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Oxidative potential and chemical speciation of size-resolved particulate matter (PM) at near-freeway and urban background sites in the greater Beirut area

Nancy Daher [a], Najat A. Saliba [b], Alan L. Shihadeh [c], Malek Jaafar [b], Rima Baalbaki [b], Martin M. Shafer [d], James J. Schauer [d], Constantinos Sioutas [a,*]

[a] *University of Southern California, Department of Civil and Environmental Engineering, Los Angeles, USA*
[b] *American University of Beirut, Department of Chemistry, Beirut, Lebanon*
[c] *American University of Beirut, Department of Mechanical Engineering, Beirut, Lebanon*
[d] *University of Wisconsin–Madison, Environmental Chemistry and Technology Program, Madison, WI, USA*

HIGHLIGHTS

- Per air volume basis, ROS-activity was greater at the freeway than at background site.
- Size-resolved PM intrinsic ROS-activity was generally comparable at both sites.
- In $PM_{2.5-10}$, Mn and Co were highly associated with ROS-activity.
- In $PM_{2.5-0.25}$, Cu and Co were highly correlated with ROS production.
- In $PM_{0.25}$, V and Ni strongly correlated with ROS formation.

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ABSTRACT

To assess particle oxidative potential in the greater Beirut area, size-resolved $PM_{10-2.5}$, $PM_{2.5-0.25}$ and $PM_{0.25}$ samples were collected at near-freeway and urban background sites. Metals and trace elements, including Mn, Cr, Cu, Ba, Mo and Sb, displayed increased levels and crustal enrichment factors at the roadway, indicating their vehicular origin. These elements in addition to Co, V, Ni and Zn were mostly distributed in $PM_{2.5-0.25}$ and $PM_{0.25}$ at both sites, with moderate-to-high water-solubility (>30%). The presence of these metals, mainly air toxics, in small size ranges constitutes an added health risk. Of particular concern are elements with strong correlations ($R \geq 0.70$) with reactive oxygen species (ROS)-activity, measured by a cellular assay. In $PM_{10-2.5}$, road dust component Mn and soil-related element Co were highly correlated with ROS-activity. In $PM_{2.5-0.25}$, vehicular abrasion element Cu and soil-derived component Co were highly associated with ROS-activity. In $PM_{0.25}$, V and Ni, originating from fuel oil combustion, strongly correlated with ROS formation. ROS-activity displayed a particle-size dependency, with lowest activity associated with $PM_{10-2.5}$. On a per air volume basis, size-resolved ROS-activity was 1.5–2.8 times greater at the roadside than background location, indicating that exposure to redox-active species may be greatest near the freeway. Size-fractionated PM intrinsic activity (i.e. PM mass-normalized) was comparable at both sites, possibly suggesting a similarity in the sources of ROS-active species. Relative to other urban settings, while the intrinsic redox activity of $PM_{10-2.5}$ in Beirut is comparable to that measured at an urban site in Los Angeles (LA), its $PM_{0.25}$-induced ROS-activity is ~2.3-fold greater. Moreover, the intrinsic ROS-activity of ambient $PM_{2.5}$ in Beirut is comparable to that reported in Milan-Italy, but 3.1-times $PM_{2.5}$ activity in the heavily-polluted Lahore-Pakistan. Lastly, findings suggest a dominant role of transition metals in generating ROS compared to organic carbon in the LA area.

1. Introduction

An increasing body of epidemiological and toxicological evidence indicates robust associations between adverse health effects and exposure to particulate matter (PM) (Peters et al., 2001; Pope et al., 2002). Many of the observed health endpoints may result, at least in part, from oxidative stress initiated by the formation of reactive oxygen species (ROS) upon the interaction of PM with epithelial cells and macrophages (Li et al., 2003; Nel, 2005). ROS is a collective term comprising chemically reactive oxygen radicals or oxygen-derived species (e.g. hydroxyl radical and hydrogen peroxide) (Halliwell and Cross, 1994). However,

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* Corresponding author.
E-mail address: sioutas@usc.edu (C. Sioutas).

