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Shahana Khurshid
Steven J. Emmerich
Andrew Persily

Engineering Laboratory, National Institute of Standards and Technology
100 Bureau Drive Gaithersburg, MD 20899

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Evaluating the Oxidative Potential of Indoor and Outdoor Particles with an EPR Assay

Shahana S. Khurshid^{1,*}, Steven Emmerich¹, Andrew Persily¹

¹Energy and Environment Division, Engineering Laboratory, 100 Bureau Drive, Mail Stop 8633, Gaithersburg, MD 20899-8633, USA

*Corresponding email: shahana.khurshid@nist.gov

SUMMARY

The hydroxyl radical ($\bullet\text{OH}$) generating capacity of particles has been measured in several outdoor locations, but it remains unquantified in indoor environments where extended periods of human exposure are likely. Total suspended particle samples were collected inside and outside an unoccupied manufactured test house in Maryland, USA. The oxidative potential of particles was determined using electron paramagnetic resonance (OP^{EPR}) to quantify the $\bullet\text{OH}$ produced when particles are placed in a hydrogen peroxide solution. The mean OP^{EPR} of indoor particles was about 75 % of the mean OP^{EPR} of outdoor particles on an air sampling volume basis. Given that particle counts were lower indoors than outdoors, the ratio of indoor to outdoor particulate OP^{EPR} is bound to be higher on a particle mass basis. Air change rate, temperature, and relative humidity were concurrently measured in order to assess the role of these parameters on the oxidative potential of particles.

PRACTICAL IMPLICATIONS

The free radical generating capacity of particles may provide a more relevant health-based exposure measure for particles as compared to particle size and concentration. This study quantifies the hydroxyl radical ($\bullet\text{OH}$) generating capacity of particles collected in a test house under different conditions.

KEYWORDS

Particulate matter, Hydroxyl radical, Test house, Oxidative stress, Health effects

1 INTRODUCTION

It is widely accepted that airborne particles have adverse effects on human health but the pathophysiological mechanisms for these effects haven't been established (Bell et al., 2004, Pope et al., 2015). Particulate matter (PM) are typically characterized by their physical properties and chemical composition, but there may be more physiologically relevant properties of PM that are better suited to characterize their ability to induce cellular oxidative stress (Borm et al., 2007). The hydroxyl radical ($\bullet\text{OH}$) generating capacity of PM has been suggested as a way to assess the oxidative potential of particles (Shi et al., 2003b). Transition metals are known to drive $\bullet\text{OH}$ generation via the Fenton reaction, which involves the reduction of hydrogen peroxide (H_2O_2) by a transition metal (Shi et al., 2006). The hydroxyl radical generating capacity of outdoor PM has been measured over the last decade (Shi et al., 2003a, Shi et al., 2003b, Kunzli et al., 2006, Boogaard et al., 2012, Yang et al., 2015). Given that people are typically exposed to indoor pollutants for much more time than outdoor pollutants, it is important to also determine the oxidative potential of particles collected from indoor environments. This study is the first to measure the hydroxyl radical generating capacity of indoor PM.

2 MATERIALS/METHODS

Total suspended particle (TSP) samples were collected simultaneously inside and outside an unoccupied 3-bedroom manufactured test house built in 2002 and located on the campus of the National Institute of Standards and Technology (NIST) in Maryland, USA. The house has a floor area of 140 m² and a volume of 340 m³ (Rim et al., 2013). Particles were collected over a 4-day period on triplicate Teflon filters (37 mm) using air sampling pumps calibrated to run at 20 L/min. Indoor particles were collected 1 m above the floor in the centrally located kitchen area of the house, whereas outdoor particles were collected 1.5 m above the ground in front of the house. The house heating ventilation and air-conditioning (HVAC) system was operating on thermostatic control during all sampling periods, with the HVAC fan cycling with the thermostat in these tests. Indoor and outdoor particle counts were measured with an optical particle counter. Air change rates were measured using a tracer gas (SF₆) decay method (ASTM E741, 2011). Relative humidity and temperature were monitored inside and outside the house. Wind speed and direction were also recorded.

