Emission Factor Development for Intermittent Workplace Sources

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Final Performance Report (Option 2)

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List of Publications

Peer-Reviewed Papers

Wadden, R.A., Scheff, P.A., Franke, J.E., Conroy, L.M., Javor, M., Keil, C.B., and Milz, S.A. VOC emission rates and emission factors for a sheetfed offset printing shop. Amer. Ind. Hyg. Assoc. J. (In Press), April 1995.

Conroy, L.M., Prodans, R., Lachman, M., Yu, X., Wadden, R.A., Franke, J.E., and Scheff, P.A. Hood efficiencies of vapor degreasers under operating conditions. J. Environ. Engin., American Society of Civil Engineers, (In Press), 1995.

Wadden, R.A., Scheff, P.A., Keil, C.B., Franke, J.E., and Conroy, L.M. Determination of VOC emission rates and compositions for offset printing. J. Air Waste Manage. Assoc., (In Press), 1995.

Conroy, L.M., Wadden, R.A., Scheff, P.A., Franke, J.E., and Keil, C.B. Workplace emission factors for hexavalent chromium plating. Applied Occup. Environ. Hyg., (In Press), 1995.

Abstracts and Presentations

Milz, S.A., Wadden, R.A., Franke, J.E., Scheff, P.A., and Conroy, L.M. Characterization of source activity and emission factors for wave soldering. Paper and Abstract 95, To be presented at the American Industrial Hygiene Conference, Kansas City, May, 1995.

Keil, C.B., Conroy, L.M., Franke, J.E., Scheff, P.A., and Wadden, R.A. Applications of indoor emission factors for worker exposure modeling. Paper and Abstract 91, To be presented at the American Industrial Hygiene Conference, Kansas City, May, 1995.

Wadden, R.A., Scheff, P.A., Keil, C.B., Conroy, L.M., and Franke, J.E. Determination of offset printing VOC emission rates and compositions. Abstract 94-RA111.04, 87th Annual Meeting of the AWMA, Cincinnati, June 1994.

Wadden, R.A., Scheff, P.A., Franke, J.E., and Conroy, L.M. Estimation of workroom emissions from electroplating. Paper 168, (Invited paper) Presented at the American Industrial Hygiene Conference, Anaheim, May, 1994.

Milz, S.A., Wadden, R.A., Franke, J.E., Scheff, P.A., and Conroy, L.M. Characterization of source activity and emission factors for a copper plating line. Paper 170, Presented at the American Industrial Hygiene Conference, Anaheim, May, 1994.

Wadden, R.A. Determination of VOC emission factors for offset printing. Roundtable 11, Perspectives on Exposure Assessment Modeling. Presented at the American Industrial Hygiene Conference, Anaheim, May, 1994.

Keil, C.B., Franke, J.E., Wadden, R.A., Scheff, P.A., and Conroy, L.M. D-Limonene emission factors from a terpene electronics parts degreaser. (Abstract) Paper 258, Presented at the American Industrial Hygiene Conference, New Orleans, May, 1993.

Wadden, R.A., Scheff, P.A., Franke, J.E., Conroy, L.M., Keil, C.B., Javor, M.J., and Milz, S.A. VOC emission rate determination in an offset printing shop. (Abstract) Paper 164, Presented at the American Industrial Hygiene Conference, New Orleans, May, 1993.

Milz, S.A., Wadden, R.A., Franke, J.E., Scheff, P.A., Conroy, L.M. Characterization of source activity and emission factors for uncontrolled trichloroethane degreasers. (Abstract) Paper 257, Presented at the American Industrial Hygiene Conference, New Orleans, May, 1993.

Wadden, R.A., Scheff, P.A., Franke, J.E., Conroy, L.M., and Yu, Xiao-Min. Measurements of solvent and lead release in a microcircuit production facility. Paper 285; Presented at the American Industrial Hygiene Conference, Boston, June 1992.

Milz, S.A., Wadden, R.A., Franke, J.E., Scheff, P.E., Conroy, L.M., Keil, C., Prodans, R., and Perez, S. Emission factor field test for a copper plating line. American Industrial Hygiene Conference, Boston, June, 1992.

