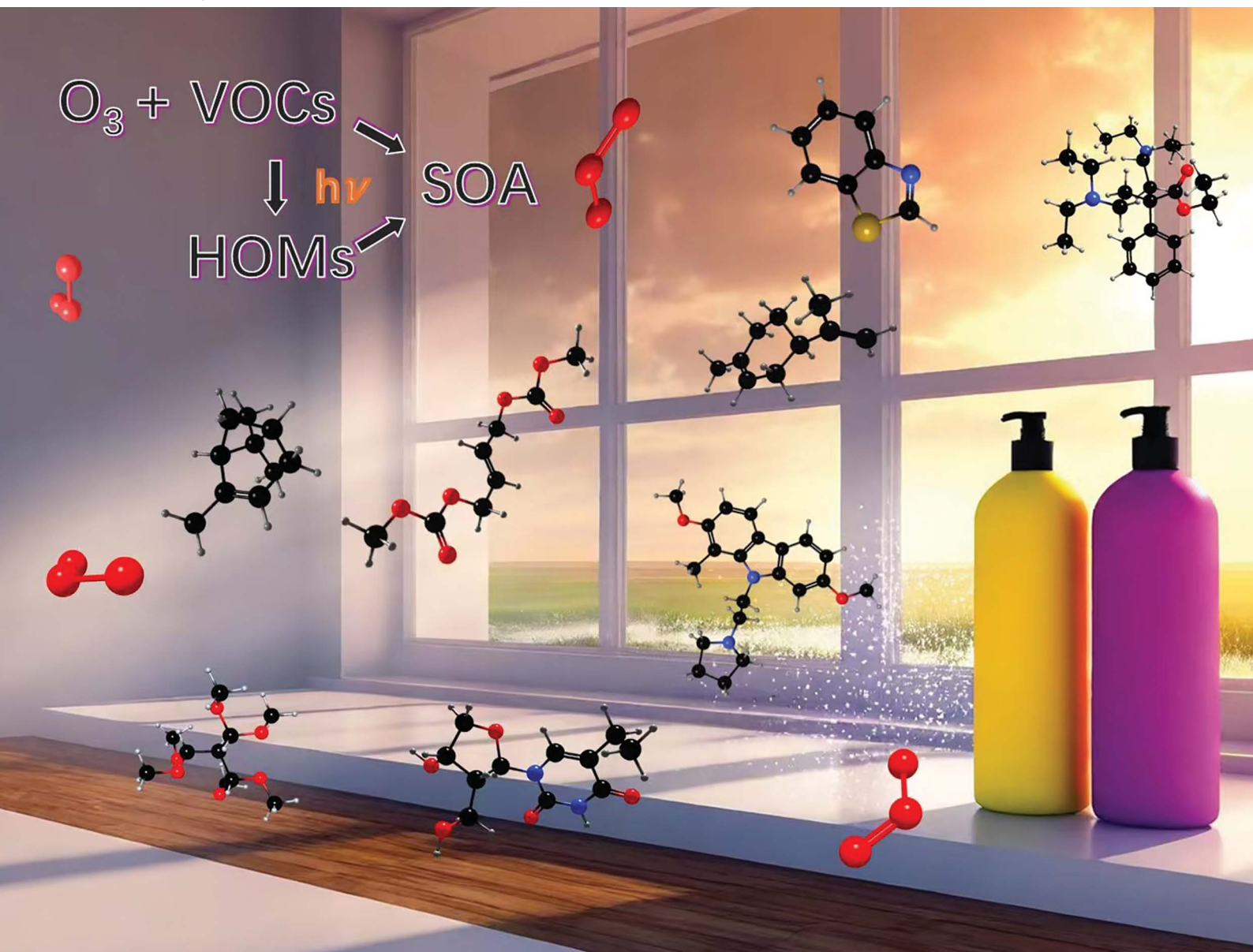


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Nitrogen-containing organic aerosols and highly oxidized molecules produced by reaction of ozone with floor cleaning detergent†

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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 nm < λ < 400 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 O₃ 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 (O₃) 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 O₃ concentration can vary from a few ppb to tens of ppb.^{2,8–10} The reactions of O₃ 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 (~15%) in particulate matter within three hours after the cleaning event

