Applied Occupational and Environmental Hygiene

ISSN: 1047-322X (Print) 1521-0898 (Online) Journal homepage: https://www.tandfonline.com/loi/uaoh20

Determination of Multiple Source Volatile Organic Compound Emission Factors in Offset Printing Shops

C. B. Keil , R. A. Wadden , P. A. Scheff , J. E. Franke & L. M. Conroy

To cite this article: C. B. Keil , R. A. Wadden , P. A. Scheff , J. E. Franke & L. M. Conroy (1997) Determination of Multiple Source Volatile Organic Compound Emission Factors in Offset Printing Shops, Applied Occupational and Environmental Hygiene, 12:2, 111-121, DOI: 10.1080/1047322X.1997.10389470

To link to this article: https://doi.org/10.1080/1047322X.1997.10389470

Determination of Multiple Source Volatile Organic Compound Emission Factors in Offset Printing Shops

C.B. Keil,[A] R.A. Wadden,[B] P.A. Scheff,[B] J.E. Franke,[B] and L.M. Conroy[B]

[A]Environmental Health Program, College of Health and Human Services, Bowling Green State University, Bowling Green, Ohio 43403; [B]Environmental and Occupational Health Sciences, School of Public Health, University of Illinois at Chicago, Chicago, Illinois 60612

The printing industry emits large quantities of volatile organic compounds (VOCs) that impact workplace and ambient air quality. Emission factors are a useful way to describe these emissions. Emission factors describe the mass release of a pollutant in terms of a process activity related to the emissions, and are useful for concentration modeling, evaluation and prioritization of engineering control efforts, and development of logical exposure assessment strategies. Three offset printing facilities of various sizes were evaluated for VOC air concentrations, ventilation characteristics, and process activities. The air concentration and ventilation data were used in mass balance models to determine the hourly VOC emission rates. Emission rates were validated with measures of bulk solvent use. Average VOC emission rates at three sites ranged from 178 to 1076 g/h. On a mass VOC emitted/area printed basis, the smallest print shop emitted up to 12 times the amount from the other sites (29 versus 3.9 and 2.3 mg/ft^2). Process variables were compared with emission rates to identify the most important determinants of VOC emissions. Activities related to press cleaning with solvents were found to account for a large portion of the VOC release. Emission factors relating cleaning activities to the mass of VOCs released were developed using single and multiple variable regression analysis. Each manual press cleaning resulted in the release of 24.9 to 65.9 g of VOCs. Emission factors were also developed for other measures of press cleaning activity. Multiple regression analysis of specific process activities resulted in more detailed emission factor information.

KEIL, C.B.; WADDEN, R.A.; SCHEFF, P.A.; FRANKE, J.E.; CONROY, L.M.: DETERMINATION OF MULTIPLE SOURCE VOLATILE ORGANIC COMPOUND EMISSION FACTORS IN OFFSET PRINTING SHOPS. APPL. OCCUP. ENVIRON. HYG. 12(2):111–121; 1997.

Emission factors have been developed for a number of indoor pollution sources.(1–6) These can be used as tools to help evaluate engineering controls and predict worker exposure to pollutants from intermittently operating sources. Emission factors describe the mass of a pollutant emitted from a process as a function of a process variable associated with the release of the pollutant (e.g., mass of pollutant per unit of process operation). Such factors are useful and generalizable tools since the source is characterized independent of the effects of the surrounding air space. This allows mass emission rates to be determined for a variety of process conditions and different industrial settings. Once the emission rate for a scenario is determined, the air flow characteristics of the space can be used to estimate indoor pollutant concentrations.

The method for determining emission factors in a work space generally involves two steps. First, the mass balance of a pollutant around the space is determined to arrive at a net emission rate for a number of time intervals. Next, the variation in the emission rates is compared with the variability in process variables or activities during the corresponding time intervals to arrive at an emission factor.

The most straightforward emission factor approach is to use a single activity variable to describe emission rates.(5) This has the advantage of being easily illustrated graphically as a two-dimensional plot of activity rate versus mass emission rate. The slope of the line through the data points is the emission factor with the dimensions of mass emitted per activity. However, this approach is limited in cases where air spaces contain different processes and activities, each having contributions to the emission of the same pollutant. This is the case in the printing industry, where each press has multiple sources of volatile organic compound (VOC) emissions and often there are different press types with different emission characteristics operating in the same work space.

This study evaluated three offset printing operations of various sizes. Overall emission rates for the printing operations were developed using ventilation and concentration measurements in mass balance models. This was followed by two-dimensional analysis of emission rates and activity to determine an overall emission factor for each site. Multiple regression analysis was then used to improve the emission factors by discriminating emission factors for all major determinants of VOC emissions.

VOCs in the Printing Industry

VOCs are ubiquitous in the air of print shops and other graphic art facilities. The sources of VOCs are numerous and widespread through the printing process. Organics are often the carrier portion of the printing inks and can also be found in dampening fountain solutions on offset presses. Organics are also used in plate making and press cleaning. There are nearly 70,000 printing facilities in the United States, making this industry the sixth largest in the nation. Offset lithography accounts for over 75 percent of magazine, catalog, and book publication, and many small and mid-sized printers use offset presses.

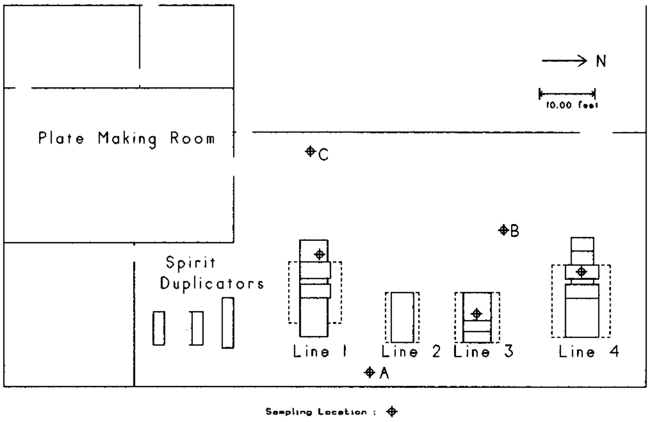

FIGURE 1. Site 1 layout and sampling locations.

The majority of printing operations have no emission control devices on the presses. Heat-set offset printing requires an ink drying unit at the end of a series of presses as a necessary part of the process. Many of these drying units have pollution control devices, but these are only effective at controlling VOCs emitted inside the drier. An important portion of the VOCs emitted during the printing process can escape into the workplace as fugitive emissions.

