# VOC and SVOC contribution of papers for hardcopy devices to indoor air pollution

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## ABSTRACT
Test chamber measurement for hardcopy devices (laser printers and copiers) showed the release of toluene, ethylbenzene, styrene and xylenes but also hexanal and acetic acid were detected. It is known that hexanal and acetic acid originate from wood which is the main component in paper production. Beneath the VOCs a large number of SVOCs were found in the test chamber air. Only a few could be identified, e.g. diisopropylnaphthalene and isopropyllaurate (dodecanoic acid, isopropylester). The sum of SVOCs (TSVOC) calculated as toluene-equivalents reached up to 28 mg/(h unit) and was up to ten times higher than the TVOC (depending on the hardcopy device).

The analysis of paper by means of direct thermal desorption showed that the SVOCs are emitted especially from recycled paper when it is heated up to 180°C which is the maximum temperature during the printing process (fixation of toner) in many hardcopy devices.

## INDEX TERMS
VOC; SVOC; Paper; Printer; Hardcopy device

## INTRODUCTION
For a revision of the German environmental label 'Blue Angel' for hardcopy devices different aspects of emissions (VOCs, ozone, particles) were investigated in test chambers (Rockstroh *et al.*, 2003). For environmental reasons, recycled paper was used for printing. The contribution of paper-emissions has not been taken into account so far in the existing testing methods (European Computer Manufactures Association, Japan Business Machine Makers Association, German environmental label 'Blue Angel' RAL UZ 62 and 85) and in the literature (Black and Worthan, 1999; Wensing *et al.*, 2002). That might be due to the use of large chambers up to 50 m³ where especially SVOC-emissions cannot be detected because of sink effects. Another reason might be the routine analysis for VOCs only up to the retention time of *n*-hexadecane. In the existing testing methods only styrene has to be specifically calculated, all other compounds are either neglected or calculated together for the TVOC as toluene-equivalents, which could mean that paper-typical emissions like, e.g. hexanal are not identified at all. Some investigations considered the toner ingredients and emissions of styrene from freshly copied paper (Wolkoff *et al.*, 1993; Henschel *et al.*, 2002).

## METHODS
### Materials
Hardcopy devices were obtained from seven producers and were taken from the current production. The papers were bought in packages of 500 sheets. The recycled paper which was used for all test chamber measurements of the hard copy devices was bought in one charge of 100 packages.

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**Emission Test Chamber**
The investigations were performed in 1 m³ chambers which are in accordance with the European prestandard ENV 13419-1.

**Printing Process**
For the printing process the printers were loaded with 500 sheets of paper and the air exchange rate was adjusted to be between 4 and 5 $h^{-1}$. The exact air exchange rate was determined by $N_2O$ measurements. This high air exchange rate was required to reach an equilibrium concentration inside the test chamber within the short printing time of only 30 min (Rockstroh *et al.*, 2003). The high air exchange rate was also necessary because, otherwise, the released water from the paper condensed inside the 1 m³ chamber (relative humidity more than 90%). The printing process was started at 10% r.h. and 23°C and ended at about 55% r.h. and 24°C. Printing time was normally between 20 and 30 min.

**Analysis of Chamber Air Samples**
Sampling was done using glass tubes (length 178 mm, od 6 mm, id 4 mm) filled with Tenax TA (200 mg, 60–80 mesh) fixed with glass wool (deactivated) stoppers. The sampling volume was between 0.5 and 2 l with an airflow of 100 ml/min.

The analysis was carried out by thermal desorption (final temperature 290°C, Gerstel TDS-2/CIS-3) combined with gas chromatography (HP 5890 II plus) and a mass spectrometer (HP MSD5972).

**Analysis of Papers by Direct Thermal Desorption**
For direct thermal desorption one strip of paper was cut out of the DIN A4 sized paper and was transferred into an empty glass tube. The strips were about 3 mm wide and 60–80 mm long and had a weight of 20 mg.

Thermal desorption was started at 40°C. The temperature was raised at a rate of 40°C/min to the final temperature of 180°C which was maintained for 5 min. The helium flow rate was 30 ml/min. The cold injection system of the GC was maintained at –150°C for the time of thermal desorption to trap the emitted compounds.

**RESULTS**
During the experiments it turned out that SVOCs were also found in the test chamber air (Figure 1). Furthermore, the concentrations of SVOCs were sometimes much higher compared to the concentrations of VOCs.

