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

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1 **Abstract**

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

19

20 **Keywords:** secondary organic aerosols, indoor air, ultrafine particles, printer
21 emissions, particle ageing.

22

1 **Introduction**

2 Nowadays, office equipment is an essential part of everyday working life due to
3 its ability to facilitate information exchange and enhance worker productivity.
4 However, many of these machines, such as printers, photocopiers and computers etc.,
5 are a potential source of indoor contaminants, including volatile organic compounds
6 (VOCs), semi-volatile organic compounds (SVOCs), ozone and particulate matter (1).
7 Exposure to pollutants emitted from office equipment may cause irritative symptoms
8 of the eyes, nose, throat and lower airways, as well as mental fatigue, headache and
9 skins reactions (2-4).

10

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

23

24 One of the most effective ways to mitigate the particle pollution caused by laser
25 printers is to locate the source and then eliminate it. However, identifying the

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

11

12 Ozone is a common air pollutant, with photocopiers and laser printers considered
13 to be major sources of ozone in office environment (9, 10, 18). Over a decade ago,
14 Wolkoff (1999) published work on the secondary products formed by reactions
15 between ozone and unsaturated VOCs from the photocopier itself, as well as by
16 thermolysis of the toner powder, or from the processed paper (i.e. paper processed in
17 printers or photocopying machines) (19). At that time, however, no one knew
18 printer-generated particles were of a secondary nature and mainly comprised of
19 secondary organic aerosols (SOA). Increasing evidences over the past decade has
20 confirmed this fact and also provoked researchers to ponder the role of ozone in the
21 particle formation during printing. In their published papers, both Kagi et al. (2007)
22 and McKone et al. (2009) hypothesized that ozone may react with printer-generated
23 VOCs to produce SOAs (6, 20) . However, the hypothesis was yet to be proven and
24 the precursors involved remained unknown.

25

1 To fill these gaps in knowledge and thus to improve the general understanding of
2 indoor SOA formation, this study aimed to confirm the existence of ozone-initiated
3 particle formation during the operation of laser printers and to investigate the SOA
4 formation and ageing processes, as well as identify the potential SOA precursors.
5

1 **Experimental Methods**

2 **Printer and Paper.**

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

9

10 **Chemicals.**

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

15

16 **Instrumentation, Sampling and Analytical Methods.**

17 *Particle Size Distribution and Concentration:* A Condensation Particle Counter
18 (CPC, 3022A, TSI Inc.) was used to monitor the total number concentration of
19 submicrometer airborne particles larger than 7 nm in diameter, with a sampling time
20 of 1 s. Particle size distribution in the submicrometer range was measured by a
21 Scanning Mobility Particle Sizer (SMPS) incorporating a TSI Model 3071
22 Electrostatic Classifier (EC) and a CPC Model 3776, with a sampling time of 150 s
23 and a size range of 16-685 nm.

24

1 *Ozone and Total VOC Concentration:* Ozone was monitored using a UV-106 Ozone
2 Analyser (Ozone Solutions, Inc. IA, USA) and ozone measurements were made at 10s
3 intervals, with an estimated uncertainty of $\pm 2\%$. A Teflon inlet filter was used to
4 prevent internal contamination of the tubing and absorption cell by particulate matter.
5 In addition, calibration was conducted annually for the Ozone Analyser according to
6 the user's manual, including the offset correction using an external ozone scrubber
7 and the comparison with a NIST-traceable standard ozone spectrophotometer in the
8 laboratory over a wide range of ozone mixing ratios. The trend of total VOC (TVOC)
9 concentrations was monitored in real time using a ppbRAE Plus Photoionisation
10 Detector (PID, RAE Systems Inc., San Jose, CA, USA,) with a super-bright 10.6 eV
11 Ultraviolet light lamp. The PID has a resolution of 1 ppbv and worked at a sampling
12 time of 10 s. The ppbRAE monitor was calibrated before the experiment by a
13 two-point process using "fresh air" and the standard reference gas, with no detectable
14 VOC and a known concentration of a given gas, respectively. In this study, real-time
15 TVOC data measured by the PID acted as a supplement to the VOC information
16 provided by offline measurements.

17

18 *Individual VOC and SVOC Species:* Active sampling was conducted on stainless steel
19 desorption tubes (Perkin Elmer) that were filled with 300 mg of Tenax TA (Buchem
20 B.V., Apeldoorn, The Netherlands), using a FLEC pump (Chematec ApS, Roskilde,
21 Denmark) that was operated at $150 \text{ ml}\cdot\text{min}^{-1}$ to collect 5 l air sample (about 34 min).
22 Tubes were cleaned by purging with Helium at 300°C for one hour. Tube background
23 was $< 1 \mu\text{g}\cdot\text{m}^{-3}$ per substances and $< 20 \mu\text{g}\cdot\text{m}^{-3}$ TVOC. Breakthrough tests showed no
24 missing chemical mass during sampling The air samples were analysed by a process
25 which included tube thermal desorption (300°C , 10 min; Perkin Elmer ATD 400) into

1 a GC/MS system (Agilent 6890/5973), and then separation of the compounds on a
2 HP-5 MS column (60 m × 0.25 mm, 0.25 μm; He at 100 kPa, constant pressure mode,
3 temperature ramp 34°C to 300°C over 36 min, 10 min hold at 300°C). General
4 performance and retention indices were checked for each measurement using internal
5 standards. Identification was done using commercial and recorded mass-spectra
6 libraries (Wiley7, NIST 05), and both retention time and mass spectrum were checked
7 against original reference substances. For the few cases where original reference
8 substances were not available, the identification is based on the commercial libraries;
9 here, a match quality better than 80% and a plausible retention time is required for a
10 substance to be listed as identified. Quantification was performed against internal and
11 external standards in EIC mode. Background samples and field blanks were also
12 collected in this study, and the background VOC concentrations were deducted from
13 the measured samples in later analysis.