Earlier studies of the printing industry have focused on the measurement of worker exposure.[7–9] While these studies have documented air concentrations of VOCs, a better understanding of VOC sources and emissions is necessary for developing systematic exposure assessment strategies and engineering control designs.

Methods

Site Descriptions

Figures 1 through 3 present plan views of the three sites, including press locations and sampling locations.

Site 1 (Figure 1) was one room of a small printing facility. The room contained two two-color sheet-fed offset presses, two one-color sheet-fed offset presses, and three spirit duplicators. The room was served by general ventilation that was 65 to 70 percent recirculated. The room volume was 1642 m^3. The presses in the room produced 262,200 ft^2 of printed material during the 2 days that air sampling took place.

Site 2 (Figure 2) was the in-house printing department of a manufacturing plant. The room contained two one-color sheet-fed offset presses, two spirit duplicators, one two-color sheet-fed offset press, and two nonheat-set web-fed offset presses capable of printing in four colors or two colors on two sides of the paper. The one-color sheet-fed presses and the spirit duplicators were similar to the presses at site 1. The two-color sheet-fed press was very different than those at site 1, and its physical configuration was unique among all the presses evaluated. The room was served by general ventilation which was greater than 90 percent recirculated. The room volume was 7777 m^3. A total of 698,580 ft^2 of printed material was produced during the site evaluation.

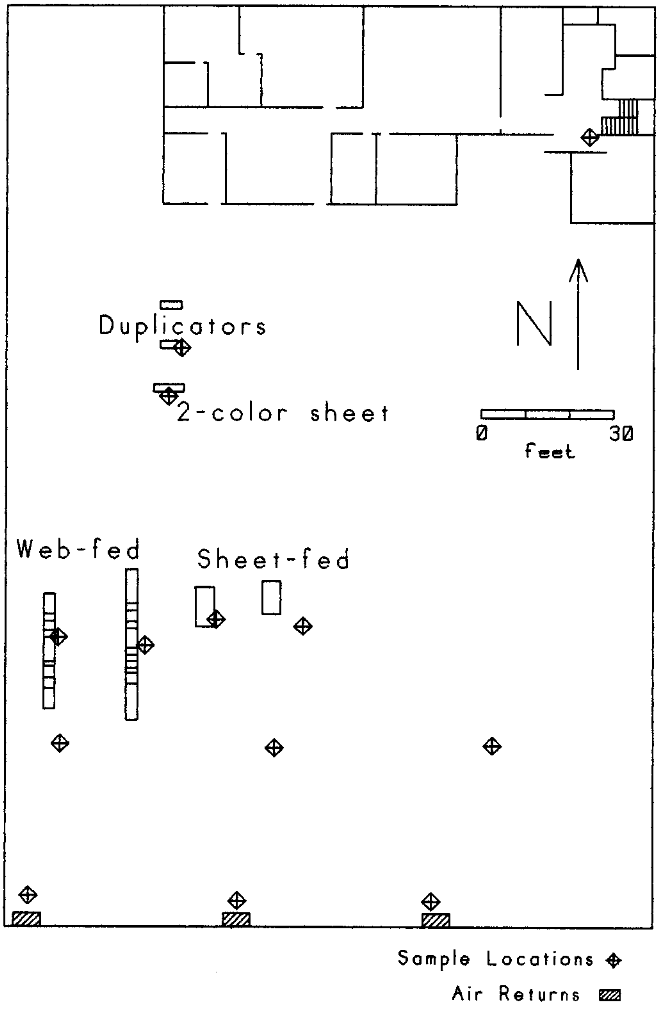

FIGURE 2. Site 2 layout and sampling locations.

Site 3 (Figure 3) was one press room of a large printing company. The facility ran three shifts and produced national weekly magazines as well as advertising material and other products. The room contained three multicolor heat-set web-fed press lines running 38-inch paper and had the capacity to run two webs simultaneously. Each press line had a two-level natural gas drier and paper cutting and folding equipment at the end. The driers had catalytic incinerator pollution control devices. The room was served by general ventilation with no recirculation. The room had a volume of 16,431 m^3. The presses printed on 1.8 million linear feet of 38-inch wide web paper during the air sampling periods (5.7 million ft^2).

Site Evaluation

Each site was characterized in terms of physical layout, ventilation, hourly VOC air concentrations, and process variables.

Ventilation rates through air entry and exit points were measured using calibrated anemometers or pitot tubes with manometers. At site 1 a sulfur hexafluoride (SF_6) tracer gas study was done to characterize the mixing in the room. SF_6 was released into the air space and allowed to mix. The SF_6 source was then shut off. Whole-air syringe samples were taken every 10 minutes at ten different locations in the room. The samples were analyzed by a portable gas chromatograph (GC)

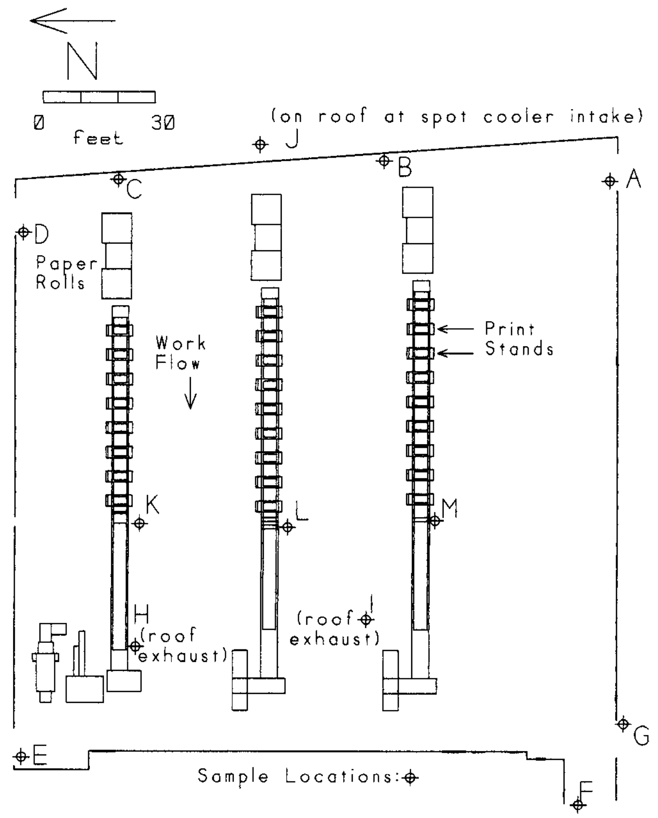

FIGURE 3. Site 3 layout and sampling locations.

with electron capture detector. The standard exponential decay equation, $C_t = C_0e^{-kt}$, was solved to determine the mixing factor at each location.

