Atmospheric formation of 9,10-phenanthraquinone in the Los Angeles air basin

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Abstract

Quinones are highly reactive and toxic compounds, capable of increasing cellular oxidative stress by raising concentrations of intracellular hydrogen peroxide. It has been suggested that these compounds, although also directly emitted by vehicular exhaust, are mostly formed in the atmosphere by photochemical reactions of their parent polycyclic aromatic hydrocarbons (PAHs). However, because of the low concentrations and instability of some quinones, relatively little is known about their levels in ambient air samples. The tricyclic compound 9,10-phenanthraquinone (PQ), one of several quinones found in the particle-phase of ambient air, is a compound that can irreversibly inactivate key cellular proteins. In this study, we report concentration changes of PQ in atmospheric samples as the air moves across the Los Angeles basin by the prevailing wind trajectory. The trajectory is, for the most part, from the coastal areas to the Inland Empire in the eastern end of the Los Angeles basin; the samples were collected during the photoactive season of early summer. For this study, five sites along the predominant wind trajectory were selected and samples were collected as the air parcel passed over each site. Particle-phase PQ concentrations ranged from 100 to 2000 pg m\(^{-3}\). A significant increase in PQ concentration was observed as the air parcel moved inland from Long Beach (source area) to Riverside, the last sampling site in the wind trajectory and considered as the final receptor area. Our results suggest that ca. 90\% of the PQ in the receptor site was photochemically formed during atmospheric transport.

Keywords: 9, 10-Phenanthraquinone; Los Angeles basin; Transport; Photochemistry; PAH

1. Introduction

There are many epidemiological findings that associate particulate matter (PM) with adverse health effects in humans (Avol et al., 2001; Kunzli et al., 2006; Seagrave et al., 2006; Yorifuji et al., 2005). The Southern California Particle Center (SCPC) has been studying the chemical properties of PM in an effort to characterize those properties of relevance to toxicity. In that context, we have focused on quinones because of their presence in PM and their chemical properties, which include the ability to transfer electrons from a donor to oxygen and to form covalent bonds with appropriate
nucleophiles (Monks et al., 1992; O’Brien, 1991; Squadrito et al., 2001). Quinones are generated as combustion products of fossil fuels (Valavanidis et al., 2006a) and as photochemical reaction products of polycyclic aromatic hydrocarbons (PAHs) (Barbas et al., 1996; Holt et al., 2005; Sasaki et al., 1997; Wang et al., 2007). Wang et al. (2007) have shown that atmospheric 9,10-phenanthraquinone (PQ) is formed by gas-phase reactions of phenanthrene (PHE) with O₃, OH, and NO₃. Quinones are present in ambient air samples both in the particle-phase and the gas-phase (Cho et al., 2004; Kishikawa et al., 2006; Schuetzle et al., 1981; Valavanidis et al., 2006) and as a result, humans are exposed to quinones associated with PM on a continuous basis. The exposure to these highly toxic compounds can result from direct inhalation or/and from their metabolic formation from precursor PAHs. Quinones can cause the overproduction of reactive oxygen species (ROS), resulting in oxidative stress (Kumagai et al., 1997; Squadrito et al., 2001) which is a causal factor in the pathology of many diseases. A continuously growing list of diseases and conditions, especially those involving inflammation, asthma, cardiovascular diseases, Alzheimer’s disease, atherosclerosis, diabetes, and motor neuron diseases, are reported to be associated with oxidative stress (Beal, 1997; Martinet et al., 2004; Steele et al., 2007). In addition to their ability to generate ROS, quinones can participate in electrophilic reactions with tissue nucleophiles which can irreversibly inactivate key cellular proteins (Rodriguez et al., 2005). Previous studies conducted in our center have demonstrated that PQ can directly inactivate glyceraldehyde-3-phosphate dehydrogenase (GAPDH) by covalent bond formation and indirectly by reactive oxygen generation (Rodriguez et al., 2005). As a result of these properties, PQ on atmospheric PM has been considered as a key participant in several diseases such as lung cancer, asthma and allergic inflammation (Hiyoshi et al., 2005; Kumagai et al., 2002; Sugimoto et al., 2005).