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while particle mass has been proven useful in demonstrating the associations between PM exposure and acute health responses, aerosol mass is probably only a surrogate for causal particle components (NRC, 2004). Specific PM species contributing to aerosol toxicity remain to be identified. Particle compounds implicated in ROS formation include organic carbon, polycyclic aromatic hydrocarbons and quinones (Cho et al., 2005; Nel et al., 2001; Squadrito et al., 2001). PM oxidative potential may also be largely related to the PM content of soluble species, particularly transition metals (Goldsmith et al., 1998; Prophete et al., 2006). Metals such as iron, copper and vanadium, can initiate ROS formation both directly and indirectly through redox-mediated mechanisms (Fantel, 1996; Valko et al., 2005). Particle-size could also be critical in mediating PM toxicity. Because of their increased number, large surface area and high pulmonary deposition efficiency (Chalupa et al., 2004; Hughes et al., 1998; Morawska et al., 1998), ultrafine particles (aerodynamic diameter, $d_p < 0.1–0.2\ \mu m$) may be more potent than larger coarse ($PM_{10–2.5}$, $10\ \mu m < d_p < 2.5\ \mu m$) or fine ($PM_{2.5}$, $d_p < 2.5\ \mu m$) particles (Cho et al., 2005; Ntziachristos et al., 2007a).

Lebanon, with a growing population and severely limited air pollution controls, is afflicted with elevated PM levels, particularly in its urban areas (Saliba et al., 2010). Lacking an efficient public transportation system (MoE/URC/GEF, 2012) and suffering from inadequate electrical power production on the national grid, its high particle levels can be mainly related to vehicular and diesel generator set emissions. Regional sources could also contribute to its PM concentrations. Being located in the eastern Mediterranean basin, aerosol emissions from industrialized areas of northern and north-eastern Europe are significant particle sources in Lebanon (Saliba et al., 2010; Saliba et al., 2007).

While the chemical composition of PM in Lebanon has been previously investigated (Massoud et al., 2011; Saliba et al., 2010; Saliba et al., 2007), its oxidative potential has yet to be explored. Because redox activity is associated with adverse health effects, accurate characterization of PM-associated redox activity at urban and roadside settings can provide impetus for policies to address air quality in Lebanon. In addition, there is a dearth of information on particle toxicity in this region as a whole. To determine PM redox activity in Lebanon, coarse, accumulation ($PM_{2.5–0.25}$, $2.5\ \mu m < d_p < 0.25\ \mu m$) and quasi-ultrafine ($PM_{0.25}$, $d_p < 0.25\ \mu m$) particle samples were collected at near-freeway and urban background sites in the greater Beirut area. Samples were analyzed for their ability to induce oxidative stress on rat alveolar macrophages based on their ROS content. Their chemical composition was also determined, with particular focus on the effect of metals and trace elements. To the best of the authors' knowledge, this is the first study to evaluate particle-induced toxicity in the Eastern Mediterranean. The intrinsic redox activity of PM in Beirut — representative of developing areas lacking air quality regulations — is also compared to that of aerosols from other worldwide urban settings for which similar ROS data, using the same assay, are available. Findings of this work provide additional insight on PM-based ROS-activity and its relationship to PM species and particle-size, as they represent areas impacted by sources distinctly different from those in typically investigated regions, such as Europe and the US.