Each site had a number of sampling locations. There were six sampling locations at site 1 and 13 sampling locations at sites 2 and 3. A sequential series of 1-hour VOC samples were collected simultaneously at each location throughout the day. At site 2 some of the locations were sampled during two of the 1-hour periods each day due to equipment limitations. Additionally, continuous VOC measurements were made at a fixed location at site 1 and at two fixed locations at site 2. The continuous measurement locations corresponded with 1-hour sampling locations.

The 1-hour VOC samples were collected onto charcoal tubes and analyzed by GC with a flame ionization detector. The total area under the chromatographic curve (minus the extraction solvent peak) was quantified using the response factor for *n*-hexane. Replicate analysis of samples at a contract lab confirmed the accuracy of the results.

The continuous VOC measurements were made by infrared analyzers (Foxboro/Wilks Miran 1A General Purpose Gas Analyzer, Foxboro, Massachusetts). Calibration of infrared analyzers for total VOC analysis is difficult. Absorbance at a given wavelength is selective, but total VOC consists of a mix of compounds. The wavelength suggested for toluene (13.9 μm) was used for the analysis since toluene is often a major component of graphic arts VOC emissions.(10) At the first site the instruments were calibrated with a closed-loop system. The total VOC results using this calibration were checked against charcoal tube results taken immediately adjacent to one instrument's inlet. The results were found to be in agreement ($r^2 = 0.99$, slope = 1.2). At site 2 the same wavelength was used; however, toluene was discovered to be a much smaller fraction of the total VOCs. In this case the instruments were calibrated using the results of charcoal tube sampling done side-by-side with the instruments. The 1-hour GC determined total VOC measurements and the corresponding average Miran voltage output were used to develop a site-specific calibration for the instruments. This site-specific calibration reflected the Miran response to the unique mix of compounds at that print shop.

Print shop activities were continuously observed during the VOC sampling periods. Process variables were recorded at 2-minute intervals. Some of the variables recorded included press speeds, maintenance events, cleaning operations, print job changes, and idle time. The bulk usage of the VOC-containing raw materials was also determined.

Emissions Modeling

The emission rates at the three sites were determined using ventilation and air concentration data in mass balance models. Two different mass balance models were used, which differ only in the way that the concentration is modeled.

The first model measures the net mass balance around a room. This approach requires a measurement of air flow and pollutant concentration at each entry or exit from the room. The product of the air concentration (mass/volume) and the volumetric flow rate (volume/time) gives the average mass flow rate at each entry or exit point during the sampling period. For a steady-state system, any difference between the mass flow out of the room and the mass flow in is due to mass emitted within the room. The mass emission rate of pollutant in the room during an air sampling period can be determined using Equation 1:(5)

$$S = \sum_{i=1}^{n} q_iC_i - \sum_{j=1}^{n} q_jC_j \qquad (1)$$

where:

S = source emission rate (mass/time)
q_i = air flow rate through each room exit (volume/time)
C_i = concentration at each room exit (mass/volume)
q_j = air flow rate through each room entrance (volume/time)
C_j = concentration at each room entrance (mass/volume)

This model is termed an "experimental mass balance model." A mass balance must exist around an air space. The model describes the balance based on experimentally measured data, and is most useful when air entry and exit points are easily identified and measured.

The second mass balance model used to determine emission rates assumes that, in some cases, the pollutant distribution in a room can approach completely mixed conditions. For a system with no filtration of outdoor or recirculated air, no significant air infiltration or exfiltration, and no indoor sinks, the emission rate into a room during a sampling period can be determined using Equation 2:[(6)]

$$S = \frac{C_{av}kq - \left[C_s \frac{V}{t_{av}}\right]\left[1 - e^{-\frac{kq}{V}t_{av}}\right]}{1 + \left[\frac{V}{kqt_{av}}\left(e^{-\frac{kq}{V}t_{av}} - 1\right)\right]} \quad (2)$$

where:

S = source emission rate (mass/time)
C_{av} = average concentration during sample period (mass/volume)
C_s = initial concentration during sample period (mass/volume)
q = net air flow through room (volume/time)
k = mixing factor (dimensionless) $(0 < k < 1)$
V = room volume
t_{av} = sampling time

This model is termed the "completely mixed space model." This model is useful when identification or measurement of all air and entry points is difficult. Examples of such cases are locations where air infiltration in negative pressure rooms or exfiltration in positive pressure rooms is a major part of the total air balance.

A series of approximately 1-hour air concentration measurements were taken at each site. The concentrations were used with the ventilation measurements in the appropriate model to determine the emissions during each sampling period.

Emission Factor Determination

Once emissions for each sampling period were modeled, they were compared with the process variables for the same sampling period. A number of process variables were evaluated for correlation with emission rates. Number of sheets printed, area printed, number of print jobs, and cleaning solvent use were all considered. Variables related to the use of cleaning solvents were found to be most correlated with the VOC emission rates. The number of times press or plate cleaning with solvents was done during the sample periods was plotted against the emission rates for the same periods. The slope of the best-fit line through these points is the emission factor with the dimensions of mass VOCs emitted per cleaning event. While this one-variable approach is easy to visualize graphically, it has the limitation of describing solvent cleaning events and the corresponding VOC emissions only in the most general terms, since the generation of emissions may be affected by a number of operating variables.

Recognizing that there may be different amounts of VOCs emitted from different types of cleaning events, a multivariable analysis was done at each site. More specific descriptions of cleaning solvent use (by press type, for example) were the independent variables compared with the dependent variable of emission rate. Regression analysis was used to determine the coefficient (emission factor) of each independent variable.

The use of least-squares calculational procedures for this application is a mathematical technique to determine the best-fit line through the data points which represents a physical model. The fact that this is a physical model must be remembered. Regression is not being used to make inferences about some underlying parameter; therefore, references to statistical significance may not be important. Rather, the least-squares procedure produces the best linear relationship through multiple-variable data.

TABLE 1. Site 1 Total VOC Concentrations (mg/m^3)

				Average Concentration	
Day	**Sample**	**Minutes**	**Initial Concentration**	**Away from Presses (A, B, C)**	**All Samples**
1	1	58	75.8	53.4	72.1
	2	61	62.4	37.9	47.8
	3	52	64.6	37.2	35.6
	4	58	37.2	37.4	38.6
	5	62	52.8	49.4	62.6
	6	58	62.9	126	155
2	7	53	29.5	20.4	21.9
	8	56	35.9	22.6	31.3
	9	58	21.2	34.0	41.6
	10	60	51.8	58.8	65.4
	11	56	83.7	114	150
	12	61	184	134	148

Results

Field Data

Tables 1 to 3 present the concentrations measured at each site and the length of the sampling periods.

