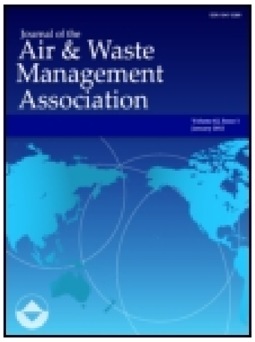

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Determination of VOC Emission Rates and Compositions for Offset Printing

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ABSTRACT

The release rates of volatile organic compounds (VOC) as fugitive emissions from offset printing are difficult to quantify, and the compositions are usually not known. Tests were conducted at three offset printing shops that varied in size and by process. In each case, the building shell served as the test "enclosure," and air flow and concentration measurements were made at each air entry and exit point. Emission rates and VOC composition were determined during production for (1) a small shop containing three sheetfed presses and two spirit duplicators (36,700 sheets, 47,240 envelopes and letterheads), (2) a medium-size industrial in-house shop with two webfed and three sheetfed presses, and one spirit duplicator (315,130 total sheets), and (3) one print room of a large commercial concern containing three webfed, heatset operations (1.16 x 10^6 ft) served by catalytic air pollution control devices. Each test consisted of 12 one-hour periods over two days. Air samples were collected simultaneously during each period at 7–14 specified locations within each space. The samples were analyzed by gas chromatography (GC) for total VOC and for 13–19 individual organics. Samples of solvents used at each shop were also analyzed by GC. Average VOC emission rates were 4.7–6.1 kg/day for the small sheetfed printing shop, 0.4–0.9 kg/day for the industrial shop, and 79–82 kg/day for the commercial print room. Emission compositions were similar and included benzene, toluene, xylenes, ethylbenzene, and hexane. Comparison of the emission rates with mass balance estimates based on solvent usage and composition were quite consistent. The average compositions of emissions from these tests were much more detailed than has been previously available, but they agreed well with previous chemical fingerprint values for toluene and o-xylene, which have been successfully applied to source-receptor modeling for graphic arts.

IMPLICATIONS

Offset printing is characterized by significant uncontrolled, and frequently unquantified, fugitive emissions of volatile organic compounds (VOC). This study demonstrates a methodology, applied to three plants of different capacities and processes, by which fugitive emissions can be quantified in printing and other surface coating operations without recourse to a Temporary Total Enclosure (TTE). The average compositions of emissions from each plant, despite process and solvent differences, were similar. These concentration data are much more detailed than have been available up until this time, but they agreed well with previous chemical fingerprint values for toluene and o-xylene, which have been successfully applied to source-receptor modeling for graphic arts.

INTRODUCTION

Offset printing has the potential to release volatile organic compounds (VOC) as fugitive emissions. In addition, under the Clean Air Act Amendments of 1990, many individual components of VOC have been identified as hazardous air pollutants (HAPs) and thus require control. Because printing operations are often not served by local exhaust ventilation control systems, the release rates are difficult to quantify and the compositions are usually not known.[1-4]

Offset printing consists of an inking system which produces and delivers a thin, uniform ink film to a printing plate. An aqueous fountain solution, which contains small amounts of phosphoric acid and *i*-propyl alcohol or glycol ethers, wets nonprinting areas of the plate. The printing plate, positioned on a cylinder, delivers only the inked images to an elastomeric, rubber-covered, multitiered lithographic blanket on the blanket cylinder. The blanket, in turn, passes images onto substrate (paper or paperboard), while the impression cylinder controls the force imposed on the substrate to insure proper transfer of inked images. Blankets and ink rollers must be cleaned before, during, and after jobs, usually with volatile solvents. Webfed presses print on a continuous sheet that is fed from an unwinding paper roll. Sheetfed printing is a slower process in which individual sheets from a stack are run through a press. Sheetfed printing and some webfed presses use nonheatset inks which are formulated to set within minutes of application and generally contain drying oil (linseed or soy), resins and pigments, and petroleum distillates. The ink is nearly dry as the sheet or web leaves the press.[1] Other webfed processes use heatset inks, typically containing about 40% by weight VOC. Most of this VOC (80–90%) is evaporated in a dryer after the ink has been applied to the web. Ordinarily, a control device, such as a catalytic incinerator, will be used to destroy the evaporated VOC.

This paper summarizes the results from tests conducted at three offset printing shops that varied in size and by process. In each case, the building shell served as the test "enclosure," and air flow and concentration measurements were made at each air entry and exit point. Emission rates and VOC composition were determined during production for (1) a small shop containing four sheetfed presses and three spirit duplicators, (2) a medium-size industrial in-house shop with two webfed and three sheetfed presses and two spirit duplicators, and (3) one print room of a large commercial concern containing three webfed, heatset operations served by catalytic air pollution control devices.

