

EXPOSURE ASSESSMENT and SAMPLING PLENARY SESSION

Part I: Sampling Methodology

Session Arranger / Moderator:

TAI L. CHAN, PhD, CIH, Mgr. Occup. Health & Safety Research, General Motors Corporation

Discussants:

DENNIS O'BRIEN, PhD, CIH, Chief, Engineering Control Branch, NIOSH

THOMAS J. SMITH, PhD, CIH, Professor, Harvard School of Public Health

JAMES H. VINCENT, PhD, ScD, Professor, Univ. of Minnesota; Editor, Journal of Aerosol Science

Technical Presenters:

THOMAS C. PEDERSON, PhD, Senior Staff Research Scientist, General Motors Corporation

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HOWARD J. COHEN, PhD, CIH, University of New Haven; Editor, AIHA Journal

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TAI L. CHAN, PhD, CIH, General Motors

Mr. DAVID FELINSKI; AAMA: Good morning. I know we have a number of new people here today, so welcome to the Metalworking Fluids Symposium. And now, I'd like to introduce today's Session Arranger.

Tai L. Chan received his Bachelors of Chemical Engineering from The Cooper Union in 1970, his Masters in Chemical Engineering from The City University of New York in 1972, and his Ph.D. in Environmental Health Sciences from New York University in 1978. He is also a certified industrial hygienist.

Dr. Chan joined General Motors Research Laboratories in 1977 in the Biomedical Science Department, and is currently program manager of occupational health and safety research in the General Motors R&D Center. He is a member of the NIH study section in Safety and Occupational Health, an editorial board member of the American Industrial Hygiene Association Journal, and also the president of the American Association for Aerosol Research.

Dr. Chan's research publications included particle deposition in the human respiratory tract, lung clearance of inhaled diesel exhaust particles, paint overspray aerosols, airbag aerosols, metalworking fluid aerosols, and hazards from emerging manufacturing technologies.

Dr. Chan, the Session is yours.

Dr. TAI CHAN: Thank you David, and good morning. He could have introduced me as the 'dust man,' because that is what I do. I

welcome all of you here. We come from different organizations, different backgrounds, and it's important that we all work together. We may have our own agenda, but we need to work together as Health and Safety professionals. We are here to serve the American worker, and what we do is going to count in the occupational environment, and we need to remember that. We have had two days of excellent critical review and today, we are getting to the main agenda - assessment and control. In Detroit, this is where 'the rubber meets the road.' Today, this morning's Session is going to focus on sampling methodology. We will start out with assessing the contaminants in the fluids, we will then move into the air component by looking at some of the vapor contaminants, and then focus on the aerosol sampling aspects. Then in the afternoon, we are going to focus on the so-called biologicals, on the bioaerosol samplers, the technology, and also the intricate details in terms of the bacterial components and endotoxins. And in the evening, we have a Poster Session. There will be nineteen very excellent posters tonight. So let's get started. The first speaker this morning is Dr. Pederson. He has been a colleague of mine for 17 years. He is a senior staff research scientist with the General Motors R&D Center, and Tom has done a lot of research in the area of polynuclear aromatic hydrocarbons. His topic today is biologically active PAH from new and used industrial lubricants.

Biologically-Active Polycyclic Aromatic Hydrocarbons from New and Used Industrial Lubricants

Thomas C. Pederson

General Motors Research and Development Center
30500 Mound Road, Building 1-3, Warren Michigan 48090-9055

ABSTRACT

The purpose of this research was to evaluate and compare the content of polycyclic aromatic hydrocarbons (PAH) found in samples of petroleum oil from new and used manufacturing lubricants. The samples analyzed also include two reference oils used to develop the recently adopted ASTM modified mutation assay method for analysis of base oils used in metal working fluids. Analysis of PAH concentrations in DMSO extracts using GC/MS with programmed selective ion monitoring show that alkylated derivatives of PAH are present in much higher concentrations than conventional parent PAH in all oil samples. Correlations between various cumulative measures of PAH content and the activities of these oils in the ASTM assay demonstrate that the alkylated PAH are also largely responsible for the mutagenic activity. Evidence of PAH formation during use was found in certain oils, but the magnitude of these changes was small in comparison to the rather wide range of PAH concentrations found in new oils. These results are discussed with consideration as to the suitability of recovering and recycling used lubricant oils for reuse in manufacturing processes.

INTRODUCTION

Although an association between industrial exposure to mineral oils and an elevated incidence of cancer was clearly evident from the historical use of poorly refined oils containing high PAH concentrations, later changes to produce severely refined oils are believed to have greatly reduced this hazard.⁽¹⁾ However, several studies using both chemical analysis and biological assays have reported varying increases in the PAH content of metalworking oils during use. Extensive animal

skin painting studies showed that the carcinogenic activity of petroleum base oils can be correlated with both the content of polycyclic aromatic compounds and the biological activity of the oil in modified versions of the *Salmonella* bacterial mutation assay.⁽²⁾ The modified mutation assay was also recently adopted as an ASTM method for evaluation of the carcinogenic hazard in base oils used in metal working fluids.⁽³⁾

This study describes the evaluation of PAH content in petroleum oil lubricants used as machining oils, hydraulic oils, gear lubes, and heat treatment quench oils. The used oils analyzed include collected waste oils from individual manufacturing plants, reclaimed oils from recovery facilities which remove water and insoluble material, and several specific types of oil which provide a direct comparison of PAH content before and after use. To establish the magnitude of PAH concentrations present in oils considered to contain hazardous amounts of PAH, analyses are presented for two reference oils that were used for the development of the ASTM modified mutation assay. One of these is reference oil R-1 that is recommended for use as a positive control in the mutation assay, and the other is test oil M-3 which was originally included in the animal skin painting studies and produced a 50% tumor incidence in the treated animals.

METHODS and RESULTS

Methods involving programmed GC/MS instrument control for selective ion monitoring and the use of multiple internal isotopic standards were developed to extend the analysis of PAH content in manufacturing oils to include a quantitative measurements of alkylated PAH compounds. The combined accuracy for extraction of PAH from oil by dimethylsulfoxide

and analysis by GC/MS was evaluated with NIST reference standards. The cumulative measures of PAH content found in the two ASTM reference oils are shown in Table I. The content of alkylated PAH in these oils and in all the manufacturing oils was roughly an order of magnitude greater than that of the parent PAH

compounds. The 4-7 ring compounds include both parent and alkylated PAH. The 2-3 ring compounds contribute the larger portion of PAH content in ASTM oil M-3 and in most manufacturing oil samples, but the carcinogenic activity of PAH mixtures is generally attributed only to compounds containing 4 or more rings.

TABLE I
Amount of Material in DMSO extracts of ASTM Oils

<u>Analytical Procedure</u>	<u>oil conc. $\mu\text{g/mL}$</u>	
	Reference Oil R-1	Test Oil M-3
Solvent evaporation weight of extract	32,000	not analyzed
GC/FID total volatile hydrocarbon	18,500	not analyzed
GC/MS(selective ion monitoring)		
Σ all parent PAH	161	202
Σ all alkylated PAH	<u>2,035</u>	<u>2,696</u>
Total measured PAH	2,196	2,898
2-3 Ring PAH	359	2,190
4-7 Ring PAH	1,838	708
IARC Carcinogens *	40	16

* Includes all PAH classified by IARC as having sufficient or limited evidence of carcinogenicity.

Figure 1 shows the comparative 4-7 ring PAH content of the manufacturing oils. With the exception of one sample of reclaimed oil, the range of PAH concentrations in used oils appears to be similar to that of the new oils. Although increases in PAH content after use were evident in three oil samples, the magnitude of the increase in 4-7 ring PAH content ranged from 18 to 62 $\mu\text{g/mL}$ which is markedly less than the range of concentrations

found in both new and used oils.

The oil samples were also submitted for evaluation of mutagenic activity using the ASTM specified method. Evaluations of the correlation between the mutagenic activity and various cumulative measures of PAH content will be described. The results demonstrate the importance of the alkylated PAH contribution to the mutagenic activity.

CONCLUSIONS

The PAH content in the oil samples analyzed in this study indicate that the extent of worker exposure to PAH from manufacturing lubricants could derive as much from the range of PAH content in new oils as from the PAH which may or may not form during use. Recycling of manufacturing lubricants offers an opportunity for considerable cost savings, but unless the reprocessing of used oils involves severe re-refining technologies, it is important that any used oil contaminated with unacceptable quantities of PAH be segregated from the oil recovered for reprocessing and reuse as a manufacturing lubricant. The correlation between differing measures of PAH content and mutagenic activity suggest improved PAH content criteria could be developed for new and recycled oils used as manufacturing lubricants.

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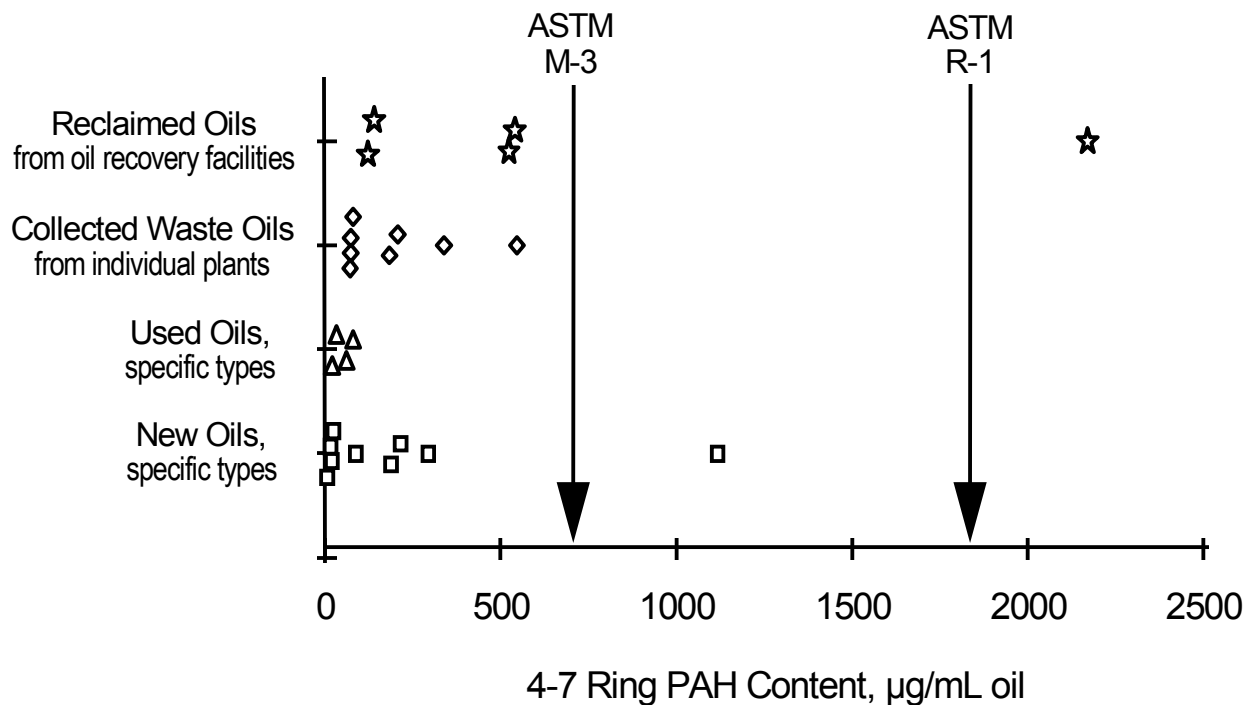


Figure 1. Comparisons of PAH content in new, used, and reclaimed manufacturing lubricants.

A Study of Formaldehyde Exposures From Metalworking Fluid Operations Using Hexahydro-1,3,5-Tris (2-Hydroxyethyl)-S-Triazine

Howard J. Cohen

University of New Haven, Department of Occupational Safety and Health
300 Orange Avenue, West Haven, CT 06516

ABSTRACT

An industry-wide study of formaldehyde exposures from metalworking fluid operations using Triazine biocides was undertaken in response to an OSHA regulation covering employers and manufacturers which use and produce materials which may off-gas formaldehyde. Triazine is one of a number of formaldehyde-condensate biocides used in the metalworking fluid industry. Twelve operations at eight different facilities were evaluated for exposure to formaldehyde. Seven of the eight different facilities involved the manufacture of metal products. A total of approximately 550 air samples were taken from workers and in areas where formaldehyde was expected to be present. Samples were taken in where no Triazine was in use to evaluate each facility's background level of formaldehyde. In addition, field blank samples, samples spiked with formaldehyde and duplicate field samples were all taken to evaluate the accuracy of three different monitoring methods to detect low levels of formaldehyde.

Employees who used metalworking fluids containing Triazine were never exposed to formaldehyde levels at or above the OSHA Action Level of 0.5 ppm or to exposures which would exceed the Short-Term Exposure Level of 2 ppm. An exception may be employees who perform maintenance operations in poorly ventilated metalworking fluid sumps. The data from this study can be used by employers, who use Triazine biocides in a manner similar to operations described in this report, to avoid the necessity of performing baseline exposure monitoring as required by OSHA. The OSHA Formaldehyde standard further requires both manufacturers and users to label products and train employees if exposures can exceed 0.1 ppm as a time-weighted

average over an eight-hour workshift. Employees monitored at nine of the twelve operations monitored had at least some exposures exceed the 0.1 ppm threshold for labeling and training. However, background levels of formaldehyde at the facilities studied and the imprecision of established monitoring methods for exposure at low levels made it impossible to determine whether Triazine was responsible for any of the low levels of formaldehyde measured during this study. When only exposure data from the use of neat Triazine were considered, no formaldehyde was detected.

INTRODUCTION

In December of 1987 OSHA published a new standard for formaldehyde. The purpose was to address both the respiratory irritant properties of formaldehyde and animal toxicity data indicating it to be a carcinogen. Several parties sued OSHA over the standard, and OSHA was required to revise their original standard. A final standard was published in May of 1992.⁽¹⁾ This standard, like other OSHA health standards, has provisions for labeling, exposure monitoring, medical surveillance, training and engineering controls. The Permissible Exposure Limit (PEL) was set at 0.75 parts per million (ppm) for eight hour time-weighted-average exposures and 2.0 ppm for short-term exposures (measured over 15 minutes). An Action Level of 0.5 ppm as an eight-hour time-weighted average was also established in this standard.

The revised OSHA Formaldehyde Standard has several unique aspects affecting manufacturers of products which may release formaldehyde and employers who use these products. Substances which contain more than 0.1% formaldehyde must have labels and Material

Safety Data Sheets (MSDS) indicating that it contains formaldehyde which is a carcinogen. This requirement is consistent with OSHA's Hazard Communication standard (29 CFR 1910.1200). A novel part of the revised Formaldehyde Standard requires manufacturers to assess whether a product may release formaldehyde, which could result in an eight hour time-weighted-average exposure above 0.1 ppm under "foreseeable conditions of use." If so, the product must be labeled indicating that it contains formaldehyde and that further information can be obtained from the MSDS. If the product may release formaldehyde above 0.5 ppm, the label must comply with appendices found in the OSHA Formaldehyde Standard, include the potential for respiratory sensitization, and contain the words, "Potential Cancer Hazard."

Employers, who purchase products which contain or can release formaldehyde as stated above, must provide hazard communication training to their employees. Employers must also obtain objective data which demonstrate that their employees will not be exposed to formaldehyde above either the Action Level or PEL. If exposures exceed these limits, then they fall under the remaining requirements of the OSHA Formaldehyde Standard.