Keil, C.B., Wadden, R. A., Scheff, P.A., Conroy, L.M., Franke, J.E. Activity related chromium emissions from an automated piston plating line. 85th Annual Meeting of the Air and Waste Management Association, Kansas City, June, 1992.

Yu, X., Wadden, R.A., Conroy, L.M., Scheff, P.A., Franke, J.E., Prodans, R.S. Concentration patterns of methylchloroform from degreasing and of lead from wave soldering. American Industrial Hygiene Conference, Salt Lake City, May, 1991.

Ph.D. Dissertations

Keil, Charles B. Process specific emission factors at three offset lithography shops. University of Illinois at Chicago, 1994.

Milz, Sheryl M. Characterization of emission rates and emission factors for three manufacturing processes. University of Illinois at Chicago, 1994.

Rationale

Engineering control of occupational health hazards ultimately depends on restricting the release (emission) of contaminants into the workspace. Emissions from indoor sources are the most significant determinants of worker exposures to air contaminants. The nature and strength of these emission sources need to be understood quantitatively so that they can be effectively controlled.

As has been the case in many areas of engineering design (e.g., mixing and filtration operations in the chemical industry; casting mold design in ferrous foundries; design of earth compaction equipment in civil engineering applications), the development of design criteria and procedures to respond to workplace problems has been essentially empirical in nature. Practitioners of industrial hygiene and occupational health engineering solved problems as they arose. And when such problems re-occurred frequently, a consensus was sought among persons knowledgeable in the field to specify a standard approach. Excellent examples of such efforts are the ACGIH's <u>Industrial Ventilation</u> (21st ed., 1992) and ASHRAE's ongoing series of design handbooks.

However, invaluable as this body of experience has been for hazard mitigation, the approach is confined bv the limitations common to any empirical approach, i.e., that the observations are of restricted generality. Typically, the experienced industrial hygienist is in the position of making a control design recommendation based on only a very few breathing zone or area concentrations; and considerable observational skills, but only applied over a limited period of time. His or her evaluation and solution will be responsive to the problem as it is now, for the particular sources and operating conditions involved, and for a specific interior space. However, the design may be incomplete, in the sense that it may not fit all typical process situations. Variation may occur because of changes in production rate, operation over extended periods, alterations in process or equipment design or operating procedures, frequency of maintenance, and differences in raw materials. In addition, as our understanding deepens about the health implications of various materials, particular design approaches adequate in the past will not continue to be so. (The steady historical reduction of TLV's (threshold limit values) is a reflection of this increase in knowledge) And such design approaches often will not intrinsically contain adequate flexibility to respond to new situations.

The conceptual thrust of this proposal was to develop a method for generalizing the design of engineering control of workplace hazards. In particular we proposed to develop a library of emission factors, based on field observations, for a series of commonly encountered, hazardous, unit operations. We concentrated on four types of open tank processes: vapor degreasing; chromium and copper electroplating; offset printing; and wave soldering. Each of these process types includes a liquid or gas vapor interface open to workspace air. Because of this interface, a significant potential exists for release of materials hazardous to health, such as organic solvent vapor, or chromium or lead particulate matter. However, aside from this common factor, there are significant differences in design and mode of operation. This process variety was selected in order to better demonstrate the generality of the evaluatory method, and from our past observations in the field that quite often the controls for such processes don't work effectively.

Significant Findings

Our proposal specified a total of 11 source tests. We actually carried out 13 evaluations. There were 3 tests of offset printing operations, 4 of degreasers, 3 of wave soldering, and 3 of electroplating. This required determination of emissions from 16 different units which discharged hazardous materials. The tests were carried out at 10 sites. One of these locations contained both a degreaser and a wave soldering line; and another contained three wave soldering lines, one of which was of older and different design that the other two. Each test consisted of 12 1-hour sampling periods which also included measurements of general and local exhaust ventilation.

