Ozone-initiated particle formation, particle ageing and precursors in a laser printer

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Abstract

An increasing number of researchers have hypothesized that ozone may be involved in the particle formation processes that occur during printing, however no studies have investigated this further. In the current study, this hypothesis was tested in a chamber study by adding supplemental ozone to the chamber after a print job without measurable ozone emissions. Subsequent particle number concentration and size distribution measurements showed that new particles were formed minutes after the addition of ozone. The results demonstrated that ozone did react with printer-generated volatile organic compounds (VOC) to form secondary organic aerosols (SOA). The hypothesis was further confirmed by the observation of correlations between VOCs, ozone and particles concentrations during a print job with measurable ozone emissions. The potential particle precursors were identified by a number of furnace tests, which suggested that squalene and styrene were the most likely SOA precursors with respect to ozone. Overall, this study significantly improved scientific understanding of the formation mechanisms of printer-generated particles, and highlighted the possible SOA formation potential of unsaturated non-terpene organic compounds by ozone-initiated reactions in the indoor environment.

Keywords: secondary organic aerosols, indoor air, ultrafine particles, printer emissions, particle ageing.
Introduction

Nowadays, office equipment is an essential part of everyday working life due to its ability to facilitate information exchange and enhance worker productivity. However, many of these machines, such as printers, photocopiers and computers etc., are a potential source of indoor contaminants, including volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), ozone and particulate matter (I). Exposure to pollutants emitted from office equipment may cause irritative symptoms of the eyes, nose, throat and lower airways, as well as mental fatigue, headache and skins reactions (2-4).

Recently, increasing concerns are focusing on the issue of ultrafine particles (UFPs, particles < 0.1 μm) emitted by laser printers, since a number of studies have demonstrated that these printers are a significant source of these particles in indoor environments (5-7), as well as VOCs and ozone (8-12). Although their emission rates vary largely between individual printers, from undetectable amounts to over $3 \times 10^{12}$ min$^{-1}$ (5, 13), the UFPs generated by laser printers of certain models can greatly elevate particle number concentrations in a large office area to the levels encountered, for example, near a busy road (5). A detailed sectional aerosol dynamic model was used by Koivisto et al. (2010) to investigate the influence of printer emissions on indoor air quality (14). They concluded that printer-emitted particles can increase the particle number concentration in an empty hypothetical office space ($4.4 \times 4.3 \times 3.3$ m$^3$) to over eleven times the background level.

One of the most effective ways to mitigate the particle pollution caused by laser printers is to locate the source and then eliminate it. However, identifying the
potential source/s was not as easy as one would expect. Earlier studies speculated that toner powder might be the particle source (8), however increasing evidence has shown that laser printers do not emit measurable toner particles (around 5-10 μm) (6, 15, 16), with UFPs dominating the particle emissions. Wensing et al. (2008) demonstrated that the release of UFPs can even occur during printing without any toner and paper present (7). Recently, an Australian study investigated the formation mechanisms of particles in relation to laser printers, and suggested that the emitted particles were seldom directly from any printer components, but formed in the air from VOCs or SVOCs which originated from the paper, toner, fuser roller and other printer components (17).

Ozone is a common air pollutant, with photocopiers and laser printers considered to be major sources of ozone in office environment (9, 10, 18). Over a decade ago, Wolkoff (1999) published work on the secondary products formed by reactions between ozone and unsaturated VOCs from the photocopier itself, as well as by thermolysis of the toner powder, or from the processed paper (i.e. paper processed in printers or photocopying machines) (19). At that time, however, no one knew printer-generated particles were of a secondary nature and mainly comprised of secondary organic aerosols (SOA). Increasing evidences over the past decade has confirmed this fact and also provoked researchers to ponder the role of ozone in the particle formation during printing. In their published papers, both Kagi et al. (2007) and McKone et al. (2009) hypothesized that ozone may react with printer-generated VOCs to produce SOAs (6, 20). However, the hypothesis was yet to be proven and the precursors involved remained unknown.
To fill these gaps in knowledge and thus to improve the general understanding of indoor SOA formation, this study aimed to confirm the existence of ozone-initiated particle formation during the operation of laser printers and to investigate the SOA formation and ageing processes, as well as identify the potential SOA precursors.
Experimental Methods

Printer and Paper.

One popular black and white laser printer was selected for this study (Printer H), whose high particle emission characteristics were reported in our previous study (17). Size A4 printer paper (PaperOne™ Copier Paper) was used in this study, along with the toner specified by the printer manufacturer. The paper was stored under laboratory conditions of approximately 22-25°C and 40-60% RH. The water content of the paper was tested and found to be 2.8%.