2. Methodology

2.1. Sampling sites

The sampling campaign was conducted in the greater Beirut area at urban background and near-freeway sites, as shown in Fig. S1. The background site was situated at the American University of Beirut (AUB). This monitoring site, which overlooks the Mediterranean coast from the north/west and AUB campus from the south/east, is mostly surrounded by dense vegetation covers and pedestrian roads. The nearest street is located about 150 m west of the site. This coastal roadway, which separates the site from the Mediterranean Sea, experiences relatively high traffic activity throughout the day, especially during peak hours (7–9 a.m. and 4–7 p.m.). Moreover, the sampling site is about 1.5 and 2.5 km away from a leisure yacht club and the commercial port of Beirut, respectively. The second sampling site consisted of 5-lane Jal El Dib freeway, along its southbound segment. The sampling point was directly adjacent to the freeway at about 1 m from its edge and 1.5 m above ground level. The site is therefore heavily influenced by vehicular emissions from the roadway. This freeway, which serves as a main conduit for vehicles traveling from Mount/North Lebanon to the capital Beirut, experiences heavy traffic throughout the day, with increased congestion during rush hours (7–11 a.m. and 4–7 p.m.). Additionally, the site is within 0.4 and 3.3 km of the Mediterranean coast and a yacht port/club, respectively. The site is also about 7.5 km from a thermal power plant running on heavy fuel oil.

2.2. Sample collection

Sampling was conducted on weekdays during July–August 2012 from 7:00 a.m. to 5 p.m. Samples were concurrently collected at both sites on a weekly basis. Three parallel Sioutas Personal Cascade Impactor Samplers (Sioutas PCIS, SKC Inc., Eighty Four, PA, USA (Misra et al., 2002)), operating at 9 lpm and fitted with PM_{10} inlets (Chemcomb 3500 speciation sampling cartridge, Thermoelectron Corp., Ohio, USA) were deployed at each location to collect size-resolved particles in the following size ranges: 10–2.5 μm (coarse PM), 2.5–0.25 μm (accumulation PM) and <0.25 μm (quasi-ultrafine PM). For chemical analysis purposes, two PCISs were loaded with Teflon filters (Pall Life Sciences, Ann Arbor, MI) while one PCIS was loaded with quartz microfiber filters (Whatman International Ltd., Maidstone, England). 25 mm filters were used as impaction substrates for $PM_{10–2.5}$ and $PM_{2.5–0.25}$ while 37 mm filters were used as collection media for $PM_{0.25}$. The collected particle mass was determined by pre- and post-weighing the Teflon filters using a UMX2 microbalance (Mettler Toledo GmbH, CH-8606 Greifensee, Switzerland), following equilibration under controlled temperature and relative humidity conditions (22–24 °C and 40–50%, respectively).

2.3. Sample analyses

To perform chemical and oxidative potential analyses of the samples, each of the collected Teflon and quartz filters was sectioned into two equal portions. Measurements of carbonaceous species and organic compounds were conducted on the quartz substrates, while all other analyses were performed on the Teflon filters. Depending on the analytical mass requirements, measurements were conducted on either individual weekly samples (carbonaceous species, ions, ROS-activity, metals and elements) or composites of the weekly samples (water-soluble organic carbon).

Elemental and organic carbon (EC and OC, respectively) contents of the filters were determined using the NIOSH Thermal Optical Transmission method (Birch and Cary, 1996). The total elemental composition of the filter substrates was measured using a high resolution (magnetic sector) Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS Thermo-Finnigan Element 2). A mixed acid (1 mL of 16 M nitric acid, 0.25 mL of 12 M hydrochloric acid and 0.1 mL of hydrofluoric acid) microwave-assisted digestion was applied for extraction of total metals and elements (Herner et al., 2006). The water-soluble elemental content of the filters was also quantified using HR-ICP-MS, but following water-extraction and filtration of the samples (Zhang et al., 2008). Ions and water-soluble organic carbon (WSOC) were respectively determined by ion chromatography and a Sievers 900 Total Organic Carbon Analyzer, after extraction of the samples with high purity water (Schauer et al., 2004; Sullivan et al., 2004).

The redox activity of the samples was measured using a macrophage-based reactive oxygen species (ROS) assay. This assay is a fluorogenic cell-based method that uses 2′,7′-dichlorodihydrofluorescein diacetate (DCFH-DA) as the fluorescent probe. This probe is responsive to the dominant cellular ROS species, including the hydroxyl radical, peroxide,