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Weiwei Hu, Sasho Gligorovski *et al.*
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Nitrogen-containing organic aerosols and highly oxidized molecules produced by reaction of ozone with floor cleaning detergent†

Jinli Xu,^{‡abcd} Tianle Pan,^{‡abcd} Tingting Feng,^{abcd} Yingkun Wang,^{abcd} Wei Chen,^{abcd} Weiwei Hu^{*abc} and Sasho Gligorovski^{‡abce}

Cleaning detergents are a source of numerous volatile organic compounds (VOCs) which are highly reactive towards ozone leading to the formation of secondary organic aerosols (SOA) in indoor environments. Here we perform real-time measurements of the organic composition of aerosols produced upon ozone reaction with floor cleaning detergent by extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) coupled to a chamber reactor. The experiments were performed in the absence of light and under light irradiation ($320\text{ nm} < \lambda < 400\text{ nm}$) simulating the fraction of sunlight that penetrates indoors. The multiple increases in particle number concentrations correspond to rise in the signal intensity of specific species. Notably, the secondary increase in particle mass concentration is mainly contributed by highly oxidized molecules (HOMs), which increased from 16.5% upon ozone oxidation to 19.9% under photo-oxidation reactions. A large fraction of CHON compounds such as imidazole, pyrazine/pyrimidine, and azaindole was observed most likely formed through the reaction of O_3 with benzothiazole (constituent of the cleaning detergent). The difference between the molecular compositions detected in the absence of light and in the presence of light indicates that sunlight penetrating through the windows can affect the SOA produced by the reaction of ozone with the floor cleaning detergent.

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Environmental significance

Secondary organic aerosols in the indoor air play an important role from a health point of view but the knowledge about their formation processes and chemical composition is still lacking. Cleaning agents which are widely used indoors represent a source of volatile organic compounds especially monoterpenes which are highly reactive toward ozone and produce organic aerosols. Understanding the formation and chemical structure of these aerosols in particular under sunlight irradiation which penetrates indoors through glass windows is essential for proper modeling of indoor air quality and a comprehensive understanding of their effect on human health.

1 Introduction

Ozone (O_3) reactions in indoor environments have attracted great attention among the scientific community.^{1–4} Previous

studies have shown that ozone can be generated indoors by photocopiers, laser printers, ozone-based air purifiers, and ozone disinfection cabinets or transported from outdoors through ventilation.^{5–7} The indoor O_3 concentration can vary from a few ppb to tens of ppb.^{2,8–10} The reactions of O_3 with unsaturated compounds *e.g.* terpenes lead to the formation of secondary organic aerosols (SOA).^{1,11–13} In the indoor environment, floor cleaning detergents contain various volatile organic compounds (VOCs) including terpenes and terpenoids which can react rapidly with ozone to generate aerosol particles.^{1,14–19} Few studies have shown that use of cleaning products, indeed leads to the formation of SOA in the indoor air.^{1,17,18,20} One of the main constituents of the cleaning products is *D*-limonene which concentration in the indoor air can reach up to 13 ppb during the cleaning event.¹⁷ Another study showed that α -pinene, *D*-limonene, and β -pinene, which are important ingredients in detergents,¹⁹ can lead to a significant increase ($\sim 15\%$) in particulate matter within three hours after the cleaning event

^aState Key Laboratory of Organic Geochemistry, Guangdong Provincial Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. E-mail: weiwei.hu@gig.ac.cn; gligorovski@gig.ac.cn

^bGuangdong-Hong Kong-Macao Joint Laboratory for Environmental Pollution and Control, Guangzhou Institute of Geochemistry, Chinese Academy of Science, Guangzhou 510640, China

^cChinese Academy of Science, Centre for Excellence in Deep Earth Science, Guangzhou 510640, China

^dUniversity of Chinese Academy of Sciences, Beijing 101408, China

^eUniversity St. Kliment Ohridski Bitola, Boulevard 1st of May B.B., Bitola 7000, North Macedonia

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‡ The first two authors contribute equally.



compared to no cleaning activities.²¹ The gas-phase emission from the cleaning detergent used in our study contains more than 30 volatile organic compounds (VOCs), including β -limonene and a variety of alcohols (dihydromyrcenol, γ -terpineol, α -terpineol) and esters (2-hydroxypropyl methacrylate and allyl heptanoate).¹⁹ These compounds have the potential to react with ozone and produce secondary organic aerosols (SOA).^{22,23} It has been found that the reaction of ozone with β -limonene produces more SOA particles than its reaction with α -pinene,^{24–26} however, it is α -pinene that exhibits higher aerosol formation potential in terms of ozone reactivity.^{27,28}

