

Source Reduction for Prevention of Methylene Chloride Hazards: Cases from four industrial sectors

Cora R Roelofs^{1*}, Michael J Ellenbecker²

¹Center for Community-Based Research, Dana-Farber Cancer Institute and Department of Health and Social Behavior, Harvard School of Public Health, Smith 271, 44 Binney Street, Boston, Massachusetts 02115 Cora_Roelofs@dfci.harvard.edu

²Department of Work Environment, University of Massachusetts Lowell, 1 University Avenue, Lowell, Massachusetts 01854 Michael_Ellenbecker@uml.edu

*Corresponding author

Abstract

Background

Source reduction, defined as chemical, equipment and process changes that intervene in an industrial process to eliminate or reduce hazards, has not figured as a front-line strategy for the protection of workers' health. Such initiatives are popular for environmental protection, but their feasibility and effectiveness as an industrial hygiene approach have not been well described.

Methods

We investigated four cases of source reduction as a hazard prevention strategy in Massachusetts companies that had used methylene chloride, an occupational carcinogen, for cleaning and adhesive thinning. Three cases were retrospective and one was prospective, where the researchers assisted with the source reduction process change. Data were collected using qualitative research methods, including in-depth interviews and site visits.

Results

Motivated by environmental restrictions, a new worker health standard, and opportunity for productivity improvements, three companies eliminated their use of methylene chloride by utilizing available technologies and drop-in substitutes. Aided by technical assistance from the investigators, a fourth case dramatically reduced its use of methylene chloride via process and chemistry changes. While the companies' evaluations of potential work environment impacts of substitutes were not extensive, and in two cases new potential hazards were introduced, the overall impact of the source reduction strategy was deemed beneficial, both from a worker health and a production standpoint.

Conclusion

The findings from these four cases suggest that source reduction should be considered potentially feasible and effective for reducing or eliminating the potential hazards of methylene chloride exposure. Especially when faced with a hazard that is both an environmental and worker health concern, companies may chose to change their processes rather than rely on local exhaust ventilation equipment or personal protective equipment that might not be as effective, might transfer risk and/or not be integrated with financial goals. However, technical assistance sensitive to environmental and health and safety impacts as well as production issues should be provided to guide companies' source reduction efforts.

Background

This paper reports on the experience of four Massachusetts companies that reduced their use of methylene chloride in a variety of industrial processes in response to increasing regulatory pressures. Rather than utilize the traditional control approaches delineated in environmental and occupational health regulation, such as pollution control equipment or local exhaust ventilation that facilitate the continued use of hazardous chemicals, these companies chose a source reduction approach. Source reduction, also called pollution prevention, includes chemical substitution, process modification, and substitute technologies that intervene in the industrial process itself to eliminate or reduce hazards.[1] In the environmental protection field, awareness of pollution “media-shifting,” e.g. protecting the air by filtering contaminants through a filter that then becomes or collects hazardous waste, has given rise to support for pollution *prevention* in place of “end-of-pipe” controls. In addition to private sector initiatives, many levels of government in industrialized countries have established source reduction as a preferred environmental policy and have dedicated resources to promote it. Danish law has since 1982 prohibiting the use of hazardous chemicals if safer substitutes are available.[2] The U.S. Pollution Prevention Act of 1990 and the 1989 Massachusetts Toxics Use Reduction Act have helped to “mainstream” source reduction in industrial production practices in the United States.[3, 4]

Source reduction activities motivated by environmental protection goals have had a significant impact on the work environment. Many of the technological breakthroughs that have occurred in chemistry, process engineering, and industrial equipment in response to demand for reducing the environmental impact of production have had the

added benefit of reducing workers' hazardous chemical exposure.[5] But while most industrial hygienists would state their philosophical commitment to "prevention at the source," source reduction strategies are not common in industrial hygiene practice. Indeed, early industrial hygienists maintained that source reduction was not a practical approach, nor even theoretically superior to local exhaust ventilation, from a prevention standpoint.[6] This latter view has been supported by an assumption that control strategies that require changes to industrial processes or products are inherently "infeasible." Thus, "add-on" controls—ventilation systems and personal protective equipment—have dominated hazard prevention guidance and practice.[7-9]

The question of the "feasibility of controls" has figured centrally in the regulation of toxic exposures in the workplace in the U.S. One of the last tasks assigned by the U.S. Congress to the now-defunct Office of Technology Assessment was a review of the U.S. Occupational Safety and Health Administration's (OSHA) procedures for determining the feasibility of control strategies to limit worker exposures to occupational hazards. The report's authors found that

The agency's demonstrations of feasibility are often based on conservative assumptions about what compliance responses will predominate across affected industries...In a good number of the cases that the Office of Technology Assessment examined, the actual compliance response that was observed included advanced or innovative control measures that had not been emphasized in the rulemaking analyses....OSHA devotes relatively little attention to examining the potential of advanced technologies or the prospect of regulation-induced innovation to provide technologically and economically superior options for hazard control. Most attention does appear to be placed on conventional control measures (e.g., increased ventilation and production enclosure), rather than on new technology ranging from sophisticated emissions control devices to technologies capable of supporting basic

shifts in production processes, including process redesigns, product reformulations, and material substitution.[10]

Evidence for the report's conclusions included industry responses to the cotton dust standard, with which industry complied by modernizing equipment and processes at a substantially reduced cost (compared to those projected for traditional control approaches) and with tremendous production benefits, and the formaldehyde standard, where industry complied not by utilizing the OSHA-recommended ventilation and enclosure strategy but with a source reduction strategy (low-formaldehyde resins) that had been available at the time of the rulemaking.

In 1997 OSHA promulgated a new comprehensive methylene chloride standard.[11] This standard presented an opportunity for innovative control approaches. Methylene chloride has been characterized as a potential occupational carcinogen by OSHA, U.S. Environmental Protection Agency, and the International Agency for Research on Cancer.[12-14] Occupational exposure to methylene chloride can occur during its production and use as a paint stripper, cleaner, degreaser, adhesive thinner, process solvent and as an aerosol carrier. With an odor threshold of around 250 parts per million (ppm), methylene chloride has poor warning properties and, due to its volatility, concentrations may rapidly approach high levels in poorly ventilated areas [15]. Fatalities due to methylene chloride vapor inhalation in furniture stripping operations have been reported.[16]

OSHA's 1997 methylene chloride standard is strict and comprehensive; it lowered the 8-hour time weighted average Permissible Exposure Limit for the chemical from 500 ppm to 25 ppm and required exposure monitoring, worker training, engineering controls, designation of restricted areas, spill and leak prevention and medical

surveillance. OSHA demonstrated that the proposed standard was technically and economically feasible with standard engineering controls and asserted that companies could comply with the new standard without eliminating methylene chloride from industrial operations. A few substitutes for methylene chloride are briefly described in the compliance guides that accompany the standard, but these guides focus on local exhaust ventilation and work practices as the best ways to lower exposure.[17] In response to complaints about the lowering of the Permissible Exposure Limit for methylene chloride, the agency replied: “OSHA has determined that the final methylene chloride standard is feasible in all affected industries without the need for substituting to alternative chemicals. It is not OSHA’s intention to force industries to abandon methylene chloride...”[18]

But abandon methylene chloride is exactly what many companies did.[19] They had begun that process several years before in response to environmental regulations that restricted methylene chloride emissions to the ambient air. Methylene chloride is regulated as a Hazardous Air Pollutant under the U.S. Clean Air Act.[20] Permits must be secured to discharge it to the atmosphere and companies must use Maximum Available Control Technology for specific sources to prevent environmental contamination. The standard for vapor degreasers specifically recommends against local exhaust ventilation because of its potential role in generating emissions to the environment.[21] Thus, OSHA’s primary recommendation for exposure control contradicted the goals of environmental protection by potentially increasing emissions of methylene chloride to the environment.