At site 1 the average concentrations determined by a Miran at a fixed location were highly correlated with the average room concentration determined by GC analysis (r^2 = 0.95, slope = 0.95). The slope of the line was used to obtain the reported estimate of the average concentration in the room at the beginning of each sampling period. Miran results were not used in the averages for site 1 since they were taken adjacent to a charcoal tube sample.

Two Mirans were available for site 2. There was no clear correlation between the Miran data and GC-obtained measurements of average room concentration. The average of the

TABLE 2. Site 2 Total VOC Concentrations (mg/m^3)

Day	Sample	Minutes	Initial Concentration	Average Concentration
1	1	63	28.3	40.8
	2	51	48.0	45.6
	3	57	42.1	51.6
	4	58	51.5	39.0
	5	65	30.8	24.3
	6	52	17.8	18.7
	7	77	15.6	69.4
	8	29	159	156
2	9	76	4.3	3.1
	10	67	0.9	3.0
	11	48	2.9	18.0
	12	60	17.2	23.0
	13	61	21.9	18.4

TABLE 3. Site 3 Total VOC Concentrations (mg/m^3)

			Sample Location												
Day	**Sample**	**Minutes**	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**	**M**
1	1	55	0.47	0.20	3.39	11.8	1.40	0.04	0.11	22.8	11.0	0.23	66.0	9.40	3.63
	2	59	0.91	0.55	2.74	7.14	1.09	0.02	0.22	14.2	7.82	0.12	26.6	10.1	1.72
	3	59	3.60	0.90	0.58	4.54	1.35	0.05	0.85	7.40	10.6	0.15	20.1	8.03	1.08
	4	63	1.06	0.76	0.22	5.91	2.80	0.04	0.64	22.8	7.68	0.13	21.6	5.28	1.30
	5	58	1.99	0.20	0.82	4.64	1.59	0.08	0.59	8.47	8.56	0.05	7.52	10.6	1.01
	6	61	2.22	1.93	3.54	7.01	10.8	0.04	0.52	15.8	19.8	0.20	13.2	5.49	3.41
2	7	62	0.69	0.26	0.04	3.92	2.09	0.01	0.83	8.98	4.77	0.07	10.0	7.07	0.86
	8	61	5.14	0.71	0.21	4.17	2.75	0.03	0.11	10.0	8.34	0.06	11.1	9.10	2.02
	9	58	1.59	0.80	0.21	3.90	3.52	0.96	2.81	7.90	3.82	0.07	9.45	5.00	3.19
	10	60	2.66	1.39	0.26	3.53	2.59	1.46	1.82	4.47	3.56	0.06	17.6	7.13	12.6
	11	63	76.1	15.9	3.84	16.2	7.07	0.25	17.0	19.0	16.0	0.04	24.1	24.0	15.2
	12	59	39.9	8.08	1.73	5.69	2.86	2.66	16.0	15.2	15.8	0.04	22.4	8.63	11.2

two Miran readings was used as the measure of initial concentration. The Miran measurements were used in determining the average room concentration for site 2. The Miran locations had charcoal tube samples for only four of the sampling hours. These charcoal tube samples were used to calibrate the Mirans as previously discussed. The Miran data then became the only data available for those locations during the other hours.

The concentration data for site 3 are all charcoal tube GC-determined values.

Ventilation measurements at each sites were taken at least twice. Little variation was observed and the reported values represent the average air flow from all measurements. Air exfiltration at site 1 and infiltration at site 2 were components of the air balance. Some of the largest points of infiltration and exfiltration (e.g., wall cracks, very low velocity movement through open doors, etc.) were identified with smoke tubes. The overall infiltration and exfiltration rates were determined using a net air balance. The SF_6 study at site 1 revealed fairly uniform decay rates throughout the room. The average k value was 0.42, and ranged from 0.37 to 0.46 with a standard deviation of 0.028. Tables 4 to 6 summarize the ventilation measurements at each site.

Activities around the presses were recorded during each sampling period. Activities that started in one sampling period and continued into the next were coded as one-half an event for each period. The activity information is reported with the modeled emissions.

Modeled Emissions

The data collected at site 1 supported the use of both Equations 1 and 2 to determine the emission rates. A good characterization of the ventilation characteristics of the room was obtained. The sample locations supported both models.

TABLE 4. Ventilation Summary of Site 1

Direction	**Location**	**m^3/min**
Into room	Make-up air (through air mover)	140
Out of room	Exfiltration	140
Recirculated	Through air mover	244

In applying the experimental mass balance model at site 1, the concentration entering the room with the make-up air was considered to be zero. There were no sources or building exhausts near the make-up inlet. Air exfiltrated from the room at a number of points along the periphery. The average concentration of the samples in the room but away from the presses (A, B, and C) was used as the measure of the concentration leaving the air space through exfiltration. With zero VOC mass coming into the air space, the generation rate will be equal to the mass flow out of the space. So in the case of the first sampling period at site 1, the average concentration at locations A, B, and C was 53.4 mg/m^3. This times the exfiltration air flow rate of 140 m^3/min gives an emission rate of 7.48 g/min or 434 g for the 58-minute sampling period.

In applying the completely mixed space model to site 1, the initial concentration for each period was determined from Miran measurements. The average concentration was calculated using all of the samples in the press room. Where in Equation 1 the desired concentration was that in the exiting air, in this case the whole room average is what is needed. The mixing factor was the value determined experimentally by SF_6 studies, k = 0.42. The emission rate during the first hour was calculated using Equation 2:

$$S = \frac{72.1\,\frac{\text{mg}}{\text{m}^3}\cdot 0.42\cdot 140\,\frac{\text{m}^3}{\text{min}} - \left[75.8\,\frac{\text{mg}}{\text{m}^3}\cdot\frac{1642\ \text{m}^3}{58\ \text{min}}\right]\left[1 - e^{-\frac{0.42\cdot 140\frac{\text{m}^3}{\text{min}}}{1642\ \text{m}^3}\cdot 58\ \text{min}}\right]}{1 + \left[\frac{1642\ \text{m}^3}{0.42\cdot 140\,\frac{\text{m}^3}{\text{min}}\cdot 58\ \text{min}}\left(e^{-\frac{0.42\cdot 140\frac{\text{m}^3}{\text{min}}}{1642\ \text{m}^3}\cdot 58\ \text{min}} - 1\right)\right]}$$

TABLE 5. Ventilation Summary of Site 2

Direction	**Location**	**m^3/min**
Into room	Infiltration (into drop ceiling space then through air mover)	120
Out of room	Down NE stairs	120
Recirculated	Through air mover	388

TABLE 6. Ventilation Summary of Site 3

Direction	Description	VOC Sample Location	m³/min
Into room	Southeast door	A	605
	South screen	B	468
	North screen	C	392
	Loading dock	F	627
	Southwest door	G	362
	Spot cooler intake	J	286
Out of room	Northeast door	D	390
	Northwest door	E	283
	North ceiling exhaust	H	847
	South ceiling exhaust	I	846
	North press drier	K	131
	Middle press drier	L	113
	South press drier	M	113

The emission rate for this period using the completely mixed space model was 4.07 g/min or 236 g for the sampling period.