METHODS

Each test consisted of 12 one-hour periods over two days. Air samples were collected simultaneously on charcoal tubes at calibrated flow rates of 300 ml/min during each period at 7–14 specified locations within each space. Each sample flow rate was checked at the beginning of the hour, on the half-hour, and at the end of the hour. The tubes were extracted with carbon disulfide and were analyzed by gas chromatography (GC) for VOC and for speciation of 13–19 organic compounds. The same sampling and extraction methodology was used for hexane equivalent VOC and the 19 speciated organics. A 30 m x 0.53 mm Supelcowax 10 column was used in a Hewlett-Packard 5890 gas chromatograph with flame ionization detection (FID), basically following the procedures of NIOSH Method 1501.[5] VOC was defined as the total area under the chromatogram trace, interpreted with the hexane response factor, after the CS_2 peak. We used the designation VOC (volatile organic compounds) in the generic sense rather than the regulatory sense. The regulatory interpretation of VOC excludes certain specific halogenated compounds. Some of these, if present, may contribute to the total area under the GC response curve. However, these compounds were not likely to have constituted major contributions to our measurement of VOC. Samples of solvents used at each shop were also analyzed by GC.

Each sample consisted of two tubes in series. Each tube was extracted and analyzed separately. However, breakthrough never occurred for either VOC or for the identified compounds because the mass collected in the backup tubes was always less than the detection limit (<0.25 μg C/m^3). Duplicate samples were collected for about 20% of the test samples. These were sent to a commercial laboratory for VOC analysis. (We did not have the resources to compare the speciated compounds.) The procedures were generally similar between the two laboratories. However, the evaluations differed somewhat because of the limitations imposed on the in-house analyses by the Supelcowax 10 column, which was the only one available. (The commercial laboratory used a different column and slightly different temperature profiles). Figure 1 shows a comparison of the VOC analyses for the paired samples. Overall, the agreement was quite good, with r^2 = 0.99 and the slope of the comparison equal to 0.88 (perhaps suggesting a small consistent offset because of the difference in methods).

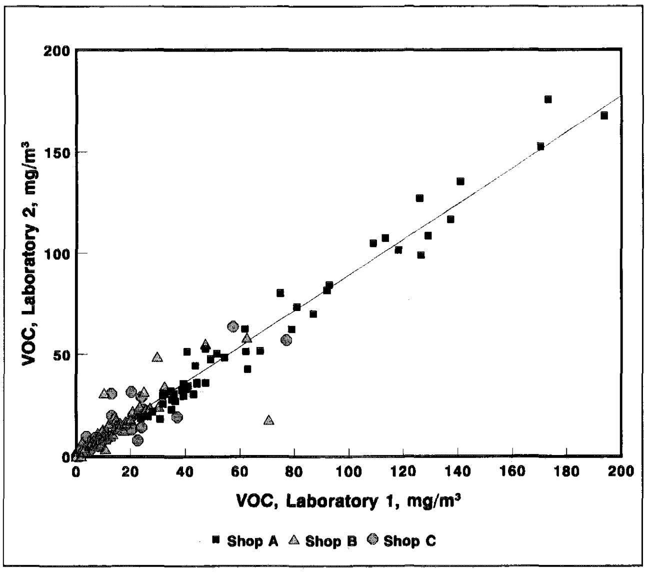

Figure 1. Hexane equivalent VOC analysis quality control comparison for two laboratories. (N = 150; $r^2 = 0.96$; [Laboratory 2 VOC] = 0.88 [Laboratory 1 VOC] + 0.81.)

Air flow was measured at each entry and exit point from each of the spaces. Air supply from diffusers was measured using an Alnor Balometer. Air return and make-up air flow rates were measured using a thermoanemometer. Cross drafts and air flow in and out of doors were determined with smoke tubes and a thermoanemometer. Air flow surveys were performed at least once each day of a test, and usually twice. (All air flows are reported at standard conditions of 25 °C and 1 atm). The mixing characteristics of the spaces were determined by SF_6 tracer concentration decay tests[6] or by decay of a residual material, such as CO from lift truck exhaust after the source had been turned off.

Plan views of the three print shops are shown in Figures 2 through 4. The sampling locations are also shown. Plant A is a small shop containing four sheetfed presses and three spirit duplicators. Three of the presses and two of the spirit duplicators in the press room were operated during the test, printing 36,700 sheets and 47,240 envelopes and letterheads. A six-color press was also operated in an adjacent room, and we measured these emissions as well. Dilution ventilation was used for control because no local exhaust ventilation control existed for either press room. The ventilation system shown in Figure 2 served all the spaces shown except the six-color press room, which was served by a separate system. Make-up outdoor air enters each system, is mixed with the air return flow, and is returned to each space through the air

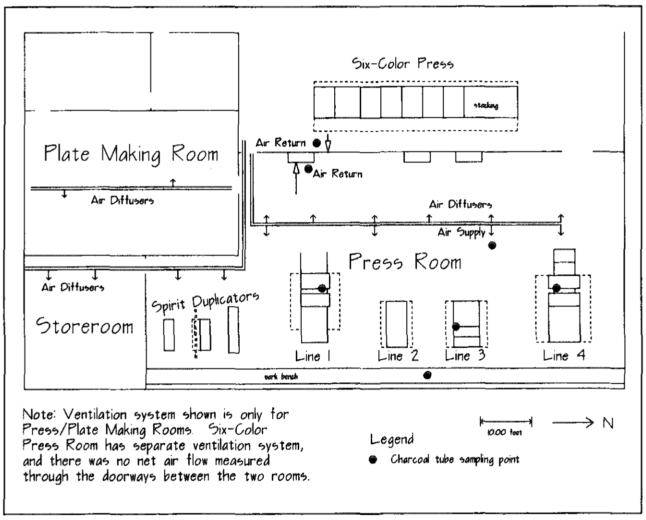

Figure 2. Plan view of Plant A (sheetfed presses). Dotted lines are raised walkways.

supply diffusers. The make-up air rate was 8391 m^3/hr for the print/plate making area and 7064 m^3/hr for the six-color press room. The air change rate based on make-up air entering the print/plate making area was 5.1 hr^{-1}.

