Environmental Research 132 (2014) 46–53

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Indoor particulate reactive oxygen species concentrations

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ARTICLE INFO

Article history:
Received 20 November 2013
Received in revised form
21 February 2014
Accepted 12 March 2014
Available online 16 April 2014

Keywords:
$PM_{2.5}$
Ozone
Air quality
Residential
Commercial

ABSTRACT

Despite the fact that precursors to reactive oxygen species (ROS) are prevalent indoors, the concentration of ROS inside buildings is unknown. ROS on $PM_{2.5}$ was measured inside and outside twelve residential buildings and eleven institutional and retail buildings. The mean ($\pm$ s.d.) concentration of ROS on $PM_{2.5}$ inside homes (1.37 ± 1.2 nmoles/m^3) was not significantly different from the outdoor concentration (1.41 ± 1.0 nmoles/m^3). Similarly, the indoor and outdoor concentrations of ROS on $PM_{2.5}$ at institutional buildings (1.16 ± 0.38 nmoles/m^3 indoors and 1.68 ± 1.3 nmoles/m^3 outdoors) and retail stores (1.09 ± 0.93 nmoles/m^3 indoors and 1.12 ± 1.1 nmoles/m^3 outdoors) were not significantly different and were comparable to those in residential buildings. The indoor concentration of particulate ROS cannot be predicted based on the measurement of other common indoor pollutants, indicating that it is important to separately assess the concentration of particulate ROS in air quality studies. Daytime indoor occupational and residential exposure to particulate ROS dominates daytime outdoor exposure to particulate ROS. These findings highlight the need for further study of ROS in indoor microenvironments.

1. Introduction

Although kinetic modeling suggests that hydrogen peroxide (a reactive oxygen species) is formed as a result of chemical reactions in indoor environments (Nazaroff and Cass, 1986), it was not until studies by Li et al. (2002) (office) and Fan et al. (2005) (simulated indoor conditions) that evidence of these mechanisms in indoor environments was found. These studies as well as chamber studies of ozone/terpene reactions (Docherty et al., 2005; Venkatachari and Hopke, 2008; Chen and Hopke, 2009; Chen et al., 2011) have shown that secondary organic aerosols (SOA) are formed in conjunction with peroxides and other reactive oxygen species (ROS). Particles, especially $PM_{2.5}$, can carry ROS into the lower respiratory tract where there is increased probability of health impacts, whereas gas phase ROS (which have high solubility and diffusivity) are likely absorbed and removed by mucus in the upper airways (Friedlander and Yeh, 1998). ROS include hydroperoxides, organic peroxides (ROOR'), hypochlorite ions (OCl^-), hydroxyl ($^{\cdot}OH$) radicals, and alkyl peroxyl radicals ($ROO^{\bullet}$). They can be formed through photochemical reactions (with NO_x, carbon monoxide, formaldehyde and volatile organic compounds (VOCs)) (Gunz and Hoffman, 1990; Finlayson-Pitts and Pitts, 2000) and via ozone-initiated reactions (Paulson and Orlando, 1996; Weschler, 2006; Venkatachari et al., 2007).

A substantial body of evidence links the endogenous production of reactive oxygen radicals, and subsequently oxidative stress and damage, to the pathogenesis of age-related and chronic diseases including cancer (Trush and Kensler, 1991; Witz, 1991; Guyton and Kensler, 1993; Klaunig and Kamendulis, 2004). Many in vitro and some in vivo studies have established the involvement of ROS in different pathologies, especially in many pulmonary diseases (Kehrer, 1993; Lansing et al., 1993; Sanders et al., 1995; Stevens et al., 1995; Bowler and Crapo, 2002; Li et al., 2003; Li et al., 2008). Exposure to exogenous sources can influence endogenous ROS production (such as greater generation of peroxynitrite anion (Lang et al., 2010)), which can lead to oxidative stress and damage (Klaunig and Kamendulis, 2004). This warrants further investigation of exogenous sources of ROS. However, studies to assess air quality have focused on measuring pollutants such as particle and VOC concentrations. While these pollutants are linked to adverse health outcomes (e.g., DALYs for particulate matter exposure (Zelm et al., 2008) and sick building syndrome symptoms for VOC exposure (e.g., Fisk and Rosenfeld, 1997)), the concentration of ROS is a metric that may be as important for assessing the quality of air in an environment. Reducing exposure to exogenous sources of ROS may reduce the likelihood of oxidative stress and subsequent disease formation (Churg, 2003).