The results of the two models were highly correlated ($r^2 = 0.82$), but the average results from Equation 2 were approximately 65 percent of the average results from Equation 1. One reason for this is the time component in Equation 2. Mass flow resulting from nonzero concentrations existing at the start of an averaging period results in a lower emission rate than if zero initial condition is assumed. If the completely mixed space model for the first 2 hours at site 1 is solved assuming a zero initial concentration, the resulting emission rates are 7.26 and 4.73 g/min. These are quite comparable to the experimental mass balance results of 7.48 and 5.31 g/min. While Equation 2 reflects the reality of nonzero initial concentrations, Equation 1 has the advantage of not requiring a mixing factor. At site 1 the mixing factor was well defined, but often it is difficult to determine. The emissions and activities for the corresponding sampling periods at site 1 are summarized in Table 7.

The air space at site 2 had many locations for air movement over walls that did not extend completely to the ceiling. For this type of space, the experimental mass balance model is difficult to apply due to the many points of air movement. However, the completely mixed space model is appropriate in these situations. Emission rates were modeled using Equation 2. The mixing factor used was 0.3. This has been found to be typical for indoor light-industrial air spaces.(11) The emissions and activity data for site 2 are presented in Table 8.

All air entry and exit points at site 3 were easily identified. Air flow and concentration measurements were taken at each point. Equation 1 was used to determine site 3 emissions. These are reported along with activity information in Table 9.

In addition to the modeled emission rates, an evaluation of bulk solvent usage was done to estimate long-term VOC emission rates. Assuming that all VOCs from cleaning solvents brought into the plant eventually escape as fugitive emissions, an emission rate based on solvent use can be determined. Each site provided an estimate of cleaning solvent consumption based on their inventories. The modeled emissions for the two sampling days at each site were 15 to 90 percent of the long-term inventory-based emission estimates.(12)

Emission Factors

SINGLE REGRESSION EMISSION FACTORS. At sites 1 and 2 the total number of cleaning events during each sampling period was used as the activity measure. Single variable regression analysis revealed no apparent correlation between total observed cleaning events and VOC emissions at site 3. Another variable, minutes of make-ready, was found to be the single variable most associated with VOC emissions. Make-ready is the time between printing jobs during which there is a large amount of cleaning solvent used in the removal of one set of printing plates and the preparation of the next. During a make-ready it was difficult for the observers to keep track of the many solvent uses. The number of minutes of make-ready is used as a surrogate for the many cleanings that took place during that period.

The total number of cleaning events at sites 1 and 2 and the combined minutes of make-ready at site 3 for each sampling period were plotted with the corresponding emissions. These plots and the least-squares fit line are shown in Figures 4 to 7. The emission factors (the slope of the least-squares fit lines) for these one-variable analyses at site 1 were 48.5 g VOC/cleaning ($r^2 = 0.78$, $p < 0.001$) and 42.2 g VOC/cleaning ($r^2 = 0.82$,

TABLE 7. Total VOC Emissions and Activities at Site 1

	Emissions (g)		Solvent Cleanings			
Sample	Equation 1	Equation 2	Total	One-color	Two-color	Duplicator
1	434	236	11	2	7	2
2	324	136	9	0	6	3
3	271	35.2	2	0	0	2
4	304	135	7	0	2	5
5	429	252	14	3	5	6
6	1023	757	17	6	6	5
7	151	49.0	4.5	1	0	3.5
8	177	91.6	5	2	3	0
9	276	192	8	2	1	5
10	494	264	9	0	2	7
11	894	660	18	8	5	5
12	1126	442	2	2	0	0

TABLE 8. Total VOC Emissions and Activities at Site 2

Sample	Emissions (g) Equation 2	Solvent Cleanings				
				Sheet-Fed		
		Total	Web	One-Color	Two-Color	Duplicator
1	278	8	3	2	2	1
2	47.8	6	3	0	0	3
3	247	5.5	1.5	0	0	4
4	0*	11.5	4.5	0	5	2
5	0	8	0.5	0	3	4.5
6	48.5	7	4.5	0	2	0.5
7	982	33.5	13.5	1.5	12.5	6
8	117	11.5	2.5	5.5	1.5	2
9	0	13.5	7	0	6	0.5
10	38.3	25	2	3.5	16	3.5
11	258	22	3	3	15	1
12	136	11.5	3	3.5	0	5
13	0	6	3	1	0	2

*Zero emissions indicated when modeled results were negative.

$p < 0.001$) using Equations 1 and 2, respectively. The results at the other sites were 20.9 g VOC/cleaning at site 2 ($r^2 = 0.46$, $p = 0.01$) and 9.91 g VOC/minute make-ready at site 3 ($r^2 = 0.24$, $p = 0.10$).

The single outlier in the site 1 figures was not used in determining the best-fit line. During that time period, cleaning solvent was transferred from a bulk container to smaller working containers by open-air pouring. This is the only time this occurred during the entire study. If the two solvent cleaning events had been the only VOC sources during the time interval, the emission factors predict 97.0 (experimental mass balance) or 84.4 (completely mixed space) grams of VOC emission. However, the modeled emissions were 1126 and 442. This analysis shows that during this period there was some other large VOC source responsible for emitting from 358 to 1029 g of VOCs. The solvent transfer occurred at this same time and the outlying location of that point in Figures 4 and 5 suggests that this operation is this large VOC source. The emissions can be estimated graphically using Figures 4 and 5 as the difference between the outlying data point and the emissions prediction if solvent cleanings are the only source of VOCs (the least-squares line on the figures). The emissions associated with the transfer process are from volatilization of the solvent during pouring, the displacement of vapor-saturated air from the containers being filled, and splashes and spills. The emissions from the entire refilling operation can be estimated as approximately 700 g of VOCs.

