Environmental Science & Technology Letters

pubs.acs.org/journal/estlcu

Letter

Aqueous OH Radical Production by Brake Wear Particles

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Cite This: *Environ. Sci. Technol. Lett.* 2024, 11, 315−322

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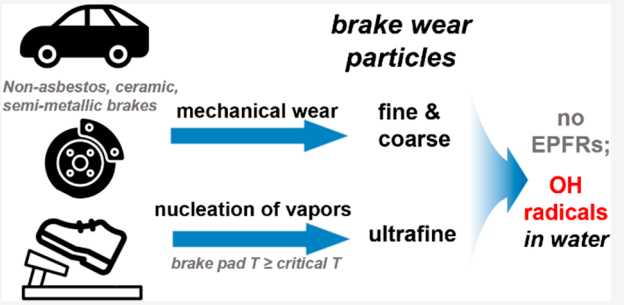
ABSTRACT: Particulate matter (PM) emitted from road traffic causes adverse health effects upon inhalation and respiratory deposition. Non-exhaust emissions will eventually become the dominant source of traffic PM upon transition to electric vehicles; however, non-tailpipe PM is currently unregulated as its health impacts are still unclear. In this study, we generated brake wear particles (BWPs) with non-asbestos organic, ceramic, and semi-metallic brake pads using custom dynamometers and measured aqueous-phase formation of reactive oxygen species (ROS). We found that BWPs do not contain environmentally persistent free radicals (EPFRs), and all types of BWPs generate exclusively ·OH radicals in water. BWPs generated by ceramic and semimetallic brakes during heavier braking lead to higher ·OH yields compared to gentle braking conditions, suggesting higher ·OH formation potential from ultrafine BWPs. Chemical characterization reveals that organic and elemental carbon correlated positively with ·OH formation while exhibiting negative correlations with abundant metals including Fe and Mn. We suggest that the source of ·OH is thermal decomposition of organic hydroperoxides derived from phenolic resin. PM oxidative potential quantified with the dithiothreitol (DTT) assay exhibited a positive correlation with the ·OH yield. These results provide critical insights into the toxicity and adverse health effects of BWPs.



KEYWORDS: *non-exhaust emissions, reactive oxygen species, ultrafine particulate matter, brake wear particles*

INTRODUCTION

The World Health Organization (WHO) reports that exposure to air pollution is estimated to cause 7 million premature deaths per year globally. In urban cities, road traffic is a leading cause of particulate matter (PM) air pollution linked to respiratory and cardiovascular diseases.[1,2] Traffic-derived PM is emitted not only from tailpipe but also from non-tailpipe or non-exhaust sources including brake and tire wear and resuspension of dust from road surfaces. It has been reported that both sources contribute almost equally by mass to the emission of traffic-related PM with a particle diameter less than 10 μm (PM_{10}).[3] With cleaner engines and more stringent regulation standards, exhaust emissions have continued to decrease over the last several decades in the US.[4] Non-exhaust emissions quickly rose to exceed exhaust emissions in many countries[5] and are expected to become the dominant source of road traffic PM emissions as early as 2035.[6] Despite their increasing importance, non-exhaust emissions have been overlooked and understudied; policy actions to target non-exhaust emissions are largely lacking and there is a major knowledge gap regarding the toxicity and health impacts of non-exhaust emissions.[6,7] Research is needed urgently to assess the potential health risks of non-exhaust PM.

One of the most important non-exhaust sources is abrasive emission from the wear of automobile brake pads. Brake wear particles (BWPs) contribute up to 55% by mass to total non-exhaust PM_{10} in urban cities.[8] Studies have shown that BWPs have toxic effects on lung cells,[9−11] although some studies observed no cytotoxicity nor oxidative stress from mice exposed to BWPs.[12] BWPs consist of various transition metals and organics,[13] some of which may induce generation of reactive oxygen species (ROS) and free radicals.[14,15] Hydroxyl radical (·OH) is the most reactive form of ROS, causing oxidative damage to lipids, proteins, and DNA.[16] ROS play a critical role in a number of physiological and pathological processes, causing aging, inflammation, and disease development;[17−21] however, the ROS formation activity of BWPs has been largely unexplored. Our previous study showed that ambient $PM_{2.5}$ collected near highways in southern California can generate ·OH and organic radicals in the aqueous phase.[22]