Additionally, for many processes, off-the-shelf technologies and chemistries were available to take methylene chloride's place. Probably in response to increasing regulation, chemical companies and equipment manufacturers have brought forth a generous array of methylene chloride source reduction strategies for its chief uses including substitute chemistries, mechanical and equipment innovations, and modernized processes. (See Table 1) Indeed, it is one leading expert's opinion that effective substitute chemistries and technologies exist for virtually every current application of methylene chloride in industry (Personal communication, K Wolf: Oct. 15, 1998).

Despite the increased use of source reduction techniques, there have been few reports of how source reduction process changes are undertaken in the "real world" and their impact on the work environment.[7] Research reports on hazard prevention strategies usually involve a description of laboratory and/or field tests of ventilation or personal protective equipment designs. While such reports may include a reporting of before and after air monitoring data, almost nowhere can you read about the process by which a prevention strategy was implemented (nor not) and its complex impact. Environmental case studies of source reduction, while more inclusive of contextual and practical factors, usually neglect to report on the impact of the source reduction strategy on the work environment.

In the wake of increased environmental and occupational health regulation of methylene chloride, we recognized an opportunity to systematically assess the issues related to source reduction that are important to the occupational health field by using a timely case study approach. Our goal in undertaking these case studies was not to

test hypotheses, but to capture the total detailed phenomena of source reduction for hazard prevention as manifested specifically in these four cases of methylene chloride source reduction for worker health hazard prevention. We were interested in information about the experiences and perceptions of the people in the process as well as the technical details. Themes distilled from these case descriptions could be used to generate hypotheses for further study and/or to guide prevention interventions. While we began our investigation with such questions as: would “safer” substitutes introduce new hazards? Would changes motivated by environmental goals improve the work environment? What is the evidence for source reduction’s feasibility and effectiveness for worker protection?—the case study approach structures open-ended exploration through observation and interrogation of key informants. The ability to discover important issues not preconceived, to provide rich descriptions, to challenge employers’ stock answers, and to get at “hows” and “whys” of their actions, are some of the several utilities of the qualitative case study approach as detailed below.

Methods

This study used qualitative research methods to investigate and describe cases of source reduction for hazard prevention. The selection of these study subjects was the result of a sampling approach that sought information-rich cases available for in-depth study in four diverse industrial settings.[22] Four companies, large and small, in four different industrial sectors were enrolled as cases. The potential cases were initially selected from the 37 companies that had reported their 1997 use of methylene chloride under the Massachusetts Toxics Use Reduction Act because they used more than 10,000 lbs of the chemical in that year. The list of potential participants was further narrowed to include only the 13 companies that had used methylene chloride

in an industrial process, such as in cleaning or thinning, and not as a component in a product. Telephone calls to each of these companies resulted in a pool of six companies with interest in participating. Two of these six agreed to participate (non-participants cited a lack of time and inability to give access to the facility as reasons for refusal). Two companies that had used methylene chloride prior to 1997 and that were participating in a Demonstration Sites program sponsored by the Toxics Use Reduction Institute at the University of Massachusetts Lowell were approached and also agreed to participate. In order to achieve representation by small furniture stripping companies, two were invited to participate, but declined. Thus, criteria for inclusion were that a company had used or was using methylene chloride in an industrial process at the time of the study, and they agreed to participate in a scientific study and provide access and information as necessary to that study. Project resources limited the study to four cases, but we achieved our sampling goal of including representation of at least one prospective case (a company still using methylene chloride at the time of the study) as well as four diverse industrial sectors (metal finishing, electrical equipment manufacture, rubber products manufacture and vessel cleaning services).

The study protocol used to build the case studies involved site visits, telephone and in-person interviews and review of company-provided and public documentation. Data source triangulation, or the use of multiple data sources to provide more than one perspective on the phenomenon under investigation, was used to enhance the depth of information about each case and internal validity.[22] For example, for two cases we were able to access the documentation provided to the Toxic Use Reduction Institute as part of the companies' participation in the Institute's Demonstration Site

program and compare the reporting of process and motivational factors between the program documentation and that provided to us in interviews. The bulk of the qualitative data was collected in in-depth interviews with key informants where the investigator used a semi-structured, open-ended interview guide for all four companies.[23] These interviews were designed to capture informants' perspectives on the motivations, processes, and impacts related to their source reduction experience. Each interview was followed by a guided tour of the industrial process that had used methylene chloride. This tour or "site visit" allowed for additional informal questioning about the process. As an additional validation step for the most complex case—that of the metal finishing company—we confirmed the investigators' findings and interpretations via a review of the written case by the president of the company.

CR conducted all the interviews and site visits and interviews notes were taken by hand. A description of the surface cleaning test methods and methylene chloride exposure assessment methods utilized in the metal finishing company case are available upon request. Institutional Review Board approval for research involving human subjects was sought and achieved for this study and all participants signed informed consent forms.

The components of the toxics use reduction implementation strategy—options identification, options assessment, implementation and evaluation—guided the design of the prospective intervention study and the evaluation of the retrospective cases. Intra-case analysis proceeded in two steps: first, data was categorized into each of the following analytic categories: description of the industrial processes involved; the

source reduction approach and the steps each company took to accomplish the change; the company's motivations for the change; and the technical, environmental, health and safety and financial assessment of the change, and second, the investigators ascertained key lessons, or salient findings, from each case. Cross-case analysis included the summary of findings by analytic categories and the culling of salient commonalities, differences, and findings perceived as useful for further study and/or recommended implementation.

Case studies are widely used in the environmental field to describe and promote pollution prevention approaches (see for example <http://www.p2gems.org>). Pollution prevention case studies are usually descriptive, focused on technical details, and written to persuade readers of the value of the approach for that application. Case studies are also a particular mode of social science investigation that is especially appropriate to intervention research. In *Case Study Research: Design and Methods*, Yin notes that case studies “are the preferred strategy when ‘how’ or ‘why’ questions are being posed, when the investigator has little control over events, and when the focus is on a contemporary phenomenon within some real-life context.”[24] Additionally, case studies are especially useful when context is key to understanding a particular phenomenon and we deem it useful to understand that phenomenon—in this case source reduction for hazard prevention—through its embodiment in particular cases.[25] The case studies in this paper combine the pollution prevention and social science case study models by providing descriptive, technical details and systematic analysis of each context-laden case.

Results

Four Massachusetts companies' experiences of methylene chloride source reduction are profiled below. The first case, compiled from three site visits, company-provided documentation, and two in-person in-depth interviews, describes a prospective study of a metal finishing company's efforts to reduce methylene chloride use over two years. The next three cases are "retrospective"; they describe the experiences of three companies (a rubber products company, an electrical equipment manufacturer and a vessel cleaning company) that had already eliminated use of methylene chloride at the time of the study. Each retrospective case was compiled from one in-person interview and site visit plus additional sources including follow-up telephone conversations to clarify observations from the in-person visits, public documentation of processes and company-provided documentation. Two of the companies were participants in the Toxics Use Reduction Institute's Demonstration Sites program and CR attended those companies' "open-house" events related to that program.

Metal Finishing Company

Background: This metal finishing company performs copper, chrome and nickel plating on aluminum, brass and steel fabricated parts on a job-ordered basis. Seventy percent of the company's business comes from a motorcycle manufacturer. The company employs 60 production workers over three shifts.