Chemicals.

Additional ozone supplied into the test chamber was produced in-situ using an ozone generator equipped with an ultra-violet lamp. Particle and VOC free air, which was produced by cleaning the compressed air using high efficiency particulate air (HEPA) filters and active carbon, was supplied to the test chamber from the top.

Instrumentation, Sampling and Analytical Methods.

Particle Size Distribution and Concentration: A Condensation Particle Counter (CPC, 3022A, TSI Inc.) was used to monitor the total number concentration of submicrometer airborne particles larger than 7 nm in diameter, with a sampling time of 1 s. Particle size distribution in the submicrometer range was measured by a Scanning Mobility Particle Sizer (SMPS) incorporating a TSI Model 3071 Electrostatic Classifier (EC) and a CPC Model 3776, with a sampling time of 150 s and a size range of 16-685 nm.
**Ozone and Total VOC Concentration:** Ozone was monitored using a UV-106 Ozone Analyser (Ozone Solutions, Inc. IA, USA) and ozone measurements were made at 10s intervals, with an estimated uncertainty of ± 2%. A Teflon inlet filter was used to prevent internal contamination of the tubing and absorption cell by particulate matter. In addition, calibration was conducted annually for the Ozone Analyser according to the user’s manual, including the offset correction using an external ozone scrubber and the comparison with a NIST-traceable standard ozone spectrophotometer in the laboratory over a wide range of ozone mixing ratios. The trend of total VOC (TVOC) concentrations was monitored in real time using a ppbRAE Plus Photoionisation Detector (PID, RAE Systems Inc., San Jose, CA, USA,) with a super-bright 10.6 eV Ultraviolet light lamp. The PID has a resolution of 1 ppbv and worked at a sampling time of 10 s. The ppbRAE monitor was calibrated before the experiment by a two-point process using “fresh air” and the standard reference gas, with no detectable VOC and a known concentration of a given gas, respectively. In this study, real-time TVOC data measured by the PID acted as a supplement to the VOC information provided by offline measurements.

**Individual VOC and SVOC Species:** Active sampling was conducted on stainless steel desorption tubes (Perkin Elmer) that were filled with 300 mg of Tenax TA (Buchem B.V., Apeldoorn, The Netherlands), using a FLEC pump (Chematec ApS, Roskilde, Denmark) that was operated at 150 ml.min⁻¹ to collect 5 l air sample (about 34 min). Tubes were cleaned by purging with Helium at 300°C for one hour. Tube background was < 1µg.m⁻³ per substances and < 20 µg.m⁻³ TVOC. Breakthrough tests showed no missing chemical mass during sampling The air samples were analysed by a process which included tube thermal desorption (300°C, 10 min; Perkin Elmer ATD 400) into
a GC/MS system (Agilent 6890/5973), and then separation of the compounds on a HP-5 MS column (60 m × 0.25 mm, 0.25 μm; He at 100 kPa, constant pressure mode, temperature ramp 34°C to 300°C over 36 min, 10 min hold at 300°C). General performance and retention indices were checked for each measurement using internal standards. Identification was done using commercial and recorded mass-spectra libraries (Wiley 7, NIST 05), and both retention time and mass spectrum were checked against original reference substances. For the few cases where original reference substances were not available, the identification is based on the commercial libraries; here, a match quality better than 80% and a plausible retention time is required for a substance to be listed as identified. Quantification was performed against internal and external standards in EIC mode. Background samples and field blanks were also collected in this study, and the background VOC concentrations were deducted from the measured samples in later analysis.

Temperature and Relative Humidity (RH) in the Chamber: The average temperature and RH in the chamber were monitored using a TSI Model 8552 Q-Trak Plus (with a sampling time of 10 s and an accuracy ± 0.6 °C for temperature and ± 3% for RH), placed in the middle of the chamber, directly above the printer. The instrument was calibrated annually according to the user’s manual.

Study Design.