Plant B (Figure 3) is a medium-size industrial in-house shop with two webfed presses, three sheetfed presses, and two spirit duplicators (one operating) (315,130 total sheets during test; 181,108 web sheets, 95,504 sheetfed, and 38,581 duplicator sheets). There was no local exhaust control. Air entered through diffusers and exhausted to a space above the false ceiling through the air return ducts. Most of the air entering from the diffusers appeared to have been recycled from this space. Net flow from the press room was down a stairwell to a factory area. Make-up air infiltrated from outdoors at a rate of 7211 m^3/hr. The air change rate based on make-up air was 0.93 hr^{-1}.

Plant C (Figure 4) is one print room of a large commercial concern containing three webfed, heatset operations (1,115,200 ft of 38-in. web during the test, or 554,496 sheets). Each web line is served by a catalytic air pollution control device. Three-shift operation is typical. The Line 1, 2, and 3 Exhausts shown in Figure 3 collect VOC vapors released from the ink dryers. These vapors are then passed to the control devices. The print room was also served by its own air intake system on the roof, which is well removed from two large roof exhaust ports. There were also several entry and exit points at doors from other parts of the plant but no recycle flow. The ventilation rate was 182,000 m^3/hr, and the air change rate was 10.9 hr^{-1}.

Emission rates were determined based on the measured concentrations C (mass/volume) and flow rates Q (volume/time) at entry and exit points.[7] The emission rate S (mass/time) is then

$$S_{mass\ balance} = \sum_{1}^{total\ exit\ points} Q_{exit} \cdot C_{exit} - \sum_{1}^{total\ entry\ points} Q_{entry} \cdot C_{entry} \qquad (1)$$

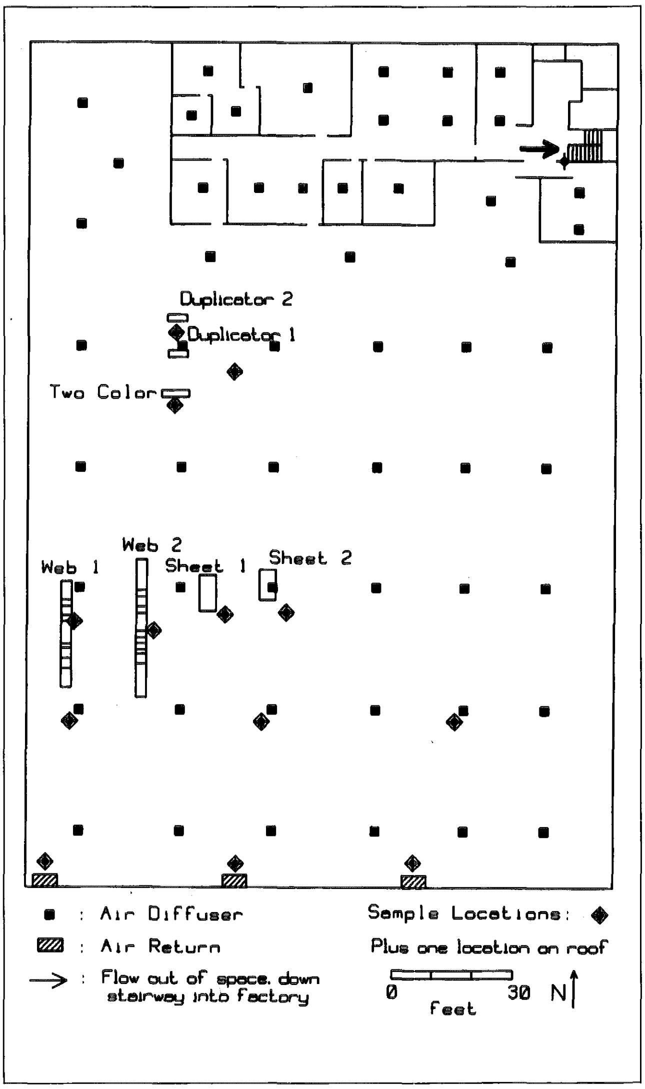

Figure 3. Plant B plan view (webfed and sheetfed presses).