Particle suspensions were prepared by placing each filter in a microcentrifuge tube with 1.5 ml nanopure water and vortexing for 2 h at 2000 rpm (33.3 Hz). An aliquot of the particle suspension was mixed with hydrogen peroxide (H₂O₂) and the spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) to make a total volume of 100 µl with 125 mmol/L H₂O₂ and 200 mmol/L DMPO. The mixture was shaken in the dark before being transferred to a 50 µl capillary and measured with a Bruker Eleksys E500 electron paramagnetic resonance (EPR) spectrometer¹. The EPR spectra were recorded at room temperature using the following instrumental conditions: modulation frequency, 100 kHz; modulation amplitude, 1.0 G (10⁻⁴ T); receiver gain, 70 dB; time constant, 20 ms; conversion time, 20 ms; sweep time, 20.97 s; center field, 3340 G (0.334 T); sweep width, 80 G (8×10⁻³ T); number of points, 1024; attenuation, 15 dB; and, number of scans, 3. The oxidative potential of each PM sample (OP^{EPR}) was calculated from the sum of the area under the four peaks in the characteristic 1:2:2:1 DMPO-•OH quartet signal and expressed in arbitrary units divided by the sampled air volume.

3 RESULTS AND DISCUSSION

The oxidative potential of indoor and outdoor particles collected at the test house is given in Table 1, along with the mean measured air change rate during each sampling period. The OP^{EPR} of indoor particles was significantly different from the OP^{EPR} of outdoor particles using the Wilcoxon matched-pairs signed-ranks test ($p=0.043$). Nonetheless, the OP^{EPR} of indoor and outdoor particles appears to be correlated (Spearman's $\rho=0.90$, $p=0.037$). The mean ratio of OP^{EPR} of indoor particles to the OP^{EPR} of outdoor particles was 72 % (± 23 % S.D.) on a sampling volume basis. The OP^{EPR} of indoor particles may be lower than that of outdoor particles on a sampling volume basis due to the removal of particles through the building envelope, to indoor surfaces, to the duct work, and by the space conditioning system filter. The HVAC filter had a minimal particle removal efficiency in the particle size ranges relevant to the indoor environment at the test house. No significant difference was observed in the OP^{EPR} of freshly collected and 1-week-old particle samples.

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Indoor particle counts were lower than outdoor particle counts during all the sampling periods. Given that the OP^{EPR} reported here is on a sampling volume basis (to better represent exposure as it is encountered in the airways), the OP^{EPR} of indoor particles on a mass basis may be equal to or even exceed that of outdoor particles. It is unclear how many of the indoor particles infiltrated from outdoors versus being generated indoors in the present study, but it is possible that processes taking place indoors (including emissions from building materials and consumer products, resuspension from carpets, and oxidative reactions) generate particles and secondary organic aerosols (SOA) with their own free radical generating capacity. Indoor particles can have different oxidative potential than outdoor particles because a major fraction of indoor particles come from indoor homogeneous and heterogeneous chemical reactions that are distinct from outdoor chemical reactions.

The air change rate at the house ranged from 0.26 h^{-1} to 0.40 h^{-1} during the sampling periods. These rates are in the range measured during previous studies at the manufactured test house (Nabinger and Persily, 2011). Increasing the indoor relative humidity from 25 % to 40 % did not appear to substantially influence the oxidative potential of indoor particles (sampling periods 4 and 5, respectively). Further testing is underway to better understand the influence, if any, of air change rate, relative humidity, and temperature on the oxidative potential of indoor particles.

Table 1. Oxidative potential of particles collected indoors and outdoors at the manufactured test house during sampling in 2015-2016.

Sampling period	OP^{EPR} / m^3 [A.U.]		Indoor / Outdoor Ratio of Oxidative Potential [%]	Air Change Rate [h^{-1}]
	Indoor	Outdoor		
1	1.04	2.44	43 %	-
2	1.95	2.49	78 %	-
3	7.97	8.94	89 %	0.26
4	2.35	2.48	95 %	0.32
5	2.82	5.28	53 %	0.40

- Air change rate was not measured during these sampling periods.

4 CONCLUSIONS

It is important to assess the toxicological characteristics of indoor particles. OP^{EPR} of particles may be a more health relevant measure than particle mass, count or other physicochemical characteristics. EPR has been used to determine the oxidative potential of particles collected from outdoor locations in the Netherlands (Boogaard et al., 2012, Janssen et al., 2014, Yang et al., 2015), Germany (Shi et al., 2003a, Shi et al., 2003b, Shi et al., 2006), as well as several other European locations (Kunzli et al., 2006), but no such study has been conducted for indoor particles to the knowledge of the authors. The OP^{EPR} of indoor particles was found to be, on average, about three-fourth of the OP^{EPR} of outdoor particles collected at the manufactured test house at NIST. The OP^{EPR} of indoor and outdoor particles appears to be correlated, but it is unclear how much of the OP^{EPR} of the particles collected indoors was due to particles that infiltrated from outdoors versus being generated indoors. Controlled experiments are being conducted to assess the effect of indoor environmental conditions (such as relative humidity, temperature and air change rate) and indoor sources on the OP^{EPR} of indoor particles.

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