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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 (O₃) 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 nm < λ < 400 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 ($R = 9$ cm, $V = 3.05$ L) (Fig. S3†). The glass reactor was placed in a stainless-steel box equipped with eight UV-A lamps (40 W, 320 nm < λ < 400 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 O₃. 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 O₃ mixing ratios of 50 ± 5 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 $m/\Delta m \sim 9000$ –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 (~ 1 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 s $\mu\text{g m}^{-3}$. 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

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 ≤ 0.5, and H/C ≥ 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

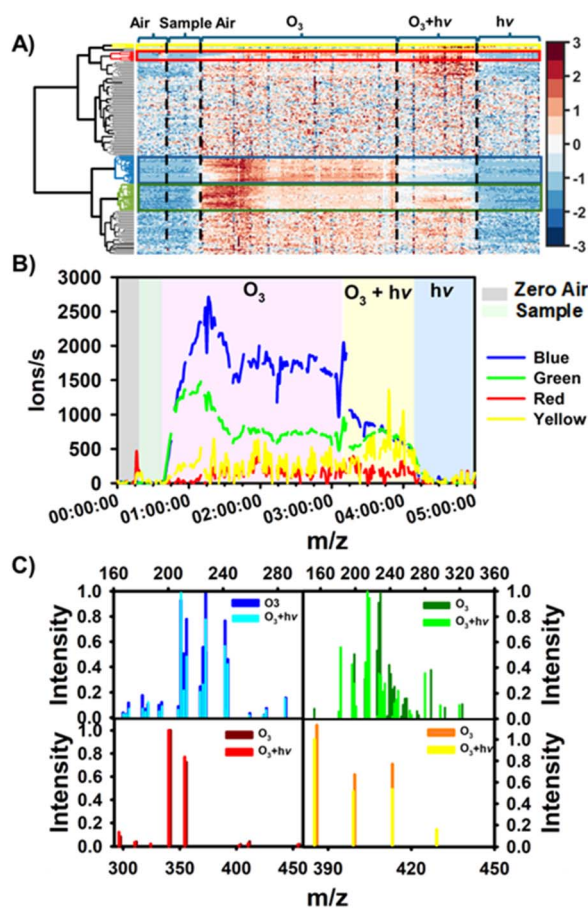
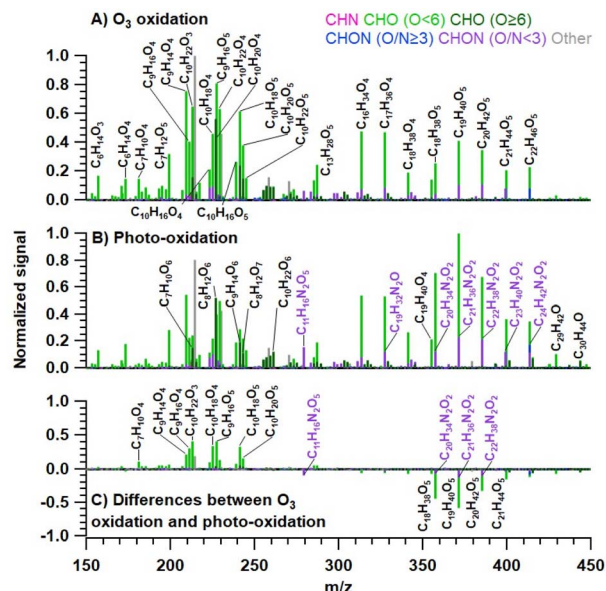


Fig. 1 (A) Hierarchical cluster analysis of 194 ions detected by EESI-TOF-MS upon ozone oxidation reaction and photo-oxidation reaction. The grouping lines of the clusters are shown in the left. The normalized signal intensity in the hierarchical cluster is presented by a color-coded scale; i.e., the 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.





suggests that the secondary organic aerosols (SOA) generated from the interaction between ozone and the surface treated with floor cleaning detergent are subject to modification by natural sunlight.

A van Krevelen (VK) diagram of the detected CHO compounds is illustrated in Fig. S8† in the form of H/C versus O/C, showing different types of compounds within the same CH₂ homologous series. The relative number abundances of the compounds produced under different conditions are shown in the pie chart in Fig. S9.† There are 43 groups of CHO compounds with different numbers of CH₂ groups shown in Fig. S8,† exhibiting a broad range of DBE values from 0 to 11. The specifics regarding the data presented in Fig. S9,† as well as the categorization of these compounds, are delineated in Table S2.† Compounds are categorized based on parameters such as O/C, H/C, DBE, and X_C. Please refer to ESI† for more information about DBE and X_C. In short, DBE refers to double bond equivalent, representing the degree of unsaturation of compounds while X_C, the aromaticity equivalent, serves as a supplement to DBE. In particular, CHO compounds with a DBE of 0 are identified as saturated alcohols or ethers; compounds with X_C = 0 are unsaturated aliphatic compounds; compounds with 0 < X_C < 2.5 are unsaturated aliphatic compounds or cyclic compounds, and compounds with X_C ≥ 2.5 are suggestive of aromatic or polycyclic structures, potentially featuring multiple unsaturated functional groups or rings.

