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Comparison of Volatile Organic Compounds from Processed Paper and Toners from Office Copiers and Printers: Methods, Emission Rates, and Modeled Concentrations

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Abstract

The emission of volatile organic compounds (VOC) from nine toner powders and eleven types of processed paper from photocopying machines (6), laser (3) and matrix printers (2), and one carbonless copy form has been measured. A total of 61 VOC from toner powders were identified by heating (185 °C) the powder for three minutes for thermal desorption and by gas chromatography followed by the use of low and high resolution EI and CI mass spectrometry. VOC from processed paper were analyzed by headspace sampling on Tenax TA from nylon bags. Thirty-one VOC with a wide range of volatility and persistency were identified from processed paper. The total VOC emission from the various types of paper differed substantially. Using the field and laboratory emission cell (FLEC), the calculated initial emission rate of styrene was 5 μg $m^{-2}h^{-1}$ from a freshly processed paper. The VOC emission from machines and the processed paper can be reduced by proper choice of office equipment. However, an evaluation should consider all potential pollutants.

KEY WORDS:
Emission, Laser printers, Matrix printers, Photocopying machines, Volatile organic compounds (VOC), Processed paper, Toner powders

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Introduction

Complaints about poor indoor air quality (IAQ) have been reported since the late sixties (Kreiss, 1989). Later, the energy crisis demanded reduced ventilation and tight buildings. The new building approach was followed by an increased use of new synthetic building materials and at the same time the use of modern office technology such as photocopying machines, computers, video display terminals (VDT), laser, matrix, and ink jet printers, carbon paper and carbonless copy paper, increased rapidly.

Based on a survey of 600 office workers, Woods et al. (1987) estimated that about 20% of all such workers are exposed to an office climate giving rise to adverse health effects such as "sick building syndrome" symptoms (WHO, 1986).

Four out of 50 patients examined by a clinical ecologist indicated office machines as the cause of their complaint (Terr, 1986). In a later review including an additional 40 patients, 19 had the office environment as their workplace (Terr, 1989). It is also striking that mucous irritation and skin problems are prevalent in the office environment (Wahlberg and Stenberg, 1991) as opposed to other non-industrial environments.

The results of two field studies suggest that handling paper from photocopying machines is associated with SBS symptom prevalence (Skov et al., 1989; Taylor et al., 1984). One of the major symptoms reported is mucous irritation in the order of 30-40% (Marbury and Woods, 1991). An office study has shown a correlation between volatile organic compounds (VOC) exposure and SBS symptom prevalence (Hodgson et al., 1991). Wallace et al. (1991) found in three building surveys that persons report-

ing odor annoyance were also more likely to report SBS symptoms such as headache, throat problems, and dizziness. Persons reporting conflicting job demands were more frequently annoyed by photocopying and printing than those without job conflicts. The concern and worry about odor from hazardous waste sites have been shown to be related to SBS-type symptoms such as headache, eye and throat irritation, and nausea (Shusterman et al., 1991). In contrast a controlled study revealed that fewer SBS symptoms were reported for persons exposed to a fresh scent (lemon) than to a malodor (Knasko, 1992). These results support the hypothesis that malodors may trigger SBS symptoms.

Controlled exposure studies have shown that some VOC are perceptible even at concentrations considerably below TLVs and may result in mucous irritation and foreign odor annoyance (Cometto-Nuñiz and Cain, 1992; Kjærgaard et al., 1989, 1991; Koren et al., 1992; Mølhave et al., 1986; Otto et al., 1992; Wolkoff et al., 1991a).

There are only a few cases reporting symptoms related to the use of a laser printer (rhinitis) (Skoner et al., 1990), a photocopying machine (irritation of the pharynx) (Selner and Staudenmayer, 1985), and heat sensitive paper (palpable purpura) (Tencati and Novey, 1983). The use of carbonless copy paper (Buring and Hennekens, 1991) and VDT (Wahlberg and Stenberg, 1991; Scansetti, 1984) have been reviewed with regard to health effects, in particular, skin effects.

The emission of ozone from office machines has been measured and its possible impact upon the indoor air quality has been discussed (Allen et al., 1978; Selway et al., 1980; Miksch et al., 1982; Hansen and Andersen, 1986; Olander, 1990). In a recent chamber study, 30 female subjects were exposed during typical clerical work to a simulated office environment with office equipment (Wolkoff et al., 1992). It was shown that the perception of eye irritation was significant among the subjects and in accord with objective eye measurements showing epithelial damage of the conjunctiva in spite of low concentrations of ozone, formaldehyde, TVOC, and particles. In addition, the air quality in decipol was worsened.