The majority of manufacturers of Triazine biocide belong to a non-profit corporation, known as the "Joint Venture," which was formed to share the costs of toxicity testing required for reregistration of the biocide by EPA. Members of the Joint Venture met in late 1992 to discuss the labeling requirements for Triazine. Triazine is the commercial name for 1,3,5-Tris(2-hydroxyethyl) hexahydro-S-Triazine, and it is the product of monoethanolamine and formaldehyde. This is one of a number of formaldehyde-condensate biocides used in the metalworking fluid industry. Limited laboratory and workplace data were shared among members. The members concluded that there were data which indicated the possibility that the use of Triazine could result in employee exposures to formaldehyde above 0.1 ppm, but that there were no data suggesting exposures

could exceed 0.5 ppm. All manufacturers confirmed that their products contained well below 0.1% formaldehyde in solution, which would also trigger labeling requirements. Members of the Joint Venture released a statement to their customers and formulators in March of 1993 indicating that they may need to label their products as containing formaldehyde, but did not need to add the cancer warnings, associated with higher expected exposures. Members of the Joint Venture decided to initiate a comprehensive workplace exposure monitoring study to assess the potential for Triazine to release formaldehyde under normal conditions of use at a number of different metalworking operations.

METHODS

A protocol was developed prior to any air monitoring which included site selection criteria, formaldehyde exposure assessment, the collection of pertinent operational data, and a method for issuing reports while maintaining the confidentiality of the participants. Every effort was made to evaluate Triazine exposures at a range of different manufacturing sites. Aluminum can manufacturers were singled out as unique operations where the highest levels of Triazine were used in metalworking fluids. In addition, some aluminum can manufacturers have automated systems as opposed to manual additions of concentrated Triazine used by most other customers. Most Triazine users add concentrated biocide once or twice a week to maintain their metalworking fluid systems, and the concentration varies during the week. Customers who agreed to participate in this study were asked to communicate when they anticipated adding Triazine so that formaldehyde monitoring could be done when Triazine levels were at their lowest, during the addition of concentrated Triazine, and immediately after addition when Triazine was at the highest concentration in the metalworking fluid. Typically, this was done in one day with monitoring for three to four hours in the morning before the addition of Triazine, monitoring for a short time (5-15 minutes) during

the addition of Triazine, and additional monitoring for three to four hours after Triazine was freshly added to the metalworking fluid. This strategy was employed to monitor the worst-case exposures when Triazine levels were at their highest, and to determine if formaldehyde exposures increased with increasing concentrations of Triazine in metalworking fluid.

Exposure monitoring was performed on employees machining parts using Triazine-containing metalworking fluid, in locations representative of where employees worked, and at sources (e.g. metalworking fluid sumps) where the highest concentrations of formaldehyde were expected. The sampling strategy consisted of monitoring the exposure of three to five employees in a specific area of a plant using Triazine-containing metalworking fluid. Samplers were removed prior to the addition of Triazine and replaced with fresh media. At nearly all locations, the exact persons, areas and sources were measured before and after the addition of Triazine to allow for comparison of these data.

During each survey a number of field blanks were taken. These samples were handled in a normal manner, but had no air drawn through the sampling media. Some samples, both on employees and in areas, were obtained in duplicate to obtain an estimate of the precision of each method. Some employees and areas were sampled with more than one type of media to allow for a comparison of these methods. During most surveys, a freshly made solution of formaldehyde (in water) was taken into the field, and samplers were spiked with known quantities of formaldehyde to approximate the quantities expected from a four hour sample at 0.1 ppm. These "spiked" samples were placed alongside normal samples to verify that the monitoring methods used could accurately determine formaldehyde at 0.1 ppm. In addition to exposure data, samples of the metalworking fluid were obtained prior to and after the addition of Triazine. These samples were taken back to a laboratory and analyzed within a week for pH and Triazine levels.

After the results of each survey were obtained, a report was prepared and issued to the facility where sampling had occurred. Data were given without regard to the effects of spiked samples or background levels in the plant (these were explained in the report when anomalies were noted). Each facility was asked to share the results of this report with all employees who participated in the survey (this is a requirement of the OSHA Formaldehyde Standard, and agreement by the facility management was required prior to conducting the study). Management at each facility were told that their company name and location would be considered confidential when preparing the overall study report.

Three methods were used to monitor formaldehyde levels in air. They included the NIOSH method 3500 which utilizes a midget impinger containing 0.1% sodium bisulfite,⁽²⁾ the GMD 570 passive dosimeter which utilizes an adsorbent impregnated with 2,4 dinitrophenylhydrazine (DNPH)⁽³⁾ and EPA method TO-11 which utilizes a silica gel impregnated with DNPH.⁽⁴⁾ The NIOSH impinger method was only used for area monitoring because of the possibility of having the liquid media spill on employees.

All air samples were analyzed by two laboratories which were accredited by the American Industrial Hygiene Association and participated in the Proficiency And Testing program for the analyses of organic vapors. One laboratory analyzed all the impinger samples, and a second laboratory analyzed all silica-gel and dosimeter samples. All samples were hand carried to the laboratories within 48 hours of sampling.

Samples of metalworking fluids from each location were obtained before and after the addition of Triazine. These samples were analyzed for pH and Triazine levels. The temperature of the metalworking fluid was noted where a facility provided measurement data.

RESULTS

Approximately 550 air samples were taken

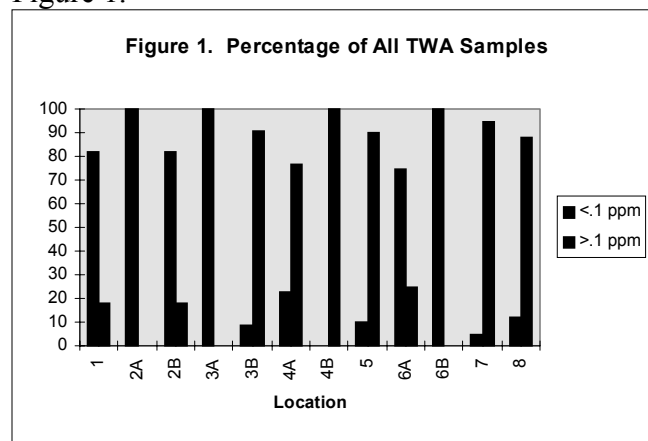
during this survey, and nearly 300 of these were obtained from workers. Every one of the personal air samples were below 0.5 ppm, the OSHA Action Level for formaldehyde. Based on the OSHA standard, none of the employees who used metalworking fluid containing Triazine received, even once, an overexposure to formaldehyde.

Background levels of formaldehyde, where no Triazine was present, were detected at five of the eight locations at levels varying from 0.018-0.135 ppm. At one of the sampling sites, the highest levels of formaldehyde measured were at operations where no Triazine was present. At another location, employees using metalworking fluid containing Triazine had similar or lower exposures than employees working with the same metalworking fluid but which contained no Triazine. When employee exposures to formaldehyde are examined from short-term operations where concentrated Triazine was added to metalworking fluid, a total of 16 air samples taken on employees from five different sites indicated non-detectable levels of formaldehyde below the OSHA Short-Term Exposure Limit of 2 ppm. These samples should represent the highest potential employee exposure to formaldehyde resulting from the use of Triazine biocide.

Given that none of the time-weighted average personal air samples taken were above 0.5 ppm, 0.1 ppm is the next and only threshold for regulatory decision making using these data. All long-term air samples taken had a maximum Limits of Quantification (LOQ) below 0.1 ppm. Many of the air samples taken throughout this survey were below the LOQ. The simplest and most statistically justified approach using these data was to examine those samples above and below 0.1 ppm. Therefore, it is possible to discuss the data in terms of whether values were above and below 0.1 ppm, and the percentage of such samples.

Examining only data that were not corrected for background formaldehyde levels or recoveries of spiked samples, nine of the 12 operations monitored had at least one personal air sample above 0.1 ppm. Six of the 12 operations

had the majority of exposures monitored above 0.1 ppm. A summary of these data are shown in Figure 1.



The same data when corrected for background levels and spiked recoveries indicated only two operations had a majority of samples above 0.1 ppm, and eight operations had the majority of samples below 0.1 ppm.

Approximately 250 air samples were taken in areas where employees normally worked or at sources where high formaldehyde levels were anticipated. While employees took breaks from work, these samples remained in the working area and vicinity of metalworking fluid. It was expected that these samples would demonstrate where the highest exposures were occurring and generally would have higher formaldehyde levels than corresponding personal air samples. The results throughout this study indicated area air samples to be lower than values obtained from employees, with the exception of those samples taken directly at metalworking fluid sumps. The majority of area air samples taken at ten of the 12 operations were below 0.1 ppm, and five of the locations had no samples above 0.1 ppm. These results are even more dramatic when corrected for background and spiked recoveries. Only one operation had the majority of area air samples above 0.1 ppm and eight of the 12 operations had ten percent or fewer samples above this level.

Collectively, the area sampling results indicate that Triazine-containing metalworking fluids are not producing levels of formaldehyde

which are likely to cause exposures above 0.1 ppm in other areas of the plant. These results also suggest that employee exposure to formaldehyde may be due to times when they open machines and work closer to the parts (and metalworking fluid) than are represented by the area air samples taken.

The study protocol was designed to test the hypothesis that Triazine in metalworking fluid was related to formaldehyde levels measured in the workplace. Formaldehyde levels were measured before and after the addition of Triazine at six of the eight locations. These data indicated that for ten operations; the percentage of exposures above 0.1 ppm remained the same at six operations, exposures increased at three operations, and exposures decreased at one operation.

There was a weak relationship between the concentration of Triazine level in use and the percentage of air samples which exceeded 0.1 ppm of formaldehyde. There was no relationship between the pH of the metalworking fluid and the percentage of air samples collected which exceeded 0.1 ppm of formaldehyde.

A number of air samples were taken on the same person or in the same area at the identical times using different air sampling methods. These data were then plotted and evaluated using regression analyses. In summary, the highest formaldehyde levels from this survey were obtained with silica-gel tubes. There was a good agreement between results obtained with silica-gel tubes and impingers (coefficient of correlation of 0.86) and a poorer agreement between dosimeters and silica-gel tubes (coefficient of correlation of 0.66). There was no relationship from results obtained between dosimeters and impingers.

At several sampling sites, duplicate samples were obtained from workers and in areas using identical devices. These results allow for an estimate of the precision from each sampling method. A total of 22 data points for dosimeters, 26 points for silica-gel tubes and only four points for impingers were obtained during this study. Each pair of points were analyzed by calculating

the difference between pairs as a percentage of the larger sample. Approximately 95% of the data for dosimeters indicated differences below 40%, while 90% of the data for silica-gel tubes were within 65% of each other.

The accuracy of each of the sampling methods is a combination of the precision and bias for each method. Bias can be estimated by examining the ability of each method to recover known quantities (spike samples) of formaldehyde. All three methods had a positive bias. The average bias was between 10-22% for the three methods. The accuracy of the dosimeters was $\pm 32\%$, the silica-gel tubes were $\pm 35\%$ and the impingers were $\pm 46\%$.

CONCLUSIONS

The results of this study indicated that employees who use metalworking fluids containing Triazine will not be exposed to formaldehyde levels at or above the Action Level of 0.5 ppm, or to exposures which would exceed the Short-Term Exposure Level of 2 ppm. An exception may be employees who perform maintenance operations in poorly ventilated sumps. These data can be used by employers, who use Triazine biocides in a manner similar to operations described in this report, to avoid having to perform baseline exposure monitoring as required by OSHA in the Formaldehyde Standard.

The OSHA Formaldehyde Standard requires manufacturers to label and employers to train employees for products which may release formaldehyde at levels above 0.1 ppm as an eight-hour time-weighted average. This standard does not consider the contributions of multiple sources of formaldehyde, each of which is responsible for less than 0.1 ppm, but which collectively may exceed this level. The standard also does not consider the accuracy of available air sampling methods for formaldehyde monitoring at 0.1 ppm, which may be significantly lower than results presented by OSHA to support a PEL of 0.75 ppm. Metalworking fluids contain numerous additives and are often used in plants where other

sources of formaldehyde are present. Therefore, the most logical data to examine in terms of the OSHA labeling requirements were the data obtained when employees handled neat Triazine. These data indicated that formaldehyde exposures were non-detectable. While the limits of quantification were below the applicable OSHA short-term exposure limit of 2 ppm, they were above the labeling limit of 0.1 ppm due to the short duration of such work.

ACKNOWLEDGEMENT

This study was sponsored by a non-profit organization comprised of five major manufacturers of Triazine: Angus Chemical Company, Stepan Chemicals, Buckman Laboratories, Lehn & Fink Products and Olin Corporation. Olin provided the technical resources for this project, while all other costs (supplies, analyses, and travel) were jointly paid for by members of the Joint Venture.

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Exposures to Metal Working Fluids and Their Components: I. Summary From a Field Study of Acute Respiratory Health Effects

Susan R. Woskie¹, M. Abbas Virji¹, David Kriebel¹, Susan R. Sama¹, Donald K. Milton², S. Katharine Hammond³, Mark Smith¹

1. Department of Work Environment, University of Massachusetts Lowell;

2. Occupational Health Program, Harvard School of Public Health;

3. Department of Family and Community Medicine, University of Massachusetts Medical Center, current affiliation: Department of Environmental Health Sciences, School of Public Health, University of California, Berkeley.

ABSTRACT

The clinical and epidemiologic literature suggests that exposures to metal-working fluids (MWF) are associated with adverse respiratory health effects. The exposure assessment summarized here is part of an epidemiologic study whose purpose was to confirm the association of metal working fluid exposures with cross-shift decrements in pulmonary function and to identify the causal agents in the MWFs.

METHODS

For each member of the cohort (216 MWF exposed and 170 MWF unexposed workers), cross-shift pulmonary function tests and environmental data were collected on the same day. For the MWF exposed workers, airborne MWF aerosol levels were measured in several ways, the inhalable mass concentration of aerosol, the inhalable levels of a variety of metals and elements found in either the MWF, machine tool or workpiece, the inhalable levels of endotoxin, and the level of culturable bacteria in the size fraction less than 8 mm. In addition, bulk samples of soluble MWFs were tested for pH, mineral and tramp oil fraction, endotoxin, culturable bacteria and lipopolysaccharide levels.

RESULTS

On the day they were tested, the majority of the workforce (56%) worked on a single machine, while 38% operated two machines and the remaining 6% operated 3 or more machines (most often concurrently). Five different brands of

machining fluids (MF) were encountered in the field and were classified into two main groups, soluble and straight. Soluble MFs were used in 60% of the machines and straight oils in 35% of the machines. Most of the machines in this plant were run on individual machine sumps, with 66% containing 50 gallons or less, while only 12% had sumps that were over 100 gallons in size. In this plant, 37% of the machines had their MF pumped out and replaced within three days of the testing, 80% had their fluid changed within 21 days. Of the 295 machines studied, 35% of the machines studied had no enclosures in place, 44% had partial enclosure. Eighty-eight percent of the machines studied had no local exhaust in place, 11% had local exhaust, although we did not evaluate the collection efficiency of these exhaust systems. Information on whether the workers cleaned the parts by dipping them in a dip tank or by blowing with air was also gathered. On 24% of the machines, parts were cleaned by dipping, while for 86% of the machines, parts were cleaned by blowing them off with compressed air.