Process and Source Reduction: All parts must be thoroughly cleaned before they can be plated. Lightly soiled parts are cleaned in-line (as part of the plating line) using acid and alkaline water-based cleaning processes. Some types of materials, particularly small parts, convoluted parts or parts coated with heavy protective oils,

were cleaned in a methylene chloride vapor degreaser before they entered the plating line. The company selected methylene chloride because of its relatively high vapor pressure (requiring less heating to enter the vapor phase) and because it was less flammable than other degreasing solvents. In the early 1990's, in response to the Clean Air Act requirements, and in order to decrease the volume of methylene chloride used to below the state and federal reporting threshold of 10,000 lb/y, the degreaser's refrigerated coils were refurbished and work practices were introduced to reduce emissions. These work practices included using the cooling coils beyond the time when the degreaser was being used, weekly monitoring of the coils, covering the degreaser when not in use, and lowering hoist speed to eight and a half feet per minute to reduce vapor drag-out. The unit is not fitted with local exhaust ventilation.

Total methylene chloride use declined by 82% between 1996 and 2002 at this company. Three factors have accounted for this dramatic reduction: improved controls on the degreaser that prevented losses and therefore conserved new use; the loss of two regular plating orders that included parts that consistently "required" methylene chloride degreasing; and source reduction process changes undertaken in conjunction with this study. In agreeing to work with the investigators to further reduce the company's use of methylene chloride, the company president reported that he was motivated by environmental regulations (Clean Air Act restrictions and Massachusetts Toxics Use Reduction Act reporting requirements), worker health concerns, and the opportunity to improve the overall efficiency of the plating process by moving cleaning operations "in-line" with the other plating operations, thereby reducing labor costs and other production inefficiencies.

During the “options identification” phase of this prospective source reduction study, the investigator and the company president determined that aqueous cleaning might be an acceptable alternative to methylene chloride cleaning because aqueous cleaning was a proven technology that was frequently used in place of vapor degreasing in other metal finishing companies. Additionally, the company had experience with aqueous cleaning in other applications and anticipated that hydrocarbon-based substitute degreasers would pose greater potential toxicity and environmental problems. Much of the work was already being cleaned aqueously in-line, and, as reported above, the company was eager to shift more of the work in-line. The barrier to doing so was inadequate aqueous cleaning effectiveness, thus “requiring” methylene chloride degreasing as a pre-cleaner.

In order to find the best-performing cleaner for the company’s applications, the investigators requested that the company submit parts for a series of test cleanings at the Toxics Use Reduction Institute’s Surface Cleaning Laboratory. Following the laboratory studies, experimental cleaning runs were conducted at the company to determine the feasibility of cleaning more of the parts in-line (aqueously with the new chemistry) thereby avoiding the methylene chloride degreasing pre-cleaning step. The company president determined that these trials were successful and quickly introduced the better performing substitute to one of the production lines. He then purchased a new pre-cleaning tank and began using the new cleaner on the two remaining plating lines. These actions significantly reduced the use of the methylene chloride degreaser; most of the work pieces were no longer diverted to solvent pre-cleaning.

Subsequent steps were consultation with the company's chemical supplier for a less expensive "generic" version of the new cleaner and tests of this cleaner, and determination of bath maintenance schedules. The company also consulted with their hazardous waste hauler to determine any potential additional costs for treatment of wastewater associated with this process. These costs were determined to be acceptable. The company president deemed the substitution of the better performing, less-expensive substitute chemistry successful. At the conclusion of the study, 70% of the work formerly degreased with methylene chloride was cleaned with water and an alkaline cleaner. In 1999, at the beginning of this study, the company operated the methylene chloride degreaser up to four hours a day, five days a week for a total of 20 hours a week. At the conclusion of the study two years later, it was used twice a week for a total of eight hours a week. No additional steps are planned to further reduce use of the methylene chloride degreaser.

Technical, environmental, health and safety and financial assessment: Technical and performance criteria dominated the company's process for determining the acceptability of the substitute. Because the aqueous cleaners had few reported health or safety hazards, especially in their diluted form, Material Safety Data Sheets were the only resources consulted by the company to gain information about potential environmental, health or safety concerns. Project staff undertook a more thorough investigation, but did not discover any concerns that would lead us to recommend that the company avoid certain products or processes associated with the new chemistry. Additionally, financial concerns did not figure prominently in the evaluation of the alternatives; the company president did not express concern about costs within the scope of the proposed project, except to find a less expensive version of our

recommended cleaner. However, financial concerns appeared to play a role in the company's decision to continue use of the degreaser on a limited basis rather than invest in alternative technology for the remaining work that could not be cleaned in-line with the substitute.

Workers are potentially over-exposed to methylene chloride (compared to the OSHA Permissible Exposure Limit of 25 ppm) when operating or maintaining the degreaser. Prior to the shifting of the majority of the work to aqueous cleaning, we conducted one day of exposure monitoring following the OSHA sampling method for methylene chloride (<http://www.osha-slc.gov/dts/sltc/methods/organic/org080/org080.html>). The estimated time-weighted eight-hour exposure for the operator was 71 ppm. In shifting much of the pre-cleaning work to in-line aqueous cleaning, the company greatly reduced potential worker exposure to methylene chloride. Workers potentially may still be exposed to methylene chloride while operating the degreaser, but the reduced schedule of use means that they are less likely to be over-exposed compared to the Permissible Exposure Limit.

What about the workers' potential exposure to the new aqueous cleaner? The company selected an alkaline liquid cleaner based on sodium metasilicate (14%). Other ingredients include diethylene glycol n-butyl ether (5%) and sodium carbonate (2%). It is used at a 10% dilution. Because of its alkalinity, repeated exposure to this undiluted alkaline cleaner could have health effects including skin, eye and respiratory irritation and burning. However, workers are unlikely to have any more than brief exposure to the chemical in its undiluted form. In its dilute form, the pH of the solution would be slightly less caustic than the concentrate, but still would be

potentially hazardous as an irritant. Workers wear chemical resistant gloves and eye protection when handling the chemical and, while they may breathe in the water vapor above the heated tanks, they are unlikely to inhale the chemical. However, no monitoring has been conducted to determine the pH of this vapor. The company president said that workers had not complained about irritation. The potential hazards associated with the use of the substitute chemical include acute irritation and burns from accidental exposure due to spills or splashes. It is not expected that routine exposure under the conditions described would result in potential long-term irritation or other health effects.

Rubber Products Company

Background: This rubber products company employs as many as 1,100 people over three shifts and makes over 3,000 rubber specialty products including windshield wipers, copier toner blades, golf grips and respirator face pieces. Their manufacturing processes utilize 4,000 different chemicals, 30 of which are used in large quantities. Processes include mixing and curing of rubber, spray coating, tumbling, forming and adhesion of rubber and metal parts.

Since 1990, the company has undertaken several projects to reduce or eliminate organic solvent use, improve material dispensing, reduce toxicity of inks, recycle, and conserve water and electricity. The Director of Environmental Health and Safety has championed these projects as well as an overall system of reducing environmental impact through their ISO 14,000 program, life cycle analysis and Design for the Environment initiatives. These projects are popular at the company, in part, because

they save an estimated \$2 million a year. The company is recognized as an environmental leader.

Process and Source Reduction: Between 1990 and 1991, the company phased methylene chloride out of their urethane mixing vessel and tool cleaning operations and phased in two drop-in substitutes: dibasic esters and polyethylene glycol. In the urethane mixing vessel operation, following the automated mixing and discharge of the urethane into a bucket, the system is automatically purged with a solvent. This solvent was methylene chloride; the company introduced dibasic esters as a substitute. While the operator is pouring the hot urethane from a bucket onto a forming belt, about 16 ounces of dibasic esters are forced through the system and into a waiting bucket. The urethane is heated to 200° F. Thus, the dibasic esters are emitted mostly as liquid, but also potentially as a component of a visible vapor resulting from contact of the liquid with the urethane-heated equipment. About three batches are run per hour.