The impact of indoor air pollution on the well-being of office workers gains particular importance when it is considered that more than 60% of the workforce in the western hemisphere is located in office or office-like environments (Wahlberg and Stenberg, 1991) and this proportion is expected to increase during the coming decades (Mage and Gammage, 1985). Additionally, another possible consequence of air pollution could be malfunction of electronic equipment (Shields and Weschler, 1992).

Building materials (Levin, 1989), household products (Knöppel and Schauenburg, 1989; Sack et al., 1992), and human activities (Wallace et al., 1987, 1989), like the use of office equipment (Brooks and Davis, 1992) and office furniture (Strobridge and Black, 1991), are the major sources of VOC to the indoor environment. Only limited information is available on the emission of VOC from office machines (Brooks and Davis, 1992; Miksch et al., 1982; Sonnino et al., 1983) and wet photocopying machines (Grot et al., 1991; Tsuchiya, 1988; Tsuchiya and Stewart, 1990; Walkinshaw et al., 1987). The emissions of VOC from building materials in a new building are dominant for up to six months (Berglund et al., 1982; Wolkoff et al., 1991b). Their decline depends on the emission characteristics of the particular material (Seifert and Ullrich, 1987). On the contrary, the use of office equipment, such as printers and photocopying machines, provides a daily contribution, which does not diminish over weeks and months.

It is important to know the potential sources of pollution in order to be able to reduce the indoor air pollution. Standardized methods have been developed for the measurement of emissions from building materials and products (ASTM, 1990; European Concerted Action, 1991) and the evaluation thereof (Wolkoff et al., 1991a). Until recently, the measurement and evaluation of emissions from office machines have focussed upon ozone. The mutagenic activity in photocopies has been tested by the Ames assay which gave a negative result (Löfroth et al., 1980; Rosenkranz et al., 1980; Malaiyandi et al., 1988).

The aim of this study was to examine VOC emitted from paper processed in laser and matrix printers, and photocopying machines as regards to the emission of their corresponding toner powder, and to develop a method for a relative comparison of the emission from office machines.

Experimental Methods

VOC Emission from Copy Machine Toner Powder

Toner powder (10.0 ± 0.4 mg) was placed in a glass tube (5.0 mm o.d.) with silanized glass wool plugs at both ends. The desorbed volatiles were cold trapped in a Perkin-Elmer ATD-50 using a standard steel

tube containing the packed glass tube. The conditions were 185 °C for 3 min. The other ATD operating parameters were: cold trap, -30 °C; flash desorption, 300 °C: interface temperature, 150 °C. The analysis was carried out with a Hewlett-Packard HP 5890A gas chromatograph equipped with a SGE split injector (2:15), between the deactivated fused silica column in the heated transfer line and the analytical column, a 50 m column, i.d. 0.32 mm, film thickness 0.20 μm (Chrompack, SIL 19 CB) and a flame ionization detector. The temperature program was 20-220 °C at 4°/min, 220 °C for 13 min.

Qualititative Analysis of VOC from Toner Powder Emissions

GC low and high EI, and CI (ammonia as reagent gas) resolution mass spectra of the effluents were obtained by coupling Perkin-Elmer ATD-50 to a KRATOS Analytical Profile HV3 GC/MS instrument. Infrared spectra of the effluent from toner powders were obtained with a Bruker IFS 85 FT-IR instrument coupled with a Carlo Erba TDAS 5000 desorber, cold trap MFA 515, and 5300 Mega GC.

Semi-quantitative Headspace GC Analysis of VOC from Processed Paper

Black sheets (10) were prepared by photocopying a dark red notebook or printing a black field generated by a text or drawing program. A comparable number of carbonless copy paper forms (4 forms of 3 sheets) were used. The papers were crumpled into balls and placed in closed nylon 6/6 foil bags. The bags were inflated with nitrogen (99.99%) to 7.3 ± 0.3 *l* and allowed to equilibrate overnight at ambient temperature (ca. 22 ± 1 °C). Gas samples were collected for analysis the following day (after 18 hours) on 200 mg Tenax TA (Chrompack) in Perkin-Elmer ATD-50 steel tubes using SKC model 224 pumps. The sampling volume was about 5.0 *l*. The ATD-50 operating parameters for Tenax TA desorption were 250 °C for 20 min. Other analysis parameters were the same as above. Total VOC (TVOC) was calculated, after subtracting artefacts, as toluene equivalents using the FID response factor of toluene determined from the standard curve by injection of 5.00 μ*l* of three stock solutions (0.0978, 1.335 and 6.068 μg/μ*l*) onto Perkin-Elmer Tenax TA tubes with a nitrogen flow of 60 m*l*/min for 3 min. Two independent experiments showed a difference of TVOC (toluene equivalents) for photocopies of ca. 10%. The TVOC values do not account for qualitative differences, cf. Table 2.

