

Available online at www.sciencedirect.com



Atmospheric Environment 42 (2008) 2312–2319



www.elsevier.com/locate/atmosenv

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

Arantza Eiguren-Fernandez<sup>a,\*</sup>, Antonio H. Miguel<sup>a</sup>, Rong Lu<sup>b</sup>, Kathie Purvis<sup>c</sup>, Bill Grant<sup>a</sup>, Paul Mayo<sup>a</sup>, Emma Di Stefano<sup>a</sup>, Arthur K. Cho<sup>a</sup>, John Froines<sup>a</sup>

<sup>a</sup>Southern California Particle Center and Supersite, Institute of the Environment, UCLA, 90095 Los Angeles, USA <sup>b</sup>Department of Atmospheric and Oceanic Sciences, University of California Los Angeles, 90095 Los Angeles, USA <sup>c</sup>Department of Chemistry, Claremont McKenna College, 91711 Claremont, USA

Received 22 June 2007; received in revised form 9 October 2007; accepted 7 December 2007

#### 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<sup>-3</sup>. 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. © 2007 Elsevier Ltd. All rights reserved.

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

fax: +1 310 206 9903.

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

<sup>\*</sup>Corresponding author. Tel.: +13108259576;

E-mail address: arantza@ucla.edu (A. Eiguren-Fernandez).

<sup>1352-2310/\$ -</sup> see front matter  $\odot$  2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.atmosenv.2007.12.029

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 O<sub>3</sub>, OH, and NO<sub>3</sub>. 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 guinones 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 casual 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 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 PM<sub>2.5</sub> collected in different locations around the world. Allen et al. (1997) found average PQ concentrations around 427 pg m<sup>-3</sup> in Boston, MA, very similar to concentrations observed by Cho et al. (2004) in the Southern California atmosphere (100–730 pg m<sup>-3</sup>), 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  $\sim 25 \text{ km}$  (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 4h 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 mediumvolume  $PM_{2.5}$  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



119°0'0"W 118°45'0"W 118°30'0"W 118°15'0"W 118°0'0"W 117°45'0"W 117°30'0"W 117°15'0"W 117°0'0"W

Fig. 1. Sampling locations, indicated by the box in the abbreviated name, and wind trajectories for all sampling dates.

dichloromethane:acetonitrile (2:1 v/v) and filtered through a  $0.45 \,\mu$ m 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  $\sim 100 \,\mu$ L 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 $PM_{2.5}$

Particle-phase PQ concentrations varied from  $0.10 \text{ ng m}^{-3}$  in Anaheim, to  $1.98 \text{ ng m}^{-3}$  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 ( $r^2 \sim 0.8$ ) 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 photochemical formation of PO 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 9,10phenanthraquinone

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 (PHE<sub>p</sub>) and PQ could be expected if both compounds were emitted by the

Table 1

Atmospheric concentrations (ng m<sup>-3</sup>) of vapor- and particle-phase PHE and particle-phase PQ for each sampling site

	Distance inland (km)	31 May		1 June		6 June		7 June					
		PQ	$\text{PHE}_{\rm v}$	PHE <sub>p</sub>	PQ	$\text{PHE}_{\rm v}$	PHE <sub>p</sub>	PQ	$\text{PHE}_{\rm v}$	PHE <sub>p</sub>	PQ	$\text{PHE}_{\rm v}$	PHE <sub>p</sub>
Long Beach (LBC)	0	0.25	8.42	2.58	0.11	2.56	2.06	0.13	0.78	0.28	0.10	10.1	0.38
Anaheim (ANA)	22	0.17	n/a	0.49	0.26	2.20	0.40	0.10	2.28	0.20	0.12	26.6	0.14
Diamond Bar (DIB)	40	0.46	1.97	0.10	0.47	0.31	0.08	1.98	1.73	0.12	0.25	6.18	0.15
Mira Loma (MRL)	65	0.35	9.77	0.19	0.23	5.75	0.30	0.27	4.49	0.15	0.26	5.63	0.14
Riverside (RIV)	80	0.39	13.4	0.01	0.19	2.58	0.02	0.29	1.07	0.01	0.30	1.61	0.04



Fig. 2. Correlation between particle-phase PQ concentrations  $(pg m^{-3})$  and inland distance (km) for each sampling day. (a) 31 May 2005, (b) 1 June 2005, (c) 6 June 2005 and (d) 7 June 2005.

same primary sources. As recently shown by a study conducted by Wang et al. (2007), secondary PQ can be formed from photochemical transformation of vapor-phase PHE (PHE<sub>v</sub>). Based on these two studies, we may use the correlation between PQ and PHE<sub>p</sub>, and PQ and PHE<sub>v</sub> 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 particlephase PHE, while higher correlations with vaporphase PHE were observed in Mira Loma and Riverside. Again, higher correlations with particlephase PHE suggest primary sources as major contributors to PQ levels in Long Beach and Anaheim, while higher correlations with vapor-

#### Table 2

Pearson correlation coefficients for PQ with vapor- and particlephase PHE at each sampling site

	Long Beach	Anaheim	Mira Loma	Riverside
PQ vs. PHE <sub>v</sub>	0.27	-0.35	<b>0.84</b>	<b>0.73</b>
PQ vs. PHE <sub>p</sub>	<b>0.66</b>	<b>0.65</b>	0.16	-0.31

Numbers in bold indicate significant correlation between the compounds.