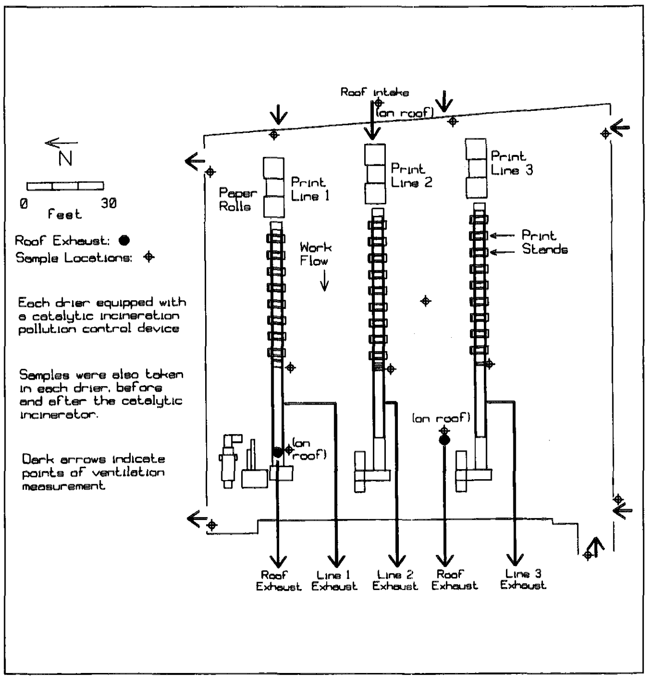

Figure 4. Plan view of Plant C (heatset webfed presses).

Table 1. Plant C average concentrations and ventilation flow rates for each sampling location.

	Flow In						*Flow Out*							
Location	SE door	S screen	N screen	Receiving door	SW door	Spot cooler intake	N ceiling exhaust	S ceiling exhaust	NE door	NW door	Line 1 dryer inlet	Line 2 dryer inlet	Line 3 dryer inlet	Leakage into dryers
Flowrate (m³/min)[a]	604.8	467.3	392.0	626.4	361.3	285.3	846.6	845.8	389.5	284.9	133.0	113.3	112.9	300.0
Component	*Concentration, mg/m³*													
n-Hexane	0.70	0.02	.005	.003	0.16	< dl	0.18	0.23	0.12	0.10	0.18	0.18	0.15	0.17
Isopropanol	0.77	0.13	0.09	< dl	0.19	< dl	2.52	0.89	1.00	0.22	4.94	0.72	0.46	2.20
Benzene	1.02	0.14	0.10	0.03	0.32	< dl	2.03	1.65	1.02	0.55	2.82	1.43	0.70	1.72
Toluene	2.90	0.11	0.04	0.06	0.67	0.02	2.16	2.42	0.91	0.56	3.71	2.33	1.01	2.43
Ethylbenzene	0.46	0.01	< dl	< dl	0.10	< dl	0.32	0.19	0.10	0.02	0.78	0.15	0.03	0.34
p-Xylene	0.23	0.01	< dl	< dl	0.03	< dl	0.09	0.05	0.05	0.01	0.39	0.06	0.01	0.17
m-Xylene	0.47	0.02	.002	0.01	0.10	< dl	0.13	0.09	0.07	0.02	0.12	0.10	0.04	0.09
Isopropylbenzene	0.50	0.02	.005	0.01	0.14	< dl	0.21	0.16	0.09	0.02	0.28	0.16	0.10	0.19
o-Xylene	0.67	0.04	0.01	0.01	0.17	< dl	0.52	0.37	0.25	0.07	0.97	0.39	0.26	0.56
n-Propylbenzene	1.12	0.07	0.02	0.02	0.32	< dl	0.42	0.32	0.22	0.07	0.56	0.34	0.23	0.39
m&p-Ethyltoluene	4.99	0.33	0.09	0.12	1.49	< dl	1.95	1.50	1.09	0.43	2.64	1.67	1.15	1.87
Isobutylbenzene	< dl[b]	< dl	< dl	< dl	< dl	< dl	0.11	0.06	0.07	< dl	0.22	0.08	0.083	0.13
1,3,5-Trimethylbenzene	1.89	0.11	0.02	0.04	0.55	< dl	0.62	0.50	0.35	0.12	0.79	0.52	0.38	0.58
o-Ethyltoluene	1.46	0.08	0.02	0.03	0.39	< dl	0.56	0.44	0.35	0.12	0.79	0.49	0.40	0.57
1,2,4-Trimethylbenzene	2.89	0.15	0.09	0.09	0.88	.002	1.73	0.96	0.79	0.31	3.56	1.31	0.96	2.03
m-Diethylbenzene	0.28	0.07	0.01	< dl	0.07	< dl	0.23	0.16	0.07	0.02	0.57	0.18	0.10	0.30
p-Diethylbenzene	0.18	0.01	0.00	< dl	0.02	< dl	0.20	0.06	0.07	< dl	0.36	0.17	0.10	0.22
o-Diethylbenzene	0.13	.001	.002	< dl	0.01	< dl	0.17	0.04	0.02	0.02	1.48	0.05	0.01	0.57
1,2,3-Trimethylbenzene	0.41	0.02	.022	0.02	0.14	< dl	0.82	0.57	0.53	0.11	1.03	0.72	0.41	0.74
Identified compounds, % hexane equivalent VOC	65.6	18.0	12.7	33.3	58.7	7.6	40.4	38.4	46.6	29.4	44.5	42.7	48.9	44.6
Total VOC	32.14	7.47	4.14	1.33	9.79	0.29	37.02	27.76	15.40	9.41	58.91	25.90	13.46	34.21

[a] All flow rates were measured entering or exiting the space except for leakage into the dryers, which was based on measured flow and energy balances around the dryer on Line 1.