MULTIPLE REGRESSION EMISSION FACTORS. The second step in emission factor development was to discriminate specific sources of VOC emissions by using multiple regression analysis. The emission estimate for each sample period was the dependent variable as in the single regression emission factors. The independent variables were still cleaning activities, but

TABLE 9. Total VOC Emissions and Activities at Site 3

Sample	Emissions (g) Equation 1	Activity		
		Make-Ready (min)	Auto Cleanings	Manual Cleanings
1	2304	55	2	10
2	1447	59	0	10
3	1053	59	1	12
4	1959	26	2	22
5	990	71	0	9
6	2115	109	2	2
7	935	64	1	14.5
8	1042	118	0	7.5
9	670	14	0	24
10	570	0	2	6
11	0*	24	1	14
12	0	9	1	3.5

*Zero emissions indicated when modeled results were negative.

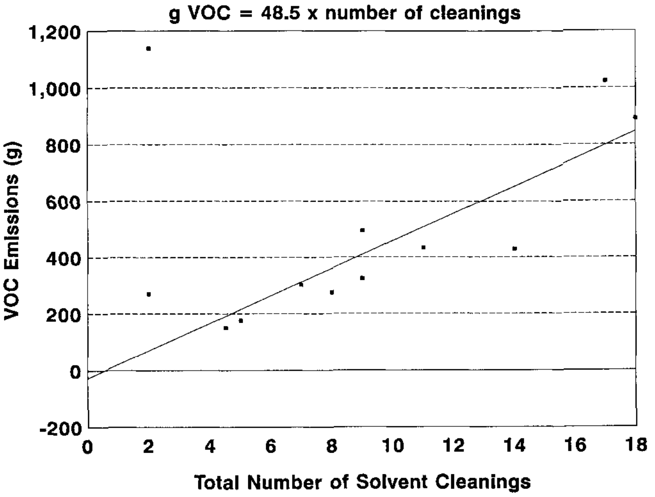

FIGURE 4. Site 1 total cleanings emission factor using the experimental mass balance model.

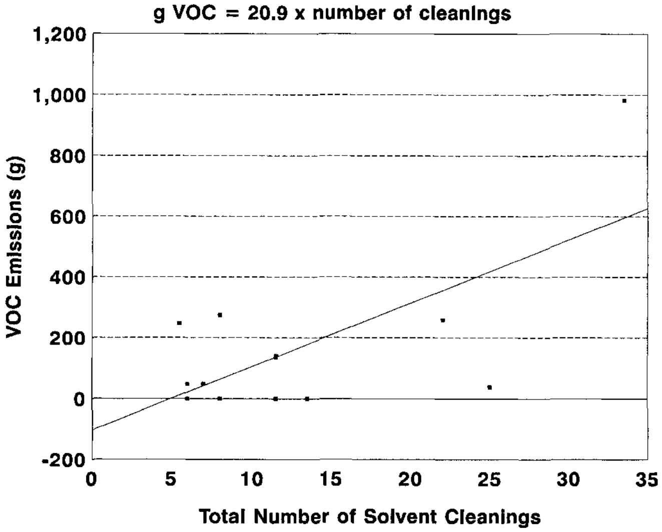

FIGURE 6. Site 2 total emission factor.

now they were specified for the various types of cleaning. At sites 1 and 2 the press cleanings were categorized by the type of press being cleaned. The presses were grouped based on paper feed type (sheet or web) and the number of colors, or whether or not it was a duplicator press. At site 3 the presses were virtually identical, but three distinct types of cleaning—manual cleaning, automatic cleaning, and make-ready cleaning (described in terms of time)—were used as the independent variables.

A series of regressions were run for each site. Each independent variable was modeled with the emissions, first independently and then in combinations. The results of these models are presented in Tables 10 to 12. In each table, a series of emission factor models are presented. Each row gives a model of grams of VOCs emitted predicted by the listed coefficient (emission factor) for the independent variables. In the last row of each table the full emission model, containing all independent variables, is presented.

The p value for each regression equation is also presented. The p value represents the probability of correctly accepting the hypothesis that a linear relationship exists between the dependent and independent variable(s). While it must be emphasized that these are physical models, not statistical models, the p value gives some indication of the degree of association between the variables. The physical appropriateness of the models can be seen in the development of the models in Tables 10 to 12. If independent variables are truly independent, their coefficients will not dramatically change as more variables are added to the model. The additional variables will describe previously unaccounted for variability in the dependent variable. For example, at site 1 the variable with the strongest association with the emissions when modeled alone was one-color press cleanings ($p < 0.001$). The value of the coefficient

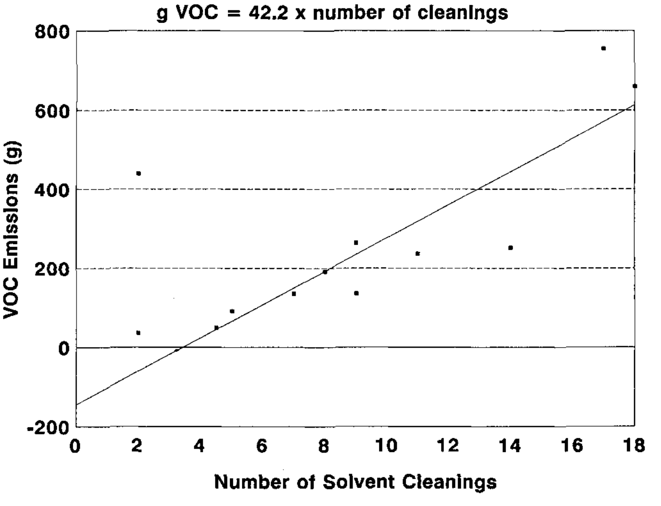

FIGURE 5. Site 1 room total emission factor using the completely mixed space model.

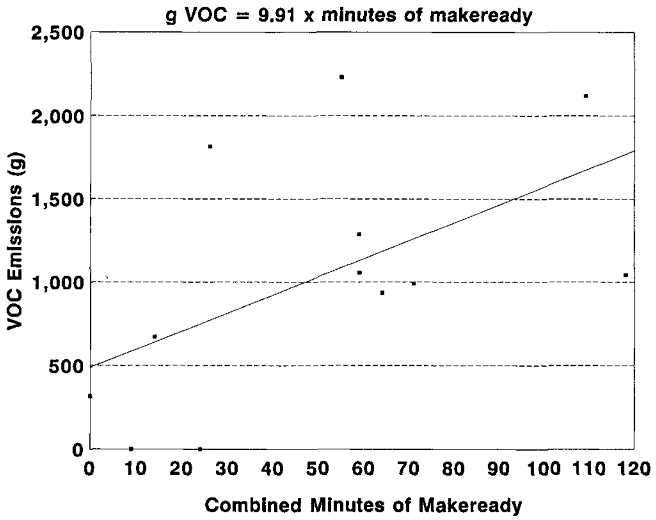

FIGURE 7. Site 3 emission factor for make-ready time.