Received: January 24, 2024
Revised: March 18, 2024
Accepted: March 20, 2024
Published: March 25, 2024

Shen et al. (2022) reported that non-tailpipe emissions in the Los Angeles area contribute significantly to PM oxidative potential (OP) for ·OH formation, which is found to be the metric most strongly correlated with adverse health outcome indicators.[23] OP characterized by dithiothreitol loss has also been suggested as an indicator for toxicity of ambient PM;[24−26] however, ambient PM is a complex mixture affected from different sources, making it hard to disentangle the specific effects of BWPs on the ROS formation and health outcomes. Therefore, studying free radical generation by BWPs independently in comparison to their OP is crucial, providing important insights for future legislation and health impacts of BWPs.

During braking, the abrasion between the disc and the brake pad generates airborne BWPs with various sizes from ultrafine to coarse modes.[27−29] Fine and coarse BWPs are emitted by mechanical wear, while substantial ultrafine particles can be formed through volatilization and nucleation of the vapors when the brake pad temperatures reach or exceed a certain level called "critical temperature".[30] Previously reported critical temperatures range from 170 to 240 °C for various brake pad materials,[31−33] while the brake pad temperatures can reach up to 720 °C or even higher at localized friction spots.[34] Upon inhalation, larger particles are likely to deposit onto upper airways, while smaller particles can travel deeper into the lung and even penetrate the air-blood barrier, causing inflammation and adverse health effects in various regions of the body.[35,36] In this study, we generated BWPs from different brake pad materials to investigate the ROS formation activities of ultrafine, fine, and coarse BWPs using electron paramagnetic resonance (EPR) spectroscopy coupled with a spin-trapping technique. We measured their chemical composition, and the role of ultrafine fractions on ROS formation was studied by comparing BWPs emitted during gentle and heavier braking.

METHODS AND MATERIALS

Brake Wear Particle Generation and Collection. A brake dynamometer, previously described by Hagino et al. (2015),[37] has specifically been designed for BWP generation under simulated driving cycles (Table S1). The test cycle is based on the WLTP-Brake Cycle.[38] In brief, a brake assembly consisting of a cast iron disc and a pair of non-asbestos organic (NAO) pads mounted on a caliper was placed inside a chamber. The brake dynamometer rotated the brake disc, and braking was achieved by pressing the brake pad against the disc. We used seven NAO pads that are used for different car types including compact car, sedan, SUV, and van (Table S1). Particle size distribution was measured with a fast mobility particle sizer (FMPS) and an aerodynamic particle sizer (APS). A detailed description of the system and test conditions are included in the SI and Figure S1. Generated BWPs were collected into fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) fractions (N = 24) using a cascade impactor (Multi-Cascade Impactor, MCI, Tokyo Dylec) with 47 mm filters. The collected filter samples (fine and coarse fractions) were used for the measurement of PM mass (N = 24), ROS generation (N = 22) and total oxidative potential based on dithiothreitol loss (OP-DTT, N = 22). A subset of samples was used for measurements of organic and elemental carbon (OC/EC, N = 10, coarse and fine fractions) and metal composition (N = 5, fine fractions).

