



Particulate ROS in an urban environment

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Technical Note: Particulate reactive oxygen species concentrations and their association with environmental conditions in an urban, subtropical climate

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Reactions between hydrocarbons and ozone or hydroxyl radicals lead to the formation of oxidized species, including reactive oxygen species (ROS), and secondary organic aerosol (SOA) in the troposphere. ROS can be carried deep into the lungs by small aerodynamic particles where they can cause oxidative stress and cell damage. While environmental studies have focused on ROS in the gas-phase and rainwater, it is also important to determine concentrations of ROS on respirable particles. Samples of PM_{2.5} collected over 3 h at midday on 40 days during November 2011 and September 2012 show that the particulate ROS concentration in Austin, Texas ranged from a minimum value of 0.02 nmolH₂O₂(m³air)⁻¹ in December to 3.81 nmolH₂O₂(m³air)⁻¹ in September. Results from correlation tests and linear regression analysis on particulate ROS concentrations and environmental conditions (which included ozone and PM_{2.5} concentrations, temperature, relative humidity, precipitation and solar radiation) indicate that ambient particulate ROS is significantly influenced by the ambient ozone concentration, temperature and incident solar radiation. Particulate ROS concentrations measured in this study were in the range reported by other studies in the US, Taiwan and Singapore. This study is one of the first to assess seasonal variations in particulate ROS concentrations and helps explain the influence of environmental conditions on particulate ROS concentrations.

1 Introduction

Peroxides are generated in ambient air from alkene ozonolysis and photochemical reactions with VOCs and NO_x (Seinfeld and Pandis, 2006). As an example, hydrogen peroxide (H₂O₂) and hydroperoxyl radical (HOO) are produced from the photooxidation of formaldehyde (Bufalini et al., 1972; Gay and Bufalini, 1972; Largiuni et al., 2002). Photochemical models suggest that peroxides can be present in both polluted and clean air (Kleinman, 1986; Heikes et al., 1996) which is confirmed by measurements (Walker

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et al., 2006; Snow et al., 2007). H_2O_2 is an important species in photochemical smog as a chain terminator. Its concentration in rainwater and snow has been measured since the late nineteenth century (Schöne, 1874) and studies have found strong seasonal and diurnal variations in the concentrations of H_2O_2 and other reactive oxygen species (ROS) in rainwater, water vapor, and air in gas-phase (Singh et al., 1986; Gunz and Hoffman, 1990 and references within; Ayers et al., 1992; Dollard and Davies, 1992; Lee et al., 2000; Yamada et al., 2002; Liu et al., 2003; Zhang et al., 2012). However, data on peroxide and ROS concentrations in the aerosol phase are limited.

It can be suggested that the concentration of peroxides in water associated with atmospheric aerosols can be estimated using gas-phase concentrations of peroxides. Hydroperoxides are thought to partition between the gas-phase and liquid water according to their Henry's law constants (e.g. $H_{\text{H}_2\text{O}_2}$ is $0.7\text{--}1.1 \times 10^5 \text{ Matm}^{-1}$ at 298 K; Hwang and Dasgupta, 1985; Staffelbach and Kok, 1993; Lind and Kok, 1994; Huang and Chen, 2010). Following this reasoning, an ambient gas-phase H_2O_2 concentration of 10 ppb would lead to a 1 mM concentration in liquid water associated with aerosols. However, studies on gas-phase ROS have found that urban hydroperoxide levels within aerosols are at least an order of magnitude higher than concentrations predicted by Henry's law (Arellanes et al., 2006; Hasson and Paulson, 2003; Hewitt and Kok, 1991). The Henry's law constant in aerosols may be different from that in liquid water (Hasson and Paulson, 2003) which makes it important to assess the concentration of peroxides and ROS in aerosols.

Reactions between hydrocarbons and ozone or hydroxyl radicals (generated during the photolysis of ozone and in catalytic cycles in the troposphere) lead to the formation of oxidized species and secondary organic aerosol (SOA). Highly soluble gases of oxidized species (such as H_2O_2) will be removed by the wet mucus lining in the upper airways when they are inhaled (Wexler and Sarangapani, 1998; Sarangapani and Wexler, 2000). However, SOA can carry the oxidized species, including ROS, deep into the respiratory tract (Morio et al., 2001) where they are more likely to cause oxidative stress and cell damage. While it would be presumptuous to declare that ROS has a

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direct toxic mechanism in tissue injury, many in vitro (Oosting et al., 1990; Holm et al., 1991; Geiser et al., 2004; Crim and Longmore, 1995; LaCagnin et al., 1990) and some in vivo studies have drawn links between endogenous ROS and cell injury and have established the involvement of ROS in different pathologies, such as oxygen toxicity disorder (Kehrer, 1993; Sanders et al., 1995; Bowler et al., 2002; Li et al., 2003, 2008). It appears likely that exposure to exogenous sources of ROS can influence endogenous production of ROS, thereby influencing the disease process.