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 3

Date	BGP (LBC)	BGP (RIV)	PQ (LBC)	BGP/PQ ratio	PQ estimated (RIV)	PQ measured (RIV)	Photochemically formed (%)
31 May	1.201	0.031	0.246	38.7	0.006	0.39	98.4
1 June	0.054	0.047	0.110	1.15	0.096	0.19	48.6
6 June	0.101	0.018	0.134	5.61	0.024	0.29	91.6
7 June	0.118	0.042	0.100	2.81	0.036	0.30	88.0

Concentrations  $(ng m^{-3})$  for BGP and PQ in Long Beach and Riverside, BGP/PQ ratios, estimated and measured concentrations  $(ng m^{-3})$  for PQ in Riverside, and estimated percentage of photochemically formed PQ

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

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

The percentage of photochemically formed PQ was calculated as

% of PQ formed photochemically

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

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 (PO) in the Los Angeles basin. The results suggest that both the air parcel origin and trajectory play an important role in the total PO 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 vaporphase PHE seems to be the major source of secondary PQ at sites located further inland. PO 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.

#### Acknowledgments

The authors thank AQMD and Mr. Phil Topard, Assistant Chief of the Lifeguard Division Office in Venice, for allowing us to use their facilities. We also thank Janet Arey, Roger Atkinson, and Lin Wang for their help with sample collection, their valuable advices and comments. This research was supported by the Southern California Particle Center and Supersite (US EPA Grants #R827352-01-0 and CR-82805901) and by the Southern California Particle Center grant RH2735201. Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

#### References

- Allen, J.O., Dookeran, N.M., Taghizadeh, K., Lafleur, A.L., Smith, K.A., Sarofim, A.F., 1997. Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. Environmental Science and Technology 31 (7), 2064–2070.
- Avol, E.L., Gauderman, W.J., Tan, S.M., London, S.J., Peters, J.M., 2001. Respiratory effects of relocating to areas of differing air pollution levels. American Journal of Respiratory and Critical Care Medicine 164 (11), 2067–2072.
- Barbas, J.T., Sigman, M.E., Dabestani, R., 1996. Photochemical oxidation of phenanthrene sorbed on silica gel. Environmental Science and Technology 30 (5), 1776–1780.
- Beal, M.F., 1997. Oxidative damage and the pathogenesis of amyotrophic lateral sclerosis. Journal of Neurochemistry 69, S256.
- Cho, A.K., Di Stefano, E., You, Y., Rodriguez, C.E., Schmitz, D.A., Kumagai, Y., Miguel, A.H., Eiguren-Fernandez, A., Kobayashi, T., Avol, E., Froines, J.R., 2004. Determination of four quinones in diesel exhaust particles, SRM 1649a, an atmospheric PM<sub>2.5</sub>. Aerosol Science and Technology 38, 68–81.
- Eiguren-Fernandez, A., Miguel, A.H., 2003. Determination of semivolatile and particulate polycyclic aromatic hydrocarbons in srm 1649a and PM<sub>2.5</sub> samples by HPLC-fluorescence. Polycyclic Aromatic Compounds 23 (2), 193–205.
- Hiyoshi, K., Takano, H., Inoue, K.I., Ichinose, T., Yanagisawa, R., Tomura, S., Kumagai, Y., 2005. Effects of phenanthraquinone on allergic airway inflammation in mice. Clinical and Experimental Allergy 35 (9), 1243–1248.
- Holt, J., Hothem, S., Howerton, H., Larson, R., Sanford, R., 2005. 9,10-Phenanthrenequinone photoautocatalyzes its formation from phenanthrene, and inhibits biodegradation of naphthalene. Journal of Environmental Quality 34 (2), 462–468.
- Hughes, L.S., Allen, J.O., Bhave, P., Kleeman, M.J., Cass, G.R., Liu, D.Y., Fergenson, D.F., Morrical, B.D., Prather, K.A., 2000. Evolution of atmospheric particles along trajectories crossing the Los Angeles basin. Environmental Science and Technology 34 (15), 3058–3068.
- Hughes, L.S., Allen, J.O., Salmon, L.G., Mayo, P.R., Johnson, R.J., Cass, G.R., 2002. Evolution of nitrogen species air pollutants along trajectories crossing the Los Angeles area. Environmental Science and Technology 36 (18), 3928–3935.
- Jakober, C.A., Riddle, S.G., Robert, M.A., Destaillats, H., Charles, M.J., Green, P.G., Kleeman, M.J., 2007. Quinone emissions from gasoline and diesel motor vehicles. Environmental Science and Technology 41 (13), 4548–4554.
- Kishikawa, N., Nakao, M., Ohba, Y., Nakashima, K., Kuroda, N., 2006. Concentration and trend of 9,10-phenanthrenequinone in airborne particulates collected in Nagasaki city, Japan. Chemosphere 64 (5), 834–838.
- Kumagai, Y., Arimoto, T., Shinyashiki, M., Shimojo, N., Nakai, Y., Yoshikawa, T., Sagai, M., 1997. Generation of reactive oxygen species during interaction of diesel exhaust

particle components with NADPH-cytochrome P450 reductase and involvement of the bioactivation in the DNA damage. Free Radical Biology and Medicine 22 (3), 479–487.