We also generated BWPs from ceramic and semimetallic brake pad materials using a custom brake dynamometer built on a heavy-duty metal working 22 in. lathe (Lodge & Shipley) (Figure S2). The braking assembly, including a rotor and brake caliper, was connected to the lathe shaft and housed in an 87 L aluminum chamber. Braking was achieved by a hydraulic brake actuator controlled by a computer program. BWPs were generated under a gentle braking cycle (regime I) followed by a heavier braking cycle (regime II). Particle size distribution was measured by using an aerodynamic particle sizer (APS; TSI) and a scanning mobility particle sizer (SMPS; TSI). The generated ceramic (N = 17) and semimetallic (N = 24) BWPs from the two different regimes were collected either (1) for regime I only onto 47 mm filters or onto aluminum foils using a Sioutas personal cascade impactor, (2) for both regimes combined onto the same 47 mm filter, or (3) for regime I and II separately onto two separate filters. Metal analysis was performed for ceramic (N = 3) and semimetallic BWPs (N = 6); EC and OC were measured for ceramic (N = 6) and semimetallic (N = 14) BWPs; ROS measurements were conducted on ceramic (N = 7) and semimetallic (N = 4) BWPs which were collected separately for regime I and II. Ceramic BWP filter samples were used for the TPT−OH measurements (see the SI for details). The brake rotor temperatures were monitored with an infrared noncontact temperature sensor (Omega model OS301-HT). Details of braking duration and temperature are provided in the SI.

OC, EC, and Elemental Composition. OC and EC were measured by a thermal-optical carbon analyzer following the predefined IMPROVE protocol.[39] Total metals for NAO BWPs including water-soluble and water-insoluble fractions were measured with energy-dispersive X-ray Fluorescence (XRF) (Epsilon 5, PANalytical B.V.). Metals in ceramic and semimetallic BWPs were measured with inductively coupled plasma mass spectrometry (ICP-MS).

EPR Measurements. A continuous-wave electron paramagnetic resonance (CW-EPR) spectrometer (EMXplus, Bruker, Germany) was used to detect ROS and free radicals. For detecting environmentally persistent free radicals (EPFRs), stable radicals contained in PM, a filter was directly inserted into an EPR tube for measurements. For measurements of radical generation in water, a half a filter sample was vortexed for 7 min in 300 μL of 10 mM spin-trapping agent 5-tert-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) in Millipore water (>18 MΩ cm). BMPO was used to trap free radicals to form stable radical adducts detectable by the EPR. ROS concentrations were calculated by normalizing the total mass of particles collected and are presented as ROS per mass of PM (in pmol μg^{-1}). Additional details are described in our previous publications[22,40] and detailed EPR parameters can be found in the SI.

DTT Assay. Total DTT activity of NAO BWPs was measured on the other half of the filter samples using a DTT-assay analytical system.[41] After extraction in deionized water via vortex, the filter and extract were incubated with 0.1 mM DTT in buffer at 37 °C and pH 7.4. At different time intervals, an aliquot of the mixture was withdrawn and mixed with TCA (trichloroacetic acid), DTNB (5,5-dithio-bis(2-nitrobenzoic acid), and Tris buffer and measured for absorbance at 412 and 700 nm wavelengths to determine the consumption rate of DTT over time. The total OP-DTT was calculated from the consumption rate of DTT normalized to the total mass of PM (in nmol min^{-1} μg^{-1}).

Statistical Analysis. For statistical analysis of multiple measurements, we applied the two-sample student t test,