In this study we use a bulk measure to assess the concentration of ROS on ambient particulate matter (PM). 2',7'-dichlorofluorescein diacetate (DCF-DA) is a non-specific fluorescent reagent for detecting ROS, such as hydrogen peroxide (H₂O₂) and hydroxyl radical (OH). Ambient concentrations of particulate ROS (Hung and Wang, 2001; Venkatachari et al., 2005, 2007; See et al., 2007) and peroxides in aerosols (Hewitt and Kok, 1991; Hasson and Paulson, 2003; Arellanes et al., 2006; Wang et al., 2010) have been measured previously. However, these studies have been conducted over short periods of time, a few months at most, and do not allow an assessment of seasonal variations in particulate ROS. Ambient particulate matter collected in different seasons has been used in studies to determine the generation of selected oxidative species in lung epithelial cells and surrogate lung fluid (Shen et al., 2011; Vidrio et al., 2009; Baulig et al., 2004). But these seasonal studies generally did not measure the ambient environmental conditions during PM sampling. It is important to understand how the ROS concentration on respirable PM varies as environmental conditions change. Thus, the main objectives of the current study are to (1) determine the concentration of ROS on PM_{2.5} in a semi-arid urban environment over a year, and (2) assess the influence of environmental conditions on these particulate ROS concentrations.

2 Materials and methods

Samples of PM_{2.5} were collected in an open area on the University of Texas at Austin campus using a Personal Environmental Monitor (PEM, SKC, PA, USA) on 40 days

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between November 2011 and September 2012. Two to five replicate samples were taken on 20 of these days to determine the average covariance in ROS concentration between multiple samplers. Sampling was conducted for 3 ± 0.5 h between 10 a.m. and 3 p.m. using air sampling pumps at 10 L min^{-1} . Pumps were calibrated before sampling with a mini-Buck Calibrator M-30 (A. P. Buck, Orlando, FL; accuracy $\pm 0.5\%$). Samplers were placed 1 m above the ground. Teflon tape was wrapped around the edges of the support screen in the PEMs to ensure a proper seal of the thin PTFE filters inside the PEMs. All sampling filters were assessed within 1 h of collection.

DCF-DA has been used as a bulk measure of ROS (Hung and Wang, 2001; Venkatachari et al., 2005, 2007; See et al., 2007) since it becomes fluorescent in the presence of a wide variety of ROS including, but not limited to, hydrogen peroxide (H_2O_2), organic peroxy (ROO) and hydroxyl (OH) radicals and the peroxyxynitrite anion (ONOO^-) (Zhu et al., 1994; Kooy et al., 1997). The use of a bulk measure enables a better understanding of the overall toxicity potential of the PM. For instance, H_2O_2 is generally considered to be less toxic than hydroxyl radicals (Valavanidis et al., 2008), but H_2O_2 likely has significant indirect biological effects since it can diffuse across membranes easily because of its lack of charge (LaCagnin et al., 1990). The method for quantifying ROS with DCF-DA was modified slightly from previous studies (Hung and Wang, 2001; Venkatachari et al., 2005, 2007; See et al., 2007) to help reduce high fluorescence intensity of field blanks. Briefly, 0.5 mL of 1 mM DCF-DA (Cayman Chemical, MI, USA) in ethanol was incubated with 2 mL of 0.01 N NaOH at room temperature for 30 min in the dark to cleave off the acetate groups. The 2',7'-dichlorofluorescein (DCFH) solution was neutralized with 10 mL sodium phosphate buffer (pH 7.2) and the solution was kept on ice in the dark till needed. Each sampled filter was sonicated in 5 mL sodium phosphate buffer for 10 min. Horseradish peroxidase (HRP, ThermoScientific, IL, USA) in sodium phosphate buffer (pH 7.0) was mixed with the DCFH solution and added to the sampled filter in the dark to yield a final volume of 10 mL with a concentration of $5 \mu\text{M}$ of DCFH and 1 unit mL^{-1} of HRP. The sample was then incubated in the dark at 37°C for 15 min, after which 0.1 mL aliquots were placed in triplicate in a 96-well plate

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and the fluorescence intensity was read at 530 nm with excitation at 485 nm (Synergy HT, Biotek, VT, USA). The concentration of ROS on the sampled filters was expressed in terms of H_2O_2 per volume of air sampled (rather than per mass of particles) because this describes exposure to ROS as it occurs in the lungs (Boogaard et al., 2012). The background fluorescence intensity produced by an unsampled filter was subtracted from the samples.