Based on 40 impactor samples, the average aerodynamic mass median diameter (AMMD) of the MWF aerosol was 3.38 microns (average GSD = 3.05). On average 65% of the mass was contributed by particles less than 3.5 mm, 19% by particles 3.5-9.8 mm and 16% by particles greater than 9.8 mm. The MWF exposed workers had a geometric mean inhalable aerosol exposure level of 0.181 mg/m³ (GSD=1.83), while the MWF unexposed workers had a geometric mean inhalable aerosol exposure level of 0.046 mg/m³

(GSD=1.60). The geometric mean mass concentration varied somewhat with operation type. Multiple-drills had the highest geometric mean mass concentration, while drill, turn and grind had the lowest geometric mean mass concentration. Broach and chucking operations had geometric mean mass concentrations in between the highest and the lowest.

MWF exposed workers had higher geometric mean airborne culturable microbial counts (102 cfu/m^3 for bacteria $< 8 \text{ mm}$; GSD=5.8) than the unexposed workers (GM = 18 cfu/m^3 ; GSD = 3.1). For a subset of the airborne culturable microbial samples, speciation on the lower impactor plate i.e., microbes less than 8 mm of the plated bacteria was performed. Among the unexposed (n = 9), bacillus was the predominant species (54% of the colonies counted) followed by pseudomonas (41%). Among the exposed workers (n = 17), pseudomonas predominated (65% of colonies counted), followed by enterobacter (19%) and bacillus (13%). Pseudomonas is a very common water contaminant and most of the MWF studied were water emulsions. Exposed workers had higher geometric mean airborne endotoxin levels (GM = 8.65 EU/m^3 ; GSD = 3.45) than the unexposed workers (GM = 2.14 EU/m^3 ; GSD = 5.96).

Elemental concentrations of iron, chlorine and sulfur were substantially higher among the exposed workers compared to the unexposed workers. Similar concentrations of bromine, chromium, nickel, lead, titanium and zinc suggest that little of these compounds are aerosolized in the MWF and/or that there is a substantial cloud effect in the plant as indicated by these tracer materials. The elemental profile of the soluble and straight MWF samples are not significantly different, except that soluble MWF aerosols contained higher concentrations of chlorine, which is a component of the soluble MWF formulations used in this plant.

The levels of bulk constituents were examined by the length of time since the MWF was pumped out and the machine sump refilled with fresh MWF. Soluble MWF sump change times were

divided into 3 categories: less than or equal to 3 days; 4 - 21 days; and greater than 21 days. The percent oil in the bulk MWF decreased with time since MWF change. The pH stayed fairly constant over time. CFU/ml $\times 10^7$ and tramp oil level increased to a maximum at 4-21 days since MWF change, and then dropped, while endotoxin and fatty acid levels consistently increased with time since change. It is surmised that the increase in culturable organisms may reach a maximum due to nutrient restrictions (oil and tramp oil) then die off, however, the endotoxin and fatty acid levels continue to rise since they measure both live and dead organisms.

SUMMARY

The inhalable mass concentrations, culturable microbial exposures and endotoxin levels measured at this plant were lower than those in previous field studies. The culturable microbial levels in the soluble bulk MWF were comparable to other field studies. Pseudomonas is the predominant type of bacteria found in both the bulk and air samples of MWF exposed workers. Levels of metals and elements were low in this plant, however, iron, chlorine and sulfur exposures were higher among MWF exposed workers.

Statistical modeling of the determinants of MWF aerosol mass exposures suggests that process emission and environmental factors such as machine type, fluid flow rate, production rate, degree of enclosure, and workplace machine density are the most significant predictors of aerosol levels in this workplace. By understanding the determinants of exposure to the MWF aerosol and its components, successful and cost-effective interventions can be developed.

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Size Distributions and Concentrations of Aerosols in Industrial Machining Environments

James B. D'Arcy, Robert G. Wooley, and Tai L. Chan
General Motors Research and Development Center
30500 Mound Road, Building 1-3 Warren, Michigan 48090-9055

ABSTRACT

The size and concentration of machining fluid aerosols were investigated in several modern automotive machining facilities. During the course of this study one large transfer line was changed from semi-synthetic fluid to soluble oil and then back to semi-synthetic fluid. Aerosol size distribution and concentration measurements obtained during these time periods were related to the percentage of fluid concentrate in the circulating fluid. The 13% soluble oil produced a proportionately larger aerosol size and higher concentrations than the 7-9% semi-synthetic fluids. The aerosol size distribution measurements from the current study indicated mass median aerodynamic diameters from 1.8 to 3.2 μm . These size measurements are somewhat smaller than related measurements in a previous study. The size distributions measured in the current work and the health data on respiratory effects of machining fluids suggest that a thoracic sampler may be appropriate for sampling this aerosol. The sampling experience from this study also suggests the use of a "splash shield," may be appropriate for personal sampling of worker exposures to avoid large non-inhalable droplets.

INTRODUCTION

General Motors has more than forty manufacturing facilities that utilize machining fluids on a large scale. The vast majority of the machining fluids are water-based fluids that contain variable amounts of mineral oil or synthetic materials. The machining fluid provides chip transport, cooling and lubrication for the machined part and tooling. The energy and speeds involved in modern machining and grinding processes can create fine aerosols from

this fluid that floods the metal removal operation.

In an earlier study, the size distributions and concentrations of machining fluid aerosols in a large automotive transmission plant were found to depend on a combination of the machining operation and the fluid type.⁽¹⁾ This study extends the previous work to other automotive machining facilities and it explores the independent effect of fluid type on aerosol size and concentration.

EXPERIMENTAL

Three sample sites in a cast-iron engine machining facility, one site in an aluminum engine machining facility, and one site in an aluminum transmission machining facility were chosen for this study. All samples are area or *general condition* samples due to the aerosol equipment used and the desire to separate process variables from the inevitable personal variables introduced in personal sampling. The sample sites were closer to the machine lines than most workers stand and might be considered *source samples*. The majority of the data reported here is from the cast-iron facility. The transmission plant used soluble oil machining fluid. The engine facilities both used semi-synthetic fluids initially, but one facility changed to a soluble oil for a period of 8 months and then switched back to a different semi-synthetic fluid during the time period of this study.

The aerosol sampling train at each site consisted of a 47 mm Teflon coated glass fiber filter (Pallflex Products Corp., Putnam, CT) operated at 10 L/min, a standard plastic 37 mm filter holder with a 5.0 μm PVC membrane filter operated at 2 L/min, an area respirable impactor operated at 30 L/min, and a MOUDI (Multi-Orifice-Uniform-Deposit-Impactor) operated at 30

L/min. On several occasions a Mercer cascade impactor sampling at 4 L/min was used to allow comparison of the aerosol size distributions with our previous work.⁽²⁾

RESULTS

The sample means of the area sampling are presented in Table I. The MOUDI and Mercer impactors compared favorably for estimation of the aerosol MMAD in this evaluation with the maximum difference in MMAD being 0.3 μm . However, the Mercer impactor suffers more interstage losses as indicated by the lower aerosol concentration estimate calculated from its individual stages. A comparison of the size distribution during the use of the 13% soluble oil as compared to a 7-9% semi-synthetic is shown in Figure 1. The mass median aerodynamic diameters for the two distributions are 2.2 μm for the semi-synthetic fluid and 2.8 μm for the soluble oil. The aerosol size distribution measurements from the current study indicated mass median aerodynamic diameters from 1.8 to 3.2 μm in the machining areas studied. No grinding operations were included in the current study. These aerosol size measurements are smaller than related measurements in the previous study. This apparent size discrepancy may reflect differences in the predominant generation mechanism between the machining operations studied.

During the course of the study several samples became contaminated by splashed fluid where a single large droplet can give erroneous readings. Problems with splashing of machining fluid caused us to abandon the use of the IOM inhalable sampler that we were evaluating as part of the sample train in early studies.

CONCLUSIONS

- The concentration of non-volatile components in the machining fluid, e.g. mineral oil, is directly related to the size distribution and concentration of the aerosol generated when all other generation factors are equal.
- The size distributions measured in the current work and the health data on respiratory effects of machining fluids suggest that a thoracic sampler may be appropriate for sampling this aerosol.⁽³⁾

The sampling experience from this study suggests the use of a "splash shield," may be appropriate for personal sampling of worker exposures to avoid large non-inhalable droplets.

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Table I
Aerosol Concentration and Size Measurements

Site	Number	Operation/Fluid	Particle Concentration	Particle Size	% Respirable
1A	9	Iron Milling/Semi-Syn	0.55 - 1.34 mg/m ³	2.2 ± 0.5 μm	85
1B	4	Iron Milling/Soluble	0.85 - 1.73 mg/m ³	2.8 ± 0.4 μm	76
2	10	Iron Drill-Mill/Semi-Syn	0.35 - 1.04 mg/m ³	2.1 ± 0.6 μm	82
3	13	Assembly	0.07 - 0.31 mg/m ³	1.0 ± 0.3 μm	98
4	3	Aluminum Mill/Semi-Syn	0.48 - 0.65 mg/m ³	3.2 μm	65
5	2	Aluminum Drill/Semi-Syn	0.72 - 0.91 mg/m ³	-	-

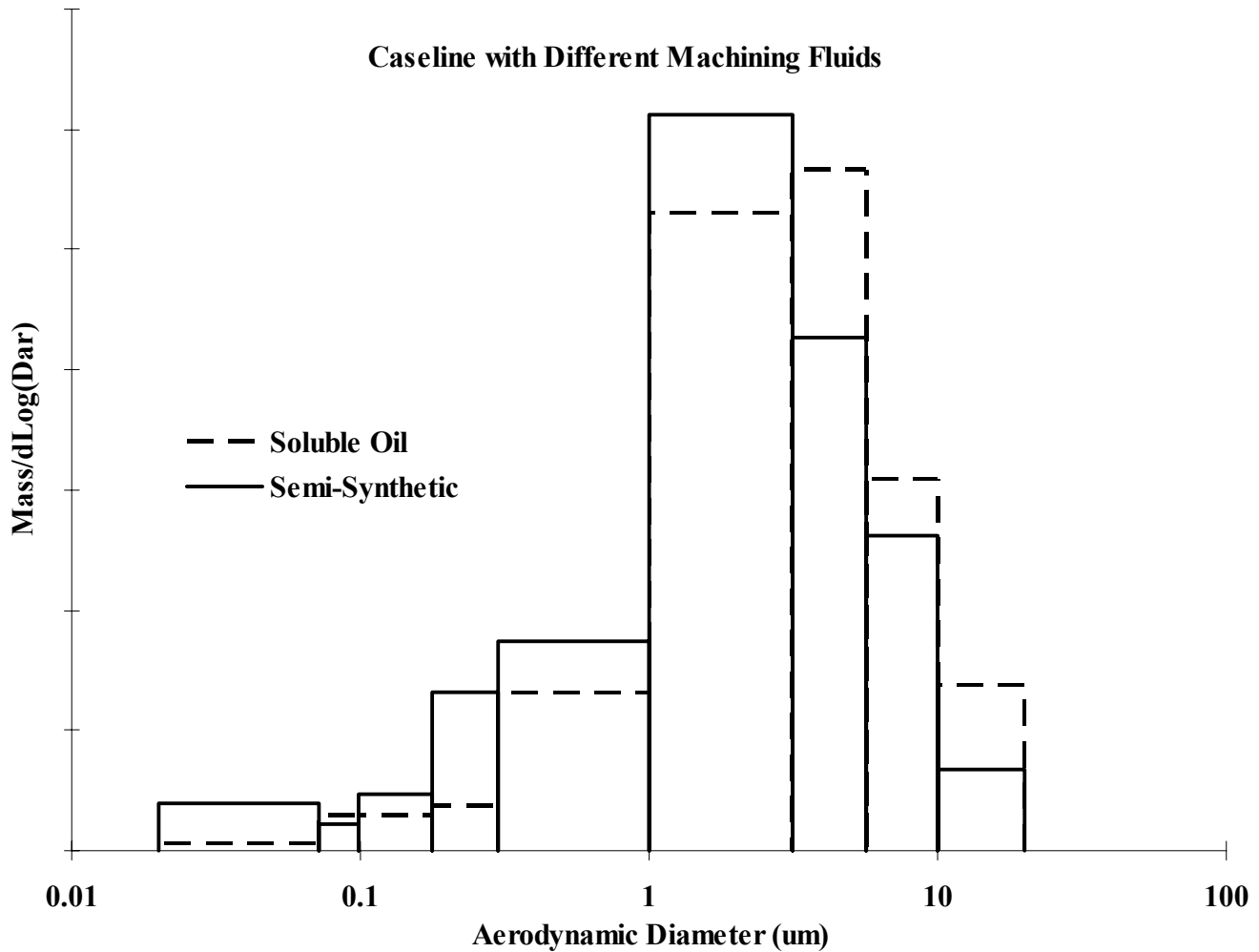


Figure 1. Size comparison of aerosol at site 1 during use of semi-synthetic and soluble oil fluids.

Measuring the Concentration of Mineral Oil Mists

David Leith, Frank A. Leith, and Maryanne G. Boundy
Aerosol Associates, Hillsborough Business Center, Hillsborough, NC
120 Muir Lane, Chapel Hill, NC 27514

ABSTRACT

This study investigates the potential for mineral oil mist to evaporate, during sampling, from filters and substrates used to assess personal exposure. Mineral oil used as a machining fluid has a low vapor pressure of about 1 mm Hg and is not normally considered volatile; however, when this oil is dispersed as a mist its aggregate surface area is so high that significant evaporation can occur. NIOSH method 5026 specifies⁽¹⁾ that oil mist concentrations should be determined by collecting mist on filters made from mixed cellulose esters (MCE) or polyvinyl chloride (PVC). After capture, collected mist droplets remain in contact with passing air and remain dispersed on the filter surface as long as sampling continues, conditions that can lead to sample evaporation. Less evaporation should occur for samples taken with an electrostatic precipitator. There, mist droplets are separated from the air flow by electrostatic force and coalesce on the precipitator wall to form a film with relatively low surface area.

Collection of mineral oil mist was investigated in paired lab tests using a precipitator designed for personal sampling and either an MCE or a PVC filter. The amounts of oil mist collected using the precipitator were significantly and substantially higher than the amounts collected using the filters, $p < 0.001$. Further tests in which clean air passed through mist-loaded precipitators and filters showed that the precipitator retained significantly more collected mist than both filters, $p < 0.001$, and further suggested that the MCE filter retained more mist than the PVC filter, $p = 0.059$. The differences in sample collection and retention between the precipitator and the filters was particularly pronounced at mist loadings below 1 mg. Overall,

the precipitator retained nearly twice as much mist as the MCE filters, and over three times as much as the PVC filters.

Mineral oil mist concentrations determined using the filter method may underestimate true mist concentrations in cases where the mist has the potential to evaporate. Exposure assessments for oil mist made using filters may have scattered data due to variations in the degree of evaporation from sample to sample as evaporation depends, in turn, on factors not readily controlled such as oil composition and plant conditions. Variability in exposure data will tend to obscure any relationship between exposure and disease. These problems can be reduced by sampling with an electrostatic precipitator.

BACKGROUND

Oil mists from machining operations have long been associated with occupational disease in exposed workers. Concern has increased with recent evidence that exposure to these mists is associated with throat, pancreas, rectum, and prostate cancers,⁽²⁾ as well as with breathing problems and respiratory illnesses.⁽²⁾ As a result, the ACGIH has published⁽³⁾ a notice of intent to reduce the TLV for mists of "mildly refined oils" from 5 mg/m^3 to 0.2 mg/m^3 . Accurate methods to monitor the personal exposure of workers to these mists is important.

Although water-based coolants are increasingly employed and have replaced mineral oil coolants for many applications, oil-based coolants continue to find use. Certain machining operations require straight mineral oils as coolants, whereas other operations use "soluble oil," an emulsion of oil in water. Thus, oil-based aerosols continue to be present in the workplace.