This study included a number of chamber and furnace tests. Schematic diagrams of the two experimental systems are outlined in Figure 1.
Two chamber experiments were conducted to test the hypothesis that ozone plays a role in the formation of SOAs in relation to laser printers. Printer H did not emit measurable ozone when printing with 0% toner coverage (PW-0%), as demonstrated in our previous study (17). In the first chamber experiment, supplemental ozone was added into the chamber about 80 min after the completion of printing 150 pages with 0% toner coverage. Particle number concentration and size distribution, as well as TVOC and ozone concentrations, were measured in real time to identify whether a nucleation event would occur after the addition of ozone. In the second chamber experiment, Printer H was operated to print 150 pages with 50% toner coverage (PW-50%), with the aim of further confirming the hypothesis by observing the relationship between VOCs, ozone and particle number concentrations during printing.

In the chamber experiments, a box chamber, with volume of 1 m$^3$ and equipped with a stirring fan, was used. Before each test, the chamber was cleaned with particle and VOC free air until the inside particle number concentration decreased to less than 1.0 particles.cm$^{-3}$. A constant air change rate (ACH = 0.5 h$^{-1}$) was achieved through the whole experiment by adjusting the flow rate of supplied air. The decay constant of ozone in the chamber was about 0.023 min$^{-1}$. Temperature and humidity in the chamber were measured but not controlled.

In addition, furnace experiments were carried out to identify the SOA precursors involved in ozone-initiated reactions. It had been demonstrated that some printer components have particle formation potentials (17). In the current study, these materials (including paper, toner powder, brand-new fuser roller and lubricant oil)
were individually heated in a furnace with the temperature increased at a steady pace, in increments of 5 °C. The emitted VOCs and SVOCs were collected by Tenax tubes and analysed to identify the SOA precursors. In the period of experiments, particle and VOC free air was introduced into the furnace at a flow rate of 1.4 l.min⁻¹.

**Results and Discussion**

In the print phase, the chamber temperature increased from 26.4 to 29.0°C and RH inside the chamber also increased, but remained below 75%, which is similar to that which was observed in previous studies ([13, 14, 21]). In addition, at the beginning of each experiment, the ozone concentration in the chamber was below the detection limit of the instrument (2 ppbv).

**Ozone-Initiated SOA Formation and Ageing.** The time series of total particle number (TPN), TVOC and ozone concentrations, as well as particle size distribution during and after PW-0%, are shown in Figure 2 and Figure 3, respectively.

As seen in Figure 2, TPN immediately increased after ozone was introduced into the test chamber, and after about 10 min of slow growth, the rate of growth increased quite rapidly. Meanwhile, TVOC concentration also increased, though at a relatively moderate rate. Additionally, TPN concentration reached its peak far earlier than the cease to add ozone.

Figure 3 indicates that printer-generated particles had a single mode with an average diameter of around 45 nm at the time right before ozone was added. After that, the size of these particles started increasing immediately. Interestingly, about 7 min
later, a group of much smaller particles (about 20 nm) appeared in the chamber and then increased in size quite quickly. In order to investigate the two groups of particles in detail, the size-dependent particle number counts measured by the SMPS were initially separated into two different size groups: (1) ~ 16 nm to 30 nm; (2) 30 nm to 685 nm. With time (and the growth of the particles), both these windows were shifted upwards. The re-calculated time-dependent particle number concentrations for different processes are presented in Figure 4. This figure shows that the major contribution to the increase in TPN after the ozone addition was the occurrence of smaller particles. Furthermore, it is observed that the decreasing trend of the number concentrations of larger particles immediately ceased during the addition of ozone. This result indicates that some new larger particles appeared at this stage and that the increase magnitude of TPN of larger particles was roughly comparable to the decrease caused by deposition and air exchange removal loss.

A time discrepancy was seen between the highest particle number concentration measured by the CPC3022 (Figure 2) and the same variable measured by the SMPS (Figure 3) likely resulting from differences in the detectable particle size limit between the two instruments. The CPC3022 has a capacity to measure particles with a diameter down to 7 nm; however the SMPS cannot measure particles less than 16 nm. Therefore, when the particle number concentration measured by the CPC3022 reached its highest value, a certain number of particles with a diameter less than 16 nm were not detected by the SMPS. With the growth of these smaller particles, the SMPS was then able to measure more particles and the readings eventually reached their peak value several minutes later.
These results provided convincing evidence that new particles were formed due to the reactions between ozone and the SOA precursors emitted during printing. The gas-phase reactions with ozone have been widely investigated (22-26), however details of the chemical mechanisms of ozone-initiated SOA formation are not well understood. The general process of SOA formation involves the oxidative formation of low-volatility products followed by nucleation or condensation onto pre-existing particles, i.e. gas-particle partitioning (27). If ozone and proper SOA precursors, such as terpenoids, are combined suddenly, nucleation usually occurs shortly after the initial combination of reactants when nucleating compounds have the ability to reach supersaturation concentrations, while partitioning occurs over the entire time of reaction, even if its gas phase concentration is below the saturation concentration (28).