Average total emissions from three uncontrolled methylchloroform degreasers were determined to be between 0.39 kg/hr and 0.74 kg/hr. These values were in good agreement with the approximate usage inventory value of 0.62 kg/hr for the same time period. Emissions were related to uncovered tank conditions, dragout, and type of parts, and 80% were identified as coming from a single line. Emission factors were about 0.2 g/part in addition to 0.22-0.4 g/in^2 of part area. Manual cleaning was also important with a rate of 58-90 g/hr·% of time on manual operation.

Total emissions from a terpene degreaser were 0.68 kg limonene/hr with an emission factor of 2.2 g limonene/circuit board cleaned. The LEV collection efficiency was 98.9-99.7%. In terms of square inches of boards degreased, the uncollected emission factor was 0.2 mg/in^2 and that for the collected emissions was 11 mg/in^2.

Methylene chloride emissions into the workspace were 0.68 g/s·m^2 of degreaser cross-sectional area from a vapor degreaser in the electronics industry. The LEV system was only 40% efficient in capturing emissions.

Uncontrolled emissions from all three Pb wave soldering lines in the same space averaged 86 mg Pb/hr. Total scrapings and dedrossings of the molten solder reservoir appeared to be the most important source activity variable with an emission factor of 4 mg of Pb/solder pot cleaning for explained area emissions. Although each line was served by a local exhaust system, the overall control efficiency for lead for the three lines was only 56%. Lead concentrations in the workspace were highly correlated (r^2= 0.7-0.9) with the combined number of scrapings and dedrossings which occurred on the open solder pot nearest to the sampling point. Two of the lines were of a much newer design than the other. One hypothesis which we examined was whether control was less effective on the older line. This proved not to be the case as the combined contribution to area lead concentrations of the two newer lines was 50% which was not different from the 23% from the older line. A chemical mass balance receptor model was used to determine these allocations.

The copper emission factor for releases into the workspace from electroplating was 0.5-2.7 μg/amp·hr. The average collection efficiency of the LEV was 97.2%. The emission factors for hexavalent chromium from piston plating were 81 μg/amp·hr for controlled (hood) emissions, and 0.3 μg/amp·hr for releases into the workspace. These findings were in good agreement with measurements carried out in California on hood emissions from hard chrome plating operations.

The release rates of volatile organic compounds (VOC) as fugitive emissions from offset printing are difficult to quantitate and the compositions are usually not known. Tests on three offset printing plants during production indicated that fugitive releases into the workplace were strongly related to press cleaning activities. 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. Air samples and solvents were analyzed by gas chromatography (GC) for total VOC and 13-18 individual organics. Average uncontrolled emissions from a sheet-fed offset print shop were 4.7-6.1 kg VOC/day, and 1.4-2.0 kg BTEX/day (the sum of benzene, toluene, ethyl benzene, and xylenes); with an emission factor of 30-50 g VOC/press cleaning depending on the type of equipment. VOC emissions of 0.4-0.9 kg/day (0.04-0.08 kg BTEX/day) were determined for a medium size industrial in-house print shop. Emission factors varied between 2.5-56 g VOC/cleaning and again depended on the type of press. Neither of these facilities had LEV systems.

Daily emissions of 79-82 kg of VOC (12-13 kg BTEX/day) were measured from one print room, within a large commercial concern, which contained 3 web-fed, heat-set lines served by catalytic air pollution control devices. Emission factors included 17 g VOC/minute of "make ready" (which included solvent cleaning), 49 g VOC/manual press cleaning, and approximately 10 times this value for automatic web blanket cleaning. The catalytic control system was effective in collecting and destroying more than 99% of the ink carrier solvents (40-50% of ink weight) driven off in the drying process. However, because of inadequate capture design, only about 40% of the cleaning solvent vapors were collected and oxidized in this system.

Emission compositions were similar for all the printing plants. In one case benzene concentrations were at the OSHA action level of 0.5 ppm. Comparison of the overall and speciated emission rates with mass balance estimates based on solvent usage and composition were quite consistent.

One more set of wave soldering emission factors are still being developed (for an advanced reflow factory installation) as well as for one for one of the electroplating lines (trivalent chromium). We also will be further evaluating emission factors for the methylene chloride degreaser (for which we already have emission rates); and emissions from one of the trichloroethane degreasers.