Quantitative Measurement of VOC Emission from Processed Paper with the Field and Laboratory Emission Cell (FLEC)

A round piece (14.8 cm diameter) of photocopied paper was placed one hour after processing on a clean 21.0 cm square piece of glass and covered with the stainless steel FLEC (volume 35 m*l*) as described previously (Wolkoff et al., 1991c). The cell was flushed with nitrogen humidified to 50% RH at 0.030 *l*/min. The effluent was sampled on the same Tenax TA tubes as above using two Alpha-1 sampling pumps (Dupont) at 0.010 *l*/min over 8 hours at 24 hour intervals. Desorption and GC analysis were carried out as described above. Sampling midpoints were used for calculations.

Results

Table 1 illustrates the various experiments performed.

Toner Powders

Since the odors emitted during operation of photocopying machines and printers clearly indicated the presence of odorous compounds, such as acrylates, photocopy and laser printer toner powders were heated to the temperature of the "fusion" roller of most of the photocopying machines examined, 185 °C. The compounds identified from nine toner powders (A-I) are listed in Table 2. Powders A-F are photocopy toners while G-I are laser printer toners. Toner

Table 1 The qualitative and quantitative VOC emission of toners and papers examined

Material	Photocoping machines		Laser printers		Matrix printers	Carbonless copy paper
Analysis	Toner	Processed paper	Toner	Processed paper	Processed paper	
Qualitative VOC	A-F	A-F	G-I	G-I		
Semi-quantitative TVOC		A-F		G-I	J-K	L
Quantitative, emission		E				

Table 2 Volatile organic compounds from copying machine toner powders, (listed according to GC retention time)

	A	B	C	D	E	F	G	H	I
1. 3-butene-2-one*						x			
2. butanal	x								
3. benzene		x	x	x	x	x		x	
4. trimethylsilanol									x
5. 2,2,4-trimethyl-1-pentene	x								
6. methyl methacrylate*					x				
7. 1-butanol*	x	x			x	x	x		x
8. pentanal					x				
9. toluene	x	x	x	x	x		x	x	x
10. C_8H_{16} isomer	x								
11. 4-methyl-2-pentanone		x		x					
12. 2-ethoxyethanol									x
13. pyridine						x			
14. 1-butyl acetate*					x				
15. C_4-cyclohexane isomers				x	x		x		x
16. 1-butyl ether*						x	x	x	x
17. ethyl benzene*	x	x	x	x	x	x	x	x	x
18. m-and p-xylene	x	x	x	x	x	x	x	x	x
19. 2,2-dimethylhexanal	x								
20. o-xylene	x	x	x	x	x	x	x	x	x
21. styrene*	x	x	x	x	x	x	x	x	x
22. 1-butyl acrylate*		x			x		x		
23. 1-butyl propionate*					x				
24. 2-phenylpropane		x		x	x	x	x	x	x
25. 3-heptanol		x							
26. 1-phenylpropane		x	x	x	x	x	x	x	x
27. 2-methylbutyl propionate*					x				
28. ethyl toluene isomers		x	x	x	x		x	x	x
29. 3-ethoxy-3-ethyl-4,4-dimethylpentane $^{+\#}$		x							
30. methylstyrene isomers*				x	x			x	x
31. 1-butyl methacrylate*	x					x			
32. α-methyl styrene*									x
33. benzaldehyde	x			x	x	x		x	x
34. diethylbenzene isomers							x	x	
35. 2-ethylhexanol*,$^{-}$				x	x	x		x	x
36. aniline	x								
37. dodecane isomer						x			
38. phenol					x				
39. acetophenone	x			x	x	x			x
40. 2-ethylhexyl acetate*			x	x				x	x
41. 2,2'-azo-bis-isobutyronitrile $^{+\#}$	x	x		x					x
42. tridecane						x			
43. 2-ethylhexyl acrylate*			x	x				x	x
44. tetradecane						x			
45. benzoic acid^{+}					x				
46. 4-phenylcyclohexene*						x			
47. di-(2-methylpropyl) maleate									x
48. 2-methylpropyl cinnamate									x
49. pentadecane						x			
50. biphenyl^{+}		x			x				
51. 2, 2,4-trimethyl-1,3-pentandiol monoisobutyrate	x								
52. N,N-phenylmethylaniline	x								
53. methylbiphenyls^{-}		x							
54. nonylbenzene		x							
55. 1,3-diphenylpropane^{+}									x
56. phenyl benzoate^{-}		x			x				x
57. $C_{16}H_{18}$ isomers (including 1,3 and 2,3-diphenyl-butanes)$^{+}$								x	
58. $C_{17}H_{20}$, diphenylpentane^{+}								x	
59. $C_{18}H_{20}$, phenyl (methylphenyl)pentene^{-}					x				
60. benzyl benzoate^{-}		x							
61. 2-hydroxymethyl-2-(phenylchromiumtricarbo-nyl)-4-phenylbutan-1-ol									x