14

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

20

21 **Study Design.**

22 This study included a number of chamber and furnace tests. Schematic diagrams
23 of the two experimental systems are outlined in Figure 1.

24

1 Two chamber experiments were conducted to test the hypothesis that ozone plays
2 a role in the formation of SOAs in relation to laser printers. Printer H did not emit
3 measurable ozone when printing with 0% toner coverage (PW-0%), as demonstrated
4 in our previous study (17). In the first chamber experiment, supplemental ozone was
5 added into the chamber about 80 min after the completion of printing 150 pages with
6 0% toner coverage. Particle number concentration and size distribution, as well as
7 TVOC and ozone concentrations, were measured in real time to identify whether a
8 nucleation event would occur after the addition of ozone. In the second chamber
9 experiment, Printer H was operated to print 150 pages with 50% toner coverage
10 (PW-50%), with the aim of further confirming the hypothesis by observing the
11 relationship between VOCs, ozone and particle number concentrations during
12 printing.

13
14 In the chamber experiments, a box chamber, with volume of 1 m³ and equipped
15 with a stirring fan, was used. Before each test, the chamber was cleaned with particle
16 and VOC free air until the inside particle number concentration decreased to less than
17 1.0 particles.cm⁻³. A constant air change rate (ACH = 0.5 h⁻¹) was achieved through
18 the whole experiment by adjusting the flow rate of supplied air. The decay constant of
19 ozone in the chamber was about 0.023 min⁻¹. Temperature and humidity in the
20 chamber were measured but not controlled.

21
22 In addition, furnace experiments were carried out to identify the SOA precursors
23 involved in ozone-initiated reactions. It had been demonstrated that some printer
24 components have particle formation potentials (17). In the current study, these
25 materials (including paper, toner powder, brand-new fuser roller and lubricant oil)

1 were individually heated in a furnace with the temperature increased at a steady pace,
2 in increments of 5 °C. The emitted VOCs and SVOCs were collected by Tenax tubes
3 and analysed to identify the SOA precursors. In the period of experiments, particle
4 and VOC free air was introduced into the furnace at a flow rate of 1.4 l.min⁻¹.

5

6 **Results and Discussion**

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

12

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

16

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

22

23 Figure 3 indicates that printer-generated particles had a single mode with an
24 average diameter of around 45 nm at the time right before ozone was added. After that,
25 the size of these particles started increasing immediately. Interestingly, about 7 min

1 later, a group of much smaller particles (about 20 nm) appeared in the chamber and
2 then increased in size quite quickly. In order to investigate the two groups of particles
3 in detail, the size-dependent particle number counts measured by the SMPS were
4 initially separated into two different size groups: (1) ~ 16 nm to 30 nm; (2) 30 nm to
5 685 nm. With time (and the growth of the particles), both these windows were shifted
6 upwards. The re-calculated time-dependent particle number concentrations for
7 different processes are presented in Figure 4. This figure shows that the major
8 contribution to the increase in TPN after the ozone addition was the occurrence of
9 smaller particles. Furthermore, it is observed that the decreasing trend of the number
10 concentrations of larger particles immediately ceased during the addition of ozone.
11 This result indicates that some new larger particles appeared at this stage and that the
12 increase magnitude of TPN of larger particles was roughly comparable to the decrease
13 caused by deposition and air exchange removal loss.

14

15 A time discrepancy was seen between the highest particle number concentration
16 measured by the CPC3022 (Figure 2) and the same variable measured by the SMPS
17 (Figure 3) likely resulting from differences in the detectable particle size limit between
18 the two instruments. The CPC3022 has a capacity to measure particles with a
19 diameter down to 7 nm; however the SMPS cannot measure particles less than 16 nm.
20 Therefore, when the particle number concentration measured by the CPC3022 reached
21 its highest value, a certain number of particles with a diameter less than 16 nm were
22 not detected by the SMPS. With the growth of these smaller particles, the SMPS was
23 then able to measure more particles and the readings eventually reached their peak
24 value several minutes later.

25

1 These results provided convincing evidence that new particles were formed due to
2 the reactions between ozone and the SOA precursors emitted during printing. The
3 gas-phase reactions with ozone have been widely investigated (22-26), however
4 details of the chemical mechanisms of ozone-initiated SOA formation are not well
5 understood. The general process of SOA formation involves the oxidative formation
6 of low-volatility products followed by nucleation or condensation onto pre-existing
7 particles, i.e. gas-particle partitioning (27). If ozone and proper SOA precursors, such
8 as terpenoids, are combined suddenly, nucleation usually occurs shortly after the
9 initial combination of reactants when nucleating compounds have the ability to reach
10 supersaturation concentrations, while partitioning occurs over the entire time of
11 reaction, even if its gas phase concentration is below the saturation concentration (28).
12 In this study, it seems that the active SOA precursors were consumed before the
13 addition of ozone had ceased. That is possibly the reason why TPN concentration
14 reached its peak before the addition of ozone had ceased.