Although quinones are important compounds from a toxicological point of view, only few studies have measured their atmospheric levels (Allen et al., 1997; Cho et al., 2004; Kishikawa et al., 2006). Most of these studies have measured PQ levels in PM₁₀ collected in different locations around the world. Allen et al. (1997) found average PQ concentrations around 427 pg m⁻³ in Boston, MA, very similar to concentrations observed by Cho et al. (2004) in the Southern California atmosphere (100–730 pg m⁻³), and by Kishikawa et al. (2006) in Nagasaki, Japan. There are still questions regarding the sources of quinones, i.e., individual contribution of different sources, either primary or secondary from parent compounds. Several studies have shown that quinones are emitted by light and heavy duty vehicles (Valavanidis et al., 2006; Jakober et al., 2007; Kishikawa et al., 2006). In particular, Kishikawa et al. (2006) examined the relationship between particle-phase PQ and particle-phase PHE. However, to our knowledge there are no other studies evaluating the photochemical formation of PQ in ambient atmospheres.

In this report, we describe results of a study of ambient air PQ concentrations measured on different days, at different locations in the Los Angeles basin, as the air parcel is transported by prevailing winds. Samples were collected at several sites in the basin, with sampling periods timed according to the predicted wind trajectories from the coast toward Riverside, located at the eastern end of the basin. The results show that, during the summer when experiments were conducted, most of the PQ measured in Riverside resulted from photochemical gas-to-particle processes.

2. Experimental

This study was conducted during the last week of March and the first week of June 2005. Sampling was only conducted when the predicted air parcel trajectory was favorable for sample collection at all sites.

2.1. Prediction of the air parcel trajectory

This study was designed following similar studies previously conducted in Southern California (Hughes et al., 2000, 2002). Sampling dates were selected based on predicted wind trajectories for individual days. Wind trajectories were predicted using the MM5 model (www.mmm.ucar.edu/mm5). The PSU/NCAR mesoscale model (known as MM5) is a limited-area, nonhydrostatic, terrain-following sigma-coordinate model designed to simulate or predict mesoscale atmospheric circulation. In this model, terrestrial and isobaric meteorological data are horizontally interpolated from a latitude–longitude mesh to a variable high-resolution domain on either Mercator, Lambert conformal, or polar stereographic projection.
Back-trajectories for the sampling dates were calculated later using actual wind fields obtained from the California Air Resources Board database. Back-trajectories (Fig. 1) calculated with measured meteorology data were consistent with the predicted trajectories for each measurement site.

For the 1 June 2005 data, the origin of the air parcel during the sampling periods was different from the other 3 days. During this sampling day, the air parcel was coming from the south and did not pass over the Long Beach site. Therefore, we expect to observe differences in PQ concentrations when comparing this day with other days of the campaign.

2.2. Sampling sites

Five sampling sites were selected in the Los Angeles basin based on the dominant wind direction in the basin. The sites were Long Beach, Anaheim, Diamond Bar, Mira Loma and Riverside. Distance between sites was ~25 km (Fig. 1). Long Beach, with its international port, refineries, and major freeways, was considered a source site and sampling was conducted during the morning hours just as the air parcel started moving. For the purpose of this study, Riverside, our last site in the trajectory, was considered a receptor site. Sampling was conducted for 4 h at each site, starting at 8:00 a.m. in Long Beach (LBC), 10:00 a.m. in Anaheim (ANA), 12:00 p.m. in Diamond Bar (DIB), 14:00 p.m. in Mira Loma (MRL), and 16:00 p.m. in Riverside (RIV). The sampling time was scheduled so that at least 2–3 h of the sampling overlapped with the expected air parcels.

Samples were only collected during the days when the predicted air trajectory was favorable, totaling 4 experimental days: 31 May, 1 June, 6 June, and 7 June of 2005.

2.3. Sampling and analyses

Aerosol samples were collected using medium-volume PM$_{2.5}$ samplers (Model 1202, TISCH Environmental, Cleves, OH). XAD-4 resin and Teflon-coated glass fiber filters (TCGFF), purchased from Fisher Scientific, were used to collect vapor- and particle-phase PAHs and quinones, respectively. Samples were extracted by sonication over three periods of 8 min using a mixture of
dichloromethane:acetonitrile (2:1 v/v) and filtered through a 0.45 μm filter (Millipore).

2.3.1. PAH assays
Fluorescence-based HPLC analyses were performed using a previously published procedure (Eiguren-Fernandez and Miguel, 2003). A 1 mL aliquot of the extract was evaporated to ~100 μL and injected directly in the HPLC-FL system.

2.3.2. Quinone assays
Quinones were assayed by a GC/MS procedure described earlier (Cho et al., 2004). In the assay, the remaining extract was derivatized with acetic anhydride and zinc to obtain the acetylated reduced quinones which were analyzed by selected ion monitoring GC/MS.