General practice in the industrial hygiene

field as well as NIOSH method 5026⁽⁴⁾ employ filters to assess exposure to mineral oil mist. The mineral oils used in some machining operations contain semi-volatile compounds that, during mist collection itself, may evaporate from the filter surface.^(2,3) To the extent that evaporation from a sampling filter occurs, the data obtained may have unnecessary scatter and a bias toward the underestimation of true exposures.

The purpose of this study was to investigate the potential for samples to evaporate from filters and substrates used to collect mineral oil mist. As NIOSH method 5026 specifies that polyvinyl chloride (PVC) filters or mixed cellulose ester (MCE) filters should be used, they were employed in the present tests. In addition, we investigated use of a small electrostatic precipitator (ESP) designed for personal sampling. In the ESP, mist droplets are first electrically charged and separated from the air stream by electrostatic force, then collected on the inside surface of the collection cylinder. Once collected, the mist in the ESP can coalesce to form a film that is separated from the gas stream and that has much less aggregate surface than the uncoalesced droplets on the filter. Thus, evaporation from the ESP substrate should, in principle, be less than from a filter.

METHODS

Aerosol was generated by a Collison nebulizer (BGI, Waltham, MA), within a 265 liter chamber as shown in Figure 1. The concentration of aerosol in the chamber was controlled using a hi-vol sampler (BGI, Waltham, MA). The hi-vol drew chamber aerosol through a fibrous glass filter to remove excess droplets at a rate that could be controlled, then recirculated the cleaned air to the chamber.

The electrostatic precipitator used in this work (Aerosol Associates, Hillsborough, NC) was designed for personal sampling at 2 L/min. It had a central ionizing wire within a grounded collection cylinder that was about 7.5 cm long and 1 cm in diameter. A disposable collection substrate made from coated aluminum foil was

placed within the cylinder for mist collection. The precipitator was powered by a miniature high-voltage power supply that consumed less than one watt and could run from a small, rechargeable battery.

A 37 mm filter holder containing a pre-weighed filter of either PVC or MCE (SKC Inc., Eighty Four, PA) and the ESP with a pre-weighed substrate were placed next to each other in the chamber at position 1 and position 2 as shown in Figure 1.

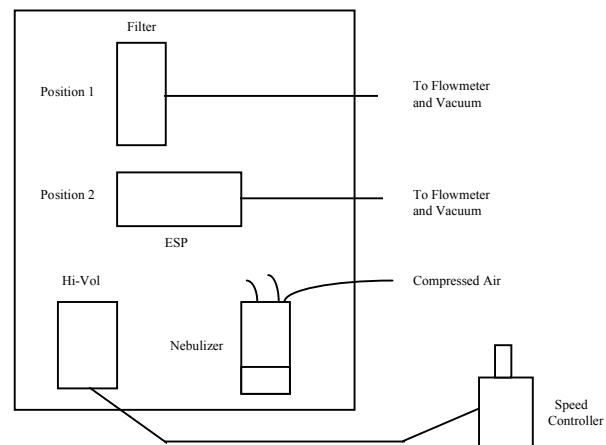


Figure 1. Apparatus used to load mist onto filters and ESP substrates.

Flow through both samplers was set at 2.0 L/min, and sufficient aerosol was generated to draw the target amount of mist through both the filter and the ESP in about 30 minutes. The target loadings, designated "low," "medium" and "high," corresponded to loadings for hypothetical samples taken at 2 L/min for about 8 hours at mist concentrations of about 1, 2.5, and 8 mg/m³, to correspond with what might occur in the field. After loading, air flow was stopped, the chamber was opened, and the filter and substrate were re-weighed to determine the mass of mist collected by each. All weights were measured using a Cahn 27 electrobalance (Cahn/Ventron, Cerrito, CA). A balance-room blank was weighed each day to determine the sensitivity of the filter and substrate to changes in balance-room humidity.

To evaluate further the potential for samples

to evaporate, the loaded filter and substrate were then returned to their samplers and clean lab air was passed through each at 2.0 L/min for four hours. The filter and substrate were then removed and weighed once again to determine whether any of the mist previously collected was lost to evaporation during this time. Although workers would not ordinarily pass their day in the exact same exposure pattern as our test program, mist exposure followed by exposure to relatively clean air might occur as workers spend time on the job then move about the plant, eat lunch, or take breaks.

Paired tests were conducted with the ESP and each of two filters for three mist loading conditions, and with the filter and ESP in each of the two sampling positions. Each test condition was replicated twice so that in all, 24 experiments were conducted as listed in Table 1. Sample blanks for both filters and ESP substrates were carried in all experiments, and all experiments were conducted in random order. Logarithms of data for loading and evaporation were taken before statistical analysis.

Table 1. Experimental conditions

Variable	Level Investigated
Sampler type	ESP and MCE, ESP and PVC
Mist loading	low, medium, high
Position in chamber	position 1, position 2
Replicates	2

The mineral oil used in these tests was Metalite SV-5 obtained from a supplier of commercial machining oil (Metal Lubricants, Co., Harvey, IL). This oil is comprised of a wide range of compounds, but is predominantly straight-chain, aliphatic hydrocarbons from C₁₄ to C₂₀ in length.⁽⁹⁾

After use, each filter and substrate was placed in its own sealed container. Filters were stored in sealed, plastic dishes and the cylindrical

ESP substrates were stored in plastic tubes with screw caps. To determine the stability of the used filter and substrate weights over several weeks, each used filter and substrate was repeatedly removed from its container, re-weighed, then replaced in its container.

RESULTS

Analysis of variance for the data found that any effect of sampler position in the chamber was not significant statistically for amounts loaded, evaporated, or left after evaporation for the ESP substrates and for both types of filters, $p > 0.21$ for all tests. Thus, the data for the effect of sampler position were pooled to give a total of four replications for each condition.

Figure 2 shows, for each loading category, the mass of mineral oil initially collected by the ESP substrate and by both the MCE and the PVC filters. On average for each loading category, the ESP substrate collected more mist than the MCE or PVC filters, and a Wilcoxon signed ranks test^(2,3) found that this difference was significant, $p < 0.001$. Although the MCE filter collected more than the PVC filter under the "high" loading condition, collection for the two filters under other loading conditions was similar. The Wilcoxon test found no significant difference in loading with filter type, $p = 0.18$.

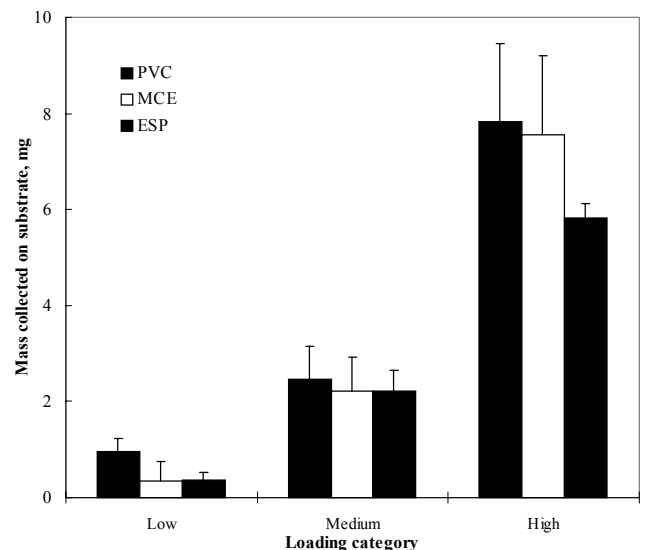


Figure 2. Mass initially collected vs. target loading for collection by the ESP and by MCE

and PVC filters

Under the “low” loading condition, the difference between the collection on the ESP substrate and the collection on each of the filters was particularly pronounced. At “low” loading the ESP collected, on average, 0.98 mg of oil mist whereas the MCE and PVC filters collected 0.34 and 0.35 mg, respectively, a factor of about 2.8 less.

Figure 3 shows the loss in the mass of mineral oil from the filters and ESP substrates caused by passing clean lab air through each for four hours.

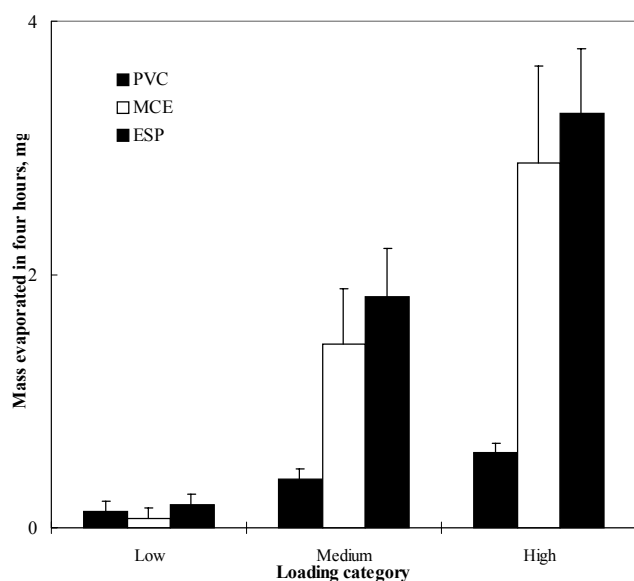


Figure 3. Mass lost after passing clean air through loaded substrates and filters for four hours vs. target loading for the ESP, and for MCE and PVC filters

These losses, presumably due to evaporation of the collected mineral oil, were substantially greater for the PVC filters than for the MCE filter or ESP, $p=0.033$ and $p=0.003$ respectively. Overall, losses from the filters were significantly greater than losses from the ESP substrates, $p<0.001$, although this situation varied with loading category. For the “medium” and “high” loading categories, Figure 3 shows that losses from both MCE and PVC filters were much greater than the losses from the ESP substrate.

For the “low” loading category this situation changed somewhat, as losses from the ESP were between those for the PVC filter and the MCE filter. However for the “low” category, as discussed above, the ESP collected about 2.8 times as much oil as the filters so that more oil was available to evaporate from the ESP substrate. If evaporative losses are expressed as a percentage of initial load, the evaporative losses for all filters under all loading conditions were substantially greater than the corresponding losses from the ESP substrates, $p<0.001$.

Figure 4 shows, for each loading category, the mass of mineral oil that remained on the ESP substrate and on both the MCE and PVC filters after clean lab air passed through each for four hours.

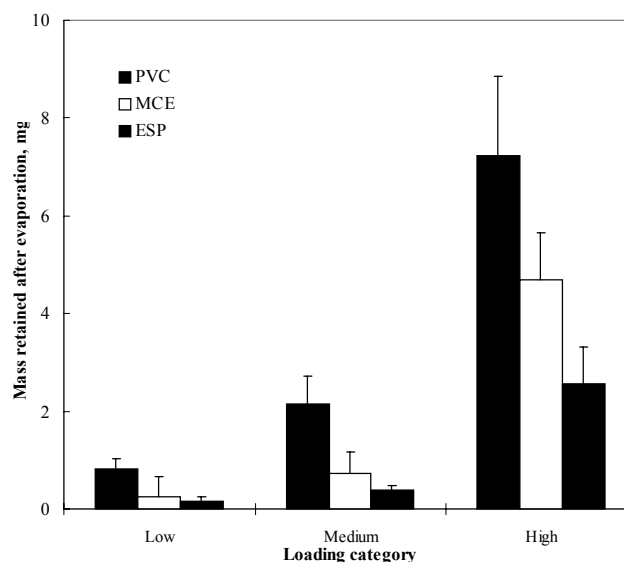


Figure 4. Mass retained on loaded substrates and filters after passing clean air through them for four hours vs. target loading for the ESP, and for MCE and PVC filters.

The values in this figure were obtained by subtracting the evaporative losses from Figure 3 from the amounts of oil initially collected from Figure 2. Figure 4 shows that overall, the ESP retained nearly twice as much oil as the MCE filters, and over three times as much as the PVC filters; this difference was significant, $p<0.001$. Figure 4 shows that the differences in oil retention

among the three samplers were particularly marked for the "low" loading category in which the ESP retained 3.3 and 5.0 times as much oil as the MCE and PVC filters, respectively. Although overall, the MCE filters retained nearly twice as much oil as the PVC filters this difference was of marginal significance, $p=0.059$.

The balance-room blanks were analyzed to determine whether relative humidity affected their weights. Humidity varied from about 25% to over 60% for the period when these experiments were conducted. Regression analysis showed that the weights of the ESP substrates and the PVC filters were stable and had no significant dependence on relative humidity, $p=0.91$ and $p=0.05$, respectively. Weights of the MCE substrates significantly increased with increases in humidity, $p<0.001$. This dependence was linear, and had a coefficient of 0.017 mg weight gain per 1% increase in relative humidity. Thus, a 10% increase in balance-room humidity caused an increase in the MCE filter weight of about 0.17 mg, a value comparable to some sample weights in these tests and similar to weights expected from 8-hour samples close to the proposed TLV of 0.2 mg/m³.

Re-weighing used substrates and filters over several weeks showed that all gradually lost mass over time. For each day after sampling spent in a sealed container, the ESP substrates lost about 0.8% of the mass originally collected and this dependence was significant, $p=0.01$. The filters lost approximately 0.5% of the mass they originally collected for each day after sampling, and this dependence was also significant, $p=0.01$. The loss coefficients of 0.8%/day for the ESP substrates and 0.5%/day for the filters were not significantly different. For both the ESP substrates and for the filters, the percentage loss depended significantly on the initial mass load, $p<0.02$ for both, with the highest percentage losses in cases where the initial loading was "low" and the lowest percentage losses when the initial loading was "high." Thus, delay in analyzing a sample after it is taken may reduce the resultant concentration reported, with the greatest

percentage reductions associated with the lightest substrate loadings.

DISCUSSION

Data given in Figures 2 and 3 support the idea that sample evaporation can occur, particularly when samples of mineral oil mist are taken using MCE and PVC filters. Figures 2 and 4 suggest that differences in sampling methods for oil mist can be especially important when measured mist concentrations are low, less than about 1 mg/m³. Evaporation from ESP substrates was substantially less than evaporation from either filter type, presumably because the ESP removes collected mist from the air stream and coalesces it to form a film with less surface area.

Figure 2 shows that significantly less oil was collected by the filters than by the ESP substrates. These results were obtained in tests where the filters and substrates were loaded quickly, in about one half hour. In the field, sampling would occur over several hours so that the opportunity for sample evaporation would be greater. Thus, the differences between sample loadings for the filters and ESP substrates shown from the lab results in Figure 2 could be more pronounced for field conditions where the filters and substrates are loaded more gradually.

Figure 3 shows that evaporative losses from loaded MCE and PVC filters during exposure to clean air were more substantial than losses from a loaded ESP substrate. To the extent that a worker enters clean areas while wearing a personal monitor, similar evaporative losses could occur.

Figure 4 shows residual retention after collection and evaporative losses. A comparison of the filter types shows that retention by the MCE filter was better than retention by the PVC filter; however, the weight of the MCE filter was very sensitive to small changes in lab humidity. Thus, neither filter type performed well in these tests. The ESP substrates were better at sample collection and lost less in evaporation to clean air, and consequently had greater retention than either filter. In addition, the ESP substrates had stable weights despite humidity fluctuations in the

balance room.

The results presented here suggest that mist samples are gradually lost over time when stored. Perhaps the collected mist re-partitions from the filter or substrate to the inside surface of its storage container, to the air within the container, or both. These results suggest that excessive delays in sample analysis may lead to the underestimation of sample concentration. The test methodology used here may have aggravated this trend, as repeated opening of the sealed containers to re-weigh the filters or substrates would cause repeated opportunities for replacement of vapor-saturated air in the container with unsaturated lab air.