- Kumagai, Y., Koide, S., Taguchi, K., Endo, A., Nakai, Y., Yoshikawa, T., Shimojo, N., 2002. Oxidation of proximal protein sulfhydryls by phenanthraquinone, a component of diesel exhaust particles. Chemical Research in Toxicology 15 (4), 483–489.
- Kunzli, N., Avol, E., Wu, J., Gauderman, W.J., Rappaport, E., Millstein, J., Bennion, J., McConnell, R., Gilliland, F.D., Berhane, K., Lurmann, F., Winer, A., Peters, J.M., 2006. Health effects of the 2003 Southern California wildfires on children. American Journal of Respiratory and Critical Care Medicine 174 (11), 1221–1228.
- Martinet, W., De Meyer, G.R.Y., Herman, A.G., Kockx, M.M., 2004. Reactive oxygen species induce RNA damage in human atherosclerosis. European Journal of Clinical Investigation 34 (5), 323–327.
- Monks, T.J., Hanzlik, R.P., Cohen, G.M., Ross, D., Graham, D.G., 1992. Quinone chemistry and toxicity. Toxicology and Applied Pharmacology 112 (1), 2–16.
- O'Brien, P.J., 1991. Molecular mechanisms of quinone cytotoxicity. Chemico-Biological Interactions 80, 1–41 (published erratum appears in Chemico-Biological Interactions 81 (January (1–2)) (1992) 219).
- Rodriguez, C.E., Fukuto, J.M., Taguchi, K., Froines, J., Cho, A.K., 2005. The interactions of 9,10-phenanthrenequinone with glyceraldehyde-3-phosphate dehydrogenase (GAPDH), a potential site for toxic actions. Chemico-Biological Interactions 155 (1–2), 97–110.
- Sasaki, J., Aschmann, S.M., Kwok, E.S.C., Atkinson, R., Arey, J., 1997. Products of the gas-phase OH and NO<sub>3</sub> radicalinitiated reactions of naphthalene. Environmental Science and Technology 31 (11), 3173–3179.
- Schuetzle, D., Lee, F.S.C., Prater, T.J., Tejada, S.B., 1981. The identification of polynuclear aromatic hydrocarbon (PAH) derivatives in mutagenic fractions of diesel particulate extracts. International Journal of Environmental Analytical Chemistry 9 (2), 93–144.
- Seagrave, J., McDonald, J.D., Bedrick, E., Edgerton, E.S., Gigliotti, A.P., Jansen, J.J., Ke, L., Naeher, L.P., Seilkop, S.K., Zheng, M., Mauderly, J.L., 2006. Lung toxicity of ambient particulate matter from southeastern US sites with different contributing sources: relationships between composition and effects. Environmental Health Perspectives 114 (9), 1387–1393.
- Squadrito, G.L., Cueto, R., Dellinger, B., Pryor, W.A., 2001. Quinoid redox cycling as a mechanism for sustained free radical generation by inhaled airborne particulate matter. Free Radical Biology and Medicine 31 (9), 1132–1138.
- Steele, M., Stuchbury, G., Munch, G., 2007. The molecular basis of the prevention of Alzheimer's disease through healthy nutrition. Experimental Gerontology 42 (1–2), 28–36.
- Sugimoto, R., Kumagai, Y., Nakai, Y., Ishii, T., 2005. 9,10-Phenanthraquinone in diesel exhaust particles downregulates Cu, Zn-SOD and HO-1 in human pulmonary epithelial cells: intracellular iron scavenger 1,10-phenanthroline affords protection against apoptosis. Free Radical Biology and Medicine 38 (3), 388–395.
- Valavanidis, A., Fiotakis, K., Vlahogianni, T., Papadimitriou, V., Pantikaki, V., 2006. Determination of selective quinones and

quinoid radicals in airborne particulate matter and vehicular exhaust particles. Environmental Chemistry 3 (2), 118–123.

- Wang, L., Atkinson, R., Arey, J., 2007. Formation of 9,10phenanthrenequinone by atmospheric gas-phase reactions of phenanthrene. Atmospheric Environment 41 (10), 2025–2035.
- Yorifuji, T., Yamamoto, E., Tsuda, T., Kawakami, N., 2005. Health impact assessment of particulate matter in Tokyo, Japan. Archives of Environmental and Occupational Health 60 (4), 179–185.