2.4. Statistical analysis
The statistical analysis of the data was carried out using GraphPad Prism 4 (GraphPad Software Inc., San Diego, CA). Average concentrations, standard deviation and correlations were calculated for each day and site according to measured data. No further analysis was done due to the limited data available.

3. Results and discussion

3.1. 9,10-Phenanthraquinone concentrations in PM2.5

Particle-phase PQ concentrations varied from 0.10 ng m⁻³ in Anaheim, to 1.98 ng m⁻³ in Diamond Bar (Table 1). The sampling station at Diamond Bar, located near a major freeway, is highly impacted by fresh emissions, which may be the cause of the higher concentration of PQ observed at this site. Also, as shown in Fig. 1, Diamond Bar was too far north from the back-trajectory to be considered in this study. For these reasons, we did not include the Diamond Bar site in the analysis of the results.

A significant increase in particle-phase PQ concentrations was observed as the air parcel moved inland from Long Beach to Riverside (Fig. 2). Good correlations (r²~0.8) between PQ and distance from Long Beach were observed for three of the four sampling dates, with higher correlations for days in which the air parcel passed closer to the sampling sites. For 6 and 7 June, the predicted air parcel moved from the northeast, passing closer to Long Beach (source site) exhibiting a higher correlation. The similarity in the slope values of the regression for 31 May, 6 and 7 June, indicates that the atmospheric factors controlling the photo-chemical formation of PQ were similar. As previously mentioned, the results for 1 June differed from the general trend of the other 3 days, suggesting a different origin of the air parcel. Consistent with this notion, the chemical composition and physical properties of the aerosol also differ. These data clearly suggest that a significant fraction of PQ is formed as the air parcel moves inland as a result of atmospheric chemical reactions of PQ precursors.

3.2. Primary vs. secondary formation of 9,10-phenanthraquinone

The objective of this study was to estimate the contribution of primary sources and secondary formation to the atmospheric PQ burden as the air parcel travels in the Los Angeles basin. To evaluate the impact of primary emissions on PQ concentrations, we examined the study reported by Kishikawa et al. (2006) in Nagasaki, Japan. These authors demonstrated that correlations between particle-phase phenanthrene (PHEp) and PQ could be expected if both compounds were emitted by the

<table>
<thead>
<tr>
<th>Distance inland (km)</th>
<th>31 May PQ</th>
<th>31 May PHEv</th>
<th>31 May PHEp</th>
<th>1 June PQ</th>
<th>1 June PHEv</th>
<th>1 June PHEp</th>
<th>6 June PQ</th>
<th>6 June PHEv</th>
<th>6 June PHEp</th>
<th>7 June PQ</th>
<th>7 June PHEv</th>
<th>7 June PHEp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long Beach (LBC)</td>
<td>0</td>
<td>0.25</td>
<td>8.42</td>
<td>0.11</td>
<td>2.56</td>
<td>2.06</td>
<td>0.13</td>
<td>0.78</td>
<td>0.28</td>
<td>0.10</td>
<td>10.1</td>
<td>0.38</td>
</tr>
<tr>
<td>Anaheim (ANA)</td>
<td>22</td>
<td>0.17</td>
<td>n/a</td>
<td>0.49</td>
<td>2.20</td>
<td>0.40</td>
<td>0.10</td>
<td>2.28</td>
<td>0.20</td>
<td>0.12</td>
<td>26.6</td>
<td>0.14</td>
</tr>
<tr>
<td>Diamond Bar (DIB)</td>
<td>40</td>
<td>0.46</td>
<td>1.97</td>
<td>0.10</td>
<td>0.31</td>
<td>0.08</td>
<td>1.98</td>
<td>1.73</td>
<td>0.12</td>
<td>0.25</td>
<td>6.18</td>
<td>0.15</td>
</tr>
<tr>
<td>Mira Loma (MRL)</td>
<td>65</td>
<td>0.35</td>
<td>9.77</td>
<td>0.19</td>
<td>5.75</td>
<td>0.30</td>
<td>0.27</td>
<td>4.49</td>
<td>0.15</td>
<td>0.26</td>
<td>5.63</td>
<td>0.14</td>
</tr>
<tr>
<td>Riverside (RIV)</td>
<td>80</td>
<td>0.39</td>
<td>13.4</td>
<td>0.01</td>
<td>2.58</td>
<td>0.02</td>
<td>0.29</td>
<td>1.07</td>
<td>0.01</td>
<td>0.30</td>
<td>1.61</td>
<td>0.04</td>
</tr>
</tbody>
</table>
same primary sources. As recently shown by Wang et al. (2007), secondary PQ can be formed from photochemical transformation of vapor-phase PHE (PHE\textsubscript{v}). Based on these two studies, we may use the correlation between PQ and PHE\textsubscript{p}, and PQ and PHE\textsubscript{v} as indicative of primary emissions of PQ, and secondary formation during atmospheric transport, respectively.