In this study, it seems that the active SOA precursors were consumed before the addition of ozone had ceased. That is possibly the reason why TPN concentration reached its peak before the addition of ozone had ceased.

Ozone can also change the physical and chemical properties of aerosol particles, although airborne particles are less influenced by ozone than other reactive gases due to the slower reaction rate, less frequent collisions and high number of reactions required to alter the chemical nature of the particles (29). The pathways leading to the change of particle nature, called aerosol ageing, include reactive uptake, condensed-phase processes and mass transfer caused by changes in the corresponding vapour phase (30). This class of reactions have been reviewed by Rudich et al. (2003, 2007) (30, 31). Reactions of ozone with unsaturated aerosol-associated compounds result in the formation of both volatile and non-volatile products (31). The products that remain in the aerosol phase are mostly carbonyls, carboxylic acids, and diacids. The
volatile products are aldehydes of various chain lengths and can be released into the gas phase (32). The release of volatile products to the gas phase may contribute to the increase in TVOC concentration observed in this study after the addition of ozone (see Figure 2). Another possible pathway leading to the increase in TVOC is the breakup of VOCs into smaller fragments following oxidation due to ozone. Since the TVOC monitor measures the volume fraction rather than mass concentration, the formation of smaller compounds from one larger one seems plausible. It is also aligned with current thought on how one primary ozonide molecule breaks into two molecules.

Generally, aerosol ageing can only change the particle mass but not number, which is inconsistent with the results of this study. As shown in Figure 4, the number of existing printer-generated particles increased slightly when ozone was added. To interpret this phenomenon, the following speculation was proposed: Given some large printer-generated particles are composed of several smaller ones fused together and there are unsaturated organics on the interfaces, the reactive uptake processes of ozone may alter the physical and chemical properties of the particle surface and lead to the disengagement of smaller particles, which can increase particle number.

This speculation is partially supported by evidence from the literature which reports on heterogeneous reactions of ozone with organic aerosol particles. On one hand, the reaction of ozone with unsaturated organic compounds on the surface of aerosols is efficient in atmosphere, generally with a reactive uptake coefficient between $10^{-4}$ to $10^{-3}$ (31). Compared with gas-phase reactions, the surface reactions are even faster (33). For example, Morris et al. (2002) investigated the reaction kinetics of submicron oleic acid aerosols with ozone, and concluded that submicron
aerosols of pure oleic acid in atmospheres polluted with 100 ppb ozone may have an atmospheric half-life on the order of minutes with respect to ozone reaction (34). Pöschl et al. (2001) also reported that the half-life of surface BaP molecules is about 5 min at 30 ppb ozone under dry conditions (35). In the present study, the concentrations of ozone and particles applied (up to 1.4 ppm and 4,500 particles cm$^{-3}$, respectively) were even higher than those in the cited studies. The maximum reaction rates between ozone and the existing printer-generated particles were $1.34 \times 10^7$ and $7.84 \times 10^7$ molecules.s$^{-1}$ when the ozone concentrations reached 500 ppb and 1 ppm, respectively. The detailed calculation method is provided in the supplementary material. On the other hand, the process that volatile products (such as CH$_2$O, HCOOH, CO and CO$_2$) were released to the gas phase during the reactions of ozone with organic aerosol’s surface (31) may provide additional force to accelerate the breaking up. To the best of our knowledge, however, no studies have reported similar phenomenon. Therefore, further investigation is required to test this mechanism.

In contrast to other sources of indoor ozone-generated SOAs, such as building materials, wood furniture and terpene-rich household products (36-40), laser printers can produce both ozone and VOCs. Also, considering the small space inside printers, the ozone concentration inside the printers can be expected quite high during printing. However, no data were reported about the ozone concentration inside the printers, and very few studies investigated the effect of high ozone concentration on SOA formation. At high ozone concentrations, RO$_2$ radicals, which play a central role in the production of lower-volatility products (41, 42), could be formed by traces of oxygen as well as by the sequence $R + O_3 \rightarrow RO + O_2$ and $RO + O_3 \rightarrow RO_2 + O_2$ (43). Additionally, Wolf et al. (2009) demonstrated that a high ratio of VOCs to ozone
could suppress SOA yield in laboratory ozonolysis experiments where an ozone concentration of 5 ppm was applied, and hypothesized that RO$_2$ radicals may be involved in SOA formation during ozonolysis in the presence of high ozone concentration (43).