Usefulness of Findings

The value of the emission factor approach is that the effect of the particular interior space in which the data are collected is removed. The factors are developed from the area concentration pattern surrounding each device while production is taking place, using mathematical models describing a mass balance for the contaminant in order to transform this pattern for a particular source to an emission rate. To systematically describe the variability of emissions, the release rate is related to measures of source activity, process conditions, and equipment geometry. The results of this study provide: (1) A compilation of activity-based emission factors for Cr and Cu electroplating, vapor degreasing, wave soldering, and offset printing; (2) A measure of the variability in emissions which can be expected from such processes; (3) Actual determinations, based on an emission mass balance, of control device performance for each of the processes studied; (4) A generalized basis for estimating workplace concentrations from these types of sources; and (5) A mass-balance basis for evaluating control design alternatives. In addition, all of the tests were carried out without recourse to a temporary total enclosure and without interfering with worker activities, increasing worker exposure, or increasing safety and explosion hazards.

Publications and Aims of Project

VOC emission rates and emission factors for a sheetfed offset printing shop. Amer. Ind. Hyg. Assoc. J. (In Press), April 1995.

This paper demonstrates the evaluation procedure. Emission rates were determined both from hourly charcoal tube samples, and from a continuous measure of VOC concentration using an infrared spectrometer. Both sets of emission rates were consistent with blanket roll cleaning frequency and gave emission factors which were in good agreement (30-50 g VOC/press cleaning).

Conroy, L.M., Prodans, R., Lachman, M., Yu, X., Wadden, R.A., Franke, J.E., and Scheff, P.A. Hood efficiencies of vapor degreasers under operating conditions. J. Environ. Engin., American Society of Civil Engineers, (In Press), 1995.

The thrust of this study was to measure capture efficiency of local exhaust hoods used to control solvent vapors from vapor degreasers during normal operating conditions, and to compare the observed capture efficiencies to the ACGIH design criteria. Most of the testing was supported by another NIOSH grant (5 RO 3 OH02680) but our methylene chloride observations were included in the testing and the analyses. The ACGIH recommended flow of 0.25 $m^3/s/m^2$ (50 cfm/ft^2) of tank surface was not always adequate for all conditions, and increasing the flow above design recommendations did not necessarily improve hood efficiency.

Wadden, R.A., Scheff, P.A., Keil, C.B., Franke, J.E., and Conroy, L.M. Determination of VOC emission rates and compositions for offset printing. J. Air Waste Manage. Assoc., (In Press), 1995.

Offset printing is characterized by significant uncontrolled, and frequently unquantitated, 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 quantitated in printing and other surface coating operations without recourse to a Temporary Total Enclosure. The average composition of emissions from each of the plants, despite process and solvent differences, were quite similar. These concentration data are much more detailed than have been available up to this time.

Conroy, L.M., Wadden, R.A., Scheff, P.A., Franke, J.E., and Keil, C.B. Workplace emission factors for hexavalent chromium plating. Applied Occup. Environ. Hyg., (In Press), 1995.

Effective control of emissions from electroplating is necessary to maintain a healthy workplace. However, in many cases the emission rates are not well characterized. This study describes a methodology to determine such rates with application to a hexavalent chromium plating line under production conditions. Area concentrations were determined from particulate samples collected on open face filters using calibrated personal sampling pumps. Twelve sets of one-hour samples were collected at six locations at different distances from the plating tanks, and in the hood of the local exhaust system. The filters were analyzed using PIXE (proton induced x-ray emission spectroscopy). For each one-hour period, measurements of area concentrations were transformed to emission rates by using a multi-point diffusion mass balance model in conjunction with measured ventilation rates. In addition source activities such as area plated, amp·hours consumed, and total power usage were recorded simultaneously with concentration measurements. Comparison of the emission rates with source activities allowed us to determine emission factors as well as the emission rates. The hood emission results were in good agreement with hood emissions measured in a California Air Resources Board study of hard chrome plating (which did not measure workroom emissions). The workroom emissions were related to plating line throughput such as total area plated or amp·hr of plating current. The methods provide a first estimate for determining workroom emissions when no other data are available, and are a useful way to extend field test measurements.