[b] less than detection limit = 0.25μg c/m³.

RESULTS

As an example of the emission rate calculation, Table 1 shows the volumetric flow rates and average compositions over the 12 hours of the test for each entry and exit point at Plant C. The air balance was good, with total measured flow rates in and out being within 0.5%. In addition to the stream compositions and flow rates summarized in Table 1, we also made temperature and flow measurements around the dryer for Line 1. These indicated that additional room air leaked into the dryer. For Line 1, this amounted to 3924 cfm. We estimated similar leakage volumes for Line 2 (3343 cfm) and Line 3 (3332 cfm). The composition given for leakage into the dryers in Table 1 is a composite of the dryer inlet compositions for Lines 1 through 3 weighted by the respective leakage volumes. Table 2 shows the mass balance for VOC. The net release into the room was 57 g/min, and the amount released to the atmosphere was 55 g/min.

Emission rates were similarly calculated for each hour of measurement for each plant. A range of emission rates is reported for Plants A and B because there were several ways to characterize the concentration of air leakage from the spaces. We were able to identify obvious exit and entrance points such as doors, windows, and forced-air ventilation

Table 2. Summary of mass flow rates for Plant C.

Location	*VOC flow rate, mg/min*
FLOW IN	
SE door	19,452
S screen	3,495
N screen	1,626
Receiving door	835
SW door	3,539
Spot cooler intake	82
Air leakage from outdoors[a]	87
TOTAL VOC FLOW IN	29,116
FLOW OUT	
N ceiling exhaust	31,361
S ceiling exhaust	23,497
NE door	5,998
NW door	2,683
Press Line 1 dryer inlet	7,834
Press Line 2 dryer inlet	2,934
Press Line 3 dryer inlet	1,520
Room air leakage into dryers	10,261
TOTAL VOC FLOW OUT	86,088
VOC EMISSION RATE INTO ROOM	56,972
VOC EMISSION RATE TO ATMOSPHERE *(ceiling exhaust fans)*	*54,858*

[a] 10,599 cfm; same composition as spot cooler intake.

Table 3. Composition of emissions.

	Average Weight % of VOC [1]						
	Plant A			Plant B		Plant C	
	Press/plate making rooms						
	Air return	Avg. of six sites[2]	Six-color press air return	Avg. of all rooms	Stairwell air	Roof fans	Room composition
	(N = 12)	(N = 72)	(N = 12)	(N = 68)	(N = 12)	(N = 24)	(N = 48)
n-Hexane	3.18	2.63	0.22	1.02	0.89	1.12	1.28
i-Propyl alcohol				12.78	11.11	4.67	4.43
Benzene				2.60	1.46	5.70	5.19
Toluene	31.56	29.57	31.18	3.55	3.76	7.80	7.90
Ethylbenzene	0.38	0.45	0.46	0.96	0.81	0.63	0.60
p-Xylene	0.26	0.27	0.24	0.56	0.47	0.18	0.24
m-Xylene	0.61	0.61	0.44	1.42	1.31	0.30	0.42
i-Propylbenzene				1.02	0.92	0.50	0.52
o-Xylene	0.87	0.93	0.76	1.37	1.31	1.39	1.53
n-Propylbenzene	2.30	2.43	2.51	2.29	1.95	1.03	1.07
m&p-Ethyltoluene	9.74	10.26	10.69	10.31	8.86	4.85	5.63
i-Butylbenzene				0.52	<.001	0.32	0.29
1,3,5-Trimethylbenzene	3.39	3.60	3.72	3.10	2.94	1.55	1.63
o-Ethyltoluene	2.25	2.40	2.52	2.36	1.93	1.50	2.11
1,2,4-Trimethylbenzene	4.70	5.01	5.22			3.97	4.30
m-Diethylbenzene	0.53	0.58	0.52	0.71	0.56	0.58	0.65
p-Diethylbenzene				0.24	0.12	0.46	0.53
o-Diethylbenzene				0.44	0.46	0.28	0.56
1,2,3-Trimethylbenzene	0.46	0.51	0.55	1.16	1.03	2.45	2.39

[1] If a value is not shown it means that either we could not determine a concentration because of interfering peaks, or the GC was not calibrated for a particular component.

[2] Average of compositions measured at all six sites in press room (Figure 2).

ducts, and we made flow and concentration measurements at these locations. However, room air also was likely to leak from the space through cracks and other small openings in walls and ductwork. These openings were not easy to identify. Consequently, although we had a good estimate of the total air leaving the space (equal to the measured make-up air), we were less sure of the exact composition. This was less of a problem for Plant C because the space was served by a once-through ventilation system with no recycle. Average VOC emission rates for Plant A from the press/plate making rooms ranged from 0.467 kg/hr (based only on the return air composition) to 0.608 kg/hr (based on the average concentration from all six sample sites in the space), and 0.462 kg/hr from the six-color press (based on the air return). The VOC emissions from Plant B, the industrial shop, ranged from 0.052 kg/hr (based only on the stairwell concentration) to 0.107 kg/hr based on the average of all concentration measurements in the space. The workspace release for Plant C, the commercial print room, was 3.42 kg/hr, with 3.29 kg/hr released to the atmosphere.