TABLE 10. Site 1 Individual Source Emission Factor Development

	Activity Coefficient (g VOC/Cleaning)				
VOC Emissions	**One-Color Press**	**Two-Color Press**	**Duplicator**	**p Value**	**r^2**
Equation 1 modeled emissions					
g =	87.3	—*	—	<0.001	0.67
g =	—	63.0	—	0.07	0.32
g =	—	—	60.1	0.18	0.19
g =	75.6	25.3	—	0.007	0.71
g =	81.3	—	39.7	0.004	0.75
g =	—	63.4	60.6	0.11	0.52
g =	66.8	29.8	43.5	0.007	0.81
Equation 2 modeled emissions					
g =	79.6	—	—	<0.001	0.78
g =	—	52.5	—	0.07	0.31
g =	—	—	49.7	0.19	0.18
g =	71.9	16.6	—	0.002	0.80
g =	74.9	—	30.9	0.001	0.85
g =	—	52.8	50.1	0.06	0.50
g =	65.1	20.1	33.5	0.001	0.88

*—indicates that the variable is not in the model in that row.

changes only about 25 percent as the two other independent variables are added. This illustrates that the emissions explained by one-color press cleanings are largely associated only with that variable.

The intercepts from the regression analysis generally have little physical meaning. A positive intercept may indicate a background source of emissions. The p values for any negative intercepts for the equations were too high to conclude that they were actually different than zero.

The emission factors are summarized in Table 13. The total cleanings emission factors for sites 1 and 2 are the results of the single regression analysis where all solvent cleanings were considered together, rather than grouped by press type (Figures 4 through 7). All other emission factors are the coefficients developed from the models containing all the independent variables. Site 1 values are the averages of the results using the two different emission models.

Discussion

The hourly average total solvent concentrations at all sites were below the acceptable levels for mixtures such as Stoddard solvent, gasoline, and naphtha. This does not indicate that there are no health hazards. The specific composition of the mixtures must be determined and compared with the individual compound standards and the equivalent mixture standard before making such a determination.

Both models produced good results for the short-term emission rates at the three sites. The modeled emission rates compared favorably with solvent usage-based measures of emission rates. The usage-based emission rates are long-term measures, and the agreement, in some cases up to 90 percent, with the modeled emission rates for only two days of measurements supports validation of the models. Additionally, at site 1, where the data set supported the use of both models, the results were very similar. This further validates the approach.

TABLE 11. Site 2 Individual Source Emission Factor Development

	Activity Coefficient (g VOC/cleaning)					
VOC Emissions	**Web Press**	**One-Color Sheet Press**	**Two-Color Sheet Press**	**Duplicator**	**p Value**	**r^2**
Equation 2 modeled emissions						
g =	61.3	—*	—	—	0.003	0.57
g =	—	18.5	—	—	0.68	0.02
g =	—	—	17.4	—	0.2	0.14
g =	—	—	—	73.2	0.09	0.24
g =	63.5	32.7	—	—	0.008	0.62
g =	57.6	—	5.71	—	0.01	0.58
g =	55.3	—	—	52.2	0.003	0.69
g =	61.9	30.3	2.26	—	0.03	0.62
g =	55.4	24.7	2.98	49.6	0.02	0.73

*—indicates that the variable is not in the model in that row.

TABLE 12. Site 3 Individual Source Emission Factor Development

VOC Emissions	Activity Coefficient (g VOC/activity) Minutes Make-Ready	Automatic Blanket Wash	Manual Blanket Wash	p Value	r²
Equation 1 modeled emissions					
g =	9.91	—*	—	0.10	0.24
g =	—	350	—	0.20	0.16
g =	—	—	1.21	0.97	<0.01
g =	12.0	458	—	0.043	0.50
g =	11.6	—	25.2	0.22	0.29
g =	—	362	8.92	0.8	0.16
g =	15.3	547	44.7	0.04	0.63

*—indicates that the variable is not in the model in that row.

The experimental mass balance model is a good model when the air balance of a room can be accurately determined. In cases where the air inlets and exits are less well defined or difficult to measure, the completely mixed space model can be used if supported by appropriate concentration measurements, measures of effective air flow, and a means of estimating the mixing factor. Also, Equation 2 is more appropriate in air spaces with lower net air change rates, which result in a longer residence time for the pollutant.

On a total mass basis, site 3, the largest of the sites, was the largest emitter of VOCs. Table 14 presents the total VOC mass emissions, the area printed, and the emissions per square foot of material printed. The modeled VOC emissions were extrapolated to the entire time for which the amount printed was available. If VOC mass emissions are described in terms of emissions per square foot of product printed, the smallest of the shops, site 1, is the most significant VOC emitter. This is probably due to the lack of any control equipment and the large amount of cleaning activities associated with the number of job and plate changes at small-order press shops. This information may be important in establishing regulatory policy for the printing industry. There are a large number of small press shops that as a group produce a large amount of the printed material in the country. These shops process small jobs and have a high VOC emission rate on a per sheet basis. Because of their small size, these are the facilities that usually are least able to afford advanced control technologies.

The emission factors for manual cleaning processes range from 24.9 to 65.9 g VOC/cleaning. This relatively narrow range represents a wide variety of press types. The emission factors for cleaning duplicators at sites 1 and 2 are 38.5 and 49.6 g VOC/cleaning. The similarity in emission factors demonstrates that the emission rate is specific to the process. Machines as similar as the duplicators at sites 1 and 2 would be expected to have similar mass emissions from cleaning regardless of the setting in which they were used. Likewise, the manual blanket washing at all three sites produced similar emission factors. The manual cleanings of web blankets at sites 2 and 3 had emission factors within 20 percent of each other (55.4 and 44.7 g VOC/cleaning). The sheet press blanket cleanings exhibited the widest range of emission factors. The two-color sheet press at site 2 was excluded from this comparison because it was quite different from all the other presses studied. It was much smaller than all other presses in the study and was largely enclosed in a plastic outer shell.