* monomer or monomer impurity; $^{-}$ initiator or degradation product; # confirmed by GC high resolution MS determination, GC CI/MS, and GC/FT-IR spectrum

Table 3 Volatile organic compounds emitted from copied (A-F), laser printed (G-I), and matrix printed (J,K) paper (listed according to GC retention time)

	A	B	C	D	E	F	G	H	I	J	K
1. hexane	x										
2. 1,1-dichloro-1-nitroethane	x										
3. benzene	x	x+	x+	x+	*+	*+	x	x+	x	x	x
4. octene(isomer)	x										
5. pentanal	x				+						
6. trichloroethene	x										
7. 1-butanol	x+	x+		x	x+	x+	x+	x	x+		x
8. toluene	x+	*+	x+	*+	x+		*+	x+	x+	*	x
9. pyridine						x+					
10. 4-methyl-2-pentanone		x+		x+							
11. hexanal	*	x	x	x	x	x	x	x	x	*	*
12. C_4-cyclohexane isomers			+	x+			+		+		
13. 1-butyl ether		x+		+	x	+	x+	x+	x+	x	x
14. ethyl benzene	*+	*+	*+	*+	*+	*+	*+	*+	*+	x	*
15. m-and p-xylene	*+	x+	*+	*+	x+	*+	*+	*+	*+	x	*
16. o-xylene	x+	x+	*+	x+	x+	x+	x+	x+	*+	x	x
17. styrene	*+	*+	*+	*+	*+	*+	*+	*+	*+	*	*
18. 1-butyl acrylate		x+			*+		x+				
19. 2-phenylpropane	x	x+	x	x+	x+	x+	x+	x+	x+	x	x
20. 3-heptanol		x+									
21. 1-phenylpropane	x	x+	x+	x+	x+	x+	x+	x+	x+	x	x
22. ethyl toluene isomers	x	x+	x+	x+	x+	x	x+	x+	x+	x	
23. 3-ethoxy-3-ethyl-4,4-dimethylpentane		*+								*	
24. 1-butyl methacrylate	x+					+					
25. benzaldehyde	+			x+	x+	x+		x+	x+	x	x
26. diethylbenzene isomers			x	x			x+	*+	x		x
27. 2-ethyl-1-hexanol				x+	+		+	x+	x+		x
28. 2-ethylhexyl acetate			+	+				x+	+		
29. 2,2'-azo-bis-isobutyronitrile	+	x+		x+					x+		
30. 2-ethylhexyl acrylate			x+	x+				x+	x+	x	x
31. methylbiphenyl		+								x	

* four largest peaks; + detected in toner powder

powder safety data sheets describe their composition as ca. 80-90% polymeric binder and 10-20% carbon black, auxilliary pigments and additives. The VOC identified include solvent residues (benzene, toluene, xylene, octene, C_4-cyclohexanes, 1-butanol, butyl acetate, 2-ethoxy- ethanol), monomers (styrene and acrylate esters), monomer impurities (ethyl, propyl and isopropyl benzenes, and the diphenyl butane isomers), coalescent agent (Texanol, compound 51 in Table 2), monomer or polymer oxidation products (benzaldehyde, acetophenone) and polymer and toner additive decomposition products. A few of these VOC have been reported in a forensic study of toner powders (Levy and Wampler, 1986). One well known chemical from carpets with latex (SBR) backing, 4-phenylcyclohexene (Pleil and Whiton, 1990), was detected in the volatiles from toner F.

The GC/FID trace of volatiles desorbed from laser printer toner H is shown in Figure 1. Most noteworthy in the emission of this toner are polystyrene impurities or decomposition products, which consist of $C_{16}H_{18}$ isomers (Zlatkis et al., 1977). These compounds were detected at much lower concentra-

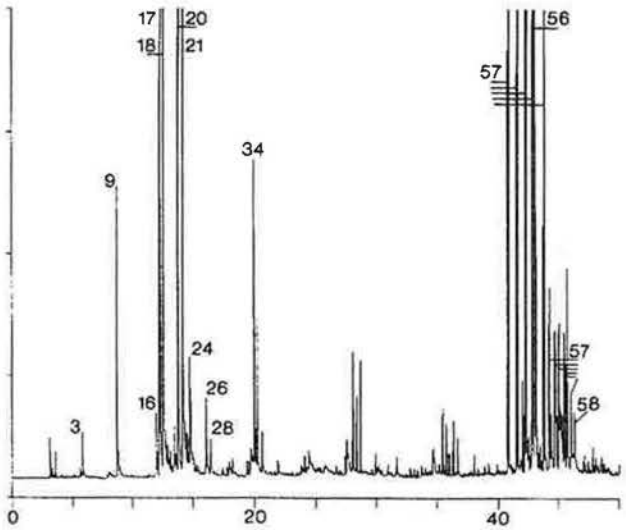

Fig. 1 Gas chromatogram. FID response for volatiles from laser printer toner H*.