In the change from methylene chloride to dibasic esters, the total volume of the solvent used was decreased through the rescheduling of batch jobs to reduce the vessel cleaning frequency and through the use of disposable and non-stick vessels that were cleaned mechanically (wiping and scraping) rather than chemically. The company also used a vacuum distillation system to reuse the dibasic esters and the company now purchases less than 1,000 gal/yr. This compares to the approximately 5,700 gal/yr of methylene chloride that the company purchased when it used the chemical.

In a second operation, mixing tools used to make urethane are soaked or agitated in buckets of dibasic esters (instead of methylene chloride) and then soaked and rinsed in a tank of hot polyethylene glycol. The company is investigating the substitution of liquid sodium chloride (salt) as a cleaning agent in place of the dibasic esters/polyethylene glycol process to further the company's goals of toxics use reduction and cost savings.

Methylene chloride was targeted in the context of an aggressive pollution prevention program in this environmentally-conscious company. The company's motivations include creating a positive image with customers, limiting liability, improving compliance with regulations, lowering insurance and accident costs, improving the company's image with employees and thereby increasing loyalty, furthering good community and employee relations, reducing waste and, most importantly, saving money. Methylene chloride was eliminated, in part, because of worker health concerns and, in part, because of its classification as a Hazardous Air Pollutant under the Clean Air Act. Additionally, the Environmental Health and Safety Director described the loss of methylene chloride to the environment (as much as 20 t/y) as "money up the stack."

Technical, environmental, health and safety and financial assessment: The company identified two potential drop-in substitutes for methylene chloride. It selected dibasic esters over n-methyl pyrrolidone because of superior technical effectiveness. The change was evaluated in a company-designed process that looked at perceived environmental and worker health and safety impact and costs. Dibasic esters were determined to be acceptable from the environmental and health and safety perspective

because they are also found in consumer products. The Environmental Health and Safety Director commented: “If this is good for a consumer product, it should be good for our employees working with it as well.” He suggested that there were few choices by the end of a technical and initial environmental assessment process. Dibasic esters were ultimately selected because they performed better than n-methyl pyrrolidone and were deemed “safer.”

Methylene chloride exposure study results were not available, but according to the company, measured methylene chloride exposure levels were “an order of magnitude below the standard,” which at the time would have been a Permissible Exposure Limit of 500 ppm. However, had workers continued to use methylene chloride to clean tools and to perform the vessel cleaning tasks, they would potentially have been exposed above the new Permissible Exposure Limit of 25 ppm. The vessel mixing and discharge rooms were relatively small, enclosed spaces and were noticeably elevated in temperature. These conditions, combined with the discharge of solvent at elevated temperature following its trip through the hot equipment, would have created the potential for over-exposure. This exposure would have been mitigated by the slot ventilation on the equipment at the point where the chemicals enter the bucket. However, other tasks with potential for high exposure were uncontrolled, such as pouring solvent into the system and pouring the used chemical into the recycling or waste containers. In the cleaning operations, the largely manual, uncontrolled processes, including pouring, stirring, mechanical cleaning, and emptying contaminated methylene chloride into either waste containers or the recycling distillation unit, would have contributed to potential over-exposure.

The substitutes have eliminated workers' exposure to methylene chloride. The introduction of substitutes with extremely low volatility has also reduced the potential for inhalation of the substitute solvent in these tasks. The initiatives undertaken to minimize the use of dibasic esters, e.g. introducing non-stick buckets, also benefited workers by lessening their potential exposure, especially skin exposure. Some manual handling tasks persist post-process change including cleaning tools and equipment and pouring used dibasic esters into the distillation unit. Workers were observed to be wearing cotton gloves. Workers were concerned that substitutes would make their jobs more difficult, but were satisfied with the change ultimately. The operator said that methylene chloride had caused skin and eye irritation (dibasic esters did not) and he was relieved to not have to worry as much about the consequences of accidental splashes.

Following the substitution, the Environmental Health and Safety Director conducted air sampling for dibasic esters in response to requests from state environmental authorities. He was not successful in monitoring the substance with an organic solvent sampling method and concluded that due to the low volatility of dibasic esters, that there was no significant air contamination. Additionally, he did an evaporation study and found that after a week, a beaker containing dibasic esters had no significant change in weight. Thus, losses in dibasic esters are largely unexplained, but may be due to spills, binding with the urethane, and/or vaporization of the product at high temperatures. Exposure to dibasic esters is not considered to be a hazard by the company. Because there is no OSHA Permissible Exposure Limit, the manufacturer of the product provided a guideline occupational exposure limit to the company upon

request and the company believes that occupational exposure to dibasic esters is well within this guideline.

Current knowledge of dibasic esters' occupational health effects would suggest that it is considerably less harmful to workers than methylene chloride. However, dibasic esters are potentially hazardous chemicals and can cause skin, eye and respiratory tract irritation. They are absorbed through the skin and prolonged exposure can cause blurry vision (dibasic esters are metabolized to formic acid). According to the Material Safety Data Sheets for polyethylene glycol, there are little or no health effects associated with exposure to the chemical. The American Industrial Hygiene Association has established a Workplace Environmental Exposure Level of 10 mg/m^3 , 8-hour, TWA for polyethylene glycol.[26] The very low vapor pressure of dibasic esters and polyethylene glycol would mitigate against inhalation.

The costs of hazardous waste disposal, raw material, and compliance related activities, were a major motivation for the elimination of methylene chloride. Dibasic esters are more expensive than methylene chloride, but a considerably lower volume of chemical is purchased due to the process changes described above and the lower volatility of the chemical. The equipment expenditures that were required during the substitution were the remanufacture of equipment O-rings that were destroyed during technical evaluation of the substitute and some new mixing tools. The new mixing tools were estimated to have cost "a couple thousand dollars." The company manufactured the new O-rings themselves. The distillation equipment had been purchased for methylene chloride recycling. All potential methylene chloride compliance-related costs were avoided. While a complete financial assessment has

not been performed by the company, the company believed that considerable savings had been generated by the project.

Electrical Equipment Manufacturer

Background: The third case is that of a company that makes electrical and electronic capacitors for original equipment manufacturers, white good manufacturers, lighting manufacturers, telecommunications and other light manufacturing companies. The company was founded in 1923. Due to environmental contamination, the company entered into a consent agreement with the EPA to mothball its plant and relocated in 2001 to a new, purpose-built facility. The company has 285 manufacturing employees over three shifts and 100 support staff.

In 2000, the company eliminated the position of Environmental Health and Safety Manager and instead moved health and safety functions to the human resources department and environmental functions became part of the facility manager's responsibilities. The company's worker/management health and safety committee has responsibility for health and safety management. Additionally, the company hires environmental and industrial hygiene consultants for specific needs. Currently, there is no Toxic Use Reduction Planning Committee, although one operated and was very active during the tenure of the former Environmental Health and Safety Manager.

Processes and Source Reduction: This company replaced methylene chloride in two processes. In the first, n-methyl pyrrolidone was a drop-in substitution for methylene chloride as an equipment cleaner. N-methyl pyrrolidone was identified as a potential

substitute by their chemical supplier. Similar to the operation described above in the rubber products company, a solvent is used to purge equipment after the equipment completes a batch coating of small capacitors with an epoxy coating. Isopropyl alcohol is preferentially used as a clean-up solvent, but n-methyl pyrrolidone is now also used (as methylene chloride was) as a general clean-up solvent for tools and equipment. N-methyl pyrrolidone is received in drums and decanted into solvent safety cans, squirt bottles and paper cups.