https://doi.org/10.1021/acs.estlett.4c00066
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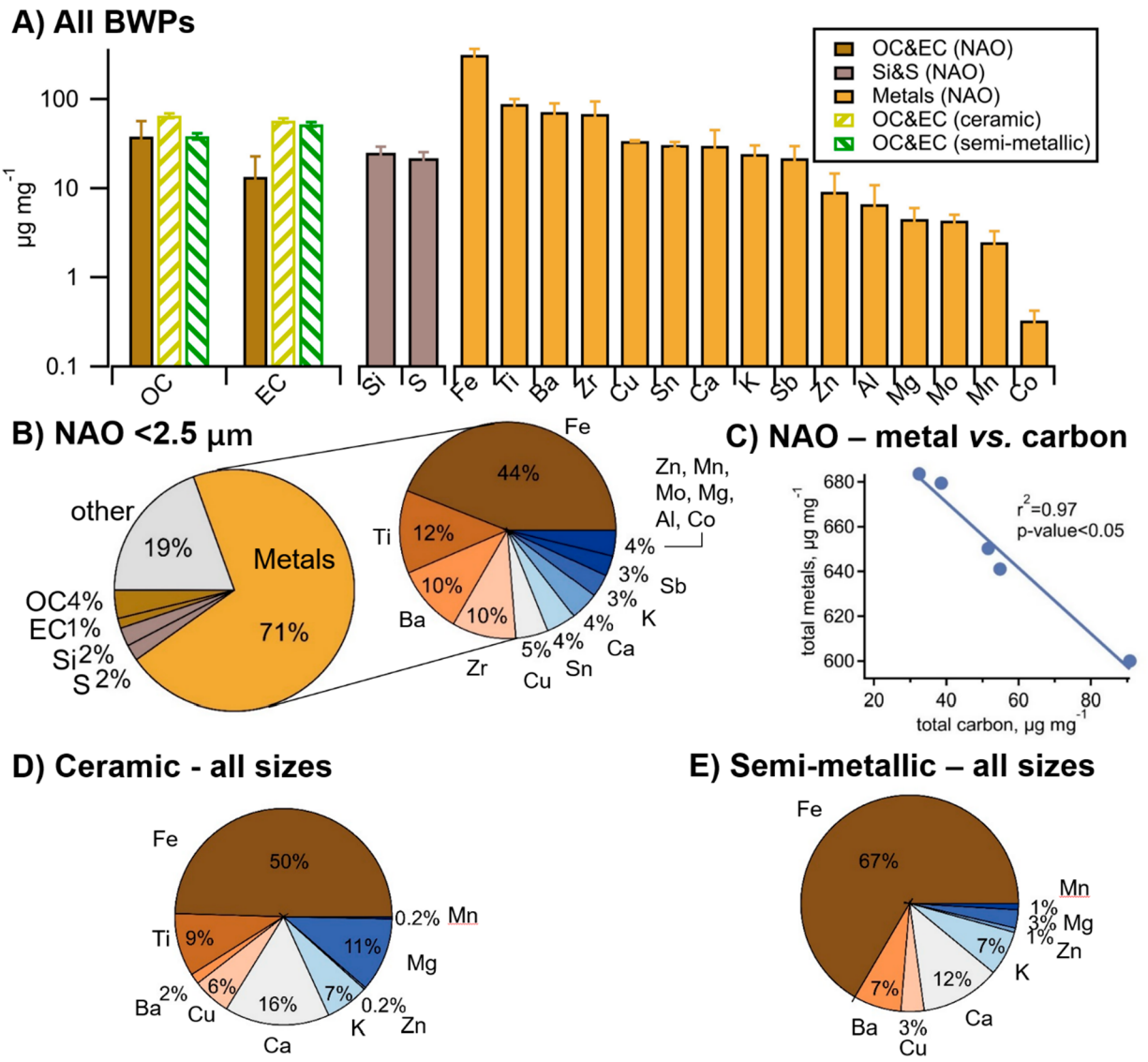

Figure 1. (A) Chemical composition of BWPs generated using non-asbestos (NAO) organics, ceramic, and semimetallic brake pads (regime I). Error bars were calculated as the standard deviations representing the variability in different samples (N = 10 for NAO, N = 6 for ceramic, N = 14 for semimetallic BWPs for OC/EC measurements, N = 5 for metal analysis for NAO BWPs). (B) Relative fractions of each composition in NAO BWPs with particle diameter <2.5 μm. Other was calculated by subtracting total mass from the sum of the masses of all measured species and elements. (C) Correlation between total metals and total carbon (sum of OC and EC) in NAO BWPs. Relative fractions of metal species in total metals in (D) ceramic (N = 3) and (E) semimetallic (N = 6) BWPs, respectively (sum of regime I and II).

assuming equal variances to obtain the mean, standard deviation, and p-values. Data normality was tested by using a Jarque-Bera test. For data that are not normally distributed, we used a Mann−Whitney U Test for comparison analysis. For correlation analysis, we applied an ANOVA test to obtain the p-values. Determination coefficient (r^2), slope, and intercept were obtained from linear regression.