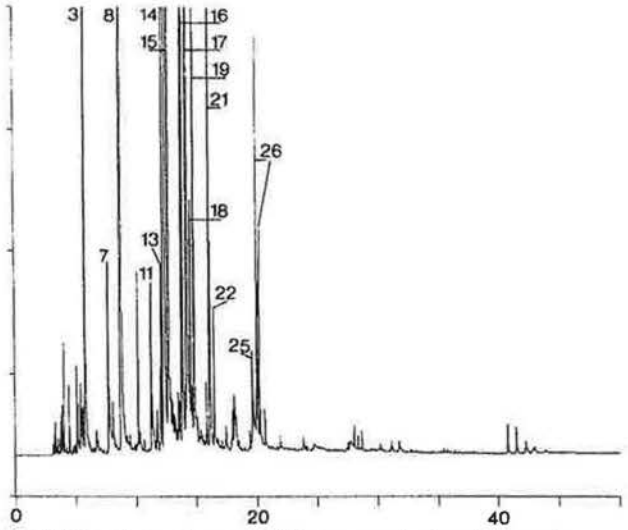

Fig. 2 Gas chromatogram. FID response for headspace of paper printed with laser printer toner H*.

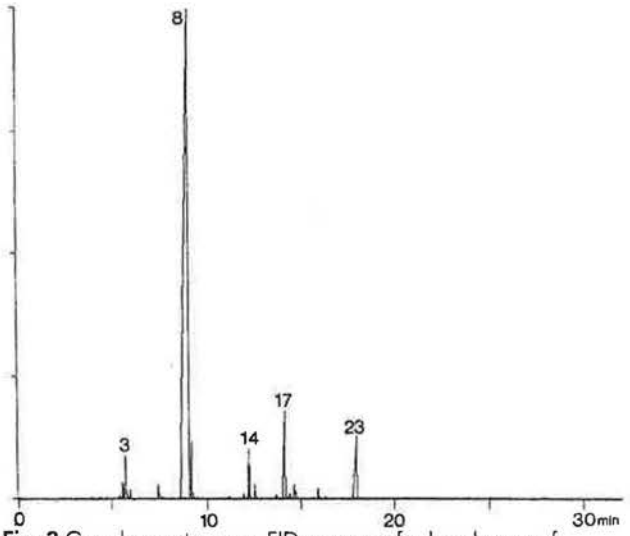

Fig. 3 Gas chromatogram. FID response for headspace of photocopied paper B*.

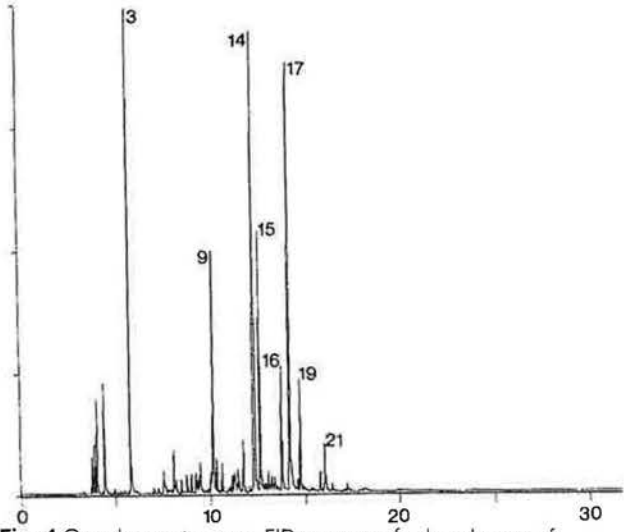

Fig. 4 Gas chromatogram. FID response for headspace of photocopied paper F*.

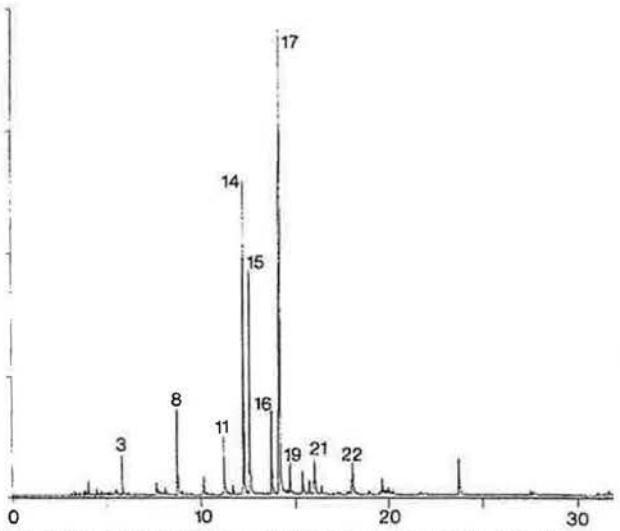

Fig. 5 Gas chromatogram. FID response for headspace of paper printed with laser printer toner I*.