Methylene chloride also had been used to dilute an adhesive used to seal the covers onto capacitor units. The adhesive also contained some methylene chloride. This process has always been a partially automated one: most covers can be automatically sprayed with adhesive, but in some cases, workers had to manually apply the thin layer of adhesive using a small oil can applicator. In both cases, workers manually mixed methylene chloride with adhesive for application. The company contacted the manufacturer of adhesive for information about what substitute materials would work with their product. The company suggested a material based on dichlorofluoroethane, also known as Freon 141b. It is a hydrochlorofluorocarbon and is one of the principal drop-in substitutes for the banned chlorofluorocarbons. The company began purchasing this chemical as a drop-in substitute for methylene chloride.

Over the two-year process to eliminate methylene chloride from this operation, the adhesive manufacturer also eliminated methylene chloride from the adhesive by substituting aromatic hydrocarbons (xylene). Additionally, the company made equipment changes that increased the amount of this work that could be automated and reduced the requirement for diluting the adhesive for automated operations. Thus,

the Freon is currently only used for manual operations, which are a small part of the process. Under pressure of the scheduled phase out of the chemical under the Clean Air Act, the company was looking for ways to change their equipment to eliminate the need for a diluent in manual application of the sealant.

Elimination of methylene chloride was motivated by the toxics use reduction planning required by Toxics Use Reduction Act and interest in a positive environmental image. There was no apparent health and safety motivation for the reduction of use; planning and program activities for reduction and elimination of methylene chloride occurred in 1997 prior to the new standard. Methylene chloride was eliminated from operations in 1999.

Technical, environmental, health and safety and financial assessment: Evaluation consisted primarily of assessing the technical performance of the substitutes. The company assumed that substitutes recommended by chemical suppliers would be acceptable from an environmental and health and safety perspective. Material Safety Data Sheets were reviewed by the former Environmental Health and Safety Manager, but not by the health and safety committee. There was no other apparent evaluation to gauge impact on the production process, environment or health or safety conditions of the change. Costs and benefits were not assessed.

Workers are no longer exposed to methylene chloride at this company. No methylene chloride exposure records were available and the facility manager did not think that any exposure monitoring had ever been done. Given methylene chloride's high volatility and the mostly uncontrolled nature of the operations using methylene

chloride, the old process would probably have resulted in over-exposure. In the cleaning operation, other than decreased exposure due to reduced volatility of n-methyl pyrrolidone, exposure potential remained the same as it had been when workers were using methylene chloride for equipment purging and general clean up. Both tasks are uncontrolled manual processes and there is the potential for skin exposure from splashes and sprays and inhalation exposure due to vaporization of bulk chemical from open containers. Work practices included throwing 20 ounce paper containers full of contaminated n-methyl pyrrolidone into an open garbage container.

N-methyl pyrrolidone exposure can cause acute and chronic health effects in workers. (The U.S. Air Force has determined that it is not a potential substitute for methylene chloride because of both potential worker health and performance concerns.[27]) It is an eye and skin irritant, has a noxious odor and it has been found to cause fetal death and fetal abnormalities in rat studies.[28] N-methyl pyrrolidone's vapor pressure at room temperature is very low, thus minimizing the chance of exposure by inhalation. However, skin adsorption is thought to be the main route of exposure. During the site visit, a worker doing the purging and cleaning operation was asked what he thought of the change. He noted that n-methyl pyrrolidone was more irritating to the skin than methylene chloride.

In the sealant operation, the mixing of the sealant had occurred without local exhaust ventilation, although the manual and automatic application work area was equipped with local exhaust ventilation. The potential for methylene chloride exposure during mixing and decanting operations probably had been quite significant. The mixing

area, which was adjacent to the process, was uncontrolled and very messy. Additionally, the work area/conveyer belt was also covered in the red sealant material. The process was not in operation during the site visit, so current work practices were not observed. The operator's chemical resistant gloves were sitting partially turned inside out on top of the machine. After the process changes, manual operations were performed far less often than they had when methylene chloride was used.

Freon 141b is quite volatile and can cause the health effects of organic solvents, plus the health effects of chlorofluorocarbons: cardiac arrhythmia. Because, in both cases, the operations were essentially unchanged from the previous ones that used methylene chloride, there was no apparent impact on noise, ergonomics or safety. It is possible that manual material handling was decreased due to the decreased volume of chemical used; barrel loading and decanting tasks became less frequent with the new chemicals.

No financial accounting of the old process or the new one was undertaken as part of the change. The facility manager noted that n-methyl pyrrolidone and the Freon 141b-based chemistry were both more expensive than methylene chloride. N-methyl pyrrolidone is estimated to be almost four times as expensive as methylene chloride on a per gallon basis. However, due to the equipment and process changes, and n-methyl pyrrolidone's lower volatility, much less of the new chemicals are used compared with methylene chloride. According to the facility manager, the proposed investment in equipment changes to facilitate the sealant project required justification ("a song and dance") to the financial managers. The company ordinarily requires an 18-month payback on capital investments (i.e., recover the cost of the investment through savings or increased revenues within 18 months) and this project was

presented as an additional cost without monetized benefits. As a result, the project was approved on environmental grounds rather than financial ones. The production manager perceived non-quantified financial benefits of the change, including increased efficiency and flexibility and reduced environmental compliance requirements.

Vessel Cleaning

Background: This vessel cleaning company employs 12 workers over two shifts and does \$1 million in business a year cleaning the inside and outside of tanker trucks and 300-gallon chemical totes. Many of the employees had worked for the company for many years and, like other small companies, management will sometimes also do the required work. The company management has experience in hazardous waste management. Common contaminants cleaned from the tanks and totes include flocculating agents for water treatment, latex, formaldehyde, acids and bases, coatings, paper industry chemicals and adhesives.

OSHA's Preamble to the methylene chloride standard noted that engineering controls, such as local exhaust ventilation were likely to be infeasible to control methylene chloride exposure below the Permissible Exposure Limit in vessel cleaning[14] The Preamble states that respiratory protection equipment has been used in the past in vessel cleaning and it expected that it would be relied upon under this standard.

Process and Source Reduction: In the usual cleaning process, workers first used hot and cold water under pressure to clean the outside and inside of the tank or tote. A

caustic sodium metasilicate-based detergent solution was then sprayed followed by a steam cleaning designed to remove solvents. As necessary, the workers would also manually scrape out dried contaminant—a process that required a confined space entry permit.

Of particular concern to the company was the process required to clean an adhesive used in the automotive industry from chemical totes. Prior to the process change described below, the workers cleaned the inside of these totes with methylene chloride and manual scraping. The cleaning process for this contaminant involved a worker pouring two gallons of methylene chloride into a tote, tipping and rolling it, releasing the lid to “degassify” it (as the manager explained it), getting into the tote and scraping for eight hours a day for three days. The workers also used methylene chloride to clean the outside of the totes.

The company management consulted the Toxics Use Reduction Institute’s Surface Cleaning Laboratory and initially selected a very effective substitute cleaner based on n-methyl pyrrolidone and dibasic esters. This change reduced the hazardous waste cost from \$250 to \$70/tote, but the cleaning process still took several days. The company also considered sand blasting, but determined that it would be too harsh on the totes. Following the receipt of a \$10,200 Toxics Use Reduction Institute Demonstration Grant, the company moved to a “baking soda blast” process where a small amount of water is mixed with baking soda (to suppress dust) and the worker directs the spray through a nozzle. The task now takes two workers one day to do each tote. For the task of cleaning the outside of totes, the workers now use high-pressure water instead of methylene chloride.