RESULTS AND DISCUSSION

Composition of Brake Wear Particles. Figure 1 summarizes the chemical compositions of major elemental constituents and their relative contributions in BWPs. Metals comprise the majority (>70%) of the mass of NAO BWPs. BWPs also contain significant fractions (~5% of mass) of OC and EC and minor fractions of nonmetal components including Si and S. For all brake types, Fe is the most dominant metal, accounting for 44−67% of total metals, followed by Ti (except semimetallic brakes), Ba, Cu Ca, and others (K, Zn, Mg, etc.). The dominance of Fe may partly be explained by the fact that rotor discs are made of gray cast iron.[42] Many studies have reported Fe, Cu, Zn, Zr, Sn, and Sb as abundant heavy metals from BWPs.[43,44] All types of BWPs exhibit substantial concentrations of OC and EC with >10 μg mg^{-1}, with both ceramic and semimetallic BWPs showing higher values of EC compared to NAO BWPs. While the total reported carbonaceous fraction of BWPs can be highly variable (5.07−75.4%),[13,45] OC and EC are likely the result of the thermal decomposition of carbonaceous constituents such as the phenolic resin and aramid fiber commonly used as binders and reinforcement materials, respectively in brake pads.[30,46−48] Interestingly, total carbon in NAO BWPs is tightly anticorrelated with total metals (sum of all metals; Figure 1C). Our data indicate that higher metal release is related with stronger mechanical friction suppressing the generation of

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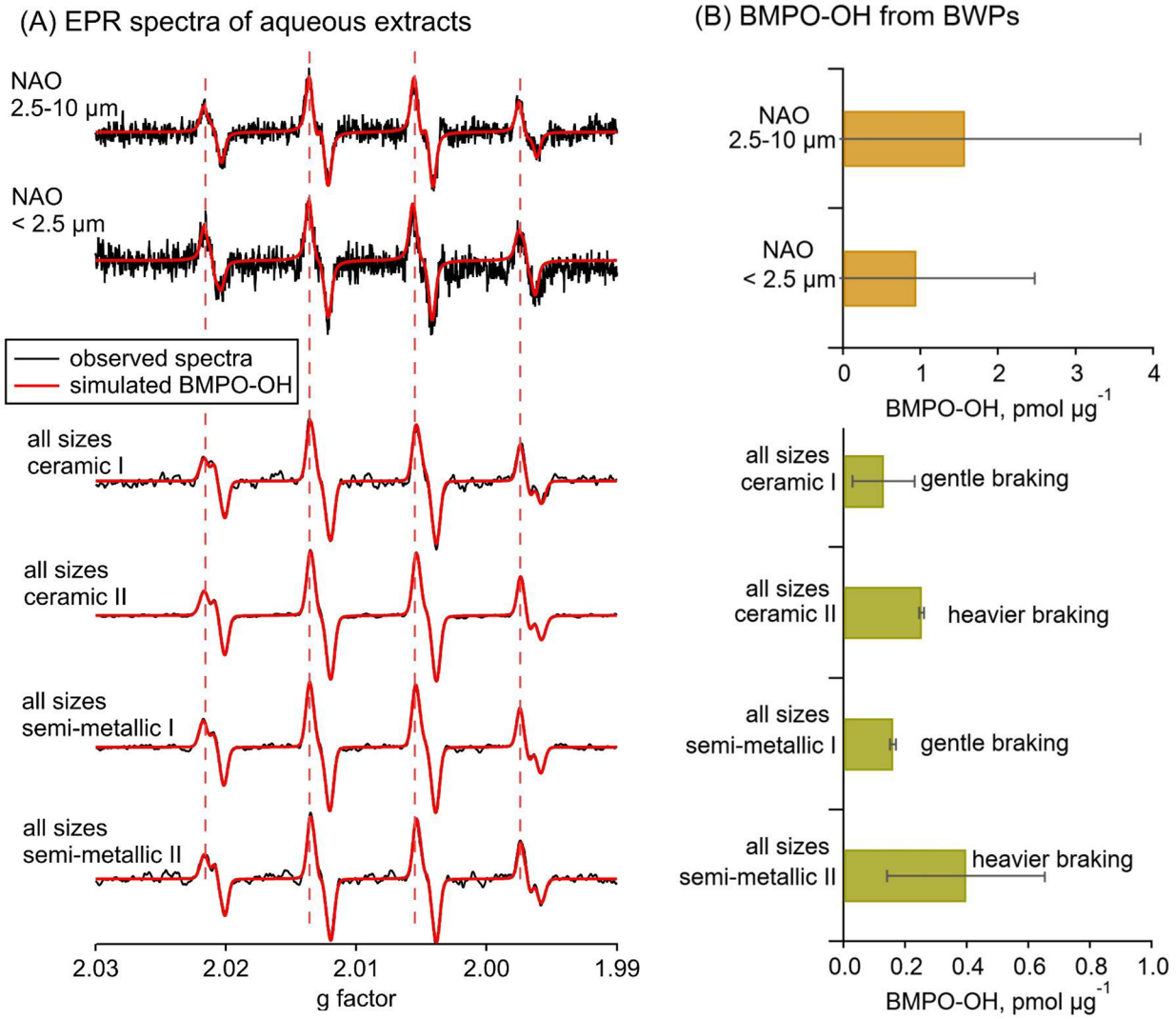