Relationship between Ozone, TVOC and Particle Concentrations. The first experiment (PW-0%) demonstrated that some VOCs/SVOCs generated by Printer H can react with ozone to form SOA. In the second chamber experiment, a normal print job (i.e. PW-50%) was conducted to investigate the relationship between ozone, TVOC and particles concentrations during printing. The time series of ozone, TVOC and particles concentrations during and after PW-50% are presented in Figure 5. Concentrations of all three pollutants rapidly increased once printing started, with the highest ozone and particle number concentration being 60 ppbv and $6 \times 10^5$ particles cm$^{-3}$, respectively. After completion of the print job, both particle number and ozone concentrations immediately decreased, while the concentration of TVOC kept increasing at a much faster rate, before reaching its peak about 5 minutes later.

The time-dependent characterisation of particle release from laser printers was investigated by Schripp et al. (2008) using emission test chambers (44). It was found that two emission profiles, constant and “initial burst”, could be easily identified for the tested nine printers. Those printers with an “initial burst” emission profile stopped producing particles soon after the print job had started, leading to a rapid decrease in particle concentration. However, the printers with a constant emission profile generated particles throughout the entire print job, as was the case with Printer H (17).
A few studies have reported the ozone emission rates of laser printers. McKone et al. (2009) tested six laser printers, two of which were found to emit detectable amounts of ozone (9.72 and 29.17 µg.min⁻¹, respectively) (20). More recently, He et al. (2010) measured 30 new laser printers and reported ozone emission rates ranging from 0.53-175 µg.min⁻¹ (13). In this study, the emission rate of ozone for Printer H was 40.14 µg.min⁻¹ calculated through a mass balance and a first-order decay model. The model has been reported in detail by Allen et al. (45) and Niu et al. (46).

VOC emissions from printers have been widely reported (1). The major VOC source is off-gassing from various printer components, such as toner powder, paper, plastic castings, circuit boards etc. (8, 47), as well as processed paper (11). Detailed VOC/SVOC emission and styrene emission from processed paper was described by Wolkoff et al. (11). In this study, TVOC concentration kept increasing up to several minutes after printing had ceased. It might be due to the fact that the temperature, both inside and outside of the printer, was still high (while decreased slowly) after the completion of a print job. For instance, the fuser roller of Printer H took more than 25 min to cool itself back to room temperature after printing (17). On the other hand, the abrupt change in the rate of increase of TVOC concentration at the end of the print task may suggest that VOC emission was suppressed or consumed during printing, though a delay of heat transfer inside the printer might also alter the trend of TVOC concentrations.

The relationship between the changes in concentration for ozone, particle number and TVOC observed in the current study is consistent with a study conducted by Morawska et al. (17), and further confirmed the initial hypothesis. Considering the
presence of ozone may lead to formation of new particles or ageing of existing particles, health risks to human beings caused by the printer-generated particles should be further investigated with the secondary particles emitted by printers, rather than just toner powders.

SOA Precursors. The chamber tests have proved that laser printers in operation generate some SOA precursors which can react with ozone to form particles. A number of furnace tests were conducted to identify the possible precursors involved in the ozone-initiated SOA formation. The VOC species emitted by the heated printer components are identified and summarised in supplementary Table S1. Little similarity was found between the emission profiles for each printer component, with the major VOC species emitted by the paper being dibutylphthalate and n-nonanal, while benzaldehyde and acetophenone were the dominant VOCs emitted from the heated toner powder. Phenol was the major species found in fuser roller emissions, accounting for over 60% of the VOCs/SVOCs emitted during heating, with sulfinylbis-methane being the principle species emitted by heated lubricant oil. Wolkoff et al. (11) also identified these compounds in the VOC emissions from nine toner powders and eleven types of processes paper. Although benzaldehyde, acetophenone and nonanal are likely Tenax degradation products by ozone (48), ozone emission was not detected during the heating of the printer components, indicating that Tenax artifacts were insignificant in this study. Actually, benzaldehyde and acetophenone are likely styrene or styrene oligomer oxidation products probably formed during the production of the toner powder.

