2. Methodology

2.1 Sampling location and schedule

PM sampling was done on the roof of the 20-meter high Chemistry building at the American University of Beirut (AUB) during the summer and fall of 2012. The university is located in the northwest region of Beirut (33°90'N, 35°50'E) in close proximity to commercial areas and high-volume roadways, thus we may assume the PM samples collected at this location are highly representative of the city's urban atmosphere (Baalbaki et al., 2013; Daher et al., 2013).

Size segregated PM samples were collected using three Sioutas Personal Cascade Impactor Samplers, or PCISs (SKC Inc., Eighty-Four, PA, USA; Misra, et al., 2002; Singh, et al., 2003), operating in parallel, each preceded by a 10 µm cut-point impactor (Chemcomb Model 3500 Speciation Sampling Cartridge) and operating at a flow rate of 9 lpm. Each PM sample was collected over a 24-hour time period. Separate coarse (PM_{10-2.5}), accumulation mode (PM_{2.5-0.25}) and ultrafine (PM_{0.25}) particle fractions were collected; however, in the current study we combine the results of accumulation mode and ultrafine PM analyses into one size fraction, i.e. PM_{2.5}.

Teflon (PTFE) filters (Pall Life Sciences, Ann Arbor, MI) were utilized in two of the PCISs and were subsequently analyzed for PM mass, inorganic secondary ions and total metals. The third PCIS utilized quartz microfiber filters (Whatman International Ltd., Maidstone, England) and analysis of these samples for water-soluble organic carbon (WSOC) as well as organic and elemental carbon (OC/EC) was subsequently performed.

Ten PM samples segregated into size fractions (6 fine, 4 coarse) were collected during dust event days, and nine PM samples (5 fine, 4 coarse) were collected during non-dust days. While this might appear to be a rather limited sample size, it should be noted that dust storms are infrequent events, therefore by its nature, this type of research is one of opportunity. Dust storm episodes are not a daily or weekly occurrence, even in the Middle

East, and during such events conditions prevail that cannot be replicated in a laboratory. Therefore, we collected samples based on the occurrence of these events within a reasonable timeframe.

Dust days were identified using the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) model (Draxler and Rolph, 2013). Confirming evidence of desert dust events was provided by the BSC-/DREAM dust maps website (<http://www.bsc.es/ess/bsc-dust-daily-forecast/>). Because aerosols resulting from dust episodes could continue to influence the local PM concentrations even after an episode ends (Zender et al., 2003), the day an event occurred as well as the two days following were considered “dust days” for the purposes of this study. Complete details of the PM sampling methodology and dust event determination procedure are documented in Dada et al. (2013) and Jaafar et al. (2014). During the campaign, four individual dust episodes were identified, for which 6 fine and 4 coarse PM samples were collected (Table 1). Sampling during dust days extended over the 24-hour average collection time in some cases.

2.2 Gravimetric and chemical analyses

Gravimetric analysis consisted of weighing all filters pre- and post-sampling with a high-precision microbalance to determine mass loading. Total metals content of the PM samples was determined by analysis of the Teflon filters using magnetic-sector Inductively Coupled Plasma Mass Spectroscopy (HR-ICP-MS Thermo-Finnigan Element 2) after acid extraction (Zhang, et al., 2008). The extraction utilized a Teflon bomb digestion protocol, using an acid mixture composed of 1 mL of 16 M nitric acid (HNO₃), 0.25 mL of 12 M hydrochloric acid (HCl), and 0.10 mL of hydrofluoric acid (HF) (Herner et al., 2006). The digestion period included a gradual increase in temperature to 180 °C over 9 minutes and holding the digestion mixture at 180 °C for an additional 10 minutes, followed by a 1-hour cool-down period. Digestates were then diluted to 15 mL with ultrapure water, and ICP-MS analysis was then conducted (Lough et al., 2005). Metal recovery rates and reference material information for this analysis are included as a Supplementary Information (SI) Excel file. Concentrations of inorganic secondary ions in PM samples were measured by ion chromatography (Model 2020i, Dionex Corp.) performed on high purity water extractions of the Teflon filters. Analysis of the quartz filters for elemental carbon (EC), organic carbon (OC) was done using the method of Thermal Evolution/Optical Transmittance (Birch and Cary, 1996). After water-extraction and filtration (0.22 µm pore size) of the quartz filter samples, WSOC content was determined using a Sievers 900 Total Organic Carbon Analyzer (Sullivan et al., 2004). Prior to sampling, all quartz filters were prebaked at 550 °C for 12 hours and then packaged in baked aluminum foil for storage.