As shown in Fig. S10,† most of the identified compounds are in the SVOC (45.1%, −0.5 < log C × ≤ 2.5) and IVOC (36.4%, 2.5 < log C × ≤ 6.5) ranges, and almost no compounds in the ELVOC range (3.28%) (see text S6† for details of the classification).

3.3 CHON compounds

We also detected CHON product compounds during the reaction of O₃ with the floor-cleaning detergent whose precursor is most likely benzothiazole (C₇H₅NS),¹⁹ among the others. It has been shown that the reaction of O₃ with azoles leads to the formation of nitrosamines which are then transformed to higher molecular weight N-heterocyclic compounds.^{69–71} Since EESI-TOF-MS of the Na⁺ ion source is mainly sensitive to CHON compounds and cannot detect compounds containing S,^{48,72} no products containing S were observed. There are 40 groups of CHON compounds with different CH₂ group numbers shown in Fig. 3 and exhibit a broad range of DBE values from 0 to 14. The CHON compounds with 0 < X_C < 2.5 should contain at least a nitro- (–NO₂), amine group, or nitroso – (–N=O) group.⁷³ CHON compounds with 2.5 ≤ X_C < 2.7143 are likely aromatics with a benzene core structure containing nitrogen functional groups, or nitrogen-containing heterocyclic compounds.⁷⁴ Compounds with X_C ≥ 2.7143 are condensed aromatic hydrocarbon.⁷⁵ To facilitate an extensive yet concise presentation of data, Table S2 in the ESI† offers an elaborate breakdown of the compounds depicted in Fig. 3. The table includes specific DBE and X_C values, alongside potential functional groups attributed to each compound class.

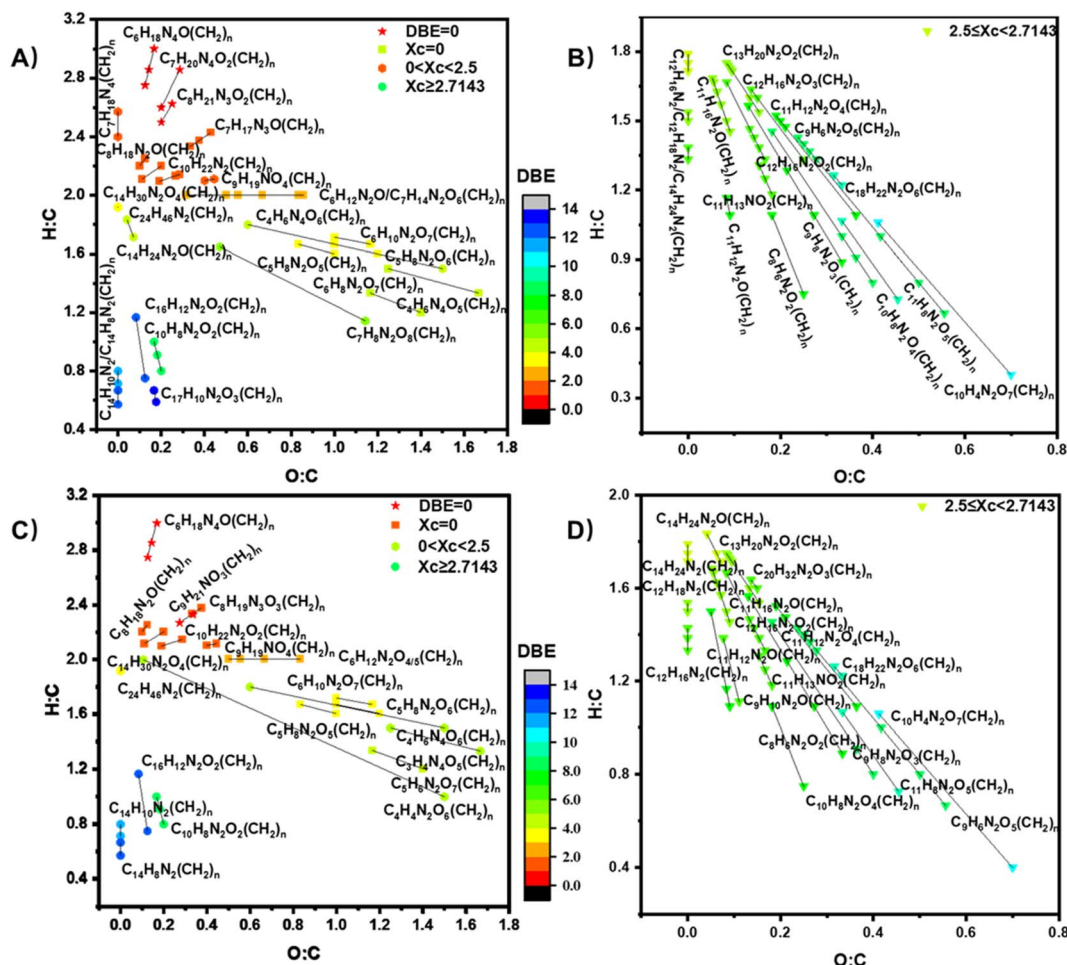
The comparative analysis of compound production, as depicted in Fig. S9,† indicates that the ozone reaction with the detergent yields a higher abundance of saturated compounds with DBE = 0 than those generated through the photo-oxidation process. Conversely, other compounds are more prevalent in the photo-oxidation scenario.