Emission compositions from each plant were similar and included benzene, toluene, xylenes, ethylbenzene, and hexane. Table 3 compares compositions for several streams from each plant in terms of weight percent. For the Plant A analyses, it was not possible to separate *i*-propyl-alcohol and benzene with the particular chromatography column used for analysis, although analyses of the solvents by a commercial laboratory with a GC/MS system and a different column indicated that both were present.[8]

DISCUSSION

In general, except for toluene, the emission compositions shown in Table 3 are quite similar despite the differences among plants in printing processes, production rate, and control. Toluene concentrations among the plants varied by a factor of about 10. The 31% toluene composition for Plant A is reflected in both the press room samples and in those from the six-color press. In addition, significant toluene concentrations were found in the solvents from this plant. At this stage, although admittedly we only have three tests on which to base judgment, we believe that the range of toluene compositions shown for the three plants is representative.

If it is assumed that all solvents used in the process are completely evaporated to workroom air, it is also possible to estimate an emission rate from measurements of solvent usage and analyses of the composition of each solvent. (It is perhaps of interest to note that the Material Data Sheets on

Table 4. Solvent compositions and usage for Plants B and C.

	Plant B Solvent Composition					*Plant C Solvent composition*						
	Weight % of hexane equivalent VOC[a]											
	V-120	Pronto	Rycoline	Stay-open	i-Propyl Alcohol	Profit Plus Kleer Gum	Dupont Kleer Gum	Flash Oil Spray	Automatic Blanket Wash	Blanket Rejuve-nator	Manual Blanket Wash	Type Wash
n-Hexane						3.1	7.6	38.4	6.2	7.8	7.1	
Isopropanol	94.0		21.2		100		1.2					62.0
Benzene				1.4		2.8	4.2		4.2		3.1	5.9
Toluene			0.2			12.7	8.2		2.8		5.5	
Ethylbenzene			15.4			0.7						0.1
p-Xylene			10.1	0.1			3.1		0.7		1.5	
m-Xylene			23.0			3.1			0.3		0.7	
Isopropylbenzene		0.04				2.2	0.4				0.1	
o-Xylene		0.04	4.1				1.1		1.2		1.9	
n-Propylbenzene		0.01				3.8					0.6	
m&p-Ethyltoluene		0.6				1.8	0.3		1.7	76.6	2.3	
Isobutylbenzene		0.02					0.3					
1,3,5-Trimethylbenzene						0.3	0.8		9.0		12.3	
o-Ethyltoluene		0.10				0.6	1.1		3.5		4.8	
1,2,4-Trimethylbenzene		0.5					0.5		2.3		3.2	0.2
m-Diethylbenzene		0.03				0.1	0.9		0.2		0.3	
p-Diethylbenzene						0.1	2.2		5.1		7.0	0.3
o-Diethylbenzene		0.01				0.1	0.4		0.6		0.6	0.3
1,2,3-Trimethylbenzene		0.06				0.6	0.4		1.2		1.2	0.4
Total VOC, g/ml	0.835	0.725	0.545	0.409	0.785	1.434	0.590	0.171	1.042	0.773	0.785	0.820
						Line 1, lbs/12 hrs			75		15	1
gallons/month	11.25	0.42	0.73	0.01	6.67	Line 2, lbs/12 hrs			0		19	0
						Line 3, lbs/12 hrs			10		14	0

[a] detection limit for all organics corresponds to < 0.0001 g C/ml

these solvents did not specify the hydrocarbon composition). Solvent compositions for Plants B and C are shown in Table 4. The composition of Plant A solvents has been reported elsewhere.[8]

One difficulty in implementing such a comparison is determining an appropriate value for solvent usage. Even if inventory values exist, these are usually for longer periods of time (a month or year) than two specific days. For Plants A and B, it was not possible to quantitatively measure actual solvent usage during the tests because of the way that the printers mixed and applied cleaning solvents and because of the relatively small amounts. Consequently, we had to determine alternative ways to estimate solvent use.

At Plant A in the press room, each line was usually operated by the same person; therefore, we asked the individual printers to estimate weekly solvent usage. We then applied the solvent compositions to the estimates of each solvent to determine VOC and component usage rates.[8] We used typical work periods of 10 hrs/day (which we observed) and 5 days/week to put the usage data on the same basis as the emission rates determined using Equation 1. For Plant B, only 12-month usage from the solvent storage cabinet was available (Table 4). The daily inventory value was estimated using 12 months and 22 working days/month. Our overall emission rate from the test data was based on an 8-hour day, which was what we observed.