2.3 Determination of PM oxidative potential via the alveolar macrophage (AM) assay

The AM assay was used to quantify the oxidative potential of the PM samples. Alveolar macrophage cells used in this assay are scavenging cells found *in vivo* in the inner epithelial lining of the rat lung. For the *in vitro* assay, the NR8383 immortalized cell line was used. During the assay, macrophage cells were exposed to PM samples, and the compound 2,7-dichlorodihydrofluorescein diacetate (DCFH-DA) was used as a fluorescent probe to quantify the cellular formation of oxidative species. As the non-fluorescent compound

DCFH-DA enters the cell, it is de-acetylated by cellular enzymes to produce 2,7-dichlorodihydrofluorescein (DCFH), also a non-fluorescent compound. DCFH is then oxidized by any reactive species generated during the cellular response to PM exposure, forming the highly fluorescent and detectable 2,7-dichlorofluorescein (DCF). Finally, DCF concentration is quantified via a spectrophotometric microplate reader (504 nm excitation and 529 nm emission) in fluorescence units per mass of PM (FU/ $\mu\text{g-PM}$), and serves as an index of reactive species formation (Rosenkranz et al., 1992; Landreman et al., 2008; Shafer et al., 2010). Fluorescence measurements are done on a dilution series for each sample extract, thus establishing a calibration curve and linear dose-response region.

Zymosan is used in the AM assay as a positive control to induce a cellular oxidative response, as it activates membrane-bound toll-like receptors (TLR) of the alveolar macrophages, thus initializing a reliably strong response. Results of the AM assay are reported in standard Zymosan units to allow data comparisons across different sample batches and experiments, minimizing difference due to variations in instrument sensitivity and cell cultures. After blank correction, the fluorescence data in units of FU/ $\mu\text{g-PM}$ is normalized to the response of a unit of Zymosan, and reported in units of $\mu\text{g-Zymosan}/\mu\text{g-PM}$. The mass concentration ($\mu\text{g-Zymosan}/\mu\text{g-PM}$) is then multiplied by the ambient PM concentration corresponding to each analyzed sample to generate standardized volumetric concentrations ($\mu\text{g-Zymosan}/\text{m}^3\text{-air}$), which are more relevant when discussing real-world population exposures to ambient PM.

2.4 Correlational analysis of oxidative potential and PM species

Bivariate correlation analysis was conducted by calculating Spearman's rho (non-parametric) coefficients for the measured air volume-based concentrations (i.e. per m^3 of air) of chemical species and oxidative potential of PM samples collected during dust and non-dust days. These correlation coefficients allowed us to identify species known to be tracers of specific sources that are highly associated with PM oxidative potential. It is noteworthy that in this work, a P-value < 0.05 was considered as statistically significant.

3. Results and Discussion

3.1 Mass concentration and chemical composition of PM

The mass concentrations ($\mu\text{g}/\text{m}^3$) of coarse and fine PM fractions collected during dust and non-dust days are presented in Figure 1. As can be seen in the figure, greater PM mass concentrations were observed during dust days as compared to non-dust days in both PM size ranges. This is quite in accordance with our expectations, and consistent with earlier findings reported in the literature, which demonstrate the impact of dust episodes on increasing ambient PM mass concentrations (e.g., Chirizzi et al., 2017; Shahsavani et al., 2012).

Figures 2 and 3 present the concentrations of ionic species and carbonaceous species, respectively, present in coarse and fine PM fractions during dust and non-dust days. When comparing dust vs. non-dust days, concentrations of Na^+ , Cl^- , EC, OC, and WSOC are not drastically different, and are within the variation indicated by error bars (Figures 2 & 3), a

finding also reflected in the data of Jaafar et al. (2014). As can be seen in Figure 2, the concentrations of Cl^- and Na^+ (tracers of sea salt aerosol) were higher in the coarse PM fraction (Fig. 2a) than in fine PM (Fig. 2b), which is expected given the nature and size of these particles (Hasheminassab et al., 2014). Concentrations of the inorganic secondary ions sulfate, nitrate, and ammonium (tracers of ammonium nitrate and ammonium sulfate), however, were higher in the fine PM size fraction, and in fact no ammonium was detected in the coarse fraction. This is most likely due to the secondary nature of these particles, which are preferentially partitioned in the accumulation mode (Daher et al., 2013, 2014). During non-dust days, concentrations of all inorganic ions present in fine PM were higher than on dust days, in agreement with previous research indicating that the background aerosol in the Mediterranean region is high in WSOC as well as in inorganic secondary ions (SI) content (Malaguti et al., 2015; Nicolas et al., 2009), and these species would be diluted by the additional crustal elements present during dust days.