The mineral oil used in this work was fresh. In a manufacturing plant the oil is recirculated, with daily makeup to replace carryover due to parts transfer, so that the average age of the used mineral oil would be greater than that tested here. If the lighter fractions of this oil evaporate during use, then mist generated from this oil would be deficient in the more volatile fractions and less prone to evaporate. By this reasoning, the lab results reported here would overestimate the tendency for sample evaporation in the field. In addition, the chemical composition of mineral oil will vary according to its proposed use and from manufacturer to manufacturer.

Evaporation rate also depends on the oil vapor concentration of the surrounding air calculated on a compound-by-compound basis; these concentrations will increase with temperature but decrease with dilution by outside air. Because the lab tests reported here were conducted within a closed chamber, the oil vapor concentrations should have been relatively high and decreased the tendency for evaporation. During summer, warm temperatures in a plant should increase vapor concentrations; however, dilution by outside air to control temperature will reduce vapor concentrations; the reverse will occur in winter. The degree to which any of these factors plays a role at a particular plant will depend on plant ventilation practice, temperature, oil properties, and the nature of the machining

operations for which the fluid is used. The present results indicate the possibility that sample evaporation can occur, but the quantitative results presented here cannot reliably be used to predict the degree of evaporation that might occur in the field.

Evaporation of collected oil mist could lead to scatter in exposure assessment data taken in the field using MCE or PVC filters. Data scatter would be aggravated if evaporation varies from location to location due to factors such as variable ventilation rates, temperature conditions, or fluid makeup. Such scatter would tend to obscure any relationship between exposure and disease. Whether this problem has occurred in past studies is difficult to say, but future studies should consider alternative sampling techniques such as the ESP that minimize the problem.

CONCLUSIONS

The vapor pressure of mineral oils used as coolants in metal machining operations is so low that evaporation of pooled liquids is not a problem; however, these materials can experience significant evaporation when dispersed as an aerosol of small droplets with high specific surface. Overall, for the sampling protocol used here, this work found that a small electrostatic precipitator retained nearly twice as much oil mist as an MCE filter and over three times as much as a PVC filter. Retention was greater in the precipitator because it separates collected mist from the air stream and coalesces it into a film that has much less aggregate surface area than that for the aerosol droplets collected on a filter. The quantitative results presented are particular to the lab tests used here and cannot reliably be extrapolated to field conditions where sample retention could be greater or less.

ACKNOWLEDGMENTS

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Comparison of Machining Fluid Aerosol Concentrations from Three Different Particulate Sampling and Analysis Methods

James B. D'Arcy (A), **David Hands** (B) and John J. Hartwig (C)

(A) General Motors Research and Development Center, 30500 Mound Road, Warren, Michigan 48090

(B) Ford Motor Company, 15000 Century Drive, 104 Central Lab, Dearborn, Michigan 48120-1220

(C) Chrysler Corporation, 12000 Chrysler Drive, Highland Park, Michigan 48288-0001

ABSTRACT

The goal of this research was to investigate the differences between three different sampling and analytical methods currently used for measuring worker exposures to machining fluid aerosols. There is currently no generally accepted method of collection and analysis of machining fluid aerosols. The three methods investigated in this work all use similar collection procedures, but different analytical procedures for reporting machining fluid exposure. All analyses were conducted by the three laboratories used for routine personal sampling with these methods. Area samples from a total of 24 sites (216 filter cassettes) involving the four basic fluid types (6 sites each) were investigated. The overall mean machining fluid concentration values, and those for specific fluid types, were not statistically different between the three methods studied. This study indicates similar machining aerosol measurement performance for the three methods within the range of concentrations and conditions studied. However, the study does not address the appropriateness of these non-specific methods for assessing health risks posed by machining fluid aerosols.

INTRODUCTION

The ability to quantitatively evaluate a hazard is essential to health protection when the hazard cannot be completely eliminated from the worksite. The subject of this research is the investigation of the differences between three different sampling and analytical methods currently used for measuring worker exposures to machining fluid aerosols in the automotive

industry. There is currently no generally accepted method of collection and analysis of machining fluid aerosol that is applicable to all fluid types. The lack of consensus is largely due to the wide range of materials in the machining fluids and the lack of a specific putative agent for the reported health effects. A current NIOSH method (5026) for *OilMist*, *Mineral*, utilizes infrared spectrophotometry to determine the total hydrocarbon content (C-H bond stretch) of filter extracts.⁽¹⁾ This method is not specific to any offending class of materials and it is not applicable to water-based fluids. The analysis of specific compounds from the circulating fluid has been used as an indicator or "tracer" of machining fluid exposure, but this technique has not been widely accepted.⁽²⁾

To evaluate the three different analytical methods used in this study eight sites were selected at each of the three domestic automobile manufacturing corporations. The sets of eight sites were equally divided between the four basic types of machining fluid: straight mineral oil, soluble oil, semi-synthetic fluid, and synthetic fluid. The sites were typical machining or grinding operations that were selected for their ability to accommodate the sampling equipment and secondarily to minimize travel from the Detroit area. All samples were collected as area samples and may not be representative of current personal exposure levels; however, all results are within the range of personal exposures that can be encountered in the machining environment.

EXPERIMENTAL Aerosol Collection

The three methods investigated in this work all use the standard 37 mm plastic filter cassette, with a 4 mm inlet opening and a 2.0 liter/minute sampling rate for aerosol collection. The collectors are operated in a manner similar to NIOSH Method 0500 for *Particulate, Total*.⁽³⁾ Method I collects the machining fluid aerosol on a pre-weighed glass-fiber filter, method II collects the machining fluid aerosol on a pre-weighed PFTE (e.g. Teflon filter) and method III collects the aerosol on a pre-weighed PVC membrane filter.

To improve the determination of the intra-method and inter-method variation of the three analytical methods, a new area sampler was designed and built at General Motors to allow the simultaneous field collection of triplicate samples for each of the three methods (9 filter cassettes) from the "same location." The sample cassettes are located around the circumference of a round manifold that uses a single vacuum source and precision valves as adjustable critical flow orifices. The maximum distance between inlets is 18 cm and the entire manifold rotates at 0.5 rpm to minimize any spatial differences in the area of sample collection. The collection device reduces collection variability to less than 2% (data not shown here).

Aerosol Analysis

The three methods investigated in this work differ most in the analysis and reporting of the analytical results. None of the three methods is specific to a class of materials or specific toxic compounds. However, methods I & II provide some selectivity by separating non-polar compounds from the total aerosol. The non-polar fraction will contain mineral oil and long-chain fatty acids and may provide a better measure of "machining fluid aerosol."

All samples collected in this study were analyzed and reported by the same laboratories used for routine workplace sampling of machining fluid exposures. The details of the three analytical methods for measurement of machining fluid exposure are given below.

Method I post-weighs the glass-fiber filter and calculates "total particulates." The glass-fiber filter is subsequently extracted with 10 mL of trichloroethylene and dried. The glass-fiber filter weight loss following extraction is used to calculate the reported "machining fluid" concentration.

Method II post-weighs the PFTE filter and calculates "total particulate." The PFTE filter is then extracted with toluene. The toluene solvent is then removed and the residue of extracted compounds is weighed and used to calculate the "machining fluid" concentration. Both total particulate and machining fluid concentrations are reported.

Method III desiccates the collected filters over calcium sulfate (e.g. Dryrite) at atmospheric pressure for 8-24 hr and then post-weighs the PVC filters. The collected mass is used to calculate the reported "machining fluid-total particulate."

RESULTS

The results from the analysis of the 216 samples is reported in Table I for each of the three methods and for each of the four basic fluid types. The mean coefficient of variation from the 6 sets of triplicate analyses for each fluid type or 24 sets in the overall analysis are presented in parentheses. One extreme value result for straight oil analysis by method III was eliminated from the analysis. Table II presents the data restricted to values of 2.0 mg/m or less (as determined by method I), which is probably more typical of current occupational exposure levels. The difference in mean values of triplicate samples for "machining fluid aerosol" by the different methods was statistically significant for 8 of the 24 sites (72 comparisons). Two of the significant differences appear to be the result of differences in reported significant figures at very low concentrations and may not be indicative of a true analytical difference.

The observed mean intra-method coefficients of variation for the three methods of measuring "machining fluid aerosol" were 0.14,

0.15, and 0.16 for methods I, II, and III, respectively. These are all greater than the 0.065 or 0.056 predicted by NIOSH for methods 5026 and 0500, respectively. Regression analysis of the results for methods I and II show a strong relationship between total particulate and "machining fluid aerosol" as determined by extraction of the collected particulate. Total particulate was found to be predictive of 92 percent of the variation in the "machining fluid aerosol" result. However, site 19, which involved a mixture of dry and wet machining, showed a strong positive bias for the total particulate results when compared to the extraction results.

CONCLUSIONS

Overall, this study indicates similar a "machining fluid aerosol" measurement performance for the three methods within the range of concentrations studied.

The coefficients of variation for the analytical techniques, as used in the field, are less precise than anticipated, in spite of a major reduction in the sample collection variability.

The study does not address the

appropriateness of these nonspecific methods for assessing health risks posed by machining fluid aerosols.

Analytical method development should focus on improvements in the specificity of the method for the fluid or fluids being used. This effort should reflect the growing health knowledge and strive to produce a method specific to attributed health effects.

REFERENCES

1. **National Institute of Occupational Safety and Health:** Method 5026, Oil Mist Mineral, in NIOSH Manual of Analytical Methods, NIOSH, Cincinnati, 1994.
2. **Lee, GL:** Oil and Coolant Mist-Assessment Criteria and Control, in *Proceeding of a Conference on the Health Hazards of cutting Oils and Their Controls*, Ed. D. C. Glass, The University of Birmingham Press, Edgbaston, UK, 1989.
3. **National Institute of Occupational Safety and Health:** Method 0500, Particulate, Total, in NIOSH Manual of Analytical Methods, NIOSH, Cincinnati, 1994.

Table I

Results of Machining Fluid Exposure Measurements

The mean coefficient of variation from the 6 sets of triplicate analyses for each fluid type or 24 sets in the overall are presented in parentheses

Fluid Type	Method I	Method I	Method II	Method II	Method III
	Total Particulate (mg/m ³)	Machining Fluid (mg/m ³)	Total Particulate (mg/m ³)	Machining Fluid (mg/m ³)	MF-Total Particulate (mg/m ³)
Straight Oil	1.39 (0.17)*^	1.26 (0.06)^	1.44 (0.14)*#	1.24 (0.15)#	1.01 (0.08)^#
Soluble Oil	1.93 (0.05)^	1.77 (0.06)^	1.85 (0.11)	1.64 (0.08)#	1.73 (0.08)^#
Semi-Synthetic	0.95 (0.07)*^	0.64 (0.19)	0.86 (0.20)*#	0.52 (0.13)#	0.76 (0.32)^#
Synthetic	1.18 (0.06)*^	0.88 (0.26)*^	1.03 (0.09)*	0.77 (0.24)*#	1.08 (0.17)^#
Overall 24 Sites	1.36 (0.09)	1.14 (0.14)	1.30 (0.13)	1.04 (0.15)	1.17 (0.20)

*Significant difference for one or more samples between method I and II ($p \leq 0.05$)

^ Significant difference for one or more samples between method I and III ($p \leq 0.05$)

Significant difference for one or more samples between method II and III ($p \leq 0.05$)

Table II**Results of Machining Fluid Exposure Measurements $\leq 2.0 \text{ mg/m}^3$**

The mean coefficient of variation from the 5 or 6 sets of triplicate analyses for each fluid type or 22 sets in the overall are presented in parentheses

<u>Fluid Type</u>	<u>Method I</u>	<u>Method I</u>	<u>Method II</u>	<u>Method II</u>	<u>Method III</u>
	Total Particulate (mg/m ³)	Machining Fluid (mg/m ³)	Total Particulate (mg/m ³)	Machining Fluid (mg/m ³)	MF-Total Particulate (mg/m ³)
Straight Oil	0.64 (0.20)*^	0.59 (0.03)	0.72 (0.16)*#	0.52 (0.17)#	0.57 (0.09)^#
Soluble Oil	1.23 (0.06)^	1.10 (0.07)	1.18 (0.12)	1.02 (0.07)#	1.00 (0.09)^#
Semi-Synthetic	0.95 (0.07)	0.64 (0.19)	0.86 (0.20)	0.52 (0.13)#	0.76 (0.32)#
Synthetic	1.18 (0.06)*^	0.88 (0.26)	1.03 (0.09)*	0.77 (0.24)#	1.08 (0.17)^#
Overall 22 Sites	1.01 (0.09)	0.80 (0.15)	0.95 (0.14)	0.70 (0.16)	0.86 (0.18)

*Significant difference for one or more samples between method **I** and **II** ($p \leq 0.05$)

^ Significant difference for one or more samples between method **I** and **III** ($p \leq 0.05$)

Significant difference for one or more samples between method **II** and **III** ($p \leq 0.05$)

DISCUSSANT'S COMMENTS and OPEN DISCUSSION

Dr. TAI CHAN, General Motors: We have heard a lot of original contributions to the scientific literature, and a lot of recent studies that were done in the last few months, and we want to focus the discussion this morning on several topics. One is the issue of sampling methodology. The second one is particle size-selective TLVs. Also, we want to focus on the contaminants in both air and the fluids. And fourth, the status of a sampling method which, perhaps, could be a sampling standard. I know Dr. Woskie has mentioned some of the data in the bioaerosol area and we may want to defer some of the more technical questions on the bioaerosols until this afternoon, because there will be a series of very in-depth presentations on that topic, but if you want to ask her about specific data, please do so.

To begin the Discussion Session, I would like to introduce the first Discussant. It's Dr. Dennis O'Brien. He is the Director of the Division of Physical Sciences from NIOSH and I'm very glad he is here with us today. As you know, there is some perturbation in Washington, D.C., but I'm glad the essential services of NIOSH are still here. Dennis.

Dr. DENNIS O'BRIEN, NIOSH: Good morning. Dave Hands, in his last presentation made reference to the statisticians in the audience. I hope there aren't any statisticians here because I'm going to say something that's probably going to offend them, but this is the definition of a statistician. This definition was actually first given by a NIOSH person of the statistical persuasion. A statistician is basically a person who really wanted to be an accountant, but lacked the warm, outgoing personality.

I would like to do a little commercial for the NIOSH Division of Physical Sciences and Engineering. This Division develops the tools to measure and control the workplace environment. This division currently provides comprehensive, analytical chemistry support to all of NIOSH's field

activities, including several current health hazard evaluations that are being conducted on metalworking fluids. We are currently developing improved measurement tools for metalworking fluids and their important constituents and contaminants, including biological agents.

We are also working with our external partners to improve the technology to limit exposure to these materials. This control technology research includes a closer look at some of the important processes and environmental factors identified by Dr. Woskie in her paper.

Before talking about specific papers, let me first go back to the basics. Why is it that we sample and second, how do we sample? First, and maybe this seems obvious, one of the primary reasons for sampling is to determine if a health hazard exists. Now this implies that we are examining a specific constituent and have identified appropriate criteria for the evaluation of the hazard.

Another reason for sampling is to determine exposure categories for the purpose of epidemiological studies. In this case, we may be examining a specific constituent or possibly some gross indicator of exposure. Hazard criteria really are not necessary.

Next, we may sample as a surveillance tool, and I'm really talking about surveillance in the broadest sense, to assure maintenance of a healthful working environment. And in this case, an exposure index may be appropriate, because factors such as cost and the easy use of the sampling method are really appropriate.