Abstracts (1993-1995)

CHARACTERIZATION OF SOURCE ACTIVITY AND EMISSION FACTORS FOR WAVE SOLDERING S.A. Milz, R.A. Wadden, J.E. Franke, P.A. Scheff, and L.M. Conroy. Paper and Abstract 95, To be presented at the American Industrial Hygiene Conference, Kansas City, May, 1995.

Emission rates and emission factors for lead particles were developed based on data collected during production in a space containing three wave soldering lines at a semiconductor manufacturing plant. Twelve 1-hour air samples for particulate matter were collected on polycarbonate filters over a two-day period at ten sampling locations around the lines. The particulate matter on the filters was analyzed for elemental composition using Proton Induced X-Ray Emission Spectroscopy. Source activity data were recorded during the entire twelve hours for each of the three lines. The observations included board type, number of boards, number and duration of hood cover openings, and number of pot scrapings and dedrossings.

The collected hourly concentration data and ventilation rates were used with a box model describing a lead mass balance on the space to calculate the combined hourly emission rate from all three lines. The average lead emission rate was 50 mg/hr. Emission factors were calculated using the emission rate estimates. The resulting relationships indicated that total board count and total pot scrapings and dedrossings best described the overall lead emissions from all three lines. These emission factors can then be used to estimate emissions for other wave soldering lines in the semiconductor industry.

In addition, chemical mass balance (CMB) receptor modeling was carried out on the area samples to determine the fraction of the measured lead concentration at each sampling site which was emitted from each of the three wave lines. In a space containing multiple sources, the CMB approach has the potential to provide a quantitative estimate of the fraction of each workplace sample which is due to emissions from each specific source. In this study, the allocation procedure resulted in individual line concentrations which were in good agreement with scraping and dedrossing activities for the specific line most likely to affect the area concentrations. This agreement suggests that the CMB can serve as a useful evaluating tool for discriminating the contribution of individual sources to area and personal concentrations.

APPLICATIONS OF INDOOR EMISSION FACTORS FOR WORKER EXPOSURE MODELING. Keil, C.B., Conroy, L.M., Franke, J.E., Scheff, P.A., and Wadden, R.A. Paper and Abstract 91, To be presented at the American Industrial Hygiene Conference, Kansas City, May, 1995.

There is a growing library of indoor emission factors that can be used to estimate worker exposure to airborne chemicals. Emission factors have the advantage of being a generalizable tool. The emission factor for a process can be used to predict chemical concentrations in a variety of ventilation and production conditions. The applications of emission factors need to be communicated in a meaningful way to the practicing industrial hygienist in order for this approach to be fully validated, developed and integrated into hygiene practice. Two examples of the use of emission factors are illustrated. Emission factors for chrome plating have been published as 26.8 g chromium emitted per rack of parts plated. Using this emission factor and process and ventilation measurements at another facility, chromium concentrations were predicted. The predicted values ranged from 1.7 $\mu g/m^3$ to 18 $\mu g/m^3$. Actual measured values ranged from 0.19 to 4.72 $\mu g/m^3$. This agreement is reasonable considering potential differences in rack types, part sizes, and plating current. As another example, an emission factor developed for offset printing VOC emissions at one print shop was used to predict concentrations at a separate shop. VOC emissions at offset printing are most closely associated with the solvent cleaning activities at the presses. An emission factor has been developed of 48.5 g VOC emitted during each solvent cleaning event. This emission factor along with appropriate process and ventilation measurements were used to estimate VOC concentrations at the second shop. Predicted VOC concentrations for the shop ranged from 35 to 109 mg/m^3. Measured concentrations at the shop ranged from 8.0 to 24 mg/m^3 and were highly correlated with predicted values ($r^2=0.85$). In both examples concentrations were overpredicted, but by no more than a factor of 4, which is reasonable given the large number of assumptions. These examples illustrate how emission factors can be effectively used to predict indoor chemical concentrations which could be used for epidemiological studies or for developing exposure assessment strategies.

DETERMINATION OF OFFSET PRINTING VOC EMISSION RATES AND COMPOSITIONS R. A. Wadden, P. A. Scheff, C. B. Keil, J. E. Franke, and L. M. Conroy. Abstract 94-RA111.04, 87th Annual Meeting of the AWMA, Cincinnati, June 1994.