Over the past two decades, extensive research has been conducted on the chemical composition of secondary organic aerosols (SOA) produced through the ozonolysis of terpenes, with a particular emphasis on the mass and number concentrations as well as the size distribution of the particles generated during indoor cleaning activities.^{1,20,29–38} Furthermore, several studies have delved into the SOA formation resulting from specific reactants, such as limonene, α -pinene, ozone, and nitrogen oxides (NOx).^{31–33,35} These investigations have also incorporated methodologies that involve the collection of filter samples and the application of various offline analytical techniques to identify the chemical constituents of the particulate phase.²⁹ Despite this extensive body of work, our understanding of the composition of indoor-generated SOA remains incomplete. This knowledge gap is significant, especially considering the implications for human health.^{20,38–42} Indeed, it has been shown that the deposited aerosol dose in the particle range of 1.2–800 nm, formed by the ozonolysis of monoterpenes during the mopping event is greater than, or comparable to, that one would inhale in an urban street canyon traffic.^{1,43,44}

In the present investigation, we conducted a real-time assessment of aerosol particle formation following the reaction between gaseous ozone (O_3) and a commonly utilized floor-cleaning detergent. This study was designed to simulate indoor environmental conditions, examining scenarios both devoid of light and exposed to UV-light within the range typical for indoor settings ($320 \text{ nm} < \lambda < 400 \text{ nm}$).^{10,45–47} The aerosols generated through the ozonolysis of the cleaning detergent were characterized using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS), which provided insights into their chemical composition. Concurrently, particle size distributions were determined utilizing a scanning mobility particle sizer (SMPS), with measurements recorded every 4 minutes. Experimental observations indicated that particulate matter mass concentrations varied from 5 to 7 $\mu\text{g m}^{-3}$, with an increase attributed to secondary particle formation during photo-oxidation reactions (Fig. S1†).

2 Materials and methods

2.1 Set up of the reactor

The experiments were carried out in a spherical borosilicate glass reactor ($R = 9 \text{ cm}$, $V = 3.05 \text{ L}$) (Fig. S3†). The glass reactor was placed in a stainless-steel box equipped with eight UV-A lamps (40 W, $320 \text{ nm} < \lambda < 400 \text{ nm}$) simulating the sunlight intensity penetrating indoors.^{10,45,46} A flow of 100 mL min^{-1}

(range 0–200 mL min^{-1} HORIBA METRON mass flow controller; accuracy, $\pm 1\%$) tank zero air passed through a commercial ozone generator (UVP, LLC Upland) to produce a stable mixing ratio of O_3 . Another flow of 500 mL min^{-1} air (0–500 mL min^{-1} HORIBA METRON mass flow controller; accuracy, $\pm 1\%$) passed through a glass bottle filled with bubbling ultrapure water (18 M-ohm, H2OMM-UV-T, Germany) to control the relative humidity (RH). These two flows were mixed to acquire the O_3 mixing ratios of $50 \pm 5 \text{ ppb}$, simulating the ozone levels in an indoor environment with the 70% RH and then introduced into the reactor through the right exit. The left exit of the reactor is connected to a diluted airflow of 1.7 L min^{-1} (0–5 L min^{-1} HORIBA METRON mass flow controller; accuracy, $\pm 1\%$) before introducing it into a scanning mobility particle sizer (SMPS) and an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS, ToFWerk AG and Aerodyne Research Inc.) (Fig. S3†). The preparation of the samples is described in the ESI.† Particle composition was measured by EESI-TOF-MS. Particle mass concentration and size distributions were measured by a scanning mobility particle sizer (SMPS, 3080, TSI Inc.). Our study specifically examines the impact of varying ozone reaction conditions on the composition of particles in the aerosol phase.