Standards were prepared with hydrogen peroxide (H_2O_2). To prepare the standards, aliquots of 0.1 mL of appropriate H_2O_2 concentration were added to 3 mL of DCFH-HRP reagent to get 0, 1.0, 2.0, 3.0, and 4.0×10^{-7} M H_2O_2 in final solutions. These solutions were incubated at 37°C for 15 min and fluorescence was measured. All glassware used in the experiments was scrubbed with soap, followed by immersion in a 10% nitric acid bath and subsequent 7x rinsing with deionized water.

The Method Detection Limit of the analytical procedure, as determined using US EPA's guidelines (EPA, 2011) is $1.2 \text{ nmol H}_2\text{O}_2 \text{ L}^{-1}$, which converts to 0.01 nmol m^{-3} assuming a 3 h sample at 10 L min^{-1} . Outliers were excluded using a more conservative approach than the Iglewicz and Hoaglin method (NIST, 2010) in that only sample concentrations with an absolute modified Z score value greater than 10 (instead of 3.5, as recommended by the method) were excluded as outliers. This was done in order to not exclude any real data resulting from variations in outdoor conditions.

Hourly averages of outdoor ozone and $\text{PM}_{2.5}$ concentrations, temperature, solar radiation, and relative humidity (RH) were obtained from the nearest Texas Commission on Environmental Quality's (TCEQ) sampling stations to report the data (located within 7 miles of the ROS sampling site, except for solar radiation which was obtained from a site 17 miles from the sampling site). Global horizontal (GH) solar radiation data was also measured during January–June 2012 on top of a 9-storey building located next to the sampling site using a rotating shadowband radiometer with a data logger (Campbell Scientific, Logan, UT). These GH measurements were taken every minute and averaged over the sampling duration. Daily precipitation data for Austin was obtained from Weather Underground (Weather Underground, 2013). Overall uncertainty

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for each measurement was calculated using standard error propagation to include variance in the measured readings and the uncertainty of the instrument when it was known. Graphical representations of the data and Shapiro–Wilk tests for normality indicated that all the datasets, except for ozone concentration, either followed lognormal distributions or did not follow normal or lognormal distributions. This led to the selection of the non-parametric Spearman Rank Correlation Coefficient test to determine the strength (ρ) and significance ($p < 0.01$) of any relationships between the concentration of particulate ROS and environmental factors. Bonferroni correction was applied to these tests. Simple linear regression analysis was also performed between particulate ROS concentrations and each environmental condition measured. All statistics were done with Stata version 11.2.

3 Results and discussion

The mean (\pm s.d.) concentration of ROS on $PM_{2.5}$ samples collected over 3 h around midday in Austin, Texas on 40 days between November 2011 and September 2012 was $1.25 \pm 1.1 \text{ nmol m}^{-3}$. The concentrations ranged from 0.02 nmol m^{-3} measured on 23 December to 3.81 nmol m^{-3} on 20 September. The concentrations on each sampled day are depicted in Fig. 1 with the error bars depicting the average standard error of replicate samples taken on 20 of the 40 sampling days. The sampling site was located away from any point sources, at a distance of about 0.7 miles from an interstate highway. Austin has a transitional, semi-arid climate, characterized by hot summers and mild winters. This is evidenced by the fact that the mean monthly temperature in November–February was 13°C whereas during June–September it was 28°C . Ambient environmental conditions measured at the nearest TCEQ sampling sites during the ROS sampling are given in Table S1. During the sampling periods on the 40 days, the ozone concentration ranged from 8 to 72 ppb, $PM_{2.5}$ concentration ranged from 1 to $22 \mu\text{g m}^{-3}$, temperature ranged from 3 to 35°C , relative humidity ranged from 21

to 95 %, precipitation ranged from 0 to 80 mm, and solar radiation ranged from 23 to 928 W m⁻².