Offset printing has the potential to release volatile organic compounds (VOC) as fugitive emissions. In addition, with the Clean Act Amendments of 1990, many individual components of VOC have been identified as hazardous air pollutants (HAPs) which will require control. Because printing operations are often not served by local exhaust ventilation control systems, the release rates are difficult to quantitate and the compositions are usually not known. This paper summarizes the results from tests carried out at three offset printing shops which 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 a small shop containing 3 sheet-fed presses and 2 spirit duplicators (36,700 sheets, 47,240 envelopes and letterheads), a medium size industrial in-house shop with 2 web-fed and 3 sheet-fed presses, and 1 spirit duplicator (315,130 total sheets), and one print room of a large commercial concern containing 3 web-fed, heat-set operations (1.16×10^6 feet) served by catalytic air pollution control devices. Each test consisted of 12 1-hour periods over two days. Air samples were collected simultaneously during each period at 7-14 locations within each space. The samples were analyzed by gas chromatography (GC) for total VOC and 13-18 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 sheet-fed 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, ethyl benzene, and hexane. Comparison of the emission rates with mass balance estimates based on solvent usage and composition were quite consistent. The average composition of emissions from these tests was much more detailed than has been available to this time but was in good agreement with previous chemical fingerprint values for toluene and o-xylene which have been successfully applied to source-receptor modeling for graphic arts.

ESTIMATION OF WORKROOM EMISSIONS FROM ELECTROPLATING
R.A.Wadden, P.A.Scheff, J.E.Franke, L.M.Conroy. Paper 168, (Invited paper) Presented at the American Industrial Hygiene Conference, Anaheim, May, 1994.

Effective control of emissions from electroplating is necessary to maintain a healthy workplace. However, in many cases the emission rates are not well characterized. Based on intensive testing of 8 plating operations during production we have developed a number of methods for estimating emissions of chromium, nickel, copper, and sulfur. For each test area concentrations were determined from particulate samples collected on open face filters using calibrated personnel pumps. The samples were collected hourly at several locations in the vicinity of each source. The filters were analyzed using PIXE (proton induced x-ray emission spectroscopy). In each case, measurements of area concentrations were transformed to emission rates by using appropriate mass balance models in conjunction with measured ventilation rates. In addition source activities such as area plated, amp-hours consumed, and total power usage were recorded simultaneously with concentration measurements. Comparison of the emission rates with source activities often allowed us to determine emission factors as well as the emission rates. For example, the emission factor for hard and decorative chrome electroplating for three processes varied between 0.08 and 1.47 mg Cr/amp-hr. These results were consistent with limited data available from the California Air Resources Board (0.02 - 3 mg Cr/amp-hr depending on control system). The methods provide a first estimate for determining workroom emissions when no other data are available, and are a useful way to extend field test measurements. For systems with local exhaust ventilation the approach also allows determination of mass-based collection efficiency.

CHARACTERIZATION OF SOURCE ACTIVITY AND EMISSION FACTORS FOR A COPPER PLATING LINE. Milz, S.A., Wadden, R.A., Franke, J.E., Scheff, P.A., and Conroy, L.M. Paper 170, Presented at the American Industrial Hygiene Conference, Anaheim, May, 1994.

Emission rates and emission factors were developed for copper and sulfur based on data collected during production of an eleven-tank copper plating line at a semi-conductor manufacturing plant. Hourly air samples for particulate matter were collected on polycarbonate filters over a two-day period at five locations around the line. The particulate matter on the filters was analyzed for elemental composition using Proton Induced X-Ray Emission Spectroscopy. In addition, source activity data were recorded during the entire twelve-hour sampling period. The observations included board code, rack size, number of boards, tank number, plating current, and temperature of the plating bath.

The collected hourly concentration data and ventilation rates were used with mass balance models to calculate hourly emission rates. The average copper emission rate was 487 μg/min to 1232 μg/min depending on the mass balance model.