Analysis of the papers by means of direct thermal desorption showed that the SVOCs were mainly emitted from the recycled paper. VOCs were mainly emitted from the toners during the printing process or from materials used in the hardcopy devices.

Comparison of different papers (recycled paper as well as paper produced from primary fibres) showed, in general, higher SVOC-emissions from recycled paper (Figures 2 and 3). However, there were large differences between both types of paper. The resulting emissions from the papers not only depended on the papers themselves but also on the printer used (Table 1). The comparison of the printing process of nine printers using the same recycled paper gave emission rates for the TSVOC in the range from 3800 µg/(unit h) to 27 800 µg/(unit h). For two printers which were tested in a 20 $m^3$ chamber no SVOCs could be detected. This is probably due to sink effects and smaller concentrations (compared to the 1 $m^3$ chamber) because of a larger chamber volume.

**Test Chamber Measurement**

A gas chromatogram of a sample taken during the last 10 min of a printing process is shown in Figure 1. In the VOC-range acetic acid (1), hexanal (2), ethylbenzene (3), xylenes (4), styrene (5), benzaldehyde (6), acetophenone (7), cyclodecane (internal standard, 8), tetradecane (9), 2,6-di-tert.-butyl-*p*-benzoquinone (10), pentadecane (11), and hexadecane (12) were detected. In the SVOC-range isopropyllaurate (13), diisopropylnaphthalene (six isomers, 14) and octadecane (15) were detected.

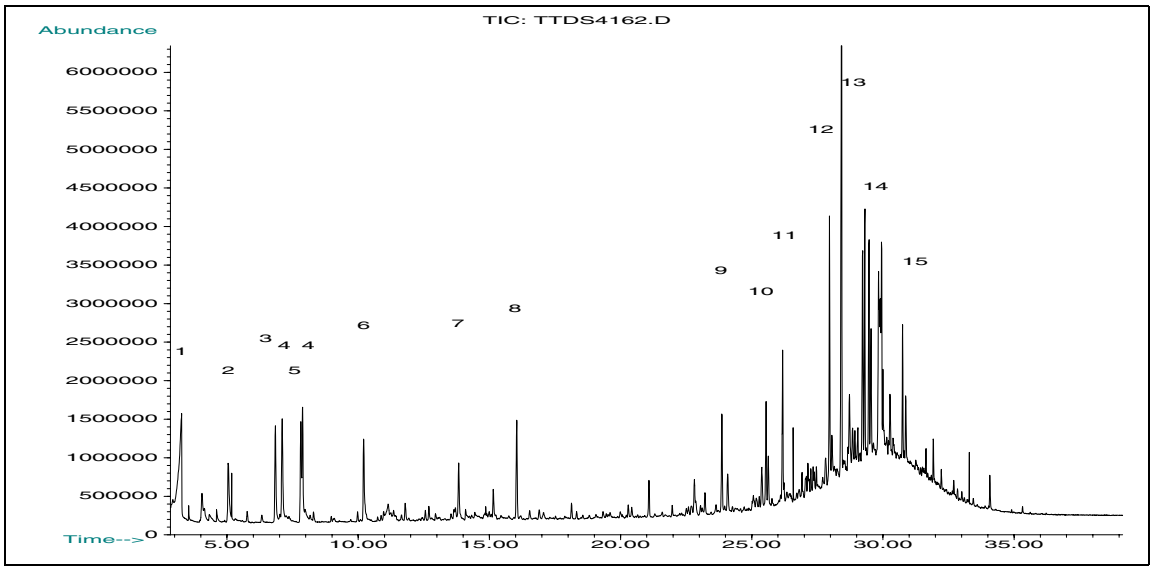


**Figure 1** Gas chromatogram of an air sample from the test chamber measurement.

Table 1 shows emission rates for the TVOC and TSVOC for nine different hardcopy devices calculated from the final printing phase (lasting 5–10 min, equilibrium approach (Rockstroh *et al.,* 2003)). The same recycled paper was used for printing. For test conditions see Methods, subsection Printing Process. Printer 6 printed 2000 sheets in 30 min.