Studies have found strong seasonal and diurnal variations in the concentrations of H₂O₂ in air, rainwater and water vapor, typically with higher concentrations measured during the summer than the winter (references within Gunz and Hoffman, 1990; references within Sakugawa et al., 1990; references within Lee et al., 2000; Yamada et al., 2002; Liu et al., 2003). However, other studies have found that some ROS species, e.g. peroxyacetyl nitrates (RCO₂ONO₂) and methyl hydroperoxide (CH₃OOH), follow the opposite trend because of greater sensitivity to NO_x precursor pollutants (Singh et al., 1986; Zhang et al., 2012). In this study, we found that particulate ROS concentrations tend to be higher in the warmer months than in the colder months, implying that particulate ROS follows trends similar to gas-phase and rainwater H₂O₂ in the atmosphere.

Table 1 displays the results of the Spearman Rank Correlation tests between particulate ROS concentrations and measured environmental conditions (ozone and PM_{2.5} concentrations, temperature, relative humidity, precipitation and solar radiation). The concentration of ROS on PM_{2.5} was statistically significantly correlated with ozone concentration ($\rho = 0.61$, $p = 0.0000$), temperature ($\rho = 0.56$, $p = 0.0002$) and solar radiation ($\rho = 0.61$, $p = 0.0000$). Several studies have assessed the correlation between particulate ROS concentrations and ozone (Hung and Wang, 2001; Venkatachari et al., 2005, 2007) and also between gas-phase H₂O₂ and ozone (Liu et al., 2003). These studies have found moderate correlations between the concentrations of ROS and ozone, with the strongest correlations occurring around midday. Complexities in the chemistry of formation of ROS have been cited as the reason for the relatively moderate correlations with ozone (Venkatachari et al., 2007). Meteorological conditions, such as solar radiation, water vapor concentration, temperature and pressure, are thought to influence the atmospheric concentration of H₂O₂ and peroxides (Logan et al., 1981; Jackson and Hewitt, 1999). Only a few studies have assessed the relationship between particulate ROS concentrations and meteorological conditions other than ozone

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concentration. Venkatachari et al. (2007) had found a weak, but statistically significant, correlation between particulate ROS and estimated secondary organic carbon concentrations in the atmosphere. Given the evidence for ROS being photochemically driven, one of the objectives of this study was to study the relationship between particulate ROS and certain meteorological conditions that influence photochemical reactions.

The statistically significant correlations observed in this study between particulate ROS concentrations and ozone concentrations, temperature and solar radiation agree with observations by studies on gas-phase H_2O_2 . Yamada et al. (2002) found that gas-phase H_2O_2 was positively correlated with solar radiation, UV radiation and temperature, while it was negatively correlated with relative humidity. Liu et al. (2003) found that gas-phase H_2O_2 was positively correlated with ozone, and negatively correlated with NO_x . Similar to Liu et al. (2003), we did not find a discernible correlation between ROS and relative humidity. While not significant, the inverse relationship between particulate ROS and daily precipitation could be because of the reduction in gas-phase H_2O_2 during rain events (Gunz and Hoffman, 1990) which could lead to reduction in adsorption of gas-phase ROS onto atmospheric aerosols.

The nearest TCEQ sampling site to measure solar radiation was located 17 miles from the ROS sampling site (all other environmental conditions were obtained from TCEQ sites within 7 miles of the ROS sampling site). In order to ensure that the conditions at the ROS sampling site were similar to those at the TCEQ sampling site, solar radiation was measured next to the ROS sampling site during January to June 2012. The solar radiation data from the two sources was seen to match well ($\rho = 0.78$, $p = 0.0002$), and data from the TCEQ site were used for analysis over the entire study period. In addition, other environmental conditions were correlated with each other in ways that were expected. When solar radiation during the sampling event was strong, ozone concentrations and temperatures also tended to be high, as indicated by significant correlations between these parameters. In contrast, solar radiation was lower on days when it rained or had high RH, as indicated by the significant inverse correlations between solar radiation and daily precipitation/RH. Ozone concentrations were also

inversely correlated with RH and daily precipitation. Higher temperatures tended to increase the concentration of $PM_{2.5}$, as indicated by a significant correlation between temperature and $PM_{2.5}$ concentration, possibly due to an increase in reaction rates leading to SOA formation.