Source activity variables were averaged (rack size, current, temperature) or totaled (number of boards) for each of the twelve sampling hours. In addition, three other activity variables were calculated for each sampling hour. These calculated activity variables included the total square inches of boards entering the plating baths each hour, the total square inches of boards being plated each hour, and the total effective energy each hour, which was calculated by multiplying the current by the plating time. As expected, the area plated was highly correlated with the product of current and time interval in the plating bath.

Emission factors were then calculated for all four emission rate estimates. The resulting equations indicated that the total effective energy and the total square inches of boards entering the plating baths each best described the copper and sulfur emissions. These emission factors can then be used to estimate emissions for other copper plating lines in the semi-conductor industry.

DETERMINATION OF VOC EMISSION FACTORS FOR OFFSET PRINTING. R. A. Wadden Roundtable 11, Perspectives on Exposure Assessment Modeling. Presented at the American Industrial Hygiene Conference, Anaheim, May, 1994.

Almost half of U.S. printing is carried out using offset lithography. Operation of offset printing presses requires use of solvents containing various volatile organic compounds (VOC) including benzene, toluene and xylene. While significant quantities of these materials may be released to workroom air, actual emission rates and emission factors are usually not known. Based on field testing of three offset printing plants during operation we have developed techniques to quantitate the emissions and, by relating emission rates to source activities, to develop emission factors. We will report on these techniques and will also summarize the emission rates and factors, and the work station exposure data collected during the tests.

CHARACTERIZATION OF SOURCE ACTIVITY AND EMISSION FACTORS FOR UNCONTROLLED TRICHLOROETHANE DEGREASERS S.A. Milz, R.A. Wadden, J.E. Franke, P.A. Scheff, and L.M. Conroy. (Abstract) Paper 257, Presented at the American Industrial Hygiene Conference, New Orleans, May, 1993.

Hourly air samples for 1,1,1-trichloroethane (TCA) were collected on charcoal adsorption tubes over a two-day period during normal working conditions at 10 locations surrounding 3 open-top vapor degreasers at a semi-conductor plant. Continuous air monitoring was also conducted using 2 Foxboro/Wilks Miran IA General Purpose Gas Analyzers calibrated for TCA. In addition, degreaser source activity was recorded for each minute during the sampling periods for each of the 3 lines. The hourly concentration data were used with the completely mixed space model ($V=2798$ m^3 and an experimentally determined $k=0.3$) to estimate the overall emission rates from all 3 lines. These rates were compared with an experimental mass balance based on the measurement of air concentration and air flow at each exit and entry point. The hourly results from these 2 approaches were highly correlated ($r^2 = 0.728$) with an average emission rate from the completely mixed space model of 6551.62 mg/min and an average emission rate from the experimental mass balance of 11717.72 mg/min. An inventory check based on the daily additions by maintenance personnel to the solvent reservoir resulted in an emission rate of approximately 10400 mg/min. The 1-minute Miran concentrations (420 observations) were then regressed against the activity observations from all 3 lines. The significant activities determined from the regressions were the times during which the degreasing tanks were uncovered (tank), the number of boards degreased during each cycle (part), the amount of time previously degreased boards remained near the sampling pumps (basket), and the board identification number (travel). A fit of the first day's hourly values using the fraction of time the tanks were uncovered indicated that $\text{tank}_{\text{line2}}$ (5908 mg/min) and $\text{tank}_{\text{line3}}$ (3726 mg/min) contributed almost all of the emissions for this period. The 6 source characteristics were then used to model 10-minute emission rates based on Miran concentrations. This approach enables us to determine short-term emissions from each line individually based on the activity data.

D-LIMONENE EMISSION FACTORS FROM A TERPENE ELECTRONICS PARTS DEGREASER C.B. Keil, J.E. Franke, R.A. Wadden, P.A. Scheff and L.M. Conroy. (Abstract) Paper 258, Presented at the American Industrial Hygiene Conference, New Orleans, May, 1993.