Despite their potential health effects, ROS have mainly been studied in outdoor environments and only one study has assessed the concentration of ROS in an indoor environment (in a university

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http://dx.doi.org/10.1016/j.envres.2014.03.026
0013-9351/

building in Singapore: See et al., 2007). Unsaturated hydrocarbons, which can react with ozone to produce ROS, are prevalent inside buildings (Wallace et al., 1987, 1991; Brown et al., 1994) and are emitted from sources such as cleaning products (Zhu et al., 2001), air fresheners (Steinemann, 2009; Steinemann et al., 2011), and wood products (Hodgson et al., 2000). A few studies have studied the factors that influence the formation of ROS under controlled conditions in chambers (Docherty et al., 2005; Chen and Hopke, 2009; Chen et al., 2011). However, indoor environments are much more complex in that several ROS precursors are present and there is the possibility that unfiltered outdoor ROS and precursors penetrate indoors.

Given that Americans spend more than 85% of their time inside buildings (Klepeis et al., 2001), it is crucial to determine actual indoor concentrations of ROS. Residential environments have the greatest potential for exposure because people spend almost 70% of their time at home (Klepeis et al., 2001). Exposure to pollutants in commercial buildings can be very different from that in residential buildings because commercial buildings have higher air exchange rates (Chao and Chan, 2001; Bennett et al., 2012), higher recirculation rates (Thornburg et al., 2001; Bennett et al., 2012), and different operation and ventilation strategies. Employed Americans spend 8.8 h on average working on weekdays (U.S. Department of Labor, Bureau of Labor Statistics, American Time Use Survey (ATUS), 2011a), a major portion of which may be spent in office buildings. Retail stores are frequented by a large section of the population and 7.6 million Americans work as retail salespeople and cashiers (U.S. Department of Labor, Bureau of Labor Statistics, Occupational Employment Statistics Tables, National Cross-Industry, 2011b and U.S. Department of Labor, Bureau of Labor Statistics, News Release, American Time Use Survey (ATUS), 2011c). In this study, samples of $PM_{2.5}$ were collected at twelve homes, six institutional buildings and five retail stores in Austin, Texas to compare the indoor and outdoor concentrations of particulate ROS, and to determine the influence of environmental factors on particulate ROS concentrations. Because several studies have reported high background ROS values for blank filters (22–75% of field samples) (Hung and Wang, 2001; Venkatachari et al., 2005; Venkatachari et al., 2007), steps were taken in this study to improve the analytical method before collecting field samples.

2. Methods

2.1. Sample collection at homes, institutional buildings and retail stores

$PM_{2.5}$ was collected inside and outside twelve homes during March and August 2012 on Teflon filters (TF-1000, 1 μm pore size, 37 mm, Pall, NY, USA) using Personal Environmental Monitors (PEM, SKC, PA, USA). Similarly, indoor and outdoor samples of $PM_{2.5}$ were collected at seven institutional buildings located on the University of Texas at Austin campus on different days in March and July 2012, and at five retail stores during January–April 2012. Teflon tape was wrapped around the edges of the support screen in the PEMs to ensure a proper seal of the thin Teflon filters inside the PEMs. Sampling was conducted for 3 ± 0.25 h between 11 am and 2 pm using air sampling pumps at 10 L/min. All pumps were calibrated before sampling with a mini-Buck Calibrator M-30 (A.P.Buck, Orlando, FL; accuracy $\pm 0.5\%$). Duplicate samplers were placed 1 m above the ground outside and in a central location inside the buildings (variations from this protocol are described in the next paragraph). All buildings were located in Austin, Texas. Field blanks were periodically used to check that there was no significant difference in fluorescence between laboratory blanks and field blanks. The background fluorescence intensity produced by an unsampled filter was subtracted from the samples. All sampling filters were transported to the lab and assessed with the fluorescence assay described below within 1 h of collection.

For the institutional buildings, indoor sampling was conducted in an office at street level except for I2 (where the sampling room was on the 3rd floor), I3 (2nd floor), I4 (6th floor), and I1 (where the sampling room was a classroom on the 7th floor). Replicate samples were collected for 10 out of the 14 measurements. For the retail buildings, single samplers were used both indoors and outdoors. At retail sites 1–3, indoor and outdoor sampling was not conducted simultaneously, but rather on consecutive days.

ROS concentrations measured inside or outside the buildings that were greater than 3.5 times the median absolute deviation (MAD) away from the median were considered outliers (5 out of 48 samples for the commercial buildings and 6 out of 64 samples for the residential buildings), based on the Iglewicz and Hoaglin method (NIST, 2010).