15
16 Ozone can also change the physical and chemical properties of aerosol particles,
17 although airborne particles are less influenced by ozone than other reactive gases due
18 to the slower reaction rate, less frequent collisions and high number of reactions
19 required to alter the chemical nature of the particles (29). The pathways leading to the
20 change of particle nature, called aerosol ageing, include reactive uptake,
21 condensed-phase processes and mass transfer caused by changes in the corresponding
22 vapour phase (30). This class of reactions have been reviewed by Rudich et al. (2003,
23 2007) (30, 31). Reactions of ozone with unsaturated aerosol-associated compounds
24 result in the formation of both volatile and non-volatile products (31). The products that
25 remain in the aerosol phase are mostly carbonyls, carboxylic acids, and diacids. The

1 volatile products are aldehydes of various chain lengths and can be released into the gas
2 phase (32). The release of volatile products to the gas phase may contribute to the
3 increase in TVOC concentration observed in this study after the addition of ozone (see
4 Figure 2). Another possible pathway leading to the increase in TVOC is the breakup of
5 VOCs into smaller fragments following oxidation due to ozone. Since the TVOC
6 monitor measures the volume fraction rather than mass concentration, the formation of
7 smaller compounds from one larger one seems plausible. It is also aligned with current
8 thought on how one primary ozonide molecule breaks into two molecules.

9

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

18

19 This speculation is partially supported by evidence from the literature which
20 reports on heterogeneous reactions of ozone with organic aerosol particles. On one
21 hand, the reaction of ozone with unsaturated organic compounds on the surface of
22 aerosols is efficient in atmosphere, generally with a reactive uptake coefficient
23 between 10^{-4} to 10^{-3} (31). Compared with gas-phase reactions, the surface reactions
24 are even faster (33). For example, Morris et al. (2002) investigated the reaction
25 kinetics of submicron oleic acid aerosols with ozone, and concluded that submicron

1 aerosols of pure oleic acid in atmospheres polluted with 100 ppb ozone may have an
2 atmospheric half-life on the order of minutes with respect to ozone reaction (34).
3 Pöschl et al. (2001) also reported that the half-life of surface BaP molecules is about 5
4 min at 30 ppb ozone under dry conditions (35). In the present study, the
5 concentrations of ozone and particles applied (up to 1.4 ppm and 4,500 particles cm⁻³,
6 respectively) were even higher than those in the cited studies. The maximum reaction
7 rates between ozone and the existing printer-generated particles were 1.34×10^7 and
8 7.84×10^7 molecules.s⁻¹ when the ozone concentrations reached 500 ppb and 1 ppm,
9 respectively. The detailed calculation method is provided in the supplementary
10 material. On the other hand, the process that volatile products (such as CH₂O,
11 HCOOH, CO and CO₂) were released to the gas phase during the reactions of ozone
12 with organic aerosol's surface (31) may provide additional force to accelerate the
13 breaking up. To the best of our knowledge, however, no studies have reported similar
14 phenomenon. Therefore, further investigation is required to test this mechanism.

15

16 In contrast to other sources of indoor ozone-generated SOAs, such as building
17 materials, wood furniture and terpene-rich household products (36-40), laser printers
18 can produce both ozone and VOCs. Also, considering the small space inside printers,
19 the ozone concentration inside the printers can be expected quite high during printing.
20 However, no data were reported about the ozone concentration inside the printers, and
21 very few studies investigated the effect of high ozone concentration on SOA
22 formation. At high ozone concentrations, RO₂ radicals, which play a central role in the
23 production of lower-volatility products (41, 42), could be formed by traces of oxygen
24 as well as by the sequence $R + O_3 \rightarrow RO + O_2$ and $RO + O_3 \rightarrow RO_2 + O_2$ (43).
25 Additionally, Wolf et al. (2009) demonstrated that a high ratio of VOCs to ozone

1 could suppress SOA yield in laboratory ozonolysis experiments where an ozone
2 concentration of 5 ppm was applied, and hypothesized that RO₂ radicals may be
3 involved in SOA formation during ozonolysis in the presence of high ozone
4 concentration (43).

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

17
18 The time-dependent characterisation of particle release from laser printers was
19 investigated by Schripp et al. (2008) using emission test chambers (44). It was found
20 that two emission profiles, constant and “initial burst”, could be easily identified for
21 the tested nine printers. Those printers with an “initial burst” emission profile stopped
22 producing particles soon after the print job had started, leading to a rapid decrease in
23 particle concentration. However, the printers with a constant emission profile
24 generated particles throughout the entire print job, as was the case with Printer H (17).

25

1 A few studies have reported the ozone emission rates of laser printers. McKone et
2 al. (2009) tested six laser printers, two of which were found to emit detectable
3 amounts of ozone (9.72 and 29.17 $\mu\text{g}\cdot\text{min}^{-1}$, respectively) (20). More recently, He et
4 al. (2010) measured 30 new laser printers and reported ozone emission rates ranging
5 from 0.53-175 $\mu\text{g}\cdot\text{min}^{-1}$ (13). In this study, the emission rate of ozone for Printer H
6 was 40.14 $\mu\text{g}\cdot\text{min}^{-1}$ calculated through a mass balance and a first-order decay model.
7 The model has been reported in detail by Allen et al. (45) and Niu et al. (46).

8

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

22

23 The relationship between the changes in concentration for ozone, particle number
24 and TVOC observed in the current study is consistent with a study conducted by
25 Morawska et al. (17), and further confirmed the initial hypothesis. Considering the

1 presence of ozone may lead to formation of new particles or ageing of existing
2 particles, health risks to human beings caused by the printer-generated particles
3 should be further investigated with the secondary particles emitted by printers, rather
4 than just toner powders.