Figure 2. (A) EPR spectra of the aqueous extracts of brake wear particles (BWPs) generated by two brake dynamometers. The observed spectra (black) are simulated with BMPO−OH (red) with dashed lines highlighting four characteristic peaks. (B) PM mass normalized BMPO−OH concentrations by non-asbestos organic (NAO) BWPs (particle diameter of 2.5−10 μm and <2.5 μm) as well as ceramic and semimetallic BWPs (all particle sizes) from gentle (regime I) and heavier (regime II) braking. High ultrafine particle emissions were observed under heavier braking. Error bars for NAO BWPs are based on the standard deviation of different samples. Error bars on ceramic and semimetallic BWPs are based on error propagation from background filter correction and variabilities in filter weighing.

carbonaceous compounds, but the underlying mechanism is unclear.

The EPR spectra of solid BWPs were analyzed for the presence of environmentally persistent free radicals (EPFRs), which are stable organic radicals contained in atmospheric PM in urban air affected by traffic-related pollution.[49] Figure S3 shows that EPFR were not detected in any types of BWPs, indicating that brake wear does not lead to emission of EPFRs. This is consistent with previous studies suggesting that EPFRs are associated with vehicular tailpipe emissions.[22,50] The EPR spectra from all solid samples show a strong signal at g-factors of 2.07−2.44 (Figure S3) which can be assigned to paramagnetic Fe(III).[51] This is consistent with the dominance of Fe in the total mass.

Aqueous OH Generation by Brake Wear Particles. Figure 2 shows the EPR spectra of the aqueous extracts of BWPs and the PM mass normalized concentrations of ·OH trapped by BMPO (BMPO−OH). Most interestingly, all BWPs generate exclusively ·OH radicals in aqueous solution, as indicated by the characteristic four peaks from the BMPO−OH spectra (Figure 2A; simulation parameters for BMPO−OH are given in Table S2). We also applied a disodium terephthalate (TPT)−OH method[52] to confirm that ·OH are indeed generated by BWPs (details in the SI). A previous study observed ROS generation from BWPs using a 2′,7,-dichlorodihydrofluorescein (DCFH) assay, although this assay is not selective as it can be sensitive to a range of ROS including H_2O_2 and superoxide.[53] As shown in Figure 2B, the mass normalized BMPO−OH concentration (OH_m) in the NAO BWP coarse fraction (1.57 ± 2.26 pmol μg^{-1}) is similar to OH_m in the fine fraction (0.94 ± 1.53 pmol μg^{-1}, N = 11, Jarque-Bera test, p > 0.05; Mann−Whitney U test, p > 0.05). These values are ∼1.2−4.5 times higher than the levels observed in ambient air near the highways in southern California,[22] and ∼9−20 times higher than those observed in urban cities in China (Guangzhou, Shanghai, Beijing, and Xi'an) and Germany (Mainz).[54]