Although all these dominant VOC species emitted will not react with ozone, nine unsaturated compounds were detected in the samples (listed in Table 1). Interestingly,
all of them came from the toner and the paper, including dodecenal, furfuryl alcohol, 2-furaldehyde, 2,6-di-tert-butyl-p-benzoquinone, BHT-quinone methide and squalene from the paper, and 3-buten-2-one, 2-phenylpropenal, squalene and styrene from the toner. 2,6-di-tert-butyl benzoquinone and the BHT-quinone methide are a well-known oxidation products of BHT itself, probably added as antioxidant. 2-phenylpropenal is probably derived from oxidation of styrene dimer or trimers. Styrene and other unsaturated species were also emitted from processed paper ([11]). Compared to other compounds detected, they have higher potential to react with ozone due to having double bonds ([51]). Their reaction products may contribute to the formation of SOA under favorable conditions, i.e. sufficient concentration, suitable temperature and humidity, and so on. The overall ozone reaction rate constants of these unsaturated compounds are also presented in Table 1. Based on this information, the most possible precursors are squalene, followed by styrene and BHT-Quinone Methide. Dodecenal, which has the lowest ozone reaction rate constant, is less likely to be SOA precursors.

As the most popular SOA precursors in indoor environment, limonene and alpha-pinene have an ozone rate constant of $2.1 \times 10^{-16}$ cm$^3$.molecule$^{-1}$.s$^{-1}$ and $8.7 \times 10^{-17}$ cm$^3$.molecule$^{-1}$.s$^{-1}$, respectively ([52]). This means that squalene, which has an ozone reaction rate constant of $258.0 \times 10^{-17}$ cm$^3$.molecule$^{-1}$.s$^{-1}$, will react with ozone faster than limonene and alpha-pinene, though few studies have investigated the SOA formation potential of squalene.

Based on the traditional mechanism of SOA formation, the low volatility of oxidated products can favour the transfer from the gas-phase to the particle-phase, and improves the SOA yield. Cyclic organic compounds, such as cycloalkenes, terpenes and aromatics, have long been identified as more likely to be SOA precursors since
the oxidation of these classes of compounds more likely generates low-volatility products than the oxidation of similar sized VOCs in other classes. There are two main reasons leading to the formation of low-volatility products: (1) the products of ring opening processes often have the same (or similar) carbon number as the parent compound, and (2) the oxidation occurs predominantly by an addition mechanism to produce first-generation products with two (or more) polar functional groups (53).

Aromatic compounds contribute to SOA formation mainly through photochemical reactions and in the indoor environment, terpenes (in particular α-pinene and limonene) are the dominant SOA precursor as a result of their reactions with ozone. However, no terpenes, except squalene (a type of triterpene), were detected in the emissions of the heated printer components.

Squalene has been widely detected as the single most abundant unsaturated constituent in human skin lipids (54) and can participate in reactions with indoor oxidants, such as ozone and nitrate, yielding volatile aldehydic and ketonic products (55, 56). In addition, recent studies have shown that squalene is the major scavenger of ozone at the interface between room air and the human envelope (57), however there is no evidence that squalene acts as a precursor to SOA formation in ozone-initiated reactions.

Styrene was detected in the emission from both paper and toner powder in this study. As a common constituent in paper and toner powder, styrene has been widely reported in printer emissions by a number of studies (8, 16, 21, 47, 58, 59). The rate constant for reaction between ozone and styrene was calculated by Tuazon et al. (1993) (50). Na et al. (60) reported SOA formation from a styrene-ozone system and
proposed 3,5-diphenyl-1,2,4-trioxolane and a hydroxyl-substituted ester as the major aerosol-forming products. It was also found that SOA formation can be reduced with the presence of water vapour prior to styrene oxidation.

Though all other unsaturated species can react with ozone due to their double bonds, few studies have been done to investigate their SOA formation potential possibly because of the relatively slow reaction rate with ozone under ambient environment or lack of lower-volatility reaction products. Recent studies suggested that SOA formation from VOC oxidation is not solely driven by the volatility of the gas-phase products formed, but is also influenced by the propensity of oxidation products to undergo further reactions in the condensed phase (53, 61-63). Highly volatile VOCs, such as glyoxal and acetylene, can associate with other aldehydes and organic acids in particles to add to SOA mass (64). Therefore, the formation of SOAs from the degradation of smaller molecular weight VOCs can no longer be automatically disregarded (53). As such, some oxidant products from the ozonolysis reactions of unsaturated species, which were identified in paper and toner emission but not considered as common SOA precursors, may also have the potential to be involved in ozone-initiated SOA formation via this mechanism.