5
6 **SOA Precursors.** The chamber tests have proved that laser printers in operation
7 generate some SOA precursors which can react with ozone to form particles. A
8 number of furnace tests were conducted to identify the possible precursors involved
9 the ozone-initiated SOA formation. The VOC species emitted by the heated printer
10 components are identified and summarised in supplementary Table S1. Little
11 similarity was found between the emission profiles for each printer component, with
12 the major VOC species emitted by the paper being dibutylphthalate and n-nonanal,
13 while benzaldehyde and acetophenone were the dominant VOCs emitted from the
14 heated toner powder. Phenol was the major species found in fuser roller emissions,
15 accounting for over 60% of the VOCs/SVOCs emitted during heating, with
16 sulfinylbis-methane being the principle species emitted by heated lubricant oil.
17 Wolkoff et al. (11) also identified these compounds in the VOC emissions from nine
18 toner powders and eleven types of processes paper. Although benzaldehyde,
19 acetophenone and nonanal are likely Tenax degradation products by ozone (48),
20 ozone emission was not detected during the heating of the printer components,
21 indicating that Tenax artifacts were insignificant in this study. Actually, benzaldehyde
22 and acetophenone are likely styrene or styrene oligomer oxidation products probably
23 formed during the production of the toner powder.

24
25 Although all these dominant VOC species emitted will not react with ozone, nine
26 unsaturated compounds were detected in the samples (listed in Table 1). Interestingly,

1 all of them came from the toner and the paper, including dodecenal, furfuryl alcohol,
2 2-furaldehyde, 2,6-di-tert-butyl-p- benzoquinone, BHT-quinone methide and squalene
3 from the paper, and 3-butene-2- one, 2-phenylpropenal, squalene and styrene from the
4 toner. 2,6-di-tert-butyl benzoquinone and the BHT-quinone methide are a well-known
5 oxidation products of BHT itself, probably added as antioxidant. 2-phenylpropenal is
6 probably derived from oxidation of styrene dimer or trimers. Styrene and other
7 unsaturated species were also emitted from processed paper (11). Compared to other
8 compounds detected, they have higher potential to react with ozone due to having
9 double bonds (51). Their reaction products may contribute to the formation of SOA
10 under favorable conditions, i.e. sufficient concentration, suitable temperature and
11 humidity, and so on. The overall ozone reaction rate constants of these unsaturated
12 compounds are also presented in Table 1. Based on this information, the most possible
13 precursors are squalene, followed by styrene and BHT-Quinone Methide. Dodecenal,
14 which has the lowest ozone reaction rate constant, is less likely to be SOA precursors.
15 As the most popular SOA precursors in indoor environment, limonene and
16 alpha-pinene have an ozone rate constant of $2.1 \times 10^{-16} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ and $8.7 \times$
17 $10^{-17} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, respectively (52). This means that squalene, which has an
18 ozone reaction rate constant of $258.0 \times 10^{-17} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, will react with ozone
19 faster than limonene and alpha-pinene, though few studies have investigated the SOA
20 formation potential of squalene.

21

22 Based on the traditional mechanism of SOA formation, the low volatility of
23 oxidated products can favour the transfer from the gas-phase to the particle-phase, and
24 improves the SOA yield. Cyclic organic compounds, such as cycloalkenes, terpenes
25 and aromatics, have long been identified as more likely to be SOA precursors since

1 the oxidation of these classes of compounds more likely generates low-volatility
2 products than the oxidation of similar sized VOCs in other classes. There are two
3 main reasons leading to the formation of low-volatility products: (1) the products of
4 ring opening processes often have the same (or similar) carbon number as the parent
5 compound, and (2) the oxidation occurs predominantly by an addition mechanism to
6 produce first-generation products with two (or more) polar functional groups (53).
7 Aromatic compounds contribute to SOA formation mainly through photochemical
8 reactions and in the indoor environment, terpenes (in particular α -pinene and
9 limonene) are the dominant SOA precursor as a result of their reactions with ozone.
10 However, no terpenes, except squalene (a type of triterpene), were detected in the
11 emissions of the heated printer components.

12

13 Squalene has been widely detected as the single most abundant unsaturated
14 constituent in human skin lipids (54) and can participate in reactions with indoor
15 oxidants, such as ozone and nitrate, yielding volatile aldehydic and ketonic products
16 (55, 56). In addition, recent studies have shown that squalene is the major scavenger
17 of ozone at the interface between room air and the human envelope (57), however
18 there is no evidence that squalene acts as a precursor to SOA formation in
19 ozone-initiated reactions.

20

21 Styrene was detected in the emission from both paper and toner powder in this
22 study. As a common constituent in paper and toner powder, styrene has been widely
23 reported in printer emissions by a number of studies (8, 16, 21, 47, 58, 59). The rate
24 constant for reaction between ozone and styrene was calculated by Tuazon et al.
25 (1993) (50). Na et al. (60) reported SOA formation from a styrene-ozone system and

1 proposed 3,5-diphenyl-1,2,4-trioxolane and a hydroxyl-substituted ester as the major
2 aerosol-forming products. It was also found that SOA formation can be reduced with
3 the presence of water vapour prior to styrene oxidation.