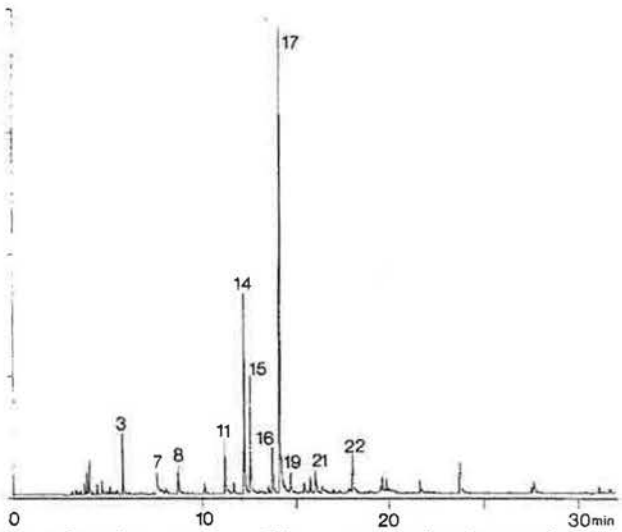

Fig. 6 Gas chromatogram. FID response for headspace of paper printed with matrix printer K*.
+ numbers refer to Table 2. * numbers refer to Table 3.

tions in copy emission due to their low volatility (see Figure 2).

Processed Paper

Most relevant for the office environment is the emission of VOC from processed/printed paper. As mentioned, the more volatile components from toner powders dominate the paper emission. The compounds identified from eleven types of printed paper (A-K) are shown in Table 3. Papers A-I are printed with their corresponding toner in Table 2 while papers J and K were printed with matrix printers. For comparison, chromatograms of emissions from four types of copied paper are included as Figures 3-6. The dominant substances are aromatic

Table 4 TVOC emission from fresh copies (μg/copy sheet)* from six photocopying machines (A-F), three laser printers (G-I), and two matrix printers (J-K), and one carbonless copy paper form (L)

Photocopy machines		Laser printers		Matrix printers	
A	1.6	G	6.5	J	0.7
B	16.4	H	2.6	K	1.0
C	0.5	I	2.0		
D	2.4				
E	6.1	Carbonless copy paper			
F	7.5	L	4.1		

* emitted from fresh black copies during 16 hours.

compounds such as toluene, the xylenes, ethyl and propyl benzenes and styrene; xylenes and styrene were dominant in all machines examined. Acrylates are usually found to be minor components. The fact that acrylates and styrene can be easily recognised in paper headspace must be due to their low odor detection threshold values 10-100 ppb (Devos et al., 1990). Hexanal is always found in the emission from photocopied paper, and is a dominant component of the headspace of paper copied without text. The reaction of NO_x with chloroalkane or alkene might give 1,1-dichloro-1- nitroethane. Pyridine and N,N-phenylmethylaniline could be additive breakdown products.

TVOC from the various types of copied and printed paper are listed in Table 4. When black copies were examined here, their emission was found to be about 1.5 times that for normal copies. There is a tendency for photocopies to emit larger amounts of organic volatiles than other types of copies but, as shown, the variation for different machines was substantial.

A concentration vs time curve for styrene emitted from normal copied paper (machine E, toner E) placed in the field and laboratory emission cell is shown in Figure 7. The decrease of the styrene is slow in spite of a high air exchange rate of 60 h^{-1}, thus indicating that the emission could be controlled by internal diffusion. A first order decay model was fitted to the concentration versus time data using non-linear regression. The resulting estimates of the initial emission rate and the first order rate constant were 4.5 μg $m^{-2}h^{-1}$ and k_1 = 0.0232 h^{-1} (r^2 = 0.89) respectively, and an initial emission mass of 193 μg m^{-2}. In this model these values are underestimated (see Figure 7). Using a model based on internal diffusion controlled emission (Clausen et al., 1993), the initial emission rate was estimated to be 5.3 μg $m^{-2}h^{-1}$, resulting in a better fit (r^2 = 0.97). These values are minimum values because of the one-hour time delay between processing and start of the emission experiment.