As shown in Figure 3, the concentrations of EC (tracer of vehicular emissions), WSOC (tracer of secondary organic aerosol (SOA) and biomass burning), and OC (from traffic, SOA, and biomass burning) were much higher in fine PM (Fig. 3b) than coarse PM (Fig. 3a). We expect to observe higher EC concentrations in fine PM (especially in the ultrafine range) than in coarse PM. OC, whether in the form of primary organic carbon (POC), that comes from traffic emissions and biomass burning, or in the form of secondary organic carbon (SOC), is a PM species having higher concentrations in the accumulation mode, or fine PM, than in the coarse PM range, which is in accordance with our results. The same applies to water soluble organic carbon (WSOC) which is mostly associated with secondary organic carbon and to a lesser extent, in the Beirut area, with biomass burning (Daher et al., 2013, 2014). When comparing the carbonaceous species composition of fine PM on dust and non-dust days, concentrations of EC, OC, and WSOC were higher on dust days as compared to non-dust days, although these differences are within the range of variation indicated by the error bars (Fig. 3b). We also calculated the OC/EC ratios in the fine PM fraction of ambient samples collected during both dust and non-dust days. Our results indicated that the OC/EC ratio did not change significantly across dust versus non-dust episodes, with corresponding values of 2.25 and 1.93, respectively. These ratios are in agreement with those previously measured in Beirut (Waked et al., 2013, 2014).

The concentrations of trace elements and metals in the coarse and fine PM fractions on dust and non-dust days are presented in Table 2. The concentrations of crustal elements and species associated with dust particles, including Mg, Ca, Ba, and Fe (Jaafar et al., 2014), are quite higher on dust days as compared to the non-dust days in both the coarse and fine PM size fractions, indicating the enrichment of these species during dust episodes. However, such a trend was not observed for many other elements that are associated with non-tailpipe vehicular emissions, particularly for coarse PM, including Cu, Zn, Cd, Ni, and Pb (Shirmohammadi et al., 2015), and in many cases the concentrations of this category of species were even higher during the non-dust days as compared to the dust days. In addition, the concentrations of crustal elements and tracers of non-tailpipe traffic emissions were higher in the coarse PM than in the fine PM size fraction, which is in agreement with previous studies (Sowlat et al., 2016b; Wang et al., 2016; Thorpe et al., 2008). K, on the other hand, which is commonly used as a tracer of biomass burning (Urban et al., 2012), has

a higher concentration in the fine PM size range, due to its predominantly primary nature as a direct product of combustion (Sanderson et al., 2014; Hasheminassab et al., 2014).

3.2 PM oxidative potential

The oxidative potential of particulate matter, as quantified by the AM assay, may be reported on either a volumetric (i.e. per m³ of air volume) or per PM mass basis concentration. When reporting the mass basis, the intrinsic toxicity of the PM is revealed, while on a volumetric basis, the extrinsic PM toxicity is indexed. The latter method is more directly applicable to the actual airborne concentrations of PM to which populations are exposed. Therefore, we present and discuss the per-volume oxidative potential of the PM samples. The volume-based oxidative potential concentrations were standardized to Zymosan, a positive control that induces a reliably strong inflammatory response in macrophage cells, and results are reported in units of µg-Zymosan/m³ air.

PM oxidative potential values determined for samples collected during dust and non-dust days are presented in Figure 4. As can be seen in the figure, the oxidative potential of coarse PM was found to be slightly higher during dust days, as compared to the non-dust days. However, the oxidative potential of fine PM was observed to be drastically higher during non-dust days (720 ± 275 µg-Zymosan/m³), as compared to that of fine PM collected during dust days (280 ± 198 µg-Zymosan/m³). This result may be due to the additional dust aerosols present in the urban atmosphere during storms diluting the concentrations of toxic PM species that are normally prevalent on non-dust days.