The emission factors developed here have a number of applications to the printing industry. They can be used to estimate potential atmospheric releases for pollution control permitting and compliance estimations. Emission factors can be used along with ventilation measurements to estimate

TABLE 13. Summary of Emission Factors

Site	Process Variable	g VOC/Activity
1*	Total number of solvent cleanings (single variable regression)	45.3
1*	Number of one-color sheet press (24″ × 29″ stock) solvent cleanings	65.9
1*	Number of two-color sheet press (25″ × 38″ stock) solvent cleanings	24.9
1*	Number of duplicator solvent cleanings (8.5″ × 11 and 4″ × 9″)	38.5
1*	Transfer of solvent from large to small containers	700
2	Total number of solvent cleanings (single variable regression)	20.9
2	Number of web press cleanings (11″ and 17.25″ wide webs)	55.4
2	Number of one-color sheet press cleanings (20.25″ × 24″ and 17.25″ × 22.25″ stock)	27.5
2	Number of two-color sheet press cleanings (11″ × 17″ stock)	2.98
2	Number of duplicator cleanings (8.5″ × 11″)	49.6
3	Minutes of make-ready	15.3
3	Automatic web press blanket cleaning (38″ wide web)	547
3	Manual web press blanket cleaning (38″ wide web)	44.7

*Site 1 values represent the average of the two emission model results.

TABLE 14. Site VOC Emissions on a Product Volume Basis

Site	mg VOC Emitted/ft^2 of Product
1	29
2	3.9
3	2.3

worker exposures. These exposure estimates can be used retrospectively to estimate historic exposures. They can be used in the present to develop systematic exposure assessment strategies. They can also be used to predict exposure differences that may result from process changes.

Emission factors can also be used for evaluating the effectiveness of existing pollution control measures and prioritizing future efforts. An example of this type of application can be illustrated at sites 1 and 3. The process for transferring solvent at site 1 clearly needs modification. During the time period that the transfer occurred the emission rate was five to ten times the expected rate based on the number of solvent cleanings. The solvent transfer accounted for almost 18 percent of the VOC emissions for that day. Likewise at site 3, the mass of VOC emissions from each automatic blanket wash was much higher than manual washing. Automatic blanket washing has the advantage of being done without stopping the press. However, evaluating the metering system that delivers the solvent to the blanket may reveal ways to better control the amount of solvent used.

Conclusions

The key to the success of any emission model is to understand the ventilation and air flow in the room and to be able to measure it. All emission models are based on the principle of conservation of mass. The difference between models is in how the transport of the mass is described. For air pollutants, this transport is largely a function of ventilation. With a clear understanding of the air flow in the room, a strong hypothesis can be made about how mass is transported in the room. From this an appropriate sampling strategy can be implemented.

Multivariable regression is an effective technique to separate emission factors from multiple sources in indoor industrial air spaces. This approach provides a means of describing emissions in an air space with complex processes. While this multivariable approach, using multiple descriptions of solvent use as independent variables, is not easily graphed, it does more accurately reflect the mechanisms that result in emissions.

This study demonstrates the development of emission factors for offset printing. The development of emission factors for this and other processes is a multistep procedure. Emissions can be determined using air concentration and ventilation measurements in mass balance models. The emissions must be validated by comparison of model results and pollutant inventory measures. Emissions are then correlated with process rates to develop emission factors that describe the mass of pollutant released per process activity variable. Once emission factors have been developed, they can be used for estimating air concentrations and worker exposure, evaluating the effectiveness of existing engineering controls, and developing control priorities.

Acknowledgments

This research was made possible by National Institute for Occupational Safety and Health grants 1-R01-OH02804 and 5T15-OH07104-15. The authors also thank the members of the teams that evaluated the three sites: Joe Chung, Luke Curtis, John Dimos, Ruth Kerzee, Sheryl Milz, Steve Perez, Paul Sullivan, Steve Van Zandt, and Yichun Zhou. Donna Kenski and Jian Lin were also very helpful by providing insights and suggestions.

The print shops that participated in this study would like to remain anonymous, but the authors thank both the management and the employees for their help and cooperation.

References

1. Franke, J.E.; Wadden, R.A.: Indoor Contaminant Emission Rates Characterized by Source Activity Factors. Environ. Sci. Technol. 12:45–51 (1987).
2. Wadden, R.A.; Scheff, P.A.; Franke, J.E.: Emission Factors for Trichloroethylene Vapor Degreasers. Am. Ind. Hyg. Assoc. J. 50:496–500 (1989).
3. Wadden, R.A.; Hawkins, J.L.; Scheff, P.A.; et al.: Characterization of Emission Factors Related to Source Activity for Trichloroethylene Degreasing and Chrome Plating Processes. Am. Ind. Hyg. Assoc. J. 52:349–356 (1991).
4. Scheff, P.A.; Friedman, R.L.; Franke, J.E.; et al.: Source Activity Modeling of Freon Emissions from Open-Top Vapor Degreasers. Appl. Occup. Environ. Hyg. 7:127–134 (1992).
5. Wadden, R.A.; Baird, D.I.; Franke, J.E.; et al.: Ethanol Emission Factors for Glazing During Candy Production. Am. Ind. Hyg. Assoc. J. 55:343–351 (1994).
6. Wadden, R.A.; Scheff, P.A.; Franke, J.E.; et al.: VOC Emission Rates and Emission Factors for a Sheetfed Offset Printing Shop. Am. Ind. Hyg. Assoc. J. 56:368–376 (1995).
7. Hansen, D.J.; Whitehead, L.W.: The Influence of Task and Location on Solvent Exposures in a Printing Plant. Am. Ind. Hyg. Assoc. J. 49:259–265 (1988).
8. Veulmans, H.; Groeseneken, D.; Masschelein, R.; et al.: Survey of Ethylene Glycol Ether Exposures in Belgian Industries and Workshops. Am. Ind. Hyg. Assoc. J. 48:671–676 (1987).
9. Kalliokski, P.: Estimating Long-Term Exposure Levels in Process-Type Industries Using Production Rates. Am. Ind. Hyg. Assoc. J. 51:310–311 (1990).
10. U.S. Environmental Protection Agency: Air Emissions Species Manual. EPA 450/2-88-003. Office of Air Quality, Planning, and Standards, Research Triangle Park, NC (1988).
11. Wadden, R.A.; Scheff, P.A.: Indoor Air Pollution: Characterization, Prediction and Control. John Wiley & Sons, New York (1983).
12. Wadden, R.A.; Scheff, P.A.; Keil, C.B.; et al.: Determination of VOC Emissions and Compositions for Offset Printing. J. Air & Waste Manage. Assoc. 45:547–555 (1995).