**Table 1** Emission rates for TVOC and TSVOC from hardcopy devices

| hardcopy device | TVOC* | TSVOC** |
|---|---|---|
| | µg/(unit h) | µg/(unit h) |
| 1 | 2800 | 27800 |
| 2 | 900 | 11000 |
| 3 | 12100 | 15300 |
| 4 | 10000 | 3800 |
| 5*** | 5000 | n.d. |
| 6*** | 4700 | n.d. |
| 7 | 22700 | 4000 |
| 8 | 4100 | 11300 |
| 9 | 2500 | 9500 |

* mainly from toner, materials of printers
** mainly from paper
*** 20 m³ test chamber
n.d.: not detected

**Direct Thermal Desorption of Papers**

For the determination of the source of the surprisingly detected SVOCs, the papers used for printing were analysed by means of direct thermal desorption. First, the recycled paper was investigated because it was used for the development of the testing method for the German

environmental label 'Blue Angel'. For comparison reasons paper produced from primary fibres were also analysed. In Figures 2 and 3 examples of the emission spectra of the two different types of paper are given.

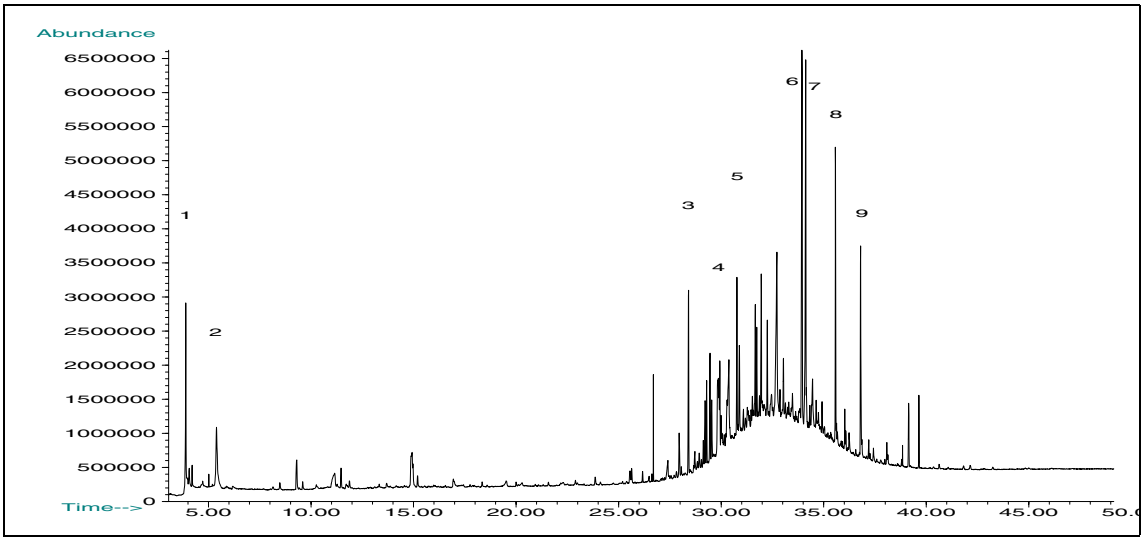


**Figure 2** Gas chromatogram obtained by direct thermal desorption of a sheet of recycled paper: 1: acetic acid, 2: hexanal, 3: isopropyllaurate, 4: diisopropylnaphthalene, 5: oktadecane 6: octadecene, 7: methyloleate, 8: eicosene, 9: docosene.