Discussion

Reports of irritation caused by office copying machines (Skoner et al., 1990; Selner and Staudenmayer, 1985) did not include identification of the pollutants, although thermal desorption or decomposition of toner powders have been proposed as the probable mode of VOC formation (Hansen and Andersen, 1986; Sonnino et al., 1983). Previous testing of photocopying machines and laser printers has fo-

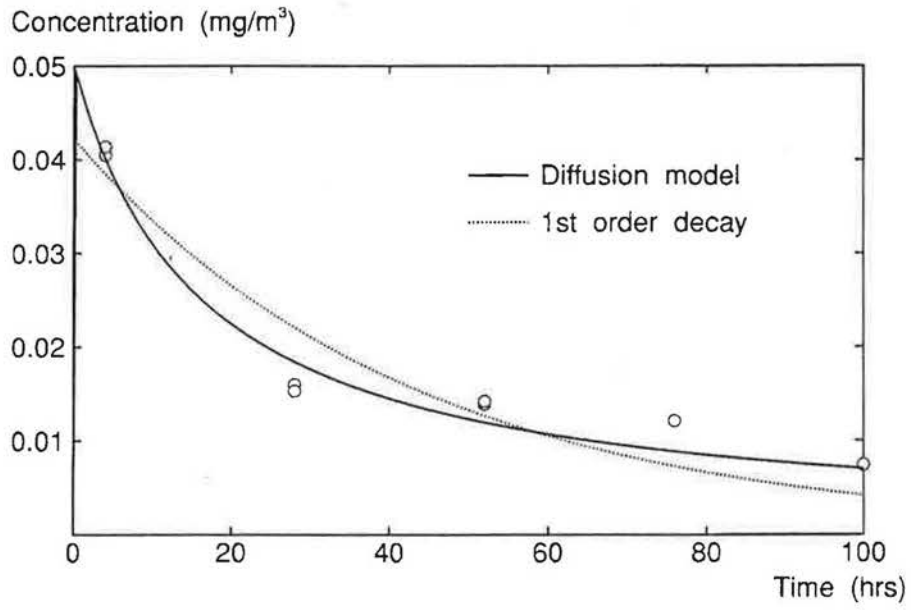

Fig. 7 Styrene concentration vs time in the FLEC emitted from processed paper from machine E.

cussed solely on the ozone emisssion (Allen et al., 1978; Selway et al., 1980; Hansen and Andersen, 1986). Ozone, a known respiratory irritant (Lippmann, 1989), is an important pollutant because of its low odor threshold (about 40 $\mu g/m^3$) (WHO, 1978). Awareness of ozone emission has resulted in the installation of filters and the development of special ventilation equipment for laser printers because they are often located near office workers.

This study showed that processed paper emits a number of different VOC which, because of their wide range of volatility and emission rates, persist for varying periods. These compounds include aromatic hydrocarbons, plastic monomer residues, and impurities as well as additivies and their decomposition products, in essential agreement with Brooks and Davis (1992). Several of the VOC have low odor thresholds (Devos et al., 1990), some are likely irritants, and some have been characterized as allergenic (acrylates) which could account for the deterioration of the local IAQ during and after photocopying. Although the absolute emission levels of photocopies, laser and matrix printer copies, and carbonless copy paper are low, large numbers of fresh copies can contribute substantially to office VOC concentration, thus reducing the indoor air quality, in particular in the microenvironment of paper handling. It is likely that VOC concentration gradients are present in copying rooms with (low) natural ventilation and in rooms in which copies are stored and used. The semi-VOC from copied paper may be very persistent and could be transported throughout buildings adsorbed to paper particles.

A realistic estimate (assuming first order decay) of handling 200 freshly processed copies in a 17 m^3 office room, 0.25 h^{-1} air exchange rate, and an emission of 6 $\mu g\ m^{-2}h^{-1}$ could reach a styrene concentration, assuming complete mixing, of 12 $\mu g\ m^{-3}$ from the processed paper. This should be considered as a minimum value because of the time delay of the emission testing. Styrene is a frequently encountered indoor VOC which is emitted from building materials and furnishings containing styrene polymers (Levin, 1989). It has been shown to be a major VOC in the headspace from carpets (Pleil and Whiton, 1990). Maximum TVOC emissions from office furniture after one hour have been reported to be in the order of 74 to 1060 $\mu g\ m^{-2}h^{-1}$ (Strobridge and Black, 1991).

The most direct approach to the reduction of indoor VOC concentrations is the limitation of the emission from materials and equipment (Tucker, 1991). Possible regulatory strategies include limitation of the VOC content in materials by legislation or the publication of comparative emission results or product ranking lists by labor unions or occupational health groups. Products could be compared using methods described herein or those used for building materials (Wolkoff, 1990) or water-based paints (Clausen et al., 1991). Since different machines and processes give a wide range of emission levels, an astute choice of copying machine and printer/process could help minimize office VOC and ozone exposure. The findings of this study support the recommendation that future tests of office copying machines include also evaluation of VOC from the machines *and* processed paper. The emission of particles should most likely also be evaluated, cf. Wolkoff et al. (1992). In addition, the findings indicate that the use of purer raw materials could aid the development of low-emission office copying systems.