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FIGURES AND TABLES
Figure 1 Schematic diagram of the instrumental set up. a) furnace and b) chamber. PID: photoionization detector; CPC: condensation particle counter; SMPS: scanning mobility particle sizer.
**Figure 2** Time series of TPN, TVOCs and ozone concentrations in the chamber during and after printing 150 pages with 0% toner coverage by Printer H (PW-0%). Additional ozone was introduced into the chamber about 80 min after the completion of the print job. Ta: start printing; Tb: stop printing; Tc: start introducing ozone; Td: stop adding ozone.
Figure 3  Particle size distributions in the chamber during and after printing 150 pages with 0% toner coverage by Printer H (PW-0%). Additional ozone was introduced into the chamber about 80 min after the completion of the print job. Ta: start printing; Tb: stop printing; Tc: start introducing ozone; Td: stop adding ozone.
Figure 4 Total particle number concentrations measured by SMPS in the experiment of ozone addition. After the addition of ozone, old particles and new particles were carefully separated in light of the change of particle size, and the corresponding total number concentrations were recalculated. Ta: start printing; Tb: stop printing; Tc: start introducing ozone;Td: stop adding ozone.
Figure 5 Time series of TPN, TVOCs and ozone concentrations in the chamber during and after printing of 150 pages with 50% toner coverage by Printer H (PW-50%). Ta: start printing; Tb: stop printing.
Table 1 Potential ozone-initiated SOA precursors during the operation of laser printers

<table>
<thead>
<tr>
<th>Possible reactants</th>
<th>Chemical structure</th>
<th>Overall ozone reaction rate constant *</th>
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<td>1.71±0.18c</td>
<td>Toner</td>
</tr>
</tbody>
</table>

* The ozone reaction rates cited in this table are based on gas-phase reactions only; the unit is $10^{-17}$ cm³.molecule⁻¹.s⁻¹; where no specific reference is given, these values are taken from a prediction model (i.e. the US Environmental Protection Agency’s EPISuite™).

a The reaction probability of ozone (50ppb) and squalene on the surface is $(45±14) \times 10^{-5}$ (J);

b Atkinson et al. (2);

c Tuazon et al. (3).
Supporting Information

This section includes a table summarizing the percentages of individual VOC concentrations from each printer component heated in a furnace, as well as the method used to calculate the maximum reaction rates between ozone and particles during printing.
**Calculation method of the maximum reaction rates between ozone and particles**

In the case of a chemical reaction between the suspending gas and a particle, there are three mass transfer steps: (1) the diffusion of specific gas molecules to the surface of the particle, (2) the transfer across the interface or reaction at the interface and (3) the diffusion into the solid or liquid particle. Any of the three steps may control the rate of reaction (1). When the size of a particle is less than the mean free path, the reaction is controlled by the rate of random molecular collisions between the particle and the vapour molecules (2). In this study, the mean free path of ozone was > 4 cm which is far more than the particle size. Therefore, the rate of arrival of ozone molecules to the entire particle surface is given by (2):

$$R = \frac{\pi d_p^2 p_\infty}{\sqrt{2\pi mkT}}$$

Where $d_p$ is the particle size, $p_\infty$ is the ambient partial pressure of vapour, $m$ is the mass of a vapour molecule and $k$ is Boltzmann’s constant.

Assuming every collision between ozone molecules and particles will trigger a reaction, $R$ is the maximum rate of reaction. Calculation has been done for two cases in our experiment: (1) $T = 300$ K, $[O3] = 500$ ppb, $d_p = 62$ nm; (2) $T = 300$ K, $[O3] = 1000$ ppb, $d_p = 106$ nm. The results indicate that the maximum reaction rates between ozone and the generated particles are $1.34 \times 10^7$ and $7.84 \times 10^7$ molecules.s$^{-1}$ for the case 1 and 2, respectively.