4
5 Though all other unsaturated species can react with ozone due to their double
6 bonds, few studies have been done to investigate their SOA formation potential
7 possibly because of the relatively slow reaction rate with ozone under ambient
8 environment or lack of lower-volatility reaction products. Recent studies suggested
9 that SOA formation from VOC oxidation is not solely driven by the volatility of the
10 gas-phase products formed, but is also influenced by the propensity of oxidation
11 products to undergo further reactions in the condensed phase (53, 61-63). Highly
12 volatile VOCs, such as glyoxal and acetylene, can associate with other aldehydes and
13 organic acids in particles to add to SOA mass (64). Therefore, the formation of SOAs
14 from the degradation of smaller molecular weight VOCs can no longer be
15 automatically disregarded (53). As such, some oxidant products from the ozonolysis
16 reactions of unsaturated species, which were identified in paper and toner emission
17 but not considered as common SOA precursors, may also have the potential to be
18 involved in ozone-initiated SOA formation via this mechanism.

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7

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21
22

FIGURES AND TABLES

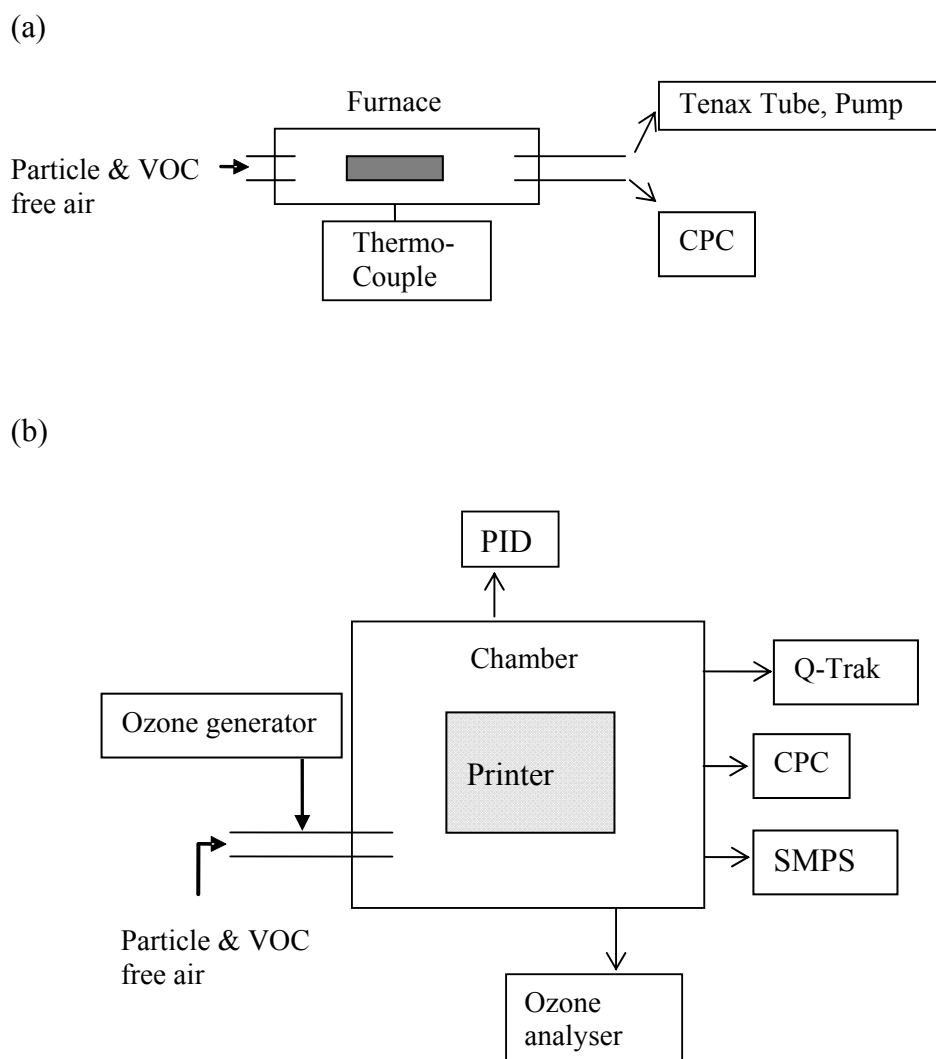


Figure 1 Schematic diagram of the instrumental set up. a) furnace and b) chamber. PID: photoionization detector; CPC: condensation particle counter; SMPS: scanning mobility particle sizer.