Last and perhaps the most common reason for sampling is to determine compliance with legal requirements and this is really the simplest situation because we merely follow the letter of the law and whatever the sampling procedure is.

Next I would like to talk a little bit about the "how" of air sampling. The air contaminant in question must first be collected. We have to get it into a sampler. We have to keep unwanted materials out of the sampler. The particular

sampler needs to reflect the target organ. In other words, its size efficiency must be appropriate for the hazard in question.

Next we need to analyze the sample that is collected. Typically we collect the particles on filters and we collect gasses and vapors adsorbed on solid surfaces. In the case of metalworking fluids, we have a problem. We normally try to exploit some chemical/physical property of the contaminant in question to be able to quantify it. In the case of metalworking fluids, though, the only property that straight oils, soluble oils, synthetics and semisynthetics have in common is the fact that they all have mass. Thus, it's not surprising that the methods used by the auto makers all rely on the weight of the collected material. Although the techniques employed by Chrysler and Ford first remove insoluble, non-oil type particles by solvent extraction, GM measures the total mass.

It's somewhat surprising, then, the results presented by Dave Hands. In this comparison there was really no significant difference between any of the three methods. These were at levels approaching one milligram per cubic meter. What happens as the oil mist or the metalworking fluid mist approaches zero? Well, there are background levels, background air pollution that typically can be about 0.1 milligrams per cubic meter. You would expect to see differences as the mean fluid concentration was lower and approached zero.

Another curiosity is that for about half of his sample sets, the amount of extractable material was greater than the total mass that was measured.

How accurate are these measurements? Dr. Leith's research indicates that there may be a negative bias present in these methods, as some of the volatile components may evaporate from the filter.

I would also like to take some time to talk about the first two papers that were presented. These didn't deal with sampling methods per se. The first paper by Dr. Pederson is very important because it addresses a strategic approach to exposure control. It tells us that the use of bulk material and chemical or mutagenicity tests can be

used to eliminate or to minimize the presence of carcinogenic materials in the base products.

This paper also addresses the issue of PAH formation in processing and recycling. What do these numbers mean though in terms of workplace exposure? I did a little 'back of the envelope' calculation in looking at some of his worst case numbers, 3,000 micrograms per milliliter of oil. In looking at present and past exposures on the order of one milligram per cubic meter to five milligrams per cubic meter of metalworking fluid mist and I came up with an estimated PAH exposure of about four to 20 micrograms per cubic meter.

How do those numbers compare to known hazardous environments? I don't keep a log of PAH levels in the back of my head, but I do know that coke oven workers were exposed to PAH concentrations about an order of magnitude higher than these levels. And they experience an approximately tenfold increased risk of lung cancer. So to me, this suggests that there is or was at least a moderate risk of cancer to workers exposed to PAH contaminated metalworking fluids.

The second paper on formaldehyde exposure from triazine-based biocide was also very intriguing to me. This paper is important because it illustrates both good product stewardship on the part of the companies in question and also, the impact and the value of government regulation in the form of the OSHA Formaldehyde Standard that really spawned that particular study.

The methods used in that particular study represent a conservative approach, as they will probably over-estimate formaldehyde exposure in these work environments. This over-estimation is due to two factors. First, the analytical methods which were used in the study will not differentiate between free formaldehyde and formaldehyde which would result from the hydrolysis of the triazine compound, if any of the metalworking fluid aerosol was collected by the samplers.

Second, no mention was made of other factors that could produce background formaldehyde levels. One observation was made,

that personal samples were higher than area air samples. Since the workers wore samplers on their breaks, this begs the question: Did cigarette smoke in some way contribute to the formaldehyde levels that were measured? Again, though not to criticize the methodology, this represents a conservative approach as it would over-estimate formaldehyde exposures.

Where do we go from here? We probably have methods that are adequate right now for surveillance purposes. However, as stated by others, these methods may not be appropriate for assessing health risks. Thank you.

Dr. TAI CHAN, General Motors: Thank you, Dr. O'Brien, for those incisive comments. Our next Discussant is Dr. Jim Vincent. In Europe I would have to introduce him as Professor Doctor Doctor Vincent. Jim is Professor of Industrial Hygiene in Occupational Health and Safety at the University of Minnesota. He's also the Editor in Chief of Journal of Aerosol Science. So with that - Jim.

Dr. JAMES VINCENT, University of Minnesota: Thank you, Tai. Since we are being politically incorrect with respect to statisticians, I might also add another comment I heard from a colleague of Dennis' at NIOSH on an occasion about three years ago when he showed two slides during a presentation. The first one said "If all the statisticians in the world were laid end to end, dot, dot, dot," and the second slide said, "It would be a good thing." I won't mention whose name that was. And since I'm not going to mention statistics, I hope there won't be too many brick bats in my direction. Well that's taken 30 seconds of my time so quickly, I'll move on.

I'm going to address some fairly broad questions about exposure assessment and then, if there's time at the end, I might try to pick up one or two specific points on issues that were raised this morning.

The first thing that I should say is that we should be prepared to take on board the fact that

sampling methodology and standards are strongly connected. That means that if we have different sampling methods or we change the sampling methods, then there is a very profound impact on the meaning of the standard. We really cannot separate the two things.

We have learned a great deal from modern aerosol science during the last 20 years, and in particular, the science of sampling for aerosols has advanced significantly. We have learned that simply drawing air through a filter does not necessarily mean we are going to sample total aerosol or any other well-defined fraction. Rather, the collected sample will depend on particle size, the flow rate, and a whole range of other factors.

The interesting thing is that the very same physical constraints or conditions apply to human exposure. So it should be reasonable that if human beings are exposed to aerosols in a certain way, the human being is in effect, therefore, an aerosol sampler. We ought to be able to devise methods of sampling which reflect how these people are exposed.

Now I should like to bring everybody up-to-date, in case there's anybody here who doesn't know, about what is happening in the area of standards setting and in the international industrial hygiene community. This involves a discussion which goes back for nearly 20 years. I attended my first meeting on the subject in 1979 in London, sponsored by the International Standards Organization. And since the very early eighties, the ACGIH has been carrying the torch in this country. The whole purpose of that discussion has been to try to point us towards an exposure assessment approach which reflects how people are physically exposed. This requires us to recognize that in fact the measurements that we have been making do not appear to relate to actual human exposures. That includes some of the methods which we are still using today.

Let me quote you brief passages from Page 7 of the new ACGIH TLV Booklet. I know Bill Wagner is at this Symposium and if you'll permit me to actually read from this so that we're all on the same page, it states at the top of Page 7: "The

term total particulate is ill-defined, since no practical sampler can collect all airborne particles with 100 percent efficiency." So we know that to be true. The intent of the Chemical Substances TLV Committee is to replace all total particulate TLVs with inhalable, thoracic or, and I think I would say and/or, respirable particulate matter TLVs. All proposed changes will be included on the notice of intended changes and comments invited. Publication of the results of side by side sampling studies using older total, that means present total, and newer inhalable thoracic or respirable sampling techniques is encouraged to aid in the appropriate replacement of current total particulate TLVs.

This, I therefore put to you, is a clear indication of where we are going, and I think that things are going to change and that there will be new TLVs. The question is: Are there practical samplers which reflect exposures according to these criteria? and the answer is sometimes yes, and sometimes no. There is a small, but growing, group of samplers which do perform according to the new criteria. For the inhalable fraction, for example, it has been declared that this will in the future replace 'total' aerosol which I always write in inverted commas since this is not time total aerosol. So we shall be required to replace current 'total' aerosol samplers inhalable samplers.

There are a number of samplers out there as candidates for this fraction, and some are available commercially. I know that in Europe there is a large study currently in progress to characterize other samplers, and hopefully this will add to the list of inhalable samplers.

Now, regarding comparisons between 'old' and 'new' methods for sampling in work places, there have been several thousands of such samples taken in wide ranges of industries. We ourselves have conducted major studies in the nickel using and producing industries, and lead production. Other experiments have been carried out in Europe and Scandinavia, as well as in this country, and what we are seeing is a very consistent trend in which the inhalable fraction is higher than what we have been measuring in the past as total aerosol.

This tells us that, currently and in the past, we have been substantially under-sampling with respect to what people actually inhale.

The factors range anywhere from 1.5 to 4, depending in part on the coarseness of the aerosol. We have ourselves conducted a relatively small study on metalworking fluids a large machine shop using straight cutting oils and found a factor of greater than two. Although there was some evidence of splashing of oil droplets, it is believed that these results do reflect the time bias between inhalable and 'total' aerosol. If I have a minute right at the end, I'll try to say something more about that.

Now, the interesting thing about this scenario is that if overnight we were to change the criteria for exposure measurement, that is to introduce the inhalable fraction, then we would observe apparently increased exposures. That could be regarded, if you like, as a step in the right direction in terms of worker protection. The complication comes if we are considering not only changing the exposure criterion, but changing the TLV numbers as well. For example, there are notices of intended changes in the ACGIH TLV booklet for many substances. Perhaps we should first get out of the way the question of the exposure criterion, make that decision and examine the impact of implementing the inhalability criterion, and then move on to develop strategies for assigning new TLV-values.

For metalworking fluids, I have heard this week discussion about carcinogenic effects and about the respiratory effects. So, therefore, we have to make a decision about whether we should be measuring exposure according to an inhalable fraction, which is what we would do if we were interested in carcinogenic effects, or whether, if the primary target is the upper respiratory system, the thoracic fraction should be used as the basis of a new standard.

But in a discussion last night with Dennis O'Brien, he made a very good point to me in that the finer you make the fraction that you are going to use as the target, and the lower the levels that you are required to comply with become, then of

course you are increasing the degree of difficulty in actually being able to detect the level for that criterion. So one good reason for sticking with the inhalable fraction is that you are going to be collecting more aerosol and, therefore, it's easier to measure. But as we have been hearing this morning, when you measure total aerosol, it actually harder to collect these coarser aerosol particles. You have more variability in the collection process.

So I think we still have some talking to do on the aerosol sampling front, and on the actual TLVs and the basis of TLVs. Well, my red light has gone on so I will not address the question of splashing here, but I will be standing a lone vigil, I hope it won't be a lone vigil, by a poster presentation tonight and if anybody wishes to debate these issues with me there, I'd be more than happy to talk to them.

Thank you.

Dr. TAI CHAN, General Motors: Thank you very much, Dr. Vincent. Our third Discussant is Professor Tom Smith from the Harvard School of Public Health and as most of you know, Tom has been involved in the very early studies almost ten years ago and we're pleased to have Tom make some comments here.

Dr. THOMAS SMITH, Harvard: Thank you, Tai. I'm very pleased to be here. I'd like to express my appreciation to the United Auto Workers and General Motors for their sponsorship of so much of the research that has been presented here. I think that it has been a critical contribution to the field. The additional joint research efforts through Chrysler and Ford are also to be recognized for their importance and critical contributions. I think this research has both led to the development of research methods, in some cases actually defining the state of the art, and it has also been strongly practical and aimed at developing our interventions to control exposures and to assess their effectiveness.

What I'd like to do is back up a little bit and

set the stage for some of the discussion of exposure monitoring. I think it's useful to review the epidemiology and sort out how we got to this point. The epidemiology has identified clear, past cancer risk in a number of areas associated with broad machining fluid types and exposures, generally 20 or more years ago. In response to those findings, there have been three major changes. Known and suspected carcinogenic agents have been removed or sharply reduced in machining fluids, polycyclic aromatic compounds are perhaps the most notable in this regard, but certainly not the only one. There has also been extensive exposure characterization, which is critical for our ability to see where we are and where we might need to go. And, of course, there has been the very important effort to generally reduce the exposure to these materials.

Unfortunately, two uncertainties remain. We have the question: Have the changes in composition and the reduction in exposure eliminated the cancer risk? It seems likely, very likely I think, that the risk has been reduced. If there is some residual risk remaining, which of the remaining machining fluid components are associated with that risk? I think that is an important question that we should pursue in the future. As you have heard from the studies of respiratory effects, there also seem to be some clear risk associated with machining fluid exposures too. We have identified some agents as being clear contributors to the risk, but again, it's not clear which of the many components of machining fluids are contributing to the problem.

The fundamental dilemma of industrial hygiene is you have to measure something. Historically we have dealt with complex mixtures such as machining fluids and cigarette smoke and diesel exhaust by using markers. In this case for a long time we have used total aerosol. More recently we have been investigating inhalable and thoracic size aerosols. Ideally you want your measurement of exposure to be the agent that's causing the effect. In this case, as we have already heard and I'm sure we're all well aware, it's not exactly clear what the agent of the effects are, or in

some cases, even if there are agents of effects.

I think that because of that, the total aerosol is really a marker for a variety of agents in a variety of settings. The problem becomes, and it has been noted, is that there are inconsistencies in the studies. I don't find that surprising because we have all heard about the variety of components, the variations in exposure. Just to mention one simple example, soluble oils can vary from three to 30 percent of the raw material, and with use, that composition can change dramatically in many different directions. So to talk about machining fluid as if the total aerosol always defines the same composition is clearly a mistake. That leaves us with some significant gaps in our knowledge that we need to continue to pursue. I think the variation in composition and the limits of our knowledge about the active agents argues that we should keep total aerosol of some variety, best defined by the aerosol researchers. I think we should keep the total aerosol exposures as low as is feasible in order to minimize exposure to all of the components as a prudent engineering approach.

In view of the problems identified by Dr. Leith and his associates, it seems clear to me that there are major losses of semi-volatile components from the filters used as our basic collection technique. This, at the very least, will add noise and under-estimation to our estimates of total aerosol exposure, but it also leads to some interesting research questions which, I think have not yet been answered.

For example, how biologically active, that is, what hazard is associated with the volatile components that are lost? Does the resulting material that we have collected under- or over-estimate the risk? Should we be measuring the volatile component exposures?

As has already been noted by Dr. Leith, there are a number of posters which will present data and begin to address these issues. One point of interest, I'm aware that there are some animal, or perhaps it was cell bioassays that looked at the C₁₂ aliphatic hydrocarbons and observed that they can be tumor promoters in some situations. That finding argues that perhaps we should look at

them. Whether they have this effect in humans is obviously a good question, and the answer is not obvious.

These findings, coupled with those of Dr. Cohen's studies, strongly suggest that we need to develop both a standard method for aerosol and for some of the volatile or maybe all of the volatile components.

It has also been suggested by Dr. Lucke, and I agree, that we should characterize short-term variations in aerosol concentration with some type of real-time monitoring. The so-called spike or peak exposures can produce responses, particularly if we're talking about sensitization to aerosol components. And this possibility really has not been assessed or addressed.

Dr. Woskie mentioned, and others have noted, the presence of tramp oil, leaked hydraulic fluid, carryover machining fluid from other operations, oil washed from parts, et cetera, et cetera. The composition of these materials is poorly characterized and their contribution to the effects are an uncertainty, and I believe these effects really need to be assessed.

Just a quick comment on Dr. D'Arcy's points about the IOM sampler as being a problem. It is a problem if your focus is on the aerosol that will penetrate into the respiratory tract. It may, in fact, be the right way to measure exposures if you're also concerned about eye irritation, nose and throat exposure, and perhaps GI exposure, where these large particles, perhaps mist droplets is a better way to characterize them, can go into the GI tract. Perhaps they are associated with the esophageal and other GI cancers that were noted in some of the epidemiologic studies.

So the question of appropriateness for aerosol methods really depends on your research question, and I think that varies as we have seen. Well, what conclusions can we draw from all of this? First a clear need is present for a standard method for a total or thoracic aerosol as a marker of all of the components of machining fluids.