Chirizzi et al. (2017) also examined the oxidative potential of ambient PM_{2.5} from dust and non-dust sources. These authors used a different assay to assess the redox properties of PM, called the dithiothreitol (DTT) assay (Rattanavaraha et al., 2011; Li et al., 2009b; Verma et al., 2009). This is a cell-free molecular assay that assesses a PM sample's oxidative potential by quantifying the transfer of electrons from DTT to oxygen, which provides an index of oxidative stress. The DTT redox reaction is similar to the naturally-occurring cellular redox reaction involving nicotinamide adenine dinucleotide phosphate (NADPH) and oxygen. The rate at which DTT is consumed during the electron transfer process is measured under standard conditions, and provides an index of the of the redox-active species concentration in a PM sample. Thus, the DTT assay is different than the cellular macrophage assay used in our study to determine oxidative potential.

Several studies have used the DTT assay to measure the oxidative potential of PM as an index of toxicity and health risk, and many different species have been implicated in the redox activity of PM. In studies of ambient ultrafine and sub-micron PM (Charrier et al., 2015), as well as PM_{2.5} (Charrier et al., 2012), fractions collected at urban and rural sites, the majority of measured DTT activity has been attributed to transition metals, especially Cu and Mn, as well as quinones. Samake et al. (2017) found that bioaerosols, specifically fungal spores, exhibit oxidative potential levels similar to those of metals and quinones. As mentioned above, and of relevance to the current study, in an examination of PM composition and oxidative potential during Saharan dust events, Chirizzi et al. (2017) found that the DTT activity of the high carbon group, which represents combustion-related PM, was more than two times greater than that of the "Saharan dust outbreak (SDO)" samples,

which are equivalent to our “dust days” samples. This is quite consistent with our observations, reinforcing the finding that for fine PM, the oxidative potential of airborne PM is much higher during non-dust periods than during dust periods.

Additionally, comparing the oxidative potential of coarse PM (Fig. 4a) to fine PM (Fig. 4b), we can see there is at least an order of magnitude difference, with the bulk of oxidative potential due to fine PM. These results are thus in agreement with previous findings that desert dust aerosols, with low oxidative potential, exist largely in the coarse PM fraction, while traffic-generated PM emissions including SOA/WSOC, which elicit a greater oxidative stress response in cells, are primarily fine PM (Kouyoumdjian et al., 2006; Shirmohammadi et al., 2015; Saffari et al., 2014).

3.3 Bivariate correlations between individual species and oxidative potential

The Spearman’s rank correlation coefficients between oxidative potential and ambient concentrations of individual marker species are presented in Table 3 for dust and non-dust days, as well as for the combined dataset. Statistically significant correlations ($p < 0.05$) are presented in bold. As can be seen in the table, oxidative potential of PM was significantly associated with markers of tailpipe vehicular emissions (i.e., EC and OC) (Schauer et al., 2003), secondary inorganic aerosol (i.e., SO_4^{2-} and NH_4^+), secondary organic aerosol (SOA) (i.e., WSOC) (Ding et al., 2008; Fine et al., 2004), and non-tailpipe emissions (i.e., Ni, Cu, Zn, As, V, Cd, and Pb) (Harrison et al., 2012; Sanderson et al., 2014). Other than secondary inorganic ions, these marker species have been statistically significantly correlated with the oxidative potential of PM in previous studies (Argyropoulos et al., 2016; Decesari et al., 2017; Shirmohammadi et al., 2015). There is no biological evidence to support toxic properties of inorganic ions, so we attribute their association with oxidative potential to their collinearity with WSOC, since all of these species are products of photochemical reactions in the atmosphere (Saffari et al., 2015). The results of the Spearman’s correlation analysis between these species and WSOC indicated R values as high as 0.73 for sulfate and 0.78 for ammonium, both of which were statistically significant ($p < 0.05$). It is noteworthy that most of the PM compounds associated with oxidative potential during non-dust days were also found to correlate highly during dust days, once again underscoring the importance of tailpipe and non-tailpipe emissions, as well as photochemistry on the overall PM toxicity. In contrast, in the case of tracers associated with soil dust, including Mg, Ca, Ba, and Fe, we clearly observed negative correlations, which are in most cases statistically significant. These species are enriched during the dust days, as indicated in Section 3.1 and Table 2, emphasizing the finding that dust events do not significantly contribute to oxidative potential of ambient PM.