The photo-oxidation reaction is characterized by a richer diversity of functional compounds. These include highly reduced species (Osc < 0, O/C ≥ 0.6) and highly oxidized functional compounds (Osc ≥ 0, O/C ≥ 0.6). The presence of low-oxidized aromatic compounds is also notable, identified by hydrogen-to-carbon (H/C) ratios not exceeding 1.0 and an O/C ratio not surpassing 0.5.

Furthermore, the photo-oxidation reaction, in contrast to the reaction conducted in the dark, is marked by a higher yield of moderately oxidized compounds, characterized by an O/N ratio within the range of 0 to 3. This observation is complemented by a notable increase in relative signal intensity of reduced CHON compounds (O/N < 3) under photo-oxidation reaction as shown in Fig. 2, and the decrease in CHN substances depicted in Fig. S11.†

Within the CHN compound group, the most prevalent subset comprises molecules with two nitrogen atoms (N₂) and DBE value exceeding 5. Notably, the series of homologous compounds, such as C₁₂H₁₆N₂(CH₂)_n, C₁₂H₁₄N₂(CH₂)_n, C₁₄H₁₀N₂(CH₂)_n, and C₁₄H₈N₂(CH₂)_n, are tentatively identified as belonging to the imidazole, pyrazine/pyrimidine, and azaindole chemical classes.^{76,77} The formation of CHON compounds with O/N = 0.5, produced by ozone reaction and photo-oxidation reaction with the floor detergent, suggests the presence of nitrosamines which could be also formed as second-generation products by ozone oxidation of N-heterocycle compounds such as imidazoles.^{69,78} Similarly, the high intensity of compounds with O/N = 1 produced during the photo-oxidation reaction, could result from light-induced ozone reaction of first-generation products (N-heterocyclic aromatic compounds), such as imidazole, pyrazole,^{69,78} piperidine, piperazine and quinoline, or compounds containing amide group. For compounds with more abundant O-atoms, it has been reported that CHON compounds with O/N < 3 are more likely to incorporate nitrogen-containing and oxygen-containing groups.⁷⁹ Conversely, CHON compounds with an O/N ratio ≥ 3 are postulated to contain groups consisting of both nitrogen and oxygen, such as nitrite (–NO₂), nitrate (–NO₃), and nitrooxy (–ONO₂) functional groups. The presence of these groups in the studied compounds implies the formation of nitrooxy (–ONO₂) amines, imines, or organonitrates in this study.^{80–83} This inference is supported by our previous findings on riverine surface microlayer, where these compounds were identified as tertiary products resulting from the ozonolysis of secondary N-heterocycle compounds, such as imidazole.^{70,71} However, the underlying reaction mechanism remains elusive at this stage, and elucidating the molecular-level formation of these compounds presents a formidable challenge. This difficulty is particularly pronounced when authentic samples are utilized instead of proxy compounds. Nevertheless, we propose that the N-containing compounds present in the detergent act





Conflicts of interest

There are no conflicts to declare.

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