2.2 Extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS)

The EESI-TOF-MS is a commercial instrument (ToFWerk AG and Aerodyne Research Inc.) coupled with positive electrospray ionization (ESI⁺) sources.⁴⁸ The aerosols were sampled using an activated carbon denuder (2 cm diameter, 4 cm height, with a 1 mm square aperture) at a flow rate of 0.37 L min^{-1} , before encountering a droplet spray from a fused silica electrospray capillary (360 μm outer diameter and 75 μm inner diameter). The extraction solvent, a 50 : 50 mixture of water and acetonitrile, was fortified with 100 ppm of sodium iodide (NaI) to facilitate the detection of aerosol molecules. The soluble constituents of the aerosol were effectively captured within the liquid phase. As the droplets evaporated, the resulting compounds were characterized as sodium ion (Na^+) adducts. The adducts were guided through a series of ion guides and were separated based on their mass-to-charge ratio in a time-of-flight mass spectrometer. During the experiments, the resolution of the mass spectrometer was $m/\Delta m \sim 9000\text{--}10\,000$. Positive ion spectra were recorded at a time resolution of 5 s and were averaged to a 1 min resolution in the latter analysis. Continuous background measurements were conducted by periodically sampling aerosols through a particulate filter (Balston disposable filter unit, model Parker 9933-11-BQ, USA) for 3 minutes within every 12 minute interval.³³ After switching from the sampling line to the filter or filter to the sampling line, transition data ($\sim 1 \text{ min}$) were recorded, which was deleted to exclude the interferences. $[(\text{NaI})_n]\text{Na}^+$ clusters are also removed from the dataset. Before the experiments, we calibrated the EESI-TOF-MS for levoglucosan, achieving a detection limit of 16.4 ng m^{-3} and a sensitivity of 2283.1 ions per $\mu\text{g m}^{-3}$. No matrix effect was found in our study, which is consistent with



what Lopez-Hilfiker *et al.* (2019) found.⁴⁸ The description of the data analysis by EESI-TOF-MS is shown in the ESI.†

3 Results and discussion

3.1 Hierarchical cluster analysis

Fig. 1 shows the hierarchical cluster analysis performed by Matlab R2018b to identify the compounds with different chronological variations during ozone-only, simultaneous ozone and light, and light-only, exposure periods.

The hierarchical cluster diagram (HKD) obtained from real-time monitoring of 194 selected ions was classified into four groups that exhibit different signal intensity–time profiles. The grouping lines of the clusters were shown in the left of Fig. 1A. The groups marked with a blue and green rectangle contain 26 and 25 species, respectively, and show increasing intensity trends (Fig. 1A and B) as the floor-cleaning detergent was



Fig. 1 (A) Hierarchical cluster analysis of 194 ions detected by EESI-TOF-MS upon ozone oxidation reaction and photo-oxidation reaction. The grouping lines of the clusters are shown in the left. The normalized signal intensity in the hierarchical cluster is presented by a color-coded scale; *i.e.*, the signal intensity increases linearly from dark blue (normalized value of -3) to wine red (normalized value of 3). (B) Curves showing signal intensity over time for different groups derived from hierarchical cluster analysis. (C) Mass spectra of observed ions in four groups produced under oxidation reaction (dark color) and photo-oxidation reaction (light color). The signal is normalized to the maximum of the highest peak in the group.

exposed to O₃. The intensity of the species categorized under ‘Blue’ diminishes when the detergent is concomitantly subjected to ozone (O₃) and light exposure, signifying that these species are likely consumed during the photo-oxidation process. Conversely, the ion intensity within the ‘Green’ group increases upon both ozone-only and photo-oxidation reactions. Additionally, the ‘Blue’ and ‘Green’ groups can be further differentiated into multiple sub-groups, as illustrated in ESI, Fig. S4 and S5.† The ‘Yellow’ group predominantly display an increase in ion intensity under photo-oxidation conditions with the cleaning detergent while the ion signals in the ‘Red’ group increase under both reaction conditions (Fig. S6†). However, the evolutionary trend of species in the ‘Red’ group is significantly distinct from that in the ‘Green’ group. Fig. 1C presents a comparative analysis of the ion intensities across all four groups under the two experimental scenarios. The ‘Yellow’ and ‘Red’ groups are predominantly composed of dimers with carbon chains ranging from C15 to C20 or even larger. In contrast, the ‘Blue’ and ‘Green’ groups are comprised of monomers with shorter carbon chains, C5 to C10. The majority of compounds within the ‘Blue’ group exhibit a $O/C \leq 0.5$, and $H/C \geq 1.5$, suggesting that aliphatic hydrocarbons are the predominant constituents. Both ‘Yellow’ and ‘Red’ groups may also include aliphatic hydrocarbons, as indicated by their H/C and O/C ratios that fall within the ranges of 1.70 to 2.13 and 0 to 0.42, respectively. Contrasting these, the ‘Green’ group is primarily composed of highly oxidized functional compounds (28%) along with a significant proportion of aliphatic hydrocarbons (16.0%).^{49–51} In the following section, is provided a detailed introduction to classifications of the observed substances.