Solvent application rates were much greater for Plant C than for the other two plants (Table 4). Consequently, we developed an estimate of usage from actual observation during the test period. Considerable imprecision remains because we were trying to measure a usage rate of about 5 kg/hr (11 lbs/hr) on three large press lines. In addition, a complicating factor was that some of the workroom emissions from solvent cleaning could be trapped in the dryers on the three lines and subsequently destroyed in the catalytic incinerators. Consequently, although the atmospheric emission rates shown in Tables 1 and 2 for Plant C are accurate, they are not exactly comparable to the inventory values because of the effect of the control devices. If we assume that 100% of the ink solvents that vaporize are driven off and destroyed in the dryer/catalytic converter, the data suggest that, at a minimum, 60% by weight of the solvents applied to the presses escaped to the workspace.

Table 5. Comparison of emission rate with estimated solvent usage.

	VOC		*BTEX*[1]	
	Mass balance[2]	*Inventory*	*Mass balance*[2]	*Inventory*
Plant A (print room), kg/day	4.7-6.1[3]	7.4[4]	1.4-2.0[3]	1.5[4]
Plant B, kg/day	0.4-0.9[5]	2.6[6]	0.04-0.08[5]	0.04[6]
Plant C, kg/12 hours	39.5-41.0[7]	62.2[8]	6.1-6.5[7]	6.4[8]

[1] BTEX = sum of benzene, toluene, ethylbenzene, and the xylenes.

[2] Emissions based on 12-hr average air exhaust concentrations and air flow rates from each exit point to the atmosphere.

[3] Based on 10-hr/day operation.

[4] Emissions based on operator estimates of weekly usage and measured solvent composition for each line adjusted on the basis of 5 working days/week.

[5] Based on 8-hr/day operation.

[6] Inventory based on 12-month usage of solvents from solvent storage cabinet and measured solvent compositions adjusted on the basis of 22 working days/month.

[7] Mass balance measurements do not include cleaning solvents drawn into the dryers with the web which are subsequently destroyed by catalytic oxidation.

[8] Inventory based on estimated and measured usage during 12 hours of testing and measured solvent compositions.

Table 6. VOC balance around heatset dryer on Line 1, Plant C.

	Six-hour average concentrations, mg/m^3		*VOC vaporized in dryer*[3]	*Ink VOC vaporized*[b]
	Inlet air	*Exit air*	*kg*	*kg*
Day 1	73.13	871.10	67.3	79.9
Day 2	44.69	617.53	48.3	43.8
12-Hour Totals			115.6	123.7
	Vaporized VOC/Ink VOC		0.93	

[a] Air flow rate = 234.25 m3/min.

[b] Based on laboratory measurements, it was assumed that 14% of the ink VOC was retained in the ink after it had heatset on the paper. VOC fractions by ink color were: black - 0.402; blue - 0.413; red - 0.409; yellow - 0.456. Usages (in lbs/6 hours): Day 1 - black, 82; blue, 131, red, 151; yellow, 123; Day 2 - black, 41; blue, 77; red, 76; yellow, 72.

Mass balance and inventory comparisons of VOC and BTEX (the sum of benzene, toluene, ethylbenzene, and xylenes) emissions for each plant are shown in Table 5. Most of the comparisons are reasonable considering the uncertainty in approximating the usage value. We suspect that the difference for Plant B BTEX arises from the inventory estimate and possibly a lack of precision in determination of toluene in the solvent compositions from this plant. (During the test on Plant B, we observed other solvent materials being used, in addition to those recorded in the solvent storage cabinet. Subsequent visits to the plant have indicated that these materials are now accounted for, possibly in response to the Clean Air Act Amendments of 1990, but they were not systematically inventoried at the time of the test.)

For Plant C, we also had specific flow and composition measurements around the dryer for Line 1, as well as daily measurements of ink usage. These data provided us with an independent check of our analytical methods for VOC. Table 6 shows the comparison between VOC based on the entry and exit concentrations, and the estimated VOC release from ink usage. We assumed that 14% of the ink VOC remains on the paper (based on a previous study by the company) and that the VOC fractions of the applied ink were typically 40–45% (also based on previous analyses by the company). The agreement was very good, as over the 12 hours of the test, the composition measurements were able to explain 93% of the vaporized ink VOC.

Emissions from the dryers are sent to the catalytic oxidation units. These devices were quite effective; the average destruction efficiency was above 99% for each unit. However, the average exit concentrations (Line 1, 6.66 mg/m^3; Line 2, 2.78 mg/m^3; and Line 3, 2.45 mg/m^3) were well above the ambient VOC level (0.10 mg/m^3), and the control devices did not regulate VOC escaping through the roof fans.

Another method of determining emission rate consistency was to compare the hourly emission rates with source activities during the same periods. Source activities were recorded at approximately five-minute intervals simultaneously with air sampling. The activity observations included number of sheets printed, number of setup and cleaning periods, number and duration of idle periods, job number, and number and duration of ink addition intervals. A typical relationship is shown for Plant A in Figure 5. VOC emission rates calculated from Equation 1 using measured flow rates, and the average concentration from the six measurement sites for leakage air, are plotted versus frequency of solvent cleaning. The emission rate and cleaning frequency are associated ($r^2 = 0.57$). Other comparisons with different data supported this relationship.[8] In addition, the slope of the least squares fit line (shown in the figure) provides an estimate of an emission factor, 70 g VOC released/press cleaning.