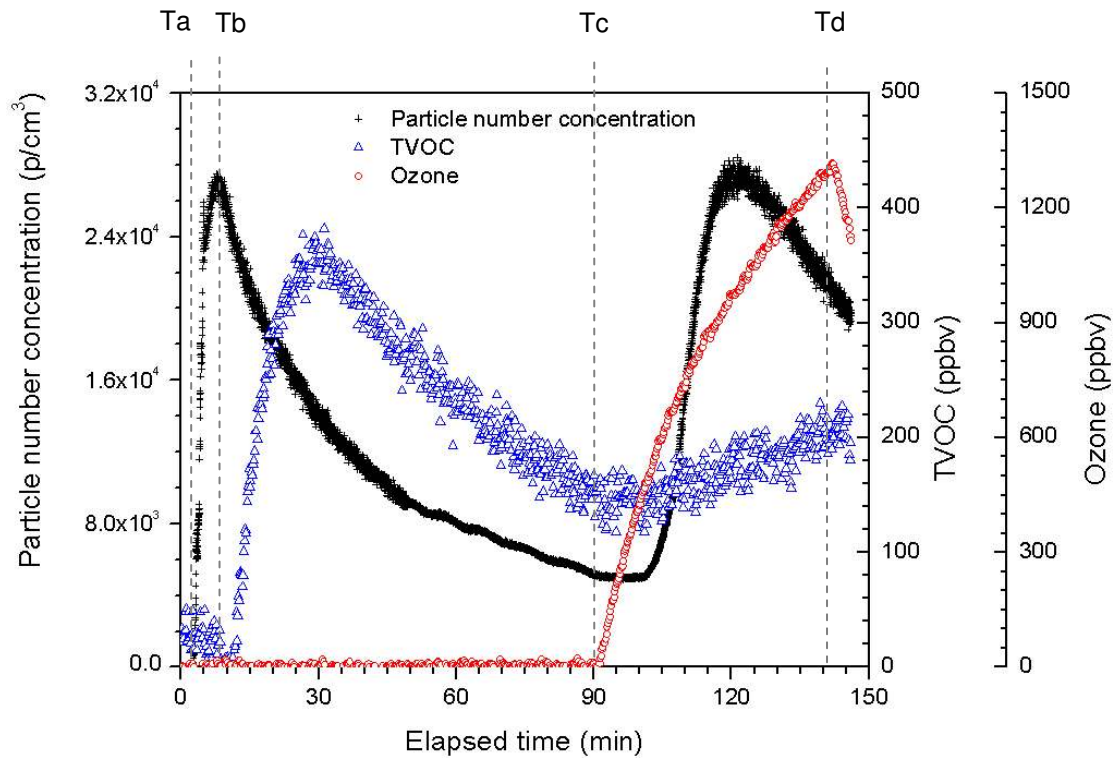


Figure 2 Time series of TPN, TVOCs and ozone concentrations in the chamber during and after printing 150 pages with 0% toner coverage by Printer H (PW-0%). Additional ozone was introduced into the chamber about 80 min after the completion of the print job. Ta: start printing; Tb: stop printing; Tc: start introducing ozone; Td: stop adding ozone.

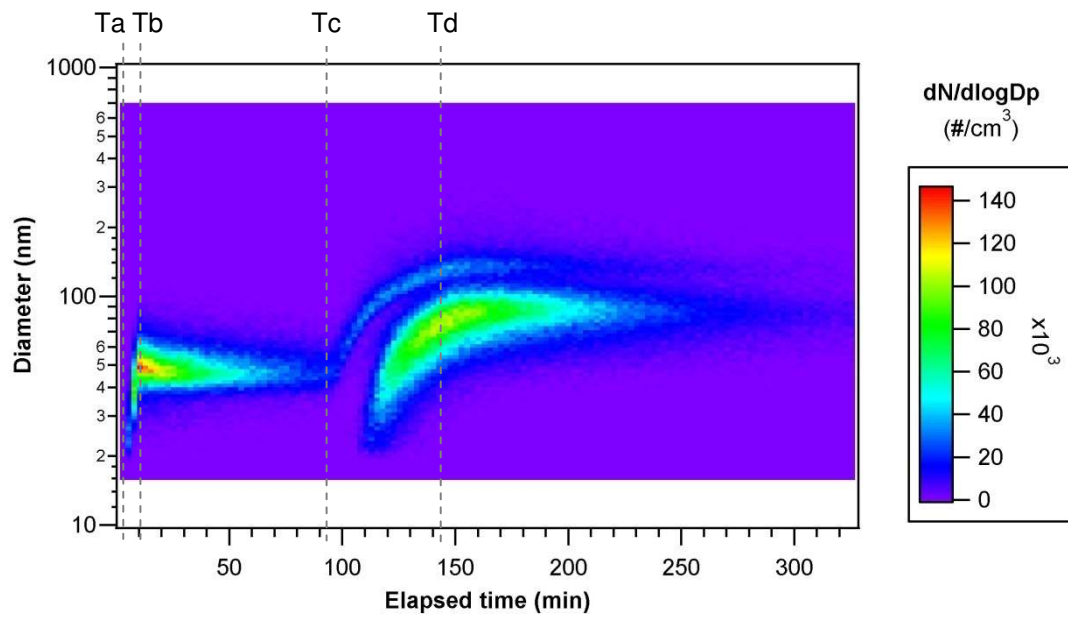


Figure 3 Particle size distributions in the chamber during and after printing 150 pages with 0% toner coverage by Printer H (PW-0%). Additional ozone was introduced into the chamber about 80 min after the completion of the print job. Ta: start printing; Tb: stop printing; Tc: start introducing ozone; Td: stop adding ozone.