The company began to look into alternatives out of concern over the volume of hazardous waste produced by this cleaning operation and methylene chloride's toxicity. Additionally, the company was looking for a faster, less labor-intensive work method. This became especially important after the company got a large contract for this work at a time when the company lost a significant portion of other work. The introduction of the 1997 OSHA standard for methylene chloride also provided a significant incentive for this change. The manager said he thought that the cost to comply with the new standard would be very expensive, especially the cost of the supplied air respirator (air-purifying respirators are not permitted for methylene chloride exposure prevention due to high breakthrough volume and limited warning properties). An additional factor that not only motivated, but also assisted with the change, was a demonstration project grant from the Toxics Use Reduction Institute that defrayed the cost of the change and was accompanied by technical assistance. The free services of the Surface Cleaning Laboratory were utilized to find substitute chemistries.

Technical, environmental, health and safety and financial assessment: As in the other cases, technical performance concerns dominated the company's evaluation efforts.

Unlike the other cases, worker chemical exposure to methylene chloride was a central concern and this change eliminated a very serious potential methylene chloride exposure. In the old process, workers were at risk of acute over-exposure from working in a confined space with this highly volatile and toxic chemical. The new process greatly minimized the toxicity of the chemical exposure in this process, but introduced new physical hazards including noise and ergonomic stress, such as

awkward postures and forceful exertions from carrying and directing the nozzle.

Thumb pressure on the nozzle is a particular ergonomic concern. Management has told workers to rest and to “alternate fingers” to reduce the risk of injury.

Noise from the new blasting equipment was not measured, but was perceived by the investigator to be potentially hazardous. Reportedly, the sales representative told management, with regard potential concerns about the noise levels of the equipment, “they’ll get used to the noise.” The baking soda is a mild respiratory irritant and for that reason, the workers wear dust masks. Additionally, they use woven gloves, hearing protection, Tyvek or cotton uniforms, safety glasses and boots. Four to six hours of this work is very hard but, according to management, the workers are much happier with the current process than they were when working with methylene chloride—a process that involved forceful manual scraping in awkward postures for days at a time.

The company estimated cost savings of \$910/tote over the old process—a savings of 74%. The manager specifically mentioned avoidance of OSHA compliance costs, especially the cost of the respirator, as a motivation behind the project. Other cost benefits included the ability to take on more of this work without expanding the labor force, and faster turnover of the work. The company’s costs of the project were minimized by the Toxics Use Reduction Institute’s grant and the savings gained from finding a used compressor. Management describes the costs of the new process, with the exception of the purchase cost of the compressor, as minor.

Discussion

Summary of source reduction process changes: Out of seven processes using methylene chloride in these four companies, two were adhesive thinning operations and five were cleaning operations. Three companies eliminated methylene chloride and one significantly reduced its use of methylene chloride. In three processes, commercially-available “drop-in” substitutes were used with little production process modification, but four process changes required some equipment or production process modification—in one case the entire process was replaced. Two process changes involved using mechanical cleaning in conjunction with new chemical substitutes. Some of the source reduction process change initiatives took advantage of the normal cycles of change in industry facilitated by increasing and decreasing demand for products and services. A loss of orders enabled one company to use less methylene chloride, while an increase in orders prompted another to seek out an alternative to methylene chloride. Two companies continue to look for substitutes for their original substitutes—one, because of environmental concerns of the substitute and, the other, to lower costs.

The three companies that eliminated methylene chloride use did not first attempt to control worker and environmental exposure with engineering controls, but looked for substitutes directly. The company that continued to use methylene chloride implemented controls required by environmental regulations—and not the OSHA recommended controls, which, if implemented, might have conflicted with environmental protection. Despite taking steps, including significant expenditures, to control methylene chloride emissions, the company was still motivated to further reduce or eliminate use of the chemical. Three of the companies relied on their

chemical suppliers for advice about safer substitutes. Two utilized technical assistance and Surface Cleaning Laboratory services of the Toxics Use Reduction Institute.

Companies were strongly motivated by environmental compliance and goals.

Specifically, they sought to improve compliance with the Clean Air Act, reduce their reporting under the Toxics Use Reduction Act, and reduce hazardous waste. Worker health concerns, including compliance with the new OSHA standard, were a partial motivating factor in three cases. Improving production efficiency was the major motivation in two cases. In a third case, the costs of using a volatile chemical such as methylene chloride also motivated the changes.

Summary of technical, environmental, health and safety and financial assessment:

Companies' evaluation efforts focused on technical performance concerns. However, potential substitute chemistries with obvious environmental problems were not evaluated to see if they would work. Financial, environmental and worker health evaluations of substitutes were minimal.

Three companies completely eliminated exposure to methylene chloride in routine and non-routine operations. The fourth significantly reduced over-exposure potential by reducing the duration of potential exposure. Based on available information, the substitute chemistries and processes appear to be less toxic and less hazardous in use than methylene chloride (see Table 2). Process changes and the physical properties of the new chemistries reduced potential exposure through reduction in quantity of total chemical used, lower volatility, and increased automation. In three cases, the principal potential hazard of the substitutes is acute eye, skin and/or respiratory irritation.

One company selected potentially hazardous substitute chemistries: one a potential reproductive hazard with potential for exposure through skin adsorption, the other an ozone-depleter and a potential cardiovascular toxin. However, in the later case, the total quantities used and potential for exposure in this operation were minimal. In one company, potential ergonomic hazards of the old process using methylene chloride were eliminated with methylene chloride, but the new process introduced new potential ergonomic hazards. A noise hazard was also introduced.

Within general constraints of not wishing to invest large amounts of money in capital equipment, the companies were not especially concerned about potential negative financial impacts of the changes. Only one company conducted a financial analysis of the change. However, the companies did try to economize on the costs of the changes. While the new chemistries cost more than methylene chloride on a volume basis, the lower volatility and improved operations from the source reduction process changes resulted in lower chemical consumption and costs. Two companies anticipated and reaped significant financial benefits from the changes—mainly through improved production efficiency.

Study limitations and strengths: This study used a case study approach to detail issues related to source reduction process change. As such, its conclusions may not be generalizable due to the small sample size and selection bias due to a sampling strategy that selected companies for participation based upon their willingness to participate. Additionally, the findings are largely the result of a single investigator's interpretation of the data and cases. Evaluation is meant to figure as a fundamental

component of the source reduction process. However, the small scope of the project, and restrictions in the amount of time and resources of the participating companies, meant that neither the companies, nor the investigators benefited from ideal systematic financial, technical and environmental, health and safety assessments. Finally, this research focused on one chemical and just a few industrial processes and may or may not apply to other cases, especially those with more specialized processes, or where the hazard in question is a formulated constituent of a company's product and change would require re-engineering of the product itself, rather than of an auxiliary process.

The study strengths include a rich, descriptive case study approach useful in understanding, in detail, source reduction as a hazard control technique, including practical limitations, potential for missed opportunities to improve the work environment, unintended consequences, future directions for preventive approaches, and research needs. The discovery of themes common across these four cases suggests their potential generalizability as categories of analysis. The findings of this study can guide further investigation of the feasibility and effectiveness of source reduction in other applications. Additionally, the investigators believe that the experience of these companies largely comports with the experience of other companies in Massachusetts who had used methylene chloride based upon an investigation of more than twenty such companies.[19]

Conclusions

These cases suggest that source reduction strategies can be a feasible and effective approach to compliance with workplace and environmental standards and reduction of

worker health hazards. In its methylene chloride standard, OSHA had concluded that engineering controls were not feasible for vessel cleaning and this industry would rely on supplied-air respirators for exposure control. We found that for a vessel cleaning company and three other diverse industrial examples, source reduction process changes that eliminated methylene chloride use were not only feasible, but beneficial to production and environmental protection goals.