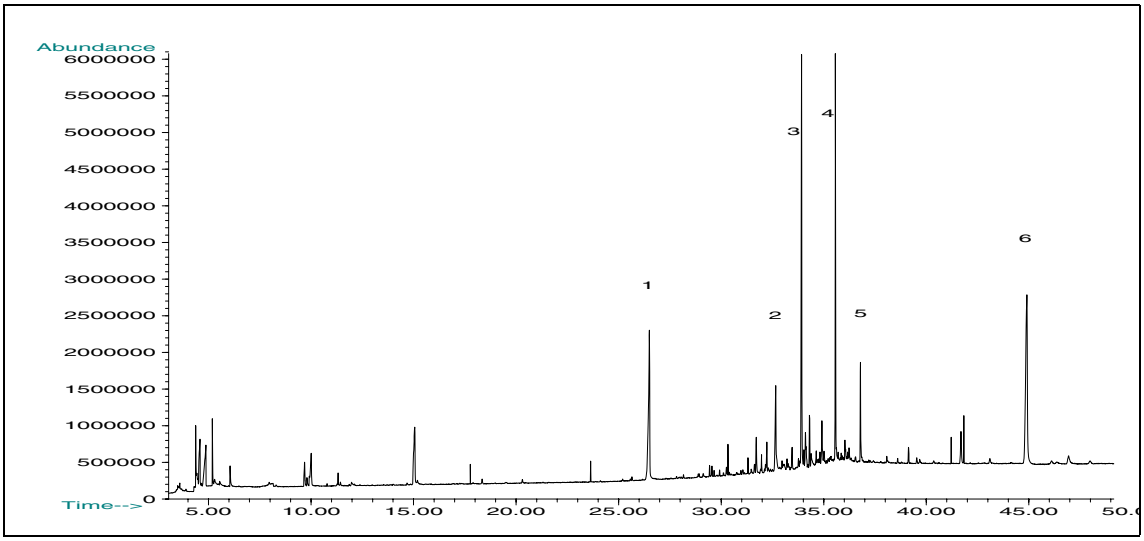


**Figure 3** Gas chromatogram obtained by direct thermal desorption of a sheet of paper produced from primary fibres: 1: *o*-hydroxybiphenyl, 2: hexadecanoic acid, 3: octadecene, 4: eicosene, 5: docosene, 6: not identified.

The two chromatograms are typical for the two different types of papers. A comparison between the chromatograms shows a higher emission potential for the recycled paper resulting from many more substances which are especially detected in the SVOC range (starting at 28 min).

**VOCs and SVOCs from Papers or (Secondary) Raw Materials**

Table 2 shows a list of identified VOCs and SVOCs from different papers and (secondary) raw materials analysed by direct thermal desorption.

**Table 2** VOCs and SVOCs detected as possible emissions from paper during printing

| VOC | SVOC |
|---|---|
| acetic acid | isopropyllaurate |
| hexanal | diisopropylnaphthlene |
| nonanal | heptadecane |
| decanal | octadecane |
| pentylfurane | nonadecane |
| ethylhexanol | eicosane |
| decadienal | octacosane |
| alkanes/isoalkanes | hexadecene |
| alkenes/isoalkenes | octadecene |
| caryophyllene | eicosene |
| longifolene | docosene |
| TXIB | lauric acid |
| BHT | myristic acid |
| hydroxybiphenyl | palmitic acid |
| pentadecane | methyloleate |
| hexadecane | dioctyladipate |
| | dibutylphthalate |
| | diisobutylphthalate |

**DISCUSSION**

The printing of 500 sheets of paper inside a 1 m³ test chamber is not a very realistic simulation of a real room (office) situation. However, the emission rates are determined under controlled conditions and can be used to estimate concentrations of emitted substances in real rooms if the air exchange rate and the number of printed papers are known (Rockstroh *et al*., 2003).

However, calculation of emission rates of SVOCs is difficult because it is not to be expected that an equilibrium between chamber air and chamber surface is reached during the short time of printing. Some SVOCs might not be detectable at all because of sink effects. It is also an analytical challenge to determine SVOCs by means of thermal desorption.

In the beginning of the project there were two reasons cited for the occurrence of SVOCs:

1. Use of chemicals for the de-inking process (flotation) during the production of recycled paper.
2. Insufficient removal of paper chemicals contained in the incoming recovered (waste) paper.

The comparison by means of direct thermal desorption of different papers produced with and without the de-inking process showed that the de-inking decreases the emission-potential of the paper. The conclusion is that the SVOCs in recycled papers come from chemicals contained in the incoming recovered (waste) paper. The main sources are probably printing inks.

The occurrence of diisopropylnaphthalene in recycled paper is explained with the processing of carbonless copy paper which is part of recovered (waste) paper.

## CONCLUSION AND IMPLICATIONS

Emissions of VOCs and especially SVOCs from papers during printing with hardcopy devices were detected. These emissions as well as emissions from toners and materials of hardcopy devices should be minimized to avoid indoor air pollution. One solution could be the reduction of the printing (fixation) temperature, which has an influence on the emission rate. Another way could be an improvement of the de-inking process to remove more chemicals during the production of recycled paper. A third method would be the development of printing inks which are easier to remove from recovered (waste) paper during the recycling process.

## ACKNOWLEDGEMENTS

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