4. Summary and conclusions

In this study, we examined the effects of aerosols arising from dust events in the Sahara and Arabian deserts on the composition and oxidative potential of airborne PM in Beirut, Lebanon. Utilizing bivariate correlation analysis, we identified marker species of ambient PM that were highly associated with PM oxidative potential observed during both dust days and non-dust periods. The major marker species that were found to be associated with the

oxidative potential of PM collected during dust days and non-dust periods included EC and OC (tracers of tailpipe emissions), WSOC (tracer of SOA), and heavy metals such as Ni, Cu, Zn, As, V, Cd, and Pb (tracers of non-tailpipe emissions), which is typical of atmospheric PM composition in dense urban areas. However, the major marker species associated with soil dust, whose concentrations were enriched during dust days, were found to be negatively correlated with the oxidative potential of PM. Therefore, we can conclude that dust events contribute minimally to health impacts caused by the oxidative potential of airborne particulate matter in Beirut.

By performing this study of PM oxidative potential during dust vs. non-dust days, we sought to gain a better understanding of Saharan and Arabian dust events, as well as the effects of the resulting dust aerosols on the chemical composition and oxidative potential of particulate pollution in the urban atmosphere of Beirut, as a representative large Middle Eastern city. Ultimately, these results will contribute to a more comprehensive understanding of the complex interactions between urban PM and such natural desert phenomena as well as the subsequent influence of such mixed atmospheric environments on human health as mediated by the oxidative stress induced by these particles. Such an understanding is crucial to many large urban cities in the entire Middle East region as well as other geographically similar regions experiencing dust events that alter the composition of their indigenous urban PM. The conclusions to be drawn from this paper may ultimately even influence the decisions of the policy-makers that will impact many urban populations throughout the Middle East.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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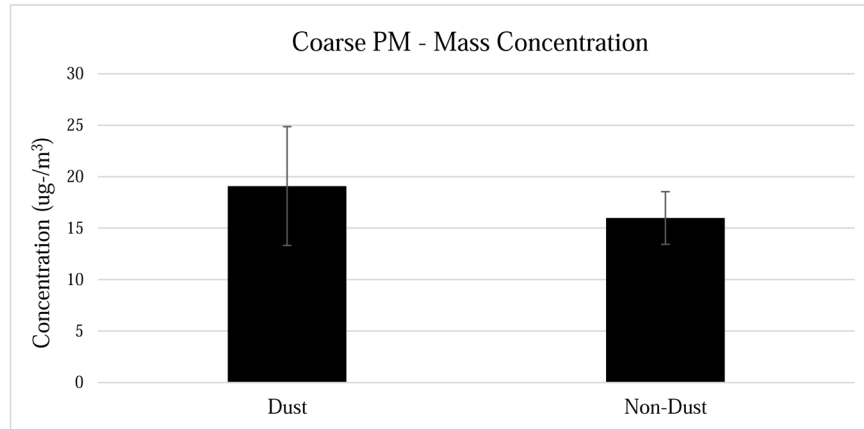
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Highlights

- Saharan and Arabian Desert dust events affect indigenous Beirut PM composition
- Coarse ambient PM contributes negligibly to oxidative potential of total PM
- Fine ambient PM was the dominant contributor to oxidative potential of total PM
- Oxidative potential of total PM was reduced during dust events
- Dust aerosol PM contributions pose no added health risk due to redox-active species
- Results have implications for the entire Middle East region affected by dust events