3.2 Mass spectral analysis

Fig. 2 shows the high-resolution mass spectra (background-subtracted) of the observed species produced under different conditions. For sake of convenience all substances in the text are shown solely in the form of organic molecular formulas excluding the Na⁺ ion. The mass spectra depicted in Fig. 2 represent the average profiles for each distinct phase of the reaction: namely, ozone oxidation (Fig. 2A), photo-oxidation reactions (Fig. 2B), and the differences between them (Fig. 2C). In the first two mass spectra (Fig. 2A and B), the ion signal intensities are normalized to the highest peak observed under the respective reaction conditions. Fig. 2C is derived by subtracting the ion signals depicted in Fig. 2B (photo-oxidation) from those in Fig. 2A (ozonolysis), thereby highlighting the differences in the products formed under different reaction conditions. Among all the detected compounds, both monomers (C5–C10) and dimers (C15–C20) are evident (Fig. 2A and B).¹⁹ The monomer region is dominated by C9 and C10 species, which together account for 71.4% of the total detected monomer compounds formed upon ozone oxidation reactions, and 66.1% produced during photo-oxidation reactions. In our previous study¹⁹ focused on the heterogenous chemistry of ozone on floor-cleaning detergent, the majority of the detected compounds were monomers retaining the skeleton of VOCs





Fig. 2 High-resolution mass spectra of the observed species produced under (A) ozone oxidation reaction, (B) photo-oxidation oxidation reaction, and (C) comparison of both spectra calculated by graph (A) minus graph (B). The signal is normalized to the maxima of the highest peaks observed. Due to space constraints, only the species with the highest relative signal intensity are labelled in this figure. The labelled species in the figure have omitted the Na^+ ion.

(C7–C10), but here products with different C-numbers were also observed. The photo-oxidation reaction is notably characterized by an increase in the average molecular size, attributable to the condensation process and the incorporation of monomers into oligomeric structures. In particular, dimers (C15–C20) and higher-molecular weight oxygenated compounds are formed as shown on the negative axis, while monomers (C5–C10) have been consumed as shown on the positive axis (Fig. 2C). Note that the CHON ($\text{O/N} < 3$) compounds in the generated dimers have increased significantly, which will be discussed in detail in the later ‘CHON compounds’ section.

In order to further distinguish the differences in oxidation products under various reaction conditions, here we subdivided the CHO and CHON compounds (for more details see section ‘CHON compounds’) into five groups according to their carbon oxidation states (OSc) and corresponding H/C and O/C ratios, as follows: aliphatic compounds which can be cyclic, saturated, and unsaturated compounds, ($\text{H/C} \geq 1.5$, $\text{O/C} \leq 0.5$);^{52,53} low oxidized aromatic compounds *e.g.* unsaturated low-oxygen-containing aromatic hydrocarbons, ($\text{H/C} \leq 1.0$, $\text{O/C} \leq 0.5$);⁵⁴ highly oxidized functional compounds *e.g.* alcohols, esters, and peroxides, ($\text{OSc} \geq 0$, $\text{O/C} \geq 0.6$); highly reduced functional compounds like organic acids and carbonyls, ($\text{OSc} < 0$, $\text{O/C} \geq 0.6$); and moderately oxygenated compounds, ($\text{OSc} \geq 0$, $\text{O/C} \geq 0$ and $\text{H/C} \leq 1.2$).^{49–51} It should be noted that the majority of CHO compounds under all conditions are aliphatic in nature, constituting over 50% of the observed species. These are followed in prevalence by highly oxidized functional compounds, which account for approximately 15%, and highly reduced functional compounds, which make up about 10%. Relative to

the ozone reactions conducted in the dark, the photo-oxidation reactions exhibit a reduced production of aliphatic compounds and an increased presence of both highly oxidized and highly reduced functional compounds, as illustrated in Fig. S12.†