Regression analysis between particulate ROS concentrations and environmental conditions shows that linear regression models between particulate ROS concentrations and ozone concentrations, temperature, and solar radiation are significant ($p < 0.001$ for the F test on the model) but with R^2 values ranging from 0.29 to 0.56. These regression models are shown in Fig. 2. t tests on the regression coefficients for these linear regression models are also significant ($p < 0.001$). A multiple regression model of particulate ROS concentration with ozone concentration, temperature and solar radiation is also significant ($p = 0.0000$) with an R^2 value of 0.6 which means that 60 % of the variance of particulate ROS concentrations is accounted for by the model. Standardized coefficients for the multiple regression model are given in supplementary information (SI). Linear regression models between particulate ROS concentrations and $PM_{2.5}$ concentrations, relative humidity and precipitation were not significant and are displayed in Fig. S1. The regression results indicate that ambient particulate ROS is likely a function of the ambient ozone concentration, temperature and incident solar radiation. Some other contributing factors to particulate ROS concentrations may include ambient particle concentrations and relative humidity, as well as parameters that were not measured in this study, such as the concentration of VOCs, NO_x , hydroxyl and other radical species.

The ROS concentration on $PM_{2.5}$ reported in the literature ranges from 0.80–0.97 $nmol\ m^{-3}$ at a location 14 km west of Manhattan during winter (Venkatachari et al., 2007), and 4.37–4.98 $nmol\ m^{-3}$ close to highway traffic during Los Angeles basin inversion conditions in summer (Venkatachari et al., 2005), to 5.71 $nmol\ m^{-3}$ in Singapore during December (See et al., 2007). A study in Taiwan reported a concentration of 0.54 $nmol\ m^{-3}$ on $PM_{3.2}$ on an urban sidewalk during summer (Hung and Wang, 2001). Some other studies use a different analytical method and report ROS concentrations

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on TSP ranging from 0–0.38 nmolm⁻³ in summer in west Los Angeles (Hasson and Paulson, 2003) to 0–0.24 nmolm⁻³ in summer at Niwot Ridge, CO (Hewitt and Kok, 1991). In the present study, we measured ROS concentrations on PM_{2.5} in the 0.02–3.81 nmolm⁻³ range during November 2011–September 2012 in Austin, Texas. The winter concentrations measured in this study are comparable to winter concentrations measured near Manhattan and summer concentrations in Taiwan. The summer concentrations measured in this study are lower than summer concentrations measured during basin inversion conditions in LA and winter concentrations in Singapore. In comparison, ROS concentrations on TSP in mainstream cigarette smoke (4–16 μmolm⁻³ for three different brands of cigarettes; Huang et al., 2005) are 3–4 orders of magnitude higher than all ambient particulate ROS concentrations reported in the literature.

4 Conclusions

Measuring the oxidative capacity of PM is important to understand the association between PM and adverse health effects including respiratory and cardiovascular illnesses (Samet et al., 2000; Pope et al., 2002; Bell et al., 2004). This study found that the ROS concentration on PM_{2.5} in an urban, semi-arid environment varies over the course of a year, with a minimum during the winter and a maximum during the summer. This is similar to observations by studies on ambient H₂O₂ concentrations in gas-phase and rainwater. Given that PM_{2.5} can carry ROS deep into the lungs where the particulate ROS can cause oxidative stress and cell damage, it is important to better understand the environmental conditions that influence the concentrations of ROS on PM_{2.5}. Results from correlation tests and linear regression analysis of particulate ROS concentrations and environmental conditions (which included ozone and PM_{2.5} concentrations, temperature, relative humidity, precipitation and solar radiation) indicate that ambient particulate ROS is significantly influenced by the ambient ozone concentration, temperature and incident solar radiation. Particulate ROS concentrations measured in this study were within the range 0.0–5.7 nmolm⁻³ reported by other studies in the US,

Taiwan and Singapore (Hewitt and Kok, 1991; Hung and Wang, 2001; Hasson and Paulson, 2003; Venkatachari et al., 2005, 2007; See et al., 2007). This study is one of the first to assess seasonal variations in particulate ROS concentrations and helps delineate the principle factors which influence this pollutant.

5 **Supplementary material related to this article is available online at**
[http://www.atmos-chem-phys-discuss.net/14/5061/2014/](http://www.atmos-chem-phys-discuss.net/14/5061/2014/acpd-14-5061-2014-supplement.pdf)
[acpd-14-5061-2014-supplement.pdf](http://www.atmos-chem-phys-discuss.net/14/5061/2014/acpd-14-5061-2014-supplement.pdf).