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Appendix

Identification of 2,2'-azo-bis-isobutyronitrile and 3-ethoxy-3-ethyl-4,4-dimethylpentane from toner powders

Two major substances detected in desorbed toner volatiles required special attention. Molecular ions were not observed in thermal desorption GC/MS experiments. The EI/MS and FTIR spectra of compound 29 (Table 2), which appears to be 3-ethoxy-3-ethyl-4,4-dimethyl- pentane, are shown in Figures 8 and 9. The molecular ion (172 dalton), was barely detectable (< 0.1%) in the EI mode but was moderate (MH+ = 173 dalton) in the CI mode (isobutane). The sum formula was determined to be $C_{11}H_{24}O$. The dominant fragmentation is the loss of t-butyl and ethyl groups by α-cleavage although the loss of methyl can also be detected. The fingerprint region of the infrared spectrum is dominated by absorption at 1200 cm^{-1}, which is typical of a highly branched compound. This ether appears to be the product of nitrogen extrusion from 3-ethoxy-3-t-butylazopentane, which is presumably a polymerization initiator similar to 2-methoxy-2-t-butylazo-4-methylpentane (Kmiec et al., 1981; Brandrup and Immergut, 1989). The spectral information, however, is compatible with the latter. Compound 41 (Table 2) was identified as 2,2'-azo-bis-isobutyronitrile. Of interest is the lack of CN stretch in the vapor phase IR spectrum of this symmetrical mole-

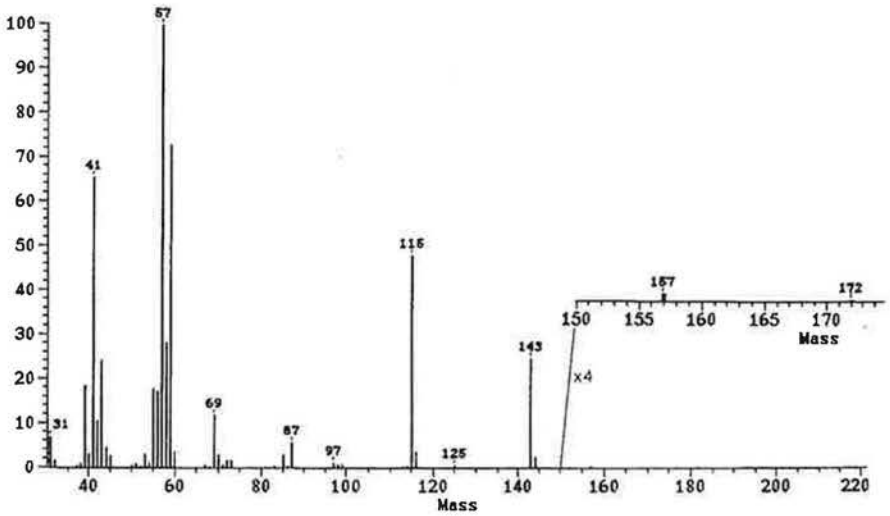

Fig. 8 Gas chromatography/electron impact mass spectrum of compound 29 (Table 2).

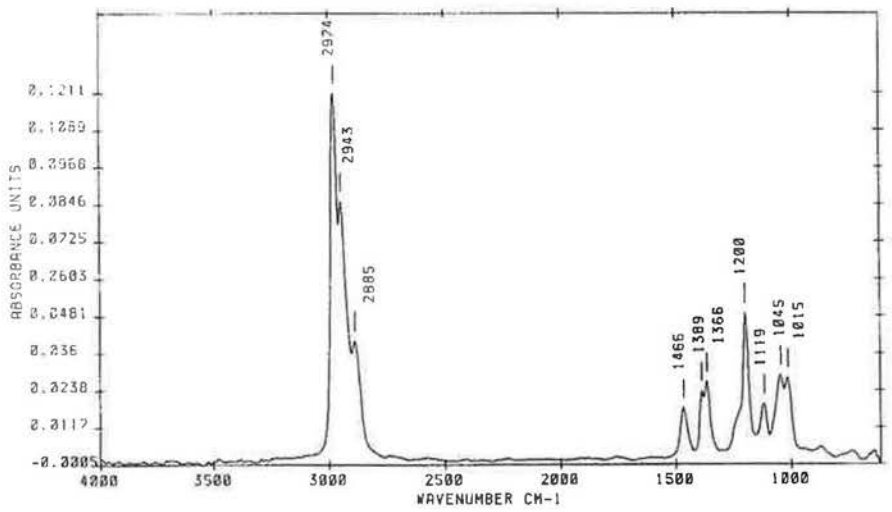

Fig. 9 Gas chromatography/gas phase infrared spectrum of compound 29 (Table 2).

cule (see below). Both of the azo compounds appear to be impurities in the polymers.

GC/FTIR results for Compound 41 (Table 2) are: (s = strong, m = medium, no indication = weak) – 3001 (s), 2954 (m), 1470 (m), 1389 (m), 1185, 1150 (m) cm^{-1}.