(a) Coarse PM



(b) Fine PM

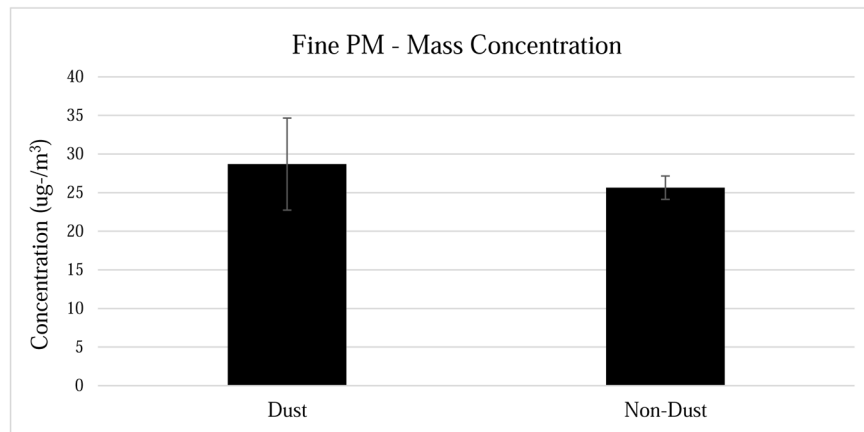
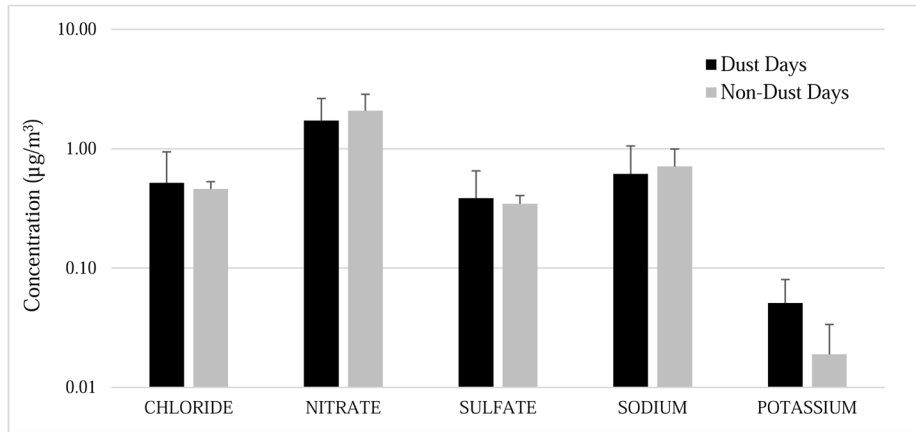


Figure 1. Mass concentrations ($\mu\text{g}/\text{m}^3$) – dust vs. non-dust days, coarse and fine PM

(a) Coarse PM



(b) Fine PM

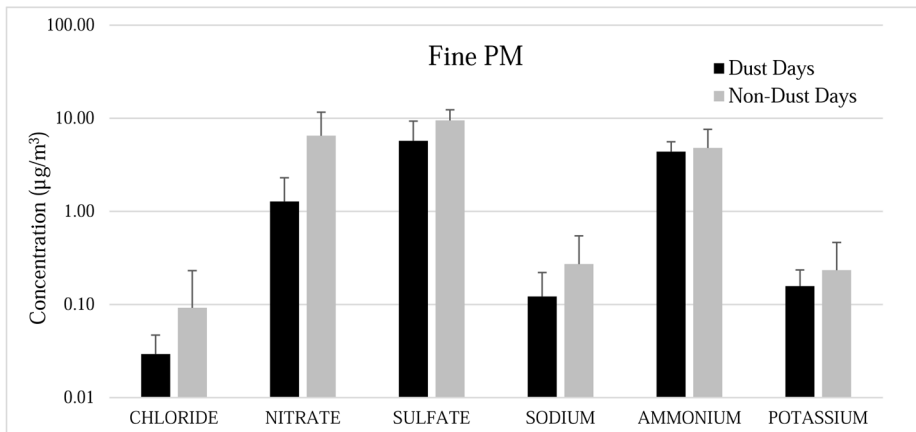


Figure 2. Concentrations of inorganic secondary ions – dust vs. non-dust days, coarse and fine PM