The phase-out of ozone depleting chloroflourocarbons (CFCs) called for in the Montreal protocol has led to a search for alternative compounds for use in various industrial processes. Terpenes are a potential replacement for CFCs in metal and electronics cleaning applications. Terpenes are a naturally occurring compound found in citrus oil. As a class of compounds terpenes have excellent solvency, rinsability, wetting, penetrating and detergent characteristics. They are considered to have low to moderate toxicity based on an incomplete but growing data base. Commercial formulations of terpenes have caused contact dermatitis and the odor is reported to produce a range of effects from headaches to nausea. Animal studies indicate that two of the terpenes, d-limonene and anethole are hepatotoxic to rodents. This study evaluated the emissions of d-limonene, the most abundant of the terpenes, around a conveyorized computer board degreaser. The degreaser was part of a prototype production facility in a 114,897 ft^3 room. The degreaser was originally designed for use with aqueous cleaners. A commercial cleaner (90% terpene, 10% anionic surfactant) was used in the unit on a trial basis. The degreaser consisted of an enclosed terpene spray wash side followed by an enclosed hot water spray rinse side with an air knife and drying oven at the exit end of the conveyor. The degreaser was equipped with local exhaust ventilation (LEV) on both enclosed spray sides and included a canopy hood over the open conveyor section between the two sides. Sulfur hexafluoride (SF_6) tracer gas studies were done to determine the effective air flow through the room. The effective airflow through the room was 10,946 cubic feet per minute or 5.7 air changes per hour. Air samples were collected at eight locations around the room including LEV ductwork. A short term sample was collected prior to the start of degreasing operations. This background d-limonene concentration was 0.03 mg/m^3. The average room concentration during degreaser operation was 0.53 mg/m^3. The LEV-captured d-limonene emissions were calculated using duct concentrations and duct flowrate. The average captured emission rate was 11,263 mg/min. These emissions were found to be strongly correlated with board throughput and can be described as mg emitted = 2,181 x number of boards degreased + 10,204 (r^2 = 0.96). Board throughput varied from 0 to 57 boards per hour with an average of 29 boards per hour.

VOC EMISSION RATE DETERMINATION IN AN OFFSET PRINTING SHOP. Wadden, R.A., Scheff, P.A., Franke, J.E., Conroy, L.M., Keil, C.B., Javor, M.J., and Milz, S.A. (Abstract) Paper 164, Presented at the American Industrial Hygiene Conference, New Orleans, May, 1993.

A two day test was carried out December 17-18, 1991, in a printing shop containing 4 sheet-fed offset presses (2 2-color; 2 1-color; 16,000 sheets/day) and 3 spirit duplicators (24,000 pieces/day). Charcoal tube samples (pumps calibrated at 300 ml/min) were collected at twelve locations for 12 hourly periods. The tubes were analyzed for hexane equivalent concentrations by gas chromatography in our laboratories and, as a quality control, 48 paired samples were analyzed at a commercial lab. The agreement was very good (r^2 = 0.969) with the slope of the relationship being 0.929 for University vs. Commercial lab analysis. Each sample was also speciated for 14 identified compounds including n-hexane, benzene, toluene, and the xylenes. The average hexane equivalent concentration over the 12 hours at a workbench in the space was 75.5 mg/m^3, 31% of which was toluene. Analysis of 10 of the cleaning solvents, blanket and plate washes indicated that 3 of these contained benzene. In addition to the hydrocarbon samples, 28 particulate samples were collected on polycarbonate filters (2 L/min for one hour), and were analyzed by proton induced x-ray emission spectroscopy (PIXE) for 14 elements including sulfur, chromium, nickel and lead. Source activities, including sheet counts, job set-up times, and cleaning periods, were also recorded. The volume of the space was 1494 m^3 with an air exchange rate of 15 hr^{-1} which included 34% makeup air from outside the building. There was no local exhaust.

The concentration and ventilation observations were used in conjunction with a completely mixed mass balance model for the interior space to estimate total emission rates of VOC and elements from all sources in the space. In addition the individual source activities were used to discriminate the contribution from each source. A chemical mass balance receptor model was also applied to the chemical pattern of elements and VOC to determine the contribution of each source to total emission. The results of these two determinations are compared. Successful application of mass balance models to determine emission rates from concentration data places the measurement information in a generalized form which can be applied to estimate workroom concentrations in other space and ventilation settings.