The experience of these cases also suggests that technical assistance sensitive to both technical and occupational and environmental health concerns could help maximize the benefits of source reduction process change projects. Typically, technical concerns are top-priority and many companies trust that “unlisted” products and products recommended by chemical sales personnel are “safe.” Companies may make sub-optimal choices, from an occupational health and safety or environmental standpoint, with inadequate information about alternatives.

And finally, it appears that source reduction strategies can result in financial benefits, without even considering the reduced costs of regulatory compliance. When companies look at processes, they often try to improve them overall, by reducing the problems they cause (environmental contamination and worker exposure) and innovating production improvements. Financial concerns associated with the change, other than significant capital investments, do not appear to be a major barrier to the utilization of source reduction strategies, especially when the changes are motivated by regulatory compliance.

A recommendation based upon these project findings is that source reduction should be included in the category of potential feasible and effective strategies for compliance with standards and reduction of health hazards. Because companies may miss opportunities to improve processes, both from an environmental, worker health, and production standpoint without adequate technical assistance that comes from non-commercial sources, worker health agencies should devote resources to this task and/or link companies to such resources. Technical assistance programs and small grants and loans can play a positive role in facilitating the innovation that can be realized from source reduction. This may be especially true for small businesses without resources to do extensive research or modeling of alternatives. The Toxics Use Reduction Institute Surface Cleaning Laboratory has played a critical role in assisting Massachusetts firms in finding alternatives and demonstrates a positive model for other states.

Intervention research is needed to find ways of coordinating technical assistance with regulation and compliance activities to maximize efficient and effective dissemination of source reduction strategies. For example, in this study it was found that chemical distribution companies may be a primary and often exclusive source of information on alternatives. Efforts could be targeted to improve the quality of information and services provided to companies through their chemical suppliers.

Competing interests

This project was funded in part by the Toxics Use Reduction Institute at the University of Massachusetts Lowell, which is funded by the fees generated to the Commonwealth of Massachusetts under the provisions of the Toxics Use Reduction Act. ME is the research director of the Toxics Use Reduction Institute.

Authors' contributions

CR designed the project, conducted the research and drafted the manuscript. ME assisted with the design of the project, advised the conduct of the research and read and approved the final manuscript.

Acknowledgements

This project was supported by the National Institute for Occupational Safety and Health Grant No. 1 R03 OH04155-01 and the Toxics Use Reduction Institute Research Fellowship. We would like to thank Drs. David Gute, Kwangseog Ahn, and Elizabeth Barbeau for their assistance and review of this project. Additionally, Jason Marshall of the Toxics Use Reduction Institute's Surface Cleaning Laboratory provided importance assistance. Finally, we would like to thank the four companies and their representatives for opening their doors and sharing their experience. Without their cooperation, this project would not have been possible.

References

1. M Ellenbecker: **Engineering Controls as an Intervention to Reduce Worker Exposure**. *Am. J. Ind. Med* 1996, **29**:303-307.
2. P Filskov, G Goldschmidt, MK Hansen, e al.:**Substitute s for Hazardous Chemicals in the Workplace**. Boca Raton, FL: Lewis Publishers; 1996.

3. U.S. Code of Federal Regulations, **Title 40 (Protection Of Environment) Chapter 133: Pollution Prevention**; 1990.
4. **Massachusetts General Law, Toxics Use Reduction Act Ch. 21I**; 1989.
5. CR Roelofs, R Moure-Eraso, MJ Ellenbecker: **Pollution Prevention and the Work Environment: The Massachusetts Experience**. *App Occup Environ Hyg* 2000, **15**:843-850.
6. AD Brandt: **Industrial Health Engineering**. New York, NY: John Wiley & Sons, Inc.; 1947.
7. CR Roelofs, EM Barbeau, R Moure-Eraso, MJ Ellenbecker: **Prevention Strategies in Industrial Hygiene: A Critical Literature Review**. *Am. Ind. Hyg. Assoc. J* 2003, **64**:62-67.
8. National Institute for Occupational Safety and Health: **National Occupational Exposure Survey Analysis of Management Interview Responses**: DHHS (NIOSH); 1988. [<http://www.cdc.gov/niosh/89-103.html>]
9. A Bracker, et al.: **Industrial hygiene recommendations as interventions**. *Appl. Occup. Environ. Hyg.* 1999, **14**:85-96.
10. Office of Technology Assessment: **Gauging Control Technology and Regulatory Impacts in Occupational Safety and Health: An Appraisal of OSHA's Analytic Approach**: U.S. Congress; 1995. [<http://www.wws.princeton.edu/cgi-bin/byteserv.prl/~ota/disk1/1995/9531/953101.PDF>]
11. U.S. Code of Federal Regulations, **Title 29 (Labor) Chapter 1910.1052: Methylene Chloride**; 1997.
12. International Agency for Research on Cancer: **Dichloromethane (Group 2B) Vol.: 71, p. 251**; 1999. [<http://www-cie.iarc.fr/htdocs/monographs/vol71/004-dichloromethane.html>]
13. U.S. Environmental Protection Agency National Toxicology Program: **10th Report on Carcinogens**; 2002. [<http://ehp.niehs.nih.gov/roc/toc10.html>]
14. U.S. Occupational Safety and Health Administration: **OSHA Preambles: Methylene Chloride V. Health Effects**; 1997. [http://www.osha-slc.gov/pls/oshaweb/owadisp.show_document?p_table=PREAMBLES&p_id=1005]
15. U.S. Environmental Protection Agency: **Methylene Chloride: Technology Transfer Network**; 2002. [<http://www.epa.gov/ttn/atw/hlthef/methylen.html>]
16. J Novak, J Hain: **Furniture Stripping Vapor Inhalation Fatalities: Two Case Studies**. *Appl. Occup. Environ. Hyg* 1990, **5**:843-847.
17. U.S. Occupational Safety and Health Administration: **Methylene Chloride: small entity compliance guide fact sheets**; 1997. [http://www.osha.gov/SLTC/methylenechloride/factsheets/meth_facts.html]
18. U.S. Occupational Safety and Health Administration: **Standards Interpretation and Compliance Letters 07/03/1997 - OSHA's Methylene Chloride Standard**; 1997. [http://131.158.51.236/osha_cd/osha/OshDoc/INTERP~2/I14928~5.HTM]
19. CR Roelofs, MJ Ellenbecker: **Results of the Massachusetts Methylene Chloride End-Users Survey**. *App. Occup. Environ. Hyg.* 2003, **18**:132-137.
20. U.S. Code of Federal Regulations, **Title 40 (Protection Of Environment) Part 61 National Emission Standards For Hazardous Air Pollutants Subpart A--General Provisions Sec. 61.01**; 1990.