Second, I think more data and a method are needed to characterize organic vapors that may be produced by the machining fluids.

Third, more work is definitely needed to evaluate and measure tramp oil. Some users and producers have, I'm sure, done work in this area, but very little has been published in the scientific literature and this is, I think, a significant need.

Fourth, we should continue to work to identify specific components whose hazards have really not been adequately described by the total aerosol marker that we are measuring. I see our monitoring strategy as a combination of a general marker for aerosols, and perhaps one for volatile organic compounds, coupled with specific component measures such as PACs, ethanalamines, et cetera.

The fifth problem is changes in formulation of the machining fluids. It has been said that many of these components are derived from materials safe for food use and I have no doubt that that's true. Unfortunately, they may not also be safe for inhalation exposure, and that has been noted by others.

I think the bottom line is that we must develop and maintain the quality of our air exposure monitoring methods for two reasons. One, we need precise and accurate estimates of exposure to assess risk and, two, we need good methods to assess our efforts to control and reduce exposures and eliminate risk. Thank you very much.

Dr. TAI CHAN, General Motors: I would like to add another bottom line and that is we need to capture the essence of science and technology and implement controls in the workplace. We're ready for the Q and A session now and as you start lining up, please make sure that you announce your name and state your questions clearly.

Mr. William Cutri: Bill Cutri, Wallover Oil Company. I have a question for David Hands. Can you give us an idea of the cost of the equipment, ease of use and the cost per test for your sampling methods and, two, can these tests be

easily run in the plethora of small machine shops that we have across the country?

Dr. JAMES D'ARCY: You're talking about the area sampler?

Mr. Cutri: Yes.

Dr. D'ARCY: The samples that were collected are normal, routine samples submitted to the same laboratories as anybody else. So the only thing that's unique is the sampler itself and it's custom-made for this purpose. I don't know, maybe we could arrange for you to borrow one, but at the moment-

Mr. Cutri: Is there just one in existence?

Dr. D'ARCY: There are four. There's four of them in existence that we used. We had two at a corporation at a time to collect the data. We can talk about it. Maybe we can loan you one.

Mr. Ike Tripp: Thank you. Ike Tripp, Etna Products. I have a question for Dr. Pederson. In your slide illustrating a comparison of four to seven ring PAH in new hydraulic oil, gear oil and quench oil versus used fluids of that nature, the PAH in the case of the gear oil actually decreased when you compared the used sample to the new sample, the new oil. Can you explain that decrease?

Dr. THOMAS PEDERSON: Well, it was a relatively small decrease.

Mr. Tripp: Relatively small decrease, but in the case of the gear oil subject to high loading and high heats, one would expect that there should be a slight increase, at least in the PAH.

Dr. PEDERSON: It depends on what you're measuring and it's how semi-volatile it is and if it's exposure to heat. In oils, the lower molecular weight PAHs in terms of mass are

predominant, starting with the two ring compounds. Three ring and four ring compounds usually predominate. If you get high enough in temperature, the three and four ring compounds are semi-volatile and will have some loss over prolonged use at elevated temperatures, but there could be other reasons related to chemical stability or something like that.

Mr. Tripp: I have a follow-up question for Susan Woskie. You noted the impact of seasonal workplace machine design, local exhaust, machine type and their effects. I was wondering if you had considered additional factors such as the actual design of the cutting tool, the binder used in the fabrication of that cutting tool, the tool coatings that are often times being utilized, the degradation thereof of those coatings, the metallurgy of the part that you're machining and additionally, the various oxides and swarf generated by the machining operation. I wonder if you could comment on these factors.

Dr. SUSAN WOSKIE: We have not looked at most of those factors. Perhaps the only thing we have done is we did indicate the kind of base metal that was being used. That's about it. We have information, for example, on speeds, cycle time, flow rate of the fluid, but we didn't collect that kind of information.

Ms. Cathy Walker: Cathy Walker, Canadian Auto Workers. I think actually Dr. Woskie you did look at cobalt, which is interesting in following up the previous question, and it was virtually at non detectable limits, as I understand it.

My question picks up from the brief comment made by Dr. Smith on edible oils and this is a question for the General Motors representatives. When the UAW-General Motors study was first published, we took the summary that appeared in Automotive News and distributed it to all our locals in the country and were rather surprised to find out we got a very fast phone call from one of our plants in Lethbridge, Alberta, a

very small plant. They said that they had a very bad problem on one of their saws that cut aluminum and of course, Canadian law permits workers to refuse to work in the case of a hazardous situation, so the workers in that plant were refusing to use this particular cutting oil.

They phoned me up and said what do we do about this, and I remembered that there had been an article that appeared in a Swedish magazine, *Work Environment* on vegetable oil substitutes for cutting oils, so I suggested they might want to try that. They wanted to know where to find it. I didn't have a clue, but they were able to chase some down quite quickly and started to use it and phoned me back and said this stuff is great. The oil mist problem is different. It's night and day. Everybody is happy. After I hung up the phone, I was rather surprised because I realized I hadn't suggested to them to do anything about ventilation, to do anything about enclosures, but simply by substituting the vegetable oil cutting fluid, there was much less oil mist in the air.

Since then, I have talked to the Swedish Metalworkers Union. They are quite pleased with this substance that's being used throughout a number of Swedish workplaces and I'm wondering for General Motors, given you are owners of Saab, what have been the results in the testing between Saab in Sweden and some of your General Motors operations in North America? What have been the differences in particulates and in PAHs between conventional cutting fluids used in North America, and vegetable oil substitutes used in Sweden? and if you don't happen to know off the top of your head --

Dr. TAI CHAN: We don't have that information now and I think it would be fair to the rest of the audience that we ask Tom [Smith] to give you a specific comment to this, otherwise we will go on.

Ms. Walker: Yes. My other question would be if you don't know, could you find out.

Dr. CHAN: Yes. You know where to find

me. I would appreciate it if people could keep the question to 30 seconds so we could respond. Frank?

Dr. Franklin Mirer: Frank Mirer, UAW. These will probably be observations more [than anything else]. I thought first that Dr. Pederson's presentation was really an excellent contribution and it shows that there's gradations of PAHs, not night and day, but a continuum there. If we have one-tenth the PAH that we used to, presumably we'd have one-tenth the risk, not zero risk.

With regard to Dr. Cohen's formaldehyde presentation, we have noted in some studies substantially higher formaldehyde levels in machining operations than you quoted. I think the best interpretation for the so-called background is simply air mixing through the whole facility that gives this apparent background of the vaporphase contaminant and recirculating facilities.

And a lesson for the UAW folks out here is if you are using triazine biocides, go out and sample the formaldehyde and see if you're above the 0.1 or the 0.5 and go out and implement the formaldehyde standard. We have, I think, a significant issue here and also one that confounds a lot of the respiratory effect studies because 0.3 parts per million of formaldehyde is certainly an effect level for some of these respiratory effects.

And then the third observation, and then I guess this does lead to a question. Frankly, the differences between the sampling methods talked about and the 20 percent of the total particulate that's not inhalable in these plants is minuscule, irrelevant and unimportant in measuring controls, because the day-to-day variability of an air sample is much, much greater than anything that arises from these different methods. If we're going to move forward to controls, we need a method that will permit multiple statistically valid air sampling, not more and more elaborate sampling methods that give us fewer and fewer samples because the variations are much more important than the sampling and analytical variability.

Dr. TAI CHAN: I would like Howard to comment quickly on the triazine and then I'll turn to a Discussant on the last question.

Dr. HOWARD COHEN: I just want to tell Frank a story that will help add to the information on formaldehyde and I'll try to do this quickly, but you can only tell stories at a certain speed.

One of the plants we were invited into was a UAW facility that both the UAW and management asked that we come in because they were having problems with irritation. We went into the facility and we looked at two somewhat different lines, but were essentially using the same fluid.

In one line, clearly the system was out of control in terms of bacteria. There were ammonia flushes, you would go in the area and you would get eye irritation, you didn't have to have any sampling equipment to say that there was a significant problem there.

The second line, everything from the workers perspective, and to myself as well, if you went in there, it seemed fine. So we did our monitoring for formaldehyde. The first line they couldn't keep triazine in the system. Bacteria, or whatever, kept eating it up. There was no triazine in the fluid that we could find, no formaldehyde in the air, and yet the eye irritation and the complaints were terrible.

Employees at the second line had determined to fix their problem by using triazine at well above the 1,500 parts per million level approved by EPA on the label. The fluid typically had 2,500 parts per million of triazine in it. We found the highest airborne levels of formaldehyde in the entire study at that facility, and the employees were pleased. They thought that the triazine had done the job and that the system was great and they wanted to switch the other system over too, again using the 2,500 parts per million triazine. Among several items, in terms of ventilation and other things, I pointed out to them that they had to require training and labeling. I also pointed out that if they continued with the

higher use level, that they would also be in violation of the EPA label directions at that level.

It led me to the conclusion, Frank, that there's a lot of things that may be out there causing eye irritation, it may not be formaldehyde at all.

Dr. TAI CHAN: Do we have a quick response on the particular sampling question?

Dr. JAMES VINCENT: If the difference in sampling methods was only 20 percent, I'd certainly agree that it would be insignificant, but it's not. It's more than 100 percent. And if you look at the statistical distributions of exposures as measured by both instruments, and we have examined these for a whole range of industries, but not specifically for metalworking fluids; what it does is significantly increase the percentage of time that you would expect to find a measurement exceeding a given level, that is, a TLV or a compliance level. And that could be a difference in maybe 30 percent or 40 percent of the time. You're increasing your probability of getting a sample above that threshold level, so I don't think that's an insignificant effect.

Dr. TAI CHAN: Okay, thank you, Jim. Let's go on.

Dr. Peter Thorne: Peter Thorne, University of Iowa. I just have a quick question for David Leith and then a general question, and that just had to do with the humidity effects seen in the MCE filters, and I wanted to clarify, was that after correcting for the humidity effect in field blanks or in your case in control filters, or was that an uncorrected drift?

Dr. DAVID LEITH: That slide that I showed was referring to blanks that were kept in the laboratory under the relative humidity of the laboratory. It did not apply to field collected samples.

Dr. Thorne: So in a field sampling regimen where you have field blanks that travel

with you and then are used to correct for any change in drift of the instrument or humidity, that effect would disappear presumably?

Dr. LEITH: Presumably it would. It was just to point out that there's potential for a problem if you don't make the correction.

Dr. Thorne: My general question has to do with the issue of personal versus area samples, particularly for oil mist or particulates, or whatever we're calling it, and whether there's a general consensus as to whether personal samples are higher than area samples, or the reverse in this worker group. Because I think I heard something about personal samples being higher, and in our experience we're finding area samples higher if the area samples are taken at the machinist's work location as opposed to the table.

Dr. TAI CHAN: Dr. O'Brien can address that.

Dr. DENNIS O'BRIEN: There isn't any generality. You can say that personal samplers are higher. Area samples really are dependent upon location, so if you are going to set an area sampler on top of a machine tool, you might expect it to be higher. On the other hand, you have to look at the nature of the workers job. If the worker is continually opening an enclosure and partially entering that enclosure, the personal sample you could see would be much higher than what an area sample would be.

In other cases, where the worker is primarily at an operating station, you could see the area samples being higher. We have even noticed in some very controlled studies that we have done where we have taken identical samples on right and left lapel, that there's even a handedness to the sample results, particularly if the worker is right-handed and the job involves a lot of right-handed activity.

Dr. Thorne: I would just comment. It seems to me that if the area sampling is performed

at a machinist's work site and they are spending considerable time away from that site because the operation is running smoothly and it isn't a tool-in, tool-out kind of thing, then the area samples are going to over-estimate exposure.

Dr. O'BRIEN: The whole purpose behind sampling is that each sample is supposed to answer a question, and if you are looking at say the effectiveness of the enclosure, you may want to look at an area sample. If you're interested in what the worker's exposure is, which is really the bottom line in most industrial hygiene sampling, then you want to do a personal sample.

Dr. TAI CHAN: Let me suggest, we're not going to be able to take all the questions in the next ten minutes. If you have a question, if you are in the back of a line, write it out, give it to Dave Felinski, and we'll make sure that it will be answered, and it will be included in the Proceedings. Is that a deal?

Dr. Sridhar Reddy: Sridhar Reddy, Wayne State University. This question is for Dr. Jim Vincent and/or Dr. Sue Woskie. Given the spectrum and size distribution of aerosols, would it be prudent to use total surface area and/or number of particles when relating this to health effects, specifically acute pulmonary effects?

Dr. JAMES VINCENT: I think there are many arguments that support the use of some exposure index other than mass, but I think for industrial hygienists and analytical chemists, this would impose considerable complications to the actual methodology. So we fall back on mass as perhaps the best, or at least the most convenient surrogate to use.

Dr. Bengt Jarvholm: Bengt Jarvholm from Sweden. I would like to make a comment about measuring of formaldehyde in cutting fluids. We have measured formaldehyde and acetic

aldehyde in two systems during one year, taking samples several times a week. We find the variation very great in the systems. You can have an order of magnitude between different days in a week in fact, and it seemed that if formaldehyde was low and vice versa, if you measure only one of them, you may have a problem. Our experience was that the highest concentration of formaldehyde in the system occurred when you refilled the system totally. And I would like to ask Dr. Cohen if you did any measurements while refilling the total system?

Dr. HOWARD COHEN: The answer is on a small system, yes, we actually did refill a small system that used just one piece of equipment. We refilled it, and the interesting aspect was that we found formaldehyde when there was no triazine in the original fluid. We then dumped out the system, added all new fresh fluid in the afternoon, and then the formaldehyde levels went down.

We tried to get this dynamic range of formaldehyde by measuring before we added triazine and after we added triazine. Our goal was to try to do what you have said. Since I was traveling around the country, I didn't have the luxury of being at one plant where I could keep going back every week or every month to sample formaldehyde. So we tried to look at that dynamic range that would occur between the before and after sampling, and there was some range in our data.

Dr. William Lucke: Bill Lucke, Cincinnati Milacron. Just a quick comment on Dr. Pederson's data that the archival oils that were studied not only were higher in PAH for the initial period compared to the newer oils, but the classification of the mutagenicity index also went from carcinogenic to noncarcinogenic. That's just a remark, not a question.

My question: The world has come to a sad state of affairs when the analytical people are more depressing than the epidemiologists. Given that the UAW has asked for a 0.5 milligram per cubic

meter PEL, and ILMA has also suggested that the limit be lowered, and given Howard's [Cohen] troubles with working with the regulation that set a limit beyond the capabilities of the analytical technology, if we went for a reasonably conservative limit and said let's go with the limit of quantitation for whatever method, what limit should be looked at there? And I'll give that to anybody that wants to take a swing at it.

Dr. TAI CHAN: I think Tom is willing. Are you?

Dr. THOMAS SMITH: I can probably say a little about that. I think that we can certainly develop methods that have reasonable quantification at that level. Now the issue of are they measuring something that's relevant, I think, is also another question. And from my own view, I think that some combination of a vapor sampler and mass sampler are what we need and I think that coupled together, you may find a better precision, but it has not been done yet, so I don't know.

Dr. Lucke: Okay. That's a good question.

Dr. SMITH: Like what? I can't know. Because I don't know what the vapor complement should be. I mean there's, as you said, some evidence that the aerosol should perhaps be in the range of one to a half or something, but I don't think we have any idea about that.

Dr. TAI CHAN: Dennis, can you give us a number?

Dr. DENNIS O'BRIEN: I could pull one out of my pocket, but no, I really can't.