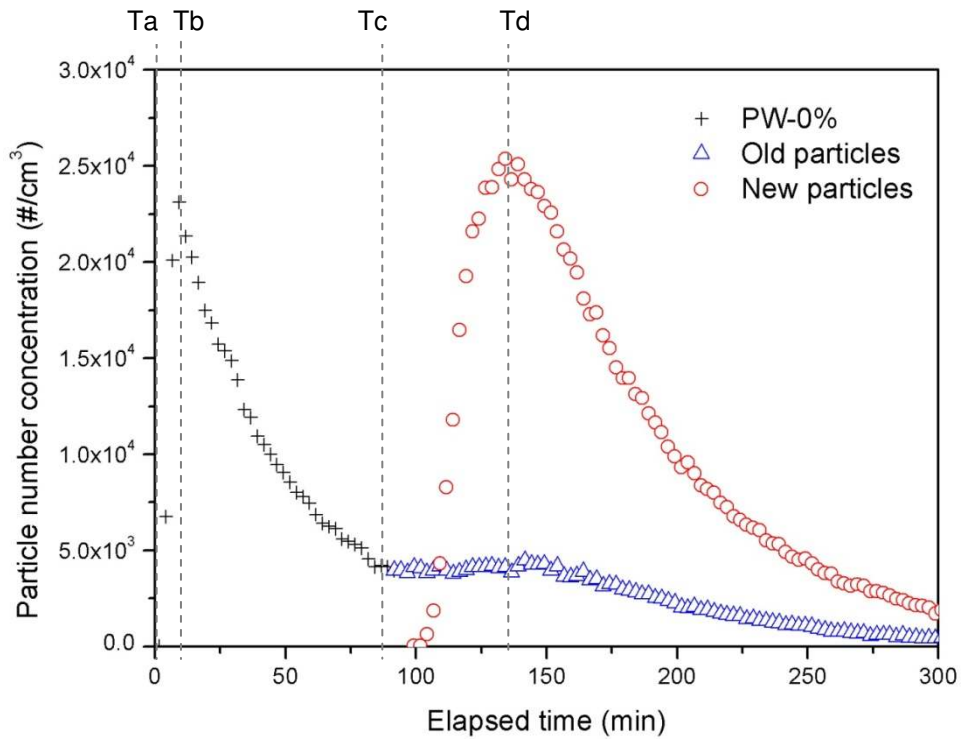


Figure 4 Total particle number concentrations measured by SMPS in the experiment of ozone addition. After the addition of ozone, old particles and new particles were carefully separated in light of the change of particle size, and the corresponding total number concentrations were recalculated. Ta: start printing; Tb: stop printing; Tc: start introducing ozone; Td: stop adding ozone.

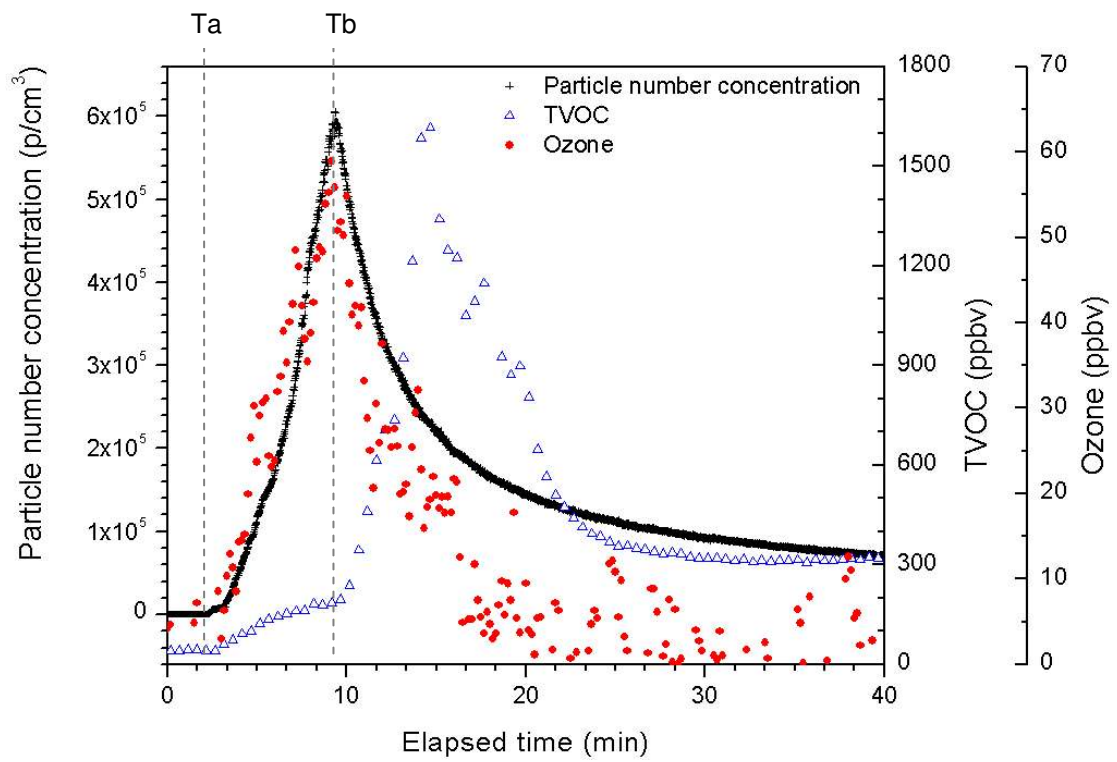

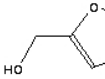
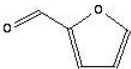
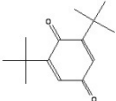
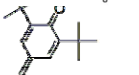
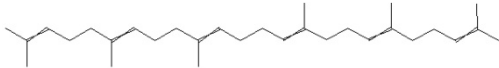


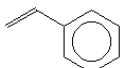


Figure 5 Time series of TPN, TVOCs and ozone concentrations in the chamber during and after printing of 150 pages with 50% toner coverage by Printer H (PW-50%). Ta: start printing; Tb: stop printing.