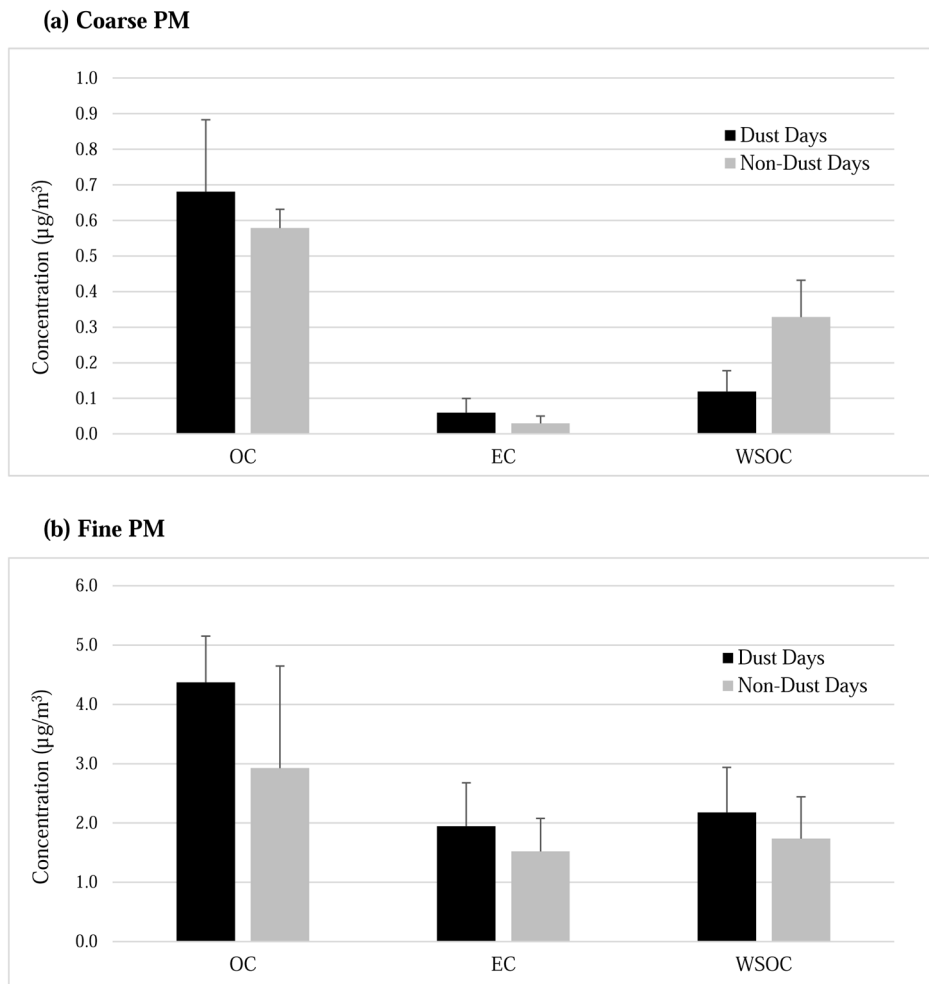
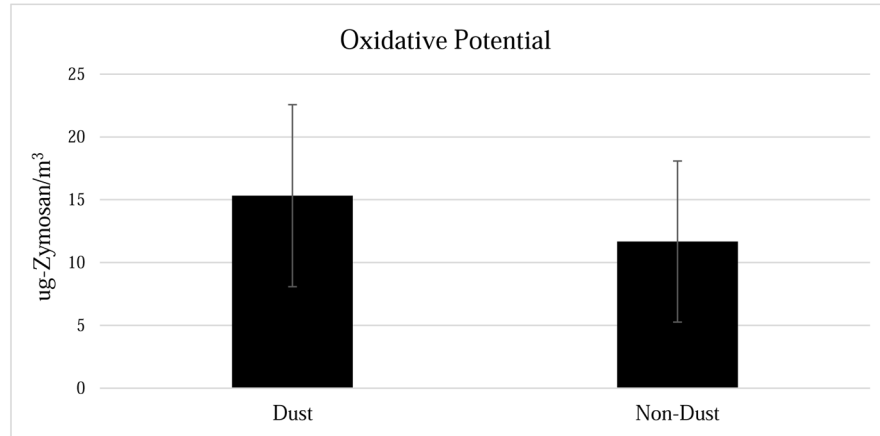


Figure 3. Concentrations of carbonaceous species – dust vs. non-dust days, coarse and fine PM