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Table 1. Spearman's rank correlation coefficients between the concentration of ROS on $PM_{2.5}$ (ROS), ozone concentration (O_3), $PM_{2.5}$ concentration, temperature (T), relative humidity (RH), precipitation (ppt), and solar radiation measured at the nearest TCEQ site (Solar Rad). Significant relationships at $p < 0.01$ are in bold and those at $p < 0.001$ are further denoted with *.

| | ROS on $PM_{2.5}$ | O_3 | $PM_{2.5}$ | T | RH | ppt |
|------------|-------------------|--------------|------------|--------------|-------------|--------------|
| O_3 | 0.61* | | | | | |
| $PM_{2.5}$ | 0.27 | 0.03 | | | | |
| T | 0.56 | 0.52 | 0.36 | | | |
| RH | -0.17 | -0.53 | 0.19 | -0.32 | | |
| ppt | -0.15 | -0.38 | 0.08 | 0.26 | 0.53 | |
| Solar Rad | 0.61* | 0.69* | 0.11 | 0.78* | -0.50 | -0.54 |

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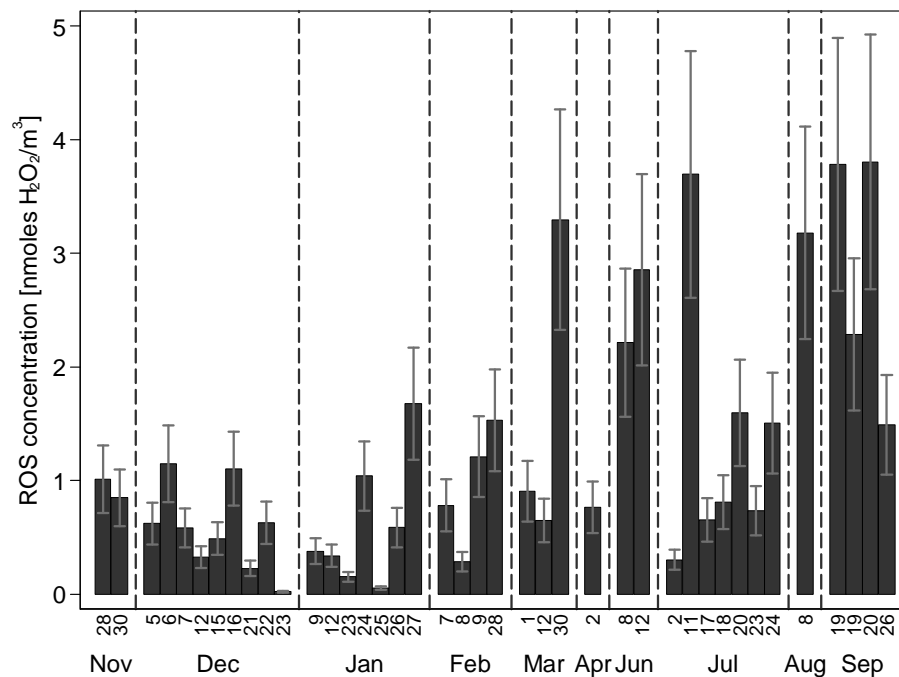


Fig. 1. Concentration of ROS on PM_{2.5} sampled at an outdoor location away from point sources in Austin, Texas. The error bars represent the average standard error of replicate samples taken on 20 of the 40 sampling days.

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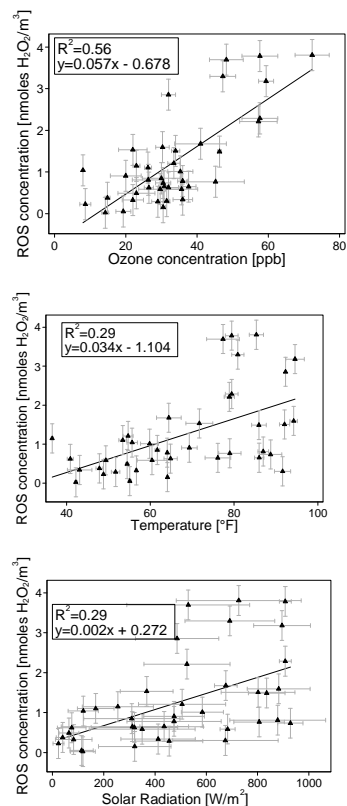


Fig. 2. Linear regression graphs showing significant relationships between particulate ROS concentrations and O₃ concentration, temperature, and solar radiation. Error bars for ROS concentration represent the average standard error of replicate ROS samples. Error bars for environmental conditions represent the variance in the measurements during the 3 h sampling period.

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