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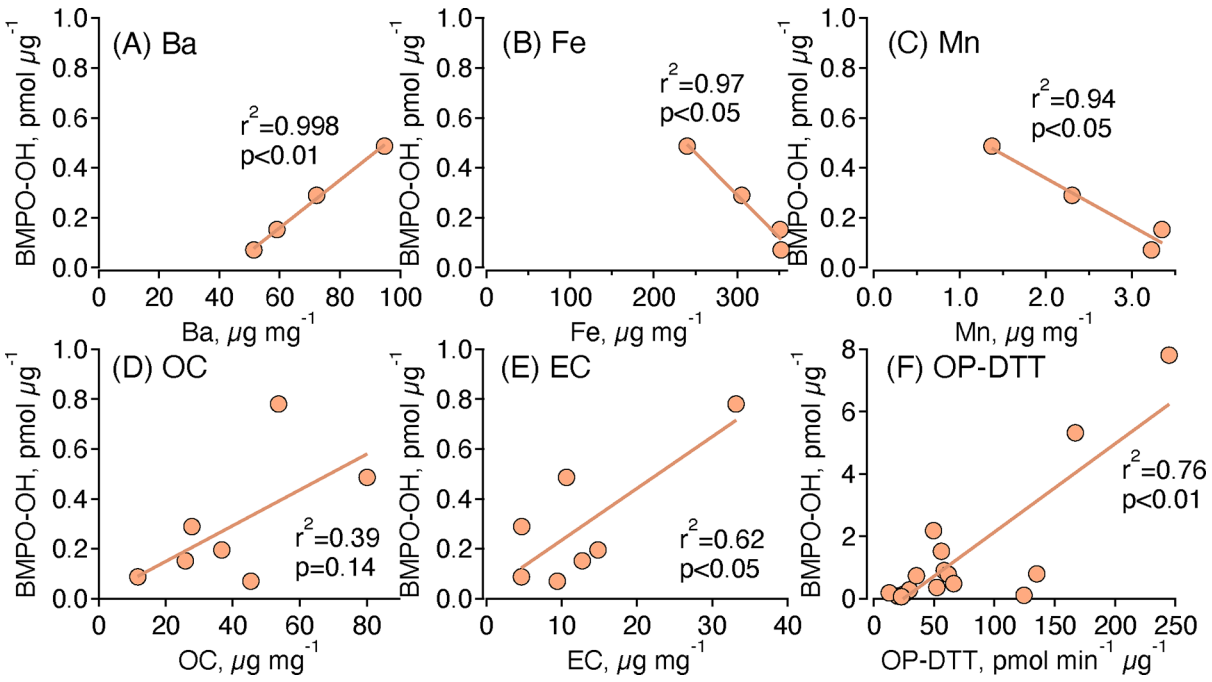

Figure 3. Correlation of ·OH generation by NAO BWPs trapped by BMPO with mass concentrations of (A) Ba, (B) Fe, (C) Mn, (D) organic carbon (OC), and (E) elemental carbon (EC), and with (F) oxidative potential measured with the dithiothreitol assay (OP-DTT).

We observed that semimetallic BWPs generate similar ·OH concentrations to ceramic BWPs for both regimes (student *t* test, $p > 0.05$). Notably, BWPs collected during heavier braking conditions (regime II) generate substantially higher OH_m values than gentle braking (regime I). It has been shown that abundant ultrafine particles can be generated through volatilization and nucleation when the temperatures of the pads reach or exceed critical temperatures, typically ranging from 170 to 240 °C.[31−33] In this work, heavier braking results in higher brake rotor temperatures (204−358 and 251−353 °C for ceramic and semimetallic pads, respectively), which likely exceed the critical temperatures for these two types of brakes. Indeed, we observed substantial increases of ultrafine particles (particle diameter less than 100 nm) as measured by the SMPS (Figure S4). For NAO BWPs, we also observed ultrafine particles, but their number concentrations were much less than fine and coarse particles (Figure S5). For fine and coarse BWPs, the governing mechanism of particle generation is mostly mechanical wear. Therefore, the higher OH_m in BWPs emitted during heavier braking suggests that the freshly nucleated ultrafine particles composed of organic compounds contribute to higher ·OH generation of BWPs. Additionally, ultrafine particles, owing to their larger exposed surface area, can potentially facilitate more surface chemistry that may lead to radical generation.[55,56]