2.2. Environmental factors measured

Indoor and outdoor air quality parameters were measured and building characteristics were recorded at all buildings. Indoor and outdoor temperature and relative humidity were measured with a HOBO U10 (Onset, Bourne, MA) with an uncertainty of ± 0.35 °C in temperature and $\pm 2.5\%$ in relative humidity (RH). A photo-ionization detector (PID, Geotechnical Services, Tustin, CA) calibrated with isobutylene was used to measure the indoor concentration of total volatile organic carbon (TVOC), with an uncertainty of the greater of ± 20 ppb or 10% of the reading. A DustTrak 8520 Aerosol Monitor with a size-selective aerosol conditioner (TSI, Shoreview, MN; uncertainty 1 $\mu g/m^3$) was used to measure indoor $PM_{2.5}$ concentration. The DustTrak was calibrated against a Tapered Element Oscillating Microbalance (TEOM) 1405D (Thermo Environmental Instruments, Franklin, MA) resulting in a gain of 0.9 and an offset of -5.3. In nine of the homes (R1–R9), a SidePak Personal Aerosol Monitor AM510 (TSI, Shoreview, MN) was used to measure indoor $PM_{2.5}$ concentrations instead of the DustTrak. The SidePak was calibrated against a TEOM resulting in a gain of 3 and an uncertainty of ± 3.2 $\mu g/m^3$ for measurements below 3 $\mu g/m^3$. Outdoor ozone and $PM_{2.5}$ concentrations, as well as wind speed, were obtained from Texas Commission on Environmental Quality's (TCEQ) nearest sampling station (# 484530014) located within 11 km of the buildings. Overall uncertainty for each measurement was calculated using standard error propagation techniques to include variance in the measured readings and the uncertainty of the instrument itself.

Additional air quality measurements were made at the retail stores using several instruments. A SidePak Personal Aerosol Monitor AM510 (TSI, Shoreview, MN), calibrated against the TEOM, was used to measure indoor $PM_{2.5}$ concentrations. The DustTrak 8520 with a size-selective aerosol conditioner, calibrated against the TEOM, was used to measure indoor PM_{10} concentrations. An Aerocet-531 Mass Particle Counter/Dust Monitor (Met One Instruments, Grants Pass, OR), calibrated against gravimetric measurements of $PM_{2.5}$ and PM_{10} with PEMs in retail stores, was used to measure outdoor $PM_{2.5}$ and PM_{10} concentrations. The air exchange rate was measured at all retail sites by measuring the decay of sulfur hexafluoride (SF_6) over a four-hour period on one of the sampling days. Measurement of four-hour average VOC concentrations (with Summa canisters and sorbent tubes) and light aldehyde concentrations (with dinitrophenylhydrazine (DNPH) tubes) were also made during this period. Summa canisters are more reliable for quantifying low molecular weight compounds, whereas the sorbent tubes used (indoor and outdoor) in this study were more adapted to quantify high molecular weight compounds. A PID was used to measure the indoor TVOC concentration during all ROS sampling events. Indoor and outdoor concentrations of ozone were measured using a UV-absorbance ozone monitor (2B Technologies model 202, uncertainty of ± 1.5 ppb or 2% of reading, lower detection limit 2 ppb). At Sites 1–3, the outdoor ozone concentration was obtained from the nearest TCEQ sampling station. Details about the instrument calibrations and the methods for air exchange rate and VOC measurements at the retail sites are given in the ASHRAE RP-1596 report (Siegel et al., 2013). For comparison with data in the RP-1596 report, it should be noted that retail sites 1–5 in this study are labeled GeT2, MbT3, FfT2, MbT4, MiT, correspondingly, in the report.

Graphical representations of the data and Shapiro–Wilk tests for normality indicated that the indoor and outdoor ROS concentrations were generally not normally distributed. The Spearman Rank Correlation Coefficient test was used to determine the strength (ρ) and significance ($p < 0.05$) of any relationships between the concentration of ROS and environmental factors with Stata version 11.2. Bonferroni adjustments were generally not used as the purpose of this study was to provide a baseline assessment of indoor ROS. The Wilcoxon matched-pairs signed-ranks test was used to assess differences between the indoor and outdoor ROS datasets at the buildings.

2.3. Method development for measuring ROS concentration

The reagent used to quantify ROS, 2′,7′-dichlorofluorescin diacetate (DCF-DA), is a non-specific indicator for ROS (Venkatachari and Hopke, 2008). It becomes fluorescent in the presence of a wide variety of ROS including, but not limited to, hydrogen peroxide (H_2O_2), peroxyl ($ROO^{\bullet}$) and hydroxyl ($^{\bullet}OH$) radicals and the peroxynitrite anion ($ONOO^-$) (Zhu et al., 1994; Kooy et al., 1997). Several studies in the last decade or so have used DCF-DA as a bulk measure of ROS (Hung and Wang, 2001; Huang et al., 2005; Venkatachari et al., 2005; Venkatachari et al., 2007; See et al., 2007; Chen and Hopke, 2009). Steps were taken to reduce the high background values reported by these studies. Sonication of the activated form of DCF-DA may cause auto-oxidation of the reagent into the fluorescent compound, dichlorofluorescein (DCF). This can lead to high fluorescence intensities being detected for blank filters (Hasson and Paulson, 2003). In order to determine the influence of sonication times on the fluorescence intensity generated by blank filters, PTFE filters (Pall TF1000) were sonicated in (i) 10 ml DCFH-HRP solution for 10 min (see below for