Dr. TAI CHAN: Let's go to Bill Watt.

Dr. William Watt: Bill Watt, Chrysler Corporation. Dr. Pederson, how much increase in the PAC or PAH content did you see in the used

oils, and was this machining fluid oil that you were looking at? Did it push it above the 1.0 mutation index point?

Dr. THOMAS PEDERSON: I have not looked at a new and used machining fluid as for PAH formation. There were two hydraulic oils, the gear oil and a quench oil. It's difficult in manufacturing facilities to find places where you can isolate a process and collect a sample of the virgin lubricant that goes into it and a used lubricant coming out of it that's not commingled with other things.

As a matter of fact, a qualifier on practically all samples that we measured is we worry about whether there's been commingling. People talk about tramp oils and things like that, I mean that's a constant problem in the real world of a manufacturing plant, to sample and characterize things according to different processes and such. So that's always a bit of a qualification on any analytical results, such as the formal one about, 'what happened with the PAH level in the gear oil?'

Dr. Watt: Were those mutagenic indexes above one, though, even if you didn't know the history of the oil?

Dr. PEDERSON: In the used machining fluid?

Dr. Watt: Yes.

Dr. PEDERSON: We haven't looked at a specific used machining fluid. The pooled waste oil samples that we have from the different plants have a heavy component in them from machining fluids, and in all of those, there was one that reached the value of 1.0. The rest were all below that.

Dr. Watt: Thank you. Another quick question. Is there a percentage of the PAHs that would be safe to use? In other words, can you give me a percentage number for PAHs so I can go out

and measure that, and I can say "it's less than one on the mutagenic index" and not worry about the oil?

Dr. PEDERSON: That is the problem. One of the things that comes from what I'm doing is to attempt to make and understand the correlation between PAH content and the mutation index. And as a matter of fact, I can use the regression coefficient I have to take a PAH analysis and say what the expected value would be for mutation index. That gives a perspective as to what that amount of PAH means, since there is a correlation of mutation index with a biological effect, mouse skin painting studies. But there is nothing in the way of an established criterion, that I'm aware of, that you can apply to the actual quantitative number for PAH content.

Dr. Christopher Skisak: Chris Skisak, Penzoil Company. I can comment on that and the answer is less than one percent. I enjoyed your presentation. I think it shows the difficulty of looking at individual PAHs, and if one adds up your PAC content, alkylated and non-alkylated, you see that your MIs [mutation indices] are all less than one when your concentration was less than 10,000 parts per million total in it. And that's been published by Gary Blackburn of Mobil by the way who is at Petro Tox, not Petro Chem, and that is in the literature.

Dr. THOMAS PEDERSON: Just one thing about the number you mentioned, the less that one percent. You are referring to PAC measurements?

Dr. Skisak: Correct.

Dr. PEDERSON: Which is the total DSMO extractable material. If you take that same number and apply it to what I'm measuring, which is total PAH by GCMS techniques, of course the quantities are over an order of magnitude.

Dr. Skisak: By GC / MS, if you have less than one percent total PAC, you will have a safe oil. That's been published.

Dr. PEDERSON: Well, I would have disagree with that because you can take the two oils in here or take one in particular, the ASTM test oil M3. That oil when it was tested in skin painting studies in the early eighties produced 50 percent tumor papilloma incidents in the mouse skin painting studies, so it had a pretty potent activity.

That falls well below your point one percent value for PAH that I measure, not the PAC measures by the other methods.

Dr. TAI CHAN: I think we are out of time. Tom has a full paper written on the subject and I think he will be happy to give you a copy of his paper.

*WRITTEN QUESTIONS SUBMITTED
SUBSEQUENT TO THIS SESSION AND
ANSWERED IN WRITING BY THE SPEAKERS
DESIGNATED BY THE QUESTIONER*

Mr. David Tepper: David Tepper, General Motors. Would you clarify the statement during your conclusion that lowering the relative humidity is a beneficial environmental control. Please consider earlier comments made by presenters about repeated problems in Winter months, which may be caused by less outside air, or may in fact result because the outside air entering the facility has significantly lower moisture content than in Summer. Also, please consider whether high humidity levels encountered are the cause of, or the result of machine fluid evaporation and mist. Is there a need to make a distinction between clean, controlled humidity and dirty, uncontrolled humidity?

Dr. SUSAN WOSKIE: If controlling humidity was done by increasing the dilution ventilation rate using fresh, clean and low humidity air, then MF

aerosol levels would decrease. Also, controlling humidity could greatly reduce the lifetime of the large MF aerosol droplets, since at lower humidities the volatile components, especially water, would evaporate and could be removed more easily by dilution ventilation. However, this does not address the concern raised at this Symposium regarding any hazard posed by the MF vapors.

Dr. Mark Entermoser: Mark Entermoser, Texaco. Your presentation has documented a couple of points that refiners have known / found: 1) 3 to 7-ring PAHs contain the carcinogenic species; and 2) alkylated PAHs predominate in crude oil.

I direct your attention to the API presentation given on Monday [by Dr. Skisak]. API is working with ACGIH on the proposed TLV revision for non-severely refined base oils. API is recommending a performance-based approach based on "weight of scientific evidence" whether an oil is classified as carcinogenic or non-carcinogenic. API has moved away from an analytical approach for two reasons, pointed out by your work: 1) all PAHs are not carcinogenic, and all carcinogenic PAHs are not equipotent; and 2) oils such as the one classed as an "outlier" are not uncommon in the wide range of oils produced. It is not uncommon to have an oil with high levels of PAHs that also "passes" the Modified Mutation Assay. These oils cannot 'simply' be discussed.

It appears from your study that the finer the focus of the analytical method on PAHs, the worse the correlation coefficient becomes. The method needs to remain broad (like IP-346) to capture other polycyclic aromatic compounds, like N- and S-containing PACs, which have similar carcinogenic potential.

Does your method capture other PACs? Not all 3-7 ring PAHs are carcinogenic. Any method of sampling must cover the broad class and set some threshold that corresponds to a non-carcinogenic oil. At present, the most effective way to evaluate the carcinogenicity of a mineral oil

comes from the scheme used by API member companies for years. The bottom line is: carcinogenic oils should not be used in metalworking fluids. The oil companies have the data. It should be requested, a non-carcinogenic oil should be selected, and the 5 mg/m³ gravimetric TLV can be used. Any PEL for a MWF depends on the fully formulated product, and its state in the plant. Thank you.

Dr. THOMAS PEDERSON: The oil sample I referred to as an "outlier" is a formulated product and would not normally be submitted for analysis in the Modified Mutation Assay. Its low mutagenic activity in proportion to its PAH content was likely attributable to inhibitory or toxic effects in the bacterial assay.

The correlations between various measures of PAH content and mutagenic activity do indeed show that the measurement method needs to remain broad. Unfortunately, method IP-346 (and other similar types of analysis) can only be used with virgin petroleum base oils. The method I have used is applicable to all manufacturing oils, including used and recycled oils.

Other PACs are recovered in the DMSO extracts of petroleum oils. In the back extraction used for the GC / MS analysis, PAC compounds with N, O, & S as ring heteroatoms are recovered with high efficiency, but back extraction of other polar PACs from the DMSO / H₂O phase is more variable. I have found, as have others, that thiophenes, primarily dibenzothiophene, benzonaphthothiaphenes, and their alkylated derivatives, are present in all the oil samples. Because of access to only a limited number of reference compounds, I have not determined the mass spectral response factors necessary for quantitative measurements, although reasonable estimates could be made and the method expanded to include these compounds. Dibenzofuran and its alkylated derivatives are similarly present, but I have found only very small amounts of the benzonaphtho-furans in comparison to the alkyl-PAH of the same molecular weight. One of the principle reasons for conducting these studies was

a concern over the possible accumulation of other polar PAH derivatives in used manufacturing oils that might contribute to the mutagenic activity in proportion to the PAH content of the used oils was indistinguishable from that of the virgin petroleum oils.

Mr. Howard Ayer: Howard Ayer, University of Cincinnati. Which of the three methods studied is the most simple and inexpensive method for a small unit to implement?

Mr. DAVID HANDS: The total particulate method is the easiest analysis to perform. The extraction methods require significant time and laboratory equipment.

Mr. Howard Ayer: Howard Ayer, University of Cincinnati. Have data on PAHs/PNAs in oils been furnished to the ACGIH TLV Committee with recommendations for the definition of threshold amount? If not, I suggest that it be done.

Dr. THOMAS PEDERSON: No, this is the first presentation of these findings. If PAH content determined by chemical analysis were to be included as part of a TLV criterion, it would first be necessary to standardize both the method for analysis and the listed chemical constituents to be included in the measure of PAH content. The preponderance of alkylated PAH in petroleum oils, and their evident importance as mutagens in the Modified Mutation Assay, increases the complexity of establishing standardized methods and measures of PAH content.

Mr. Alfred Woody: Al Woody, Giffels Associates, Inc. Please expand on the effect of seasons on oil mist levels: in the Winter, there is less ventilation (outside air) than Summertime; in the Winter you could expect lower humidity since the outside air is dryer. What would you expect if

the ventilation system could cool and thus control humidity in the Summer? Lower mist levels, or about the same?

Dr. SUSAN WOSKIE: In cold climates, less fresh outside air circulation in the Winter results in a build-up of metalworking fluid aerosol and its evaporated water in the plant. The Summer is a bit more complicated. If the building is not air-conditioned, the high temperatures and high humidity outside may also occur inside. This would foster the aerosol cloud, yet it might also result in a widespread opening of doors and windows, providing dilution ventilation. If the building is air-conditioned, reduction of energy costs may have resulted in a situation very much like the Winter, low fresh outside air circulation resulting in a build-up of metalworking fluid aerosol and its evaporated water in the plant. Thus, the MF levels in the Summer probably depend on the balance of these conditions, since in the first case high humidity from outside air entering the plant may indicate high dilution ventilation rates, while in the second case high humidity may indicate poor fresh air circulation and a build-up of MF aerosols in the plant.

Mr. Gordon Taylor: Gord Taylor, Canadian Auto Workers. Indoor air quality is a major concern in most industrial workplaces. The use of compressed air to blow off coolant covered parts, in my mind, is a major contribution to the overall air quality. What recommendations can we expect from the Symposium with respect to the use of compressed air in our manufacturing environment?

Dr. JAMES D'ARCY: The generation of specific recommendations concerning the use of metal removal fluids is not one of the goals of the Symposium. However, I agree with you that the unnecessary use of compressed air to remove fluids should be avoided. We have some plant data that shows that "air blow-offs" or air probes can be significant sources of aerosols. We are

advocating the modification of air probes to fluid probes where possible and the removal of all non-essential blow-offs. If blow-offs must be used, then specific engineering controls may be required.

Mr. Kenneth Cavanaugh: Ken Cavanaugh, Houghton International. Most components of synthetics and many in semi-synthetics are not soluble in the toluene and TCE used to extract the filters. Doesn't this skew results? Also, do you have any explanation for milligrams per cubic meter of soluble oil higher than that for straight oil?

Mr. DAVID HANDS: Yes, the lack of solubility of certain components in metalworking fluids could affect the results of analyses where extraction is used. However, the amount of solvent used in the Ford method is 10 milliliters, which is a large amount compared to the mass of material collected on the filter. Thus, if a constituent is even slightly soluble in the solvent, most or all of it may be extracted.

It is acknowledged that these methods are not specific and could yield results that vary depending on the chemistry of the metalworking fluid. However, it is interesting to note that the total particulate method indicated only slightly greater concentrations than the extractable methods.

The concentrations of soluble oils being greater than the concentrations of straight oils is most likely explained by the differences in machining processes and sampling locations. The area sampling locations for this study were based on metalworking fluid type, availability of 110-volt power, and suitability of the location to accommodate the sampling apparatus. Thus, the concentrations measured varied depending on the amount of mist generated by the machining operation, the proximity of the sampling apparatus to the machining process, and, to a lesser extent, the type of metalworking fluid used in the process.

Mr. Kenneth Cavanaugh: Ken Cavanaugh, Houghton International. With the bacteria level in the sump model, I was surprised to see that product concentration was not a determining factor. Would you comment please?

Dr. SUSAN WOSKIE: I do not have an explanation for this finding, nor is any reported in the literature I've reviewed. However, it is my understanding that the University of Michigan group (Robins, et. al.) have also found that the percentage of oil in the MF was not a significant determinant of bulk microbial levels.

Mr. Kenneth Cavanaugh: Ken Cavanaugh, Houghton International. Was the mineral oil used for misting of the type used in industrial oils?

Dr. DAVID LEITH: Yes, the oil used was a commercially available machining oil, used for machining applications.

Mr. Cavanaugh: What was the viscosity?

Dr. LEITH: The viscosity was about six centipoise.

Mr. Cavanaugh: Any plans to do other tests at manufacturing plants?

Dr. LEITH: We would like to do some tests at manufacturing plants, yes.

Mr. Howard Ayer: Howard Ayer, University of Cincinnati. Has the personal ESP been evaluated for use with water-based metalworking fluids?

Dr. DAVID LEITH: No.

Mr. Ayer: Is such a device commercially available, and if so, what is the price?

Dr. LEITH: Yes, the precipitator is available through Aerosol Associates, 120 Muirlane, Chapel Hill, North Carolina, 27514; the price is about \$2,000.

Mr. Gregory Foltz: Greg Foltz, Cincinnati Milacron. I had some comments yesterday on Dr. Kriebel's talk regarding the appearance (manual loading and lack of any obvious guarding) on the [slides shown of] machines from the plant in your study. I have a further question today regarding the fluid conditions that you reported. There was an average pH of 8, with a low of 5, maximum tramp oils of 46%, and 10^7 to 10^8 bacteria counts. These are very atypical. While they may exist for a very short period of time, they are by no means the norm. All MWF manufacturers and end users would agree that better control is needed. However, in spite of these conditions, endotoxin levels were very low, but some of your comparisons, such as local exhaust vs. complete enclosure did not show much difference. What would you expect to see if these fluid conditions were better controlled?

Dr. SUSAN WOSKIE: You raise the question of whether the levels in the sumps we measured were "typical." First, let me remind you that we measured the concentrations in the sumps of 129 machines, most of which were small sumps holding less than 50 gallons and which were often changed every few days. The levels of culturable bacteria we found in the sumps were within the ranges of previous published reports on metalworking fluids (Traver-Glass, 1991; Hill, 1979; Mattsby-Baltzer, 1989; and Wort, 1976). Our modeling suggests that the most significant

factors influencing bulk bacteria levels are the pH, the season, and the % of tramp oil, suggesting that if these factors were "controlled," the bacteria counts could be lowered. The statistical models also showed that lowering bulk counts would in turn reduce the worker's level of exposure to airborne bacteria, as would decreasing the workplace machine density, enclosing the machines and increasing the worker's distance from the machines.

Dr. John Howell: John Howell, Castrol Industrial North America. In your study, you observed exposure levels considerably lower than those previously reported (Harvard School of Public Health). On Monday, Dr. Jane Teta showed a slide showing substantially reduced exposures that have occurred over the last twenty years. Given the fact that many of the buildings were older and that there were many individual machine tools, can you comment as to whether and how your observed lower exposures were a reflection of that trend?

Dr. SUSAN WOSKIE: The reduction in exposures over the past 20 years discussed by Drs. Eisen and Teta were based on the work by Hallock *et al* using data collected from the same plants over that period. The exposure levels reported in my talk were in a completely different plant about which I know nothing about the changes in exposure levels over time. In order to make some connection between the current exposure levels found in one plant to the historical levels found in completely different plants, I would need more information.