Correlations with Elemental Composition and Oxidative Potential. Figure 3 shows the correlations of BMPO−OH with selected metals (Ba, Fe, and Mn), OC, EC, and OP-DTT in the fine fractions of NAO BWPs (see Table S3 for correlations with other species). BMPO−OH shows a strong positive correlation with barium ($p < 0.01$). Ba is the third most abundant metal in NAO BWPs (Figure 1B) and is widely used as a tracer for brake wear emissions.[3,44,57,58] Liu et al. (2022)[59] also found a strong correlation (Spearman correlation coefficient r = 0.96) between Ba and calculated ROS formation in the epithelial lining fluid. We conducted control experiments by using similar concentrations of barium sulfate, which is the most common space filler in brake pads,[60] to test if Ba^{2+} can generate ·OH. Our EPR measurements showed however no ·OH generation, indicating that Ba^{2+} may not play a role in ·OH generation. Interestingly, strong negative correlations are found for Fe ($r^2 = 0.97$) and Mn ($r^2 = 0.94$), suggesting that Fenton(-like) reactions are likely not the source of ·OH.

Positive correlations are observed for OC ($r^2 = 0.39$) and EC ($r^2 = 0.62$) with BMPO−OH, supporting the idea that ·OH generation is associated with the organic components. Our previous studies have shown that thermal decomposition of organic hydroperoxides is a prominent source of ·OH.[61,62] This process can be especially promoted in the presence of transition metals.[63,64] A previous study has shown that thermal decomposition of phenolic resin can lead to the formation of organic hydroperoxides.[65] Given that metals appear not to be a major source of ·OH as discussed above, it is very likely that the decomposition of organic hydroperoxides derived from phenolic resin is a major source of ·OH for freshly generated BWPs. It should be noted that atmospheric photochemical aging and aqueous-phase processing of BWPs may convert insoluble metals to more mobilized species, which could promote ROS formation through Fenton(-like) reactions.[66] The impact of such processes should be investigated in future studies.

Lastly, we found that BMPO−OH and OP-DTT show a positive correlation with $r^2 = 0.76$ ($p < 0.01$), which corroborates a previous ambient study finding moderate correlation between OH formation and OP-DTT.[67] While ·OH formation and OP-DTT have been separately identified as better health indicators,[23−26] an observed strong correlation suggests that OP-DTT could be used to represent the ·OH generating capability and potentially the health associations of BWPs. Overall, our study demonstrates dominant formation of ·OH radicals by BWPs in the aqueous phase, providing

https://doi.org/10.1021/acs.estlett.4c00066
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mechanistic insights into the oxidative potential and ROS formation by BWPs. Further measurements and analysis using ambient-collected PM samples are warranted to consolidate our results, and toxicological and epidemiological studies are necessary to fully evaluate the toxicity and adverse health effects of BWPs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.4c00066.

BWP generation from NAO brake pads under simulated driving conditions (Table S1, Figure S1); BWP generation from ceramic and semimetallic brake pads (Figure S2); EPR settings and measurements (Table S2, Figure S3); particle size distribution measurements (Figure S4, S5); TPT−OH assay (Figure S6); determination coefficients (r^2) between OH and OP-DTT and chemical species (Table S3) (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge funding from the California Department of Justice (No. AERTF-221620) and the Japan Automobile Research Institute (5606855, JP 22K03895). T. Fang would also like to acknowledge the support by the National Natural Science Foundation of China (Grant No. 42307528). We thank B. Finlayson-Pitts for helpful discussions. We also thank M. Steinborn and S. Embleton for assistance with the dynamometer, as well as Professors J. Bullock, B. Boden-Albala and P. Khargonekar for their support. The authors acknowledge the use of facilities and instrumentation at the UC Irvine Materials Research Institute (IMRI), which is supported in part by the National Science Foundation through the UC Irvine Materials Research Science and Engineering Center (DMR-2011967).

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https://doi.org/10.1021/acs.estlett.4c00066
Environ. Sci. Technol. Lett. 2024, 11, 315−322