21. U.S. Code of Federal Regulations, **Title 40 (Public Health) Chapter 9 and 63 National Emission Standards for Hazardous Air Pollutants: Halogenated Solvent Cleaning**; 1994.
22. P Liamputtong Rice, D Ezzy: **Qualitative Research Methods: A health focus**. South Melbourne, Australia: Oxford University Press; 1999.
23. MQ Patton: **Qualitative Evaluation and Research Methods**. Thousand Oaks, CA: Sage Publishers; 1990.
24. RK Yin: **Case Study Research: design and methods**, 3 edn. Thousand Oaks, CA: Sage Publications; 2003.
25. R Stake: **The Art of Case Study Research**. Newbury Park, NJ: Sage Publications; 1995.
26. American Industrial Hygiene Association: **Emergency Response Planning Guidelines and Workplace Environmental Exposure Level Guides**. Fairfax, VA; 2002.
27. U.S. Department of Defense: **Joint Services Pollution Prevention Opportunity Handbook: Paint Removal Process**; 2002. [http://p2library.nfesc.navy.mil/P2_Opportunity_Handbook/5_9.html]
28. O Ajayi, E Harriman: **N-Methyl Pyrrolidone: Chemical Profile**. Lowell, MA: Toxics Use Reduction Institute; 1996.
29. K Stone, JJ Springer: **Review of Solvent Cleaning in Aerospace Operations and Pollution Prevention Alternatives**. *Environmental Progress* 1995, **14**:261-265.
30. Environment Australia Eco-Efficiency Unit: **Cleaner Production - Methylene Chloride Paint Stripping Process - Intrepid Industries Pty Ltd**; 1997. [<http://www.ea.gov.au/industry/eecp/case-studies/intrepid.html>]
31. K Wolf, M Morris: **Investigation of Technologies to Reduce Emissions of Methylene Chloride from Furniture Stripping Operations**: California Air Resources Board; 2001. [<http://www.arb.ca.gov/research/abstracts/98-334.htm>]
32. U.S. Environmental Protection Agency: **Profile of the Pharmaceutical Industry**; 1997. [http://www.epa.gov/compliance/resources/publications/assistance/sectors/not_ebooks/pharmaceutical.html]
33. JA Shaeiwitz: **Coffee Decaffeination with Supercritical CO₂**: West Virginia University; 1997. [<http://www.nd.edu/~enviro/design/caffeine.pdf>]
34. Office of Technical Assistance: **Case Study No. 45: Crest Foam Eliminates Use of Methylene Chloride in Manufacturing Process**: Commonwealth of Massachusetts, Executive Office of Environmental Affairs; 1997. [<http://www.nben.org/HTMLSrc/Resources/OTAcases/crestfom.html>]
35. U.S. Environmental Protection Agency: **Best Management Practices for Pollution Prevention in the Slabstock and Molded Flexible Polyurethane Foam Industry**; 1996. [<http://www.epa.gov/ORD/NRMRL/Pubs/1996/625R96005.pdf>]
36. Institute for Research and Technical Assistance: **Case Study: Foam Fabricator Serves as Example for Industry**; 1997. [<http://home.earthlink.net/~irta/csadh001.htm>]
37. B Bilkovich: **Re: Foam**: Great Lakes Net: P2Tech Listserve; 1997. [<http://www.great-lakes.net/lists/p2tech/1997-02/msg00156.html>]
38. Research Triangle Institute: **SAGE: Solvent Alternatives Guide**; 2003. [<http://clean.rti.org/>]

39. K Thomas, M Ellenbecker: **Evaluation of Alternatives to Chlorinated Solvents for Metal Cleaning**; U.S. Environmental Protection Agency; 1997. [<http://www.epa.gov/ord/WebPubs/projsum/600sr97032.pdf>]
40. K Thomas, J Laplante, A Buckley: **Guidebook of Part Cleaning Alternatives**. Lowell, MA: Toxics Use Reduction Institute; 1997. [<http://www.state.ma.us/ota/pubs/partsguide.pdf>]
41. M Morris, K Wolf, M Swanson, J Geibig, K Kelly: **Alternative Adhesives Technologies: Foam Furniture and Bedding Industries (A Cleaner Technologies Substitutes Assessment)**: The Center for Clean Products and Clean Technologies and the Institute for Research and Technical Assistance; 2002. [<http://eerc.ra.utk.edu/ccpct/aap1.html>]
42. Pacific Northwest Pollution Prevention Resource Center: **Pollution Prevention Technology Reviews: Manufacturing Adhesives**; 1998. [<http://www.pprc.org/pprc/p2tech/p2tech.html#adhesive>]

Tables

Table 1 - Source Reduction Strategies for Principal Uses of Methylene Chloride

Industrial Activity	Source Reduction Strategy
Paint stripping (Aircraft, Ship, Metal)	Benzyl alcohol-based stripper[29]; Pyrolysis[30] Sodium Bicarbonate Medium, Carbon Dioxide Blasting Operations, Fluidized Bed Paint Stripper, High And Medium Pressure Water Paint Stripping Processes, Plastic Media Blasting (PMB) Paint Stripping, Degreasing And Paint Stripping Using Sponge Blasting, Paint Stripping Using Wheat Starch Blasting, Vacuum Sanding System Paint Stripping Process, Benzyl Alcohol Paint Stripping; N-Methyl Pyrrolidone, Laser Decoating, Waterjet Stripping, FLASHJET Coating Removal Process, UNICARB Supercritical CO ₂ Coating Spray System[27]
Paint stripping (Furniture)	No and low methylene chloride alternative strippers[31]
Pharmaceutical Tablet Coating	Water-based[32]
Caffeine Extraction	Supercritical CO ₂ [33]
Foam (Flexible/Polyurethane)	CO ₂ [34]; Reduced pressure foaming, formic acid[35],[36]
Foam (Rigid)	Self-cleaning piston system[37]
Degreasing and cleaning	Acidic Aqueous Solutions, Alkaline Aqueous Solutions, N-methyl Pyrrolidone, Terpenes, Ethyl Lactate, Surfactants, Neutral Aqueous Solutions, Petroleum Distillates, Dibasic Esters, Glycol Ethers, Pure Water, Acetone, Alcohol, Ultrasonics, Low Pressure Spray, Power Washer, Semiaqueous Cleaning, Steam, CO ₂ Snow, Abrasives, Immersion Cleaning, CO ₂ Pellets, Brushing, Megasonics, High Pressure Spray, Wiping, Plasma, Supercritical CO ₂ , Bicarbonate of Soda Stripping, Carbon Dioxide, Ice, Laser Ablation, Metal Media, Organic Media, Plastic Media Blasting, UV/Ozone Cleaning, Wheat Starch, Xenon Flash Lamp[38],[39],[40]
Adhesives	Water-based, Hot-melt, Radiant-Cured [41],[42]

Table 2 - Hazard Comparison: Methylene Chloride and Study Substitutes

	Physical Data	Acute Health	Chronic Health	Safety, Physical & Ergonomic	Environmental
Methylene Chloride	Highly volatile, low odor threshold	Central nervous system suppression: headache, dizziness, nausea; dermatitis	Suspect carcinogen, heart problems, liver damage	None observed	Chlorine persistence, Hazardous Air Pollutant; hazardous waste
Alkaline Cleaner	pH: 13-14. Packaged as liquid concentrate	Caustic irritation, Respiratory, skin, eyes	Skin defatting, tissue damage.	Electrical/hot water	Alkaline wastewater, oil and soil waste
N-Methyl Pyrrolidone	Low volatility	Moderate eye and skin irritant	Reproductive toxin: fetal death and abnormalities in second generation of exposed female and male rats. Dermatitis.	None	Hazardous waste, Toxics Release Inventory reporting
Freon 141b	High volatility	Skin and eye irritant. Central nervous system suppression: headache, dizziness, nausea; loss of concentration. Cardiac arrhythmia.	Cardiac arrhythmia; risk of heart attack.	None	Ozone-depleting HCFC (use banned as of 2003); hazardous waste
Dibasic Esters	Low volatility at room temp.; used in heated process.	Respiratory, skin, eyes irritation; blurry vision	None reported	None expected	Moderately toxic to aquatic life
Propylene Glycol	Low volatility at room temp.; used in heated process.	Respiratory and eye irritation at high temperatures	None reported	None expected	None reported
Baking Soda Blast	Slightly basic. Fine powder.	None reported on Material Safety Data Sheets. Probably a mild respiratory irritant.	None reported	Electrical/hot water, noise, physiological load, awkward posture, force, vibration	Non-toxic

Source: Material Safety Data Sheets and NIOSH Pocket Guide to Chemical Hazards, Jan. 2003