Table 1 Potential ozone-initiated SOA precursors during the operation of laser printers

| Possible reactants | Chemical structure | Overall ozone reaction rate constant * | Source |
|----------------------------------|---|--|---------------|
| Dodecenal |  | 0.091000 [Cis-] 0.182000 [Trans-] | Paper |
| Furfuryl alcohol |  | NA | Paper |
| 2-Furaldehyde |  | NA | Paper |
| 2,6-Di-tert-butyl-p-benzoquinone |  | 0.350000 | Paper |
| BHT-Quinone Methide |  | 0.985000 | Paper |
| Squalene |  | 258.000000 ^a | Paper & Toner |
| 3-Butene-2-one |  | 0.477±0.059 ^b | Toner |
| 2-Phenylpropenal |  | 0.336000 | Toner |
| Styrene |  | 1.71±0.18 ^c | Toner |

* The ozone reaction rates cited in this table are based on gas-phase reactions only; the unit is 10^{-17} $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$; where no specific reference is given, these values are taken from a prediction model (i.e. the US Environmental Protection Agency's EPISuiteTM).

^a The reaction probability of ozone (50ppb) and squalene on the surface is $(45 \pm 14) \times 10^{-5}$ (1);

^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):

$$R_R = \frac{\pi d_p^2 p_\infty}{\sqrt{2\pi m k T}}$$

Where d_p is the particle size, p_∞ 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_R is the maximum rate of reaction. Calculation has been done for two cases in our experiment: (1) $T = 300$ K, $[O_3] = 500$ ppb, $d_p = 62$ nm; (2) $T = 300$ K, $[O_3] = 1000$ ppb, $d_p = 106$ nm. The results indicate that the maximum reaction rates between ozone and the generated particles are 1.34×10^7 and 7.84×10^7 molecules.s⁻¹ for the case 1 and 2, respectively.

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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: %).

| Compounds | Function groups | PA | FR | TP | LO |
|--|-------------------|------|------|------|------|
| Furfuryl alcohol (T) | Alcohols | 2.0 | | | |
| Dodecenal (D) | Aldehydes | 3.7 | | | |
| 2-Furaldehyde | Aldehydes | 1.7 | | | |
| trans-2-Decenal (D) | Aldehydes | 7.0 | | | |
| Pentanal | Aldehydes | 2.4 | | | |
| Propanal (P) | Aldehydes | 2.3 | | | |
| Heptadecane | Aliphatic | 1.8 | | | |
| 2,6-Di-tert.butyl-4-methylphenol (B) | Aromatics | 3.8 | | | |
| 2,6-Di-tert-butyl-p-benzoquinone (B) | Aromatics | 1.2 | | | |
| BHT-Quinone Methide | Aromatics | 0.3 | | | |
| Dibutylphthalate | Carboxylic esters | 20.4 | | | |
| 2,3-Butanedione (T) | Ketones | 0.7 | | | |
| Nitrogenous (T) | N-containing | 0.9 | | | |
| Butylglycol | Alcohols | | 1.5 | | |
| Tetradecane | Aliphatic | | 2.6 | | |
| Naphtalenederivate (T) | Aromatics | | 3.7 | | |
| 1,3,5-tribromo-Benzene (T) | Aromatics | | 2.4 | | |
| Naphthalene | Aromatics | | 2.0 | | |
| N-Methyl-2-pyrrolidone | N-containing | | 7.8 | | |
| Benzaldehyde | Aldehydes | | | 35.0 | |
| 2-methyl-Benzaldehyde (T) | Aldehydes | | | 0.6 | |
| 2-Phenylpropenal (T) | Aldehydes | | | 13.7 | |
| iso-Pentane (H) | Aliphatic | | | 0.8 | |
| 3-Butene-2-one (M) | Alkenes | | | 3.1 | |
| Isocyanato-Benzene (T) | Aromatics | | | 1.6 | |
| Benzene | Aromatics | | | 1.2 | |
| Diphenylpropan (T) | Aromatics | | | 0.8 | |
| alpha-Methylstyrene (T) | Aromatics | | | 0.7 | |
| 1-phenyl-1-Propanone (T) | Aromatics | | | 0.6 | |
| Benzyl alcohol | Aromatics | | | 0.6 | |
| Butanoic acid (HA) | Carboxylic acids | | | 1.3 | |
| 5-chloro-1H-Benzotriazole (T) | N-containing | | | 0.8 | |
| C13-Benzen (T) | Aromatics | | | | 10.4 |
| Hexamethyl-cyclotrisiloxane | Siloxanes | | | | 1.6 |
| n-Heptanal | Aldehydes | 6.6 | | 1.2 | |
| n-Nonanal | Aldehydes | 16.5 | | | |
| Octanal | Aldehydes | 7.7 | | | |
| n-Hexanal | Aldehydes | 7.6 | | 0.9 | |
| Butanal | Aldehydes | 2.8 | | 2.2 | |
| Heptane | Aliphatic | | | | 5.5 |
| Hexadecane | Aliphatic | 0.9 | 2.4 | | |
| Squalene | Alkenes | 7.4 | | 5.8 | |
| BHT-Derivate (T) | Aromatics | 0.7 | 1.1 | | |
| 2,6-Diisopropyl-naphthalene | Aromatics | 0.3 | 0.4 | | |
| Styrene | Aromatics | | 0.7 | 1.6 | |
| Phenol | Aromatics | | 64.9 | 2.7 | |
| Acetophenone | Aromatics | | 5.9 | 22.9 | |
| Toluene | Aromatics | | | 1.3 | |
| Carboxylic ester (T) | Carboxylic esters | | | 0.5 | 6.6 |
| 2,2,4-Trimethylpentane-1,3-diol-monoisobutyrate (TE) | Carboxylic esters | | 4.3 | | |
| Sulfinylbis-methane (T) | Sulfide | 1.2 | | | 76.0 |

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.