**Reference:**


Table S1 Percentages of individual VOC concentrations in the test chamber emitted from paper (PA), fuser roller (FR), toner powder (TP) and Lubricant oil (LO) heated in a furnace (unit: %).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Function groups</th>
<th>PA</th>
<th>FR</th>
<th>TP</th>
<th>LO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfuryl alcohol (T)</td>
<td>Alcohols</td>
<td>2.0</td>
<td></td>
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<tr>
<td>Dodecenal (D)</td>
<td>Aldehydes</td>
<td>3.7</td>
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<tr>
<td>2-Furaldehyde</td>
<td>Aldehydes</td>
<td>1.7</td>
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</tr>
<tr>
<td>trans-2-Decenal (D)</td>
<td>Aldehydes</td>
<td>7.0</td>
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</tr>
<tr>
<td>Pentanal</td>
<td>Aldehydes</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propanal (P)</td>
<td>Aldehydes</td>
<td>2.3</td>
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<tr>
<td>Heptadecane</td>
<td>Aliphatic</td>
<td></td>
<td></td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>2,6-Di-tert-butyl-4-methylphenol (B)</td>
<td>Aromatics</td>
<td></td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,6-Di-tert-butyl-p-benzoquinone (B)</td>
<td>Aromatics</td>
<td></td>
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<td></td>
<td></td>
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<td>BHT-Quinone Methide</td>
<td>Aromatics</td>
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<tr>
<td>Dibutylphthalate</td>
<td>Carboxylic esters</td>
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<td>2,3-Butanedione (T)</td>
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<tr>
<td>Nitrogenous (T)</td>
<td>N-containing</td>
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<td>Butylglycol</td>
<td>Alcohols</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Naphtalenederivate (T)</td>
<td>Aromatics</td>
<td>3.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-tribromo-Benzene (T)</td>
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<tr>
<td>Naphthalene</td>
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<tr>
<td>N-Methyl-2-pyrrolidone</td>
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<td>2-methyl-Benzaldehyde (T)</td>
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<td>2-Phenylpropanal (T)</td>
<td>Aldehydes</td>
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<td>iso-Pentane (H)</td>
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<td>3-Butene-2-one (M)</td>
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<tr>
<td>Isocyanato-Benzene (T)</td>
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<td></td>
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<tr>
<td>Benzene</td>
<td>Aromatics</td>
<td>1.2</td>
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<tr>
<td>Diphenylpropan (T)</td>
<td>Aromatics</td>
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<td>alpha-Methylstyrene (T)</td>
<td>Aromatics</td>
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<td>1-phenyl-1-Propanone (T)</td>
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<td>0.6</td>
<td></td>
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<tr>
<td>Benzyl alcohol</td>
<td>Aromatics</td>
<td>0.6</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Butanoic acid (HA)</td>
<td>Carboxylic acids</td>
<td>1.3</td>
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<tr>
<td>5-chloro-1H-Benzotriazole (T)</td>
<td>N-containing</td>
<td>0.8</td>
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<tr>
<td>C13-Benzen (T)</td>
<td>Aromatics</td>
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<td>Hexamethyl-cyclotrisiloxane</td>
<td>Siloxanes</td>
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<tr>
<td>n-Heptanal</td>
<td>Aldehydes</td>
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<td>1.2</td>
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<td>n-Nonanal</td>
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<tr>
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<td>Aldehydes</td>
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<tr>
<td>n-Hexanal</td>
<td>Aldehydes</td>
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<td>0.9</td>
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<td>Aldehydes</td>
<td>2.8</td>
<td>2.2</td>
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<td>Squalene</td>
<td>Alkenes</td>
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<td>5.8</td>
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<tr>
<td>BHT-Derivate (T)</td>
<td>Aromatics</td>
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<td>1.1</td>
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<td>2,6-Diisopropynaphthalene</td>
<td>Aromatics</td>
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<td>0.4</td>
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<td>Aromatics</td>
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<td>Phenol</td>
<td>Aromatics</td>
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<td>2.7</td>
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<td>Acetophenone</td>
<td>Aromatics</td>
<td>5.9</td>
<td>22.9</td>
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</tr>
<tr>
<td>Toluene</td>
<td>Aromatics</td>
<td>1.3</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Carboxylic ester (T)</td>
<td>Carboxylic esters</td>
<td>0.5</td>
<td>6.6</td>
<td></td>
<td></td>
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<td>2,2,4-Trimethylpentane-1,3-diol-monoisobutyrate</td>
<td>Carboxylic esters</td>
<td>4.3</td>
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<td></td>
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<tr>
<td>(TE)</td>
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</tr>
<tr>
<td>Sulfinylbis-methane (T)</td>
<td>Sulfide</td>
<td>1.2</td>
<td></td>
<td>76.0</td>
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</tr>
</tbody>
</table>

Note: The proportion of VOC species emitted by each printer component was determined by dividing the total concentration of identified VOC species by the concentration of individual VOC. The
reference substances used are stated in the parentheses. (T): Toluene; (D): n-Decanal; (P): Pentanal; (B): BHT; (H): Hexane; (M): 2-Butanone (MEK); (HA): Hexanoic acid; (TE): Texanol.