To assess the possible role of primary sources or photochemical formation of PQ from PHE, Pearson correlation coefficients between particle-phase PQ and both vapor- and particle-phase PHE were examined for each site (Table 2). Long Beach and Anaheim showed better correlation with particle-phase PHE, while higher correlations with vapor-phase PHE were observed in Mira Loma and Riverside. Again, higher correlations with particle-phase PHE suggest primary sources as major contributors to PQ levels in Long Beach and Anaheim, while higher correlations with vapor-phase PHE suggest photochemical transformations as major PQ source as the air parcel moves inland.

To study the contribution of photochemistry to the PQ concentrations, we reasoned that if PQ is the result of only primary sources, it would follow the pattern of other compounds emitted solely by primary sources and which do not undergo significant photochemical transformations. A model compound for this purpose is the benzo[ghi]perylene (BGP), a marker for vehicular emissions, and

<table>
<thead>
<tr>
<th></th>
<th>Long Beach</th>
<th>Anaheim</th>
<th>Mira Loma</th>
<th>Riverside</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQ vs. PHE\textsubscript{v}</td>
<td>0.27</td>
<td>−0.35</td>
<td>0.84</td>
<td>0.73</td>
</tr>
<tr>
<td>PQ vs. PHE\textsubscript{p}</td>
<td>0.66</td>
<td>0.65</td>
<td>0.16</td>
<td>−0.31</td>
</tr>
</tbody>
</table>

Numbers in bold indicate significant correlation between the compounds.
commonly thought to have no significant reactivity in the atmosphere during transport. If BGP is emitted into the atmosphere in Long Beach (source site), and does not undergo transformations, then its concentration should only be affected by dilution (and local traffic) as the air parcel moves toward Riverside. A similar argument should apply to PQ if it is not photochemically formed, resulting in a constant concentration ratio of BGP to PQ across the basin. Table 3 shows BGP and PQ concentrations and BGP/PQ ratios for the Long Beach and Riverside sites, a comparison of the estimated and measured concentrations of PQ in Riverside, and the estimated percentage of PQ photochemically formed.

Estimated PQ concentrations were calculated as

$$[\text{PQ}]_{\text{RIV}} = \frac{[\text{BGP}]_{\text{RIV}}}{[\text{BGP}]/[\text{PQ}]_{\text{LBC}}}.$$  

The percentage of photochemically formed PQ was calculated as

$$\% \text{ of PQ formed photochemically} = 100 - \left[ \frac{([\text{BGP}]/[\text{PQ}]_{\text{RIV}} \times 100)}{([\text{BGP}]/[\text{PQ}]_{\text{LBC}})} \right].$$

On average, and except for 1 June, when the wind direction was not favorable, we estimated that 92.7% of the PQ present in Riverside was photochemically formed (Table 3). These results, together with the correlation observed between PQ and vapor-phase PHE, clearly suggest that during early summer a major fraction of the PQ present in the Los Angeles basin atmosphere is formed during transport.

### 4. Conclusions

The main objective of this brief study was to evaluate the extent of primary sources and secondary reactions to the atmospheric burden of 9,10-phenanthraquinone (PQ) in the Los Angeles basin. The results suggest that both the air parcel origin and trajectory play an important role in the total PQ levels measured in the air of the basin. High correlation between PQ and particle-phase PHE indicates that they have a common emission source in the Long Beach and Anaheim areas, whereas photochemical transformation of vapor-phase PHE seems to be the major source of secondary PQ at sites located further inland. PQ concentration increased downwind as the air parcel traveled inland in the Los Angeles basin, suggesting an important photochemical production. We estimate that ca. 90% of PQ present in the Los Angeles basin is secondary, formed during transport. A more extensive study is needed to measure PQ levels during different seasons, and a better model should be developed to estimate the contribution of individual primary sources and the types of photochemical reactions that contribute to the atmospheric PQ burden.

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views of the Agency and no official endorsement should be inferred.

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