(a) Coarse PM



(b) Fine PM

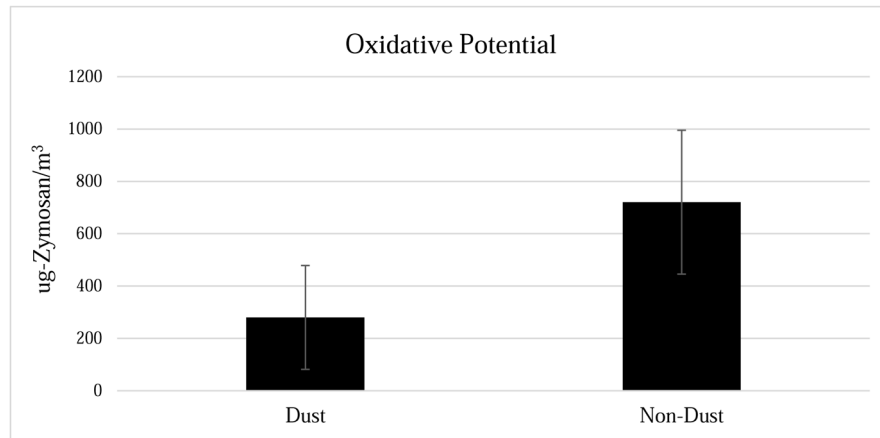


Figure 4.
PM Oxidative potential – dust vs. non-dust days, coarse and fine PM

Table 1

Sampling dates following dust episodes

Dust episodes	1	2	3	4
Sampling dates	Oct 3-4	Oct 22-24	Oct 31-Nov 2	Nov 19-21
Episode type	Arabian Remnant	Saharan - Arabian	Arabian + Saharan Remnant	Saharan - Arabian

Table 2Coarse and fine PM metals content during dust and non-dust episodes. (Mean \pm SD)

Compound	Dust Days		Non-Dust Days	
	Coarse	Fine	Coarse	Fine
<i>Total Metals (ng/m³)</i>				
Mg	225 (80.4)	85.3 (35.9)	209 (167)	52.9 (29.5)
Al	366 (99.5)	190 (89.2)	390 (380)	77.5 (44.1)
K	120 (40.3)	168 (78.5)	89.9 (53.3)	148 (51.6)
Ca	1419 (560)	269 (105)	1084 (639)	223 (153)
Ba	8.78 (1.25)	4.20 (1.56)	4.56 (2.50)	3.14 (1.95)
V	2.27 (0.74)	16.2 (9.46)	0.79 (0.44)	11.2 (5.34)
Cr	1.12 (0.15)	0.37 (0.25)	0.57 (0.46)	0.091 (0.078)
Mn	5.40 (1.37)	4.66 (1.17)	3.11 (1.84)	4.32 (1.42)
Fe	375 (72.7)	215 (64.3)	200 (107)	116 (59.5)
Ni	0.63 (0.58)	4.85 (3.13)	2.42 (4.06)	4.11 (2.28)
Cu	4.37 (0.74)	17.0 (15.9)	20.1 (13.6)	22.0 (17.8)
Zn	14.1 (3.65)	60.4 (42.4)	30.0 (13.7)	35.1 (16.0)
As	0.086 (0.018)	0.38 (0.17)	0.11 (0.089)	0.58 (0.12)
Rb	0.50 (0.29)	0.41 (0.094)	0.18 (0.14)	0.47 (0.25)
Cd	0.025 (0.0077)	0.22 (0.12)	0.016 (0.0091)	0.19 (0.084)
Pb	1.60 (0.22)	20.9 (12.0)	5.16 (6.40)	12.3 (6.25)

Table 3

Spearman's Rho correlation coefficients between the concentrations of the chemical species ($\mu\text{g}/\text{m}^3$) and the oxidative potential ($\mu\text{g-Zyosan}/\text{m}^3$) of PM during dust days ($n = 10$) and non-dust days ($n = 9$). Statistically significant correlations ($p < 0.05$) are in bold.

Species	Combined dataset	Dust days	Non-dust days
OC	0.80	0.96	0.86
EC	0.79	0.92	0.81
WSOC	0.72	0.83	0.86
SO ₄ ²⁻	0.74	0.65	0.87
NH ₄ ⁺	0.79	0.86	0.30
S	0.90	0.82	0.97
Ba	-0.34	-0.59	0.10
Mg	-0.53	-0.83	-0.20
Al	-0.52	-0.60	-0.27
Fe	-0.37	-0.64	-0.02
Ca	-0.62	-0.83	-0.42
V	0.84	0.95	0.95
Ni	0.68	0.89	0.73
Cu	0.41	0.84	0.05
Zn	0.40	0.90	0.22
As	0.91	0.82	0.98
Cd	0.79	0.92	0.82
Pb	0.54	0.93	0.30