Another very interesting finding is that the formation of HOMs appears to be correlated with the evolution trend of particulate matter. HOMs are distinguished by elevated O/C ratios, falling within the range of 0.4 to 1.1, and contain a minimum of six oxygen atoms in their molecular structures.⁵⁵ They constitute 16.5% and 19.9% of the total compounds generated during the ozone oxidation and photo-oxidation processes, respectively. These species are hypothesized to originate from auto-oxidation reactions.⁵⁵ Consequently, they are considered to represent an upper estimate of the HOMs yield.^{56–60} In this study, we report a significant increase in the normalized signal intensity of numerous HOMs observed during both oxidation and photo-oxidation reactions. The observed increase in HOMs concentration under light conditions aligns with the established research conclusion that ultraviolet light further stimulates auto-oxidation reactions.^{61–66} The highly oxidized organic compounds produced from ozone oxidation can nucleate, accumulate, and grow SOA.^{35,67,68} Taking the ‘Green’ group as an example, 56% of the species can be classified as HOMs, and the signal intensity of these species has increased again under photo-oxidation conditions (Fig. S5†). However, except for $\text{C}_{10}\text{H}_{20}\text{O}_6$, the signal intensity of other ions rapidly declines after reaching their peak, while the particle mass concentration subsequently reaches a second peak, which coincides with the increase in signal intensity of higher molecular weight species in the ‘Yellow’ group (Fig. S7†). We posit that the consumption of these HOMs and the formation of larger species, to a significant degree, are responsible for the secondary increase in mass concentration (Fig. S1†). Furthermore, our analysis of data shown in Fig. S2† suggests that the secondary increase in particulate matter mass concentration under photo-oxidation conditions is primarily attributed to the enlargement of existing particles with a diameter of 60–300 nm formed by oxidation reactions, rather than the formation of new particles. Furthermore, the multiple increases in particle number concentration are in harmony with the evolution trend of aerosol species. To elaborate, the first increase in particle concentration (red section) in Fig. S2A† corresponds to the explosive increase in signal intensity of the ‘Blue’ and ‘Green’ groups in Fig. S2B.† The second and third increases in particle concentration during the oxidation reaction phase in Fig. S2A† correspond to the two slight increases in signal intensity of the ‘Blue’ and ‘Green’ groups in Fig. S2B.† The last increase in particle concentration during the photo-oxidation reaction phase in Fig. S2A† corresponds to the significant increase in signal intensity of the ‘Yellow’ group in Fig. S2B.† This corresponding phenomenon to some extent indicates that the increase in the intensity of the ion signals shown in Fig. S2B† is contributed by the particulate matter that formed first in Fig. S2A.†

The aforementioned differences in the molecular composition of aerosols highlight the potential impact of sunlight penetrating through windows in indoor settings. Specifically, it





Fig. 3 Van Krevelen plot for homologous series of CHON compounds produced from the ozone oxidation reaction (A and B) and photo-oxidation reaction (C and D). The “*n*” refers to the number of CH₂ groups in a given family.

as precursors to the CHON product compounds, given that no NO_x species were involved in the reaction process.

4. Conclusions

Considering that in a real-life indoor environment, there is the presence of other oxidants/reactants such as NO₂, NO₃, and NH₃, the number and mass concentration of the particles generated from the use of cleaning detergent may be significantly higher than those observed in this study under laboratory conditions.^{16,84–87} The highly oxidized organic compounds produced from ozone oxidation can nucleate, accumulate, and grow SOA.^{11,35,67} It has been reported that people would inhale approximately 3.8×10^{10} to 1.8×10^{11} particles (3.0 to 7.5 μg) over the duration of a 90 min indoor mopping event, with much of the inhalation intake occurring during the first few minutes of active cleaning.¹ Therefore, it is necessary to further understand the evolution trend of particle size and composition of particulate matter produced by the reaction between ozone and common floor detergents.

In particular, the formation of nitrogen-containing aerosols may exacerbate indoor air quality and affect human health.

Here, we observed the formation of imidazole, pyrazine/pyrimidine, and azaindole compounds, which are likely to be formed by the oxidation of ozone with benzothiazole, a constituent of the floor detergent. It has been shown that imidazoles are potentially toxic compounds.⁸⁸ Therefore, from a health point of view, it is strongly recommended future studies evaluate the combined effect of oxidants on the particle formation by ozone chemistry of cleaning products in indoor environments.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

WH and SG conceived the study and designed the overall scope. JX, and TP performed the experiments and analysed the data. JX, TP, WH, and SG wrote the manuscript. TF, YW, and WC, participated in the experiments and engaged in scientific discussions regarding the manuscript.



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