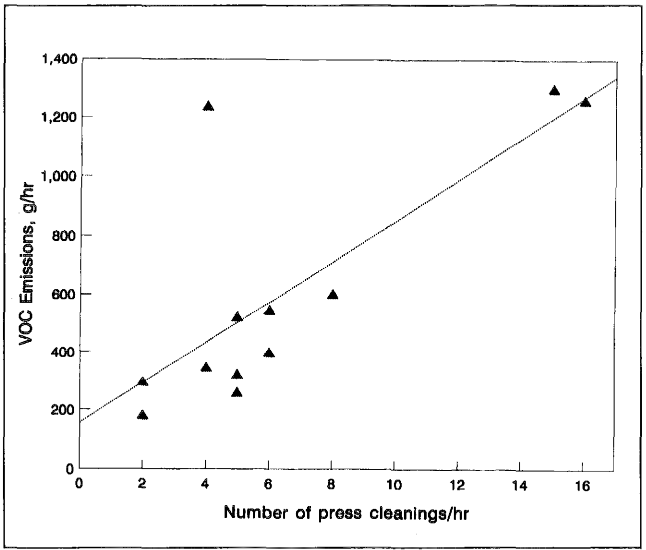

Figure 5. Plant A (sheetfed offset printing): Emission rate based on Equation 1 vs. solvent cleaning frequency. Line is least squares fit of data and slope represents an emission factor of 69.7 g VOC/press cleaning.

With reference to Figure 5, the high emission point at four press cleanings/hour occurred while another activity besides press cleaning was taking place. Small bottles were being filled with solvent from gallon jugs. Using the association between emissions and cleaning of Figure 5, we estimated that this transfer activity caused an additional emission of about 800 g/hr of VOC. Such comparisons of emission rates with source activities also give us confidence in the quality of our concentration measurements; i.e., the measurements reflect what is actually occurring in the workplace.

The relationship between emissions and press cleaning is also interesting because another study of an offset printing shop reported an association between plate changes and personal exposure of printers to VOC.[2] In addition, a recent study in a printing/bookbinding shop, which compared personal and area samples and solvent composition, identified blanket wash as a part of the printers' exposure,[9] although no attempt was made to identify specific activities. Solvent cleaning always occurs during plate changing, although as noted earlier, other periods of intensive press cleaning will also occur. The exposure relationship determined in Reference 2 includes considerable variability, which might have been caused by exposures during cleaning intervals other than plate changing.

Comparison of the emission rates with mass balance estimates based on solvent usage and composition was reasonably consistent, particularly given the variability of the inventory values. The average composition of emissions from these tests was much more detailed than has been available up until this time but agreed well with previous chemical fingerprint values for toluene and o-xylene, which have been successfully applied to source-receptor modeling for graphic arts.[10-13] For example, the graphic arts (printing) contribution to the concentration of organics in Chicago air in 1988 was determined from receptor modeling to be 6.6% of total VOC. This was in reasonable agreement with the emission inventory estimate of 9.8% of total VOC.[12]

We recognize that tests were only conducted for two days at each plant. However, these measurements were made during typical printing activity for each shop. Although the results may not precisely mirror all-year emissions, it is interesting to estimate annual VOC release on the basis of the data that we have. If we use the total emission rate from Plant A (print/plate making room and six-color press) of 929-1170 g VOC/hr, 10 hours/workday (observed during the test), and 250 days/year, the annual emissions become

$$\frac{kg_{voc}}{year} = 1.0\,\frac{kg_{voc}}{hr} \times \frac{10\ hr}{day} \times \frac{250\ days}{year} = 2500\,\frac{kg}{year}\left\{2.8\,\frac{T_{voc}}{year}\right\} \quad (2)$$

Similarly, the annual emissions rate (based on the 8 hour/day observed) would be about 200 kg/yr (0.2 T) for Plant B and about 19,700 kg/yr (21.7 T) for Plant C based on 250 days and three-shift operation. The emissions from Plant A are large considering the volume of printing being done. It is useful to recognize that most printing installations are this size. About half of all printing in the United States is done on offset presses. Eighty-five percent of offset shops employ fewer than 20 persons.[14] Both Plants A and B fall into this category. Our experience indicates that small plants are much less likely to have local exhaust capability, which exacerbates workplace exposures to benzene and other toxic materials. (As a qualitative example of such a condition, frequent complaints about poor ventilation in Plant B were made by people using the offices near the stairwell [Figure 3]). In addition, the emissions of 2 T/year or more of VOC from each such shop constitute a significant contribution to ozone precursors and also to HAPs such as toluene and xylene. In the case of Plant C, the catalytic incinerators destroy some of the cleaning solvents that are evaporated into the room, but a significant amount evidently is released into the atmosphere.

CONCLUSIONS

The application of this method may have general implications for the printing industry and for other surface coating operations. Presently these types of processes, characterized by significant uncontrolled and frequently unquantified fugitive emissions, must be surrounded by a Temporary Total Enclosure (TTE) for the purpose of determining VOC emissions.[15,16] We were able to determine the emission rate without recourse to a TTE, and without interfering with worker activities, increasing worker exposure to air pollutants and noise, or increasing